Aqueous organic dye discoloration induced by contact glow discharge electrolysis

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ABSTRACT

In this study, effects of applied voltage, types of electrolytes, initial substrate concentration, radical scavengers and iron salts on the aqueous polar brilliant B (PBB) discoloration induced by contact glow discharge electrolysis (CGDE) were examined. Experimental results showed that the PBB discoloration proceeded faster in chloride solution than in phosphate or sulfate solutions. Increasing the applied voltage from 450 V to 550 V did not enhance the discoloration when the applied current was kept constant. Addition of a small amount of hydroxyl scavengers (methanol) to the solution decreased the discoloration, whereas addition of a large amount of methanol increased the discoloration. During the treatment, TOC of the solution smoothly decreased whereas COD of the solution gradually increased due to the production of H_2O_2 in the liquid phase. Iron salts enhanced the discoloration significantly due to the additional Fenton reaction. Higher initial PBB concentration resulted in lower color removal efficiency, indicating that the PBB discoloration by CGDE did not observe the first-order reaction kinetics in inert electrolytic solutions.

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1. Introduction

Color is one of the most important indicators of water pollution. Being toxic to microbes, dyes-containing wastewater cannot be treated well by biological processes. In addition, aquatic metabolism is suppressed due to the shortage of sunlight, which in turn decreases the self-purification ability of the colored water. Therefore, development of effective dyeing wastewater treatment technologies is of practical interest.

Recently, water treatment by electrical discharges has attracted considerable interests from the environmental researchers [1]. The electrical discharges can take place directly under water or in close proximity to the water surface. Contact glow discharge electrolysis (CGDE) is an electrical process where plasma is sustained between a rode anode and an electrolytic surface. Using a thin platinum anode in contact with an electrolytic solution, normal electrolysis develops spontaneously to CGDE if the applied voltage is sufficiently high [2,3]. During CGDE, many species such as $OH^\bullet$, $H^\bullet$, $O^\bullet$, H_2O_2 are produced with yields much higher than those expected from the conventional electrolysis [3]. Furthermore, these species, especially hydroxyl radicals ($OH^\bullet$), are particularly reactive toward the organic pollutants present in water. A variety of organic pollutants could be mineralized by means of CGDE [3–13]. In addition, energy yields for pollutants removal and H_2O_2 formation in CGDE are comparable to those in pulsed corona discharges [5,11], while the equipment and operation of CGDE are much simpler than those of pulsed corona discharges.

Discoloration of dyes by CGDE has been reported by some authors [12,13]. Much confusion exists concerning the reaction kinetics. For example, Ref. [12] deemed that the discoloration of dyes by CGDE obeyed the first-order kinetics. However, the authors only investigated the discoloration in a dilute substrate solution. Whether the discoloration still obeys the first-order kinetics in concentrated solution is not known yet. Therefore, further studies on the discoloration of dyes by CGDE are needed.

As azo dyes constitute the largest class of dyes, polar brilliant B (PBB) is chosen as a model pollutant in the present study to examine the CGDE-induced decolorizing kinetics in aqueous solutions. The molecular structure of PBB is shown in Fig. 1.

2. Experimental

Experimental apparatus is shown in Fig. 2. The anode was a pointed platinum wire (diameter: 0.6 mm) sealed into a glass tube with 5.0 mm protruding from the glass body. The cathode was a stainless steel plate (surface area: 7.0 cm²) immersed in the electrolyte and separated from the anodic compartment by a glass tube with a glass frit of medium porosity at the bottom. The reaction vessel was coated by a water jacket, where the temperature of the solution in the reactor was kept at 298 ± 4 K by running tap water.

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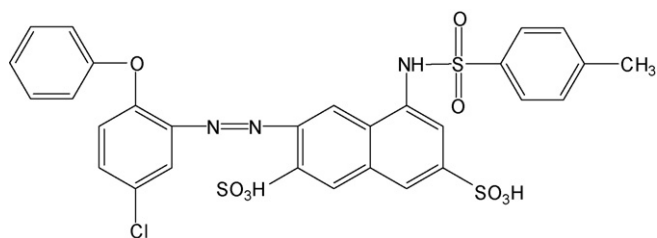 E-mail address: wangl@xmut.edu.cn.

Fig. 1. Molecular structure of PBB.

PBB was dissolved in a certain electrolytic solution (conductivity: 6.4 mS/cm) and 150 mL portion was subjected to treatment. DC voltage was applied from a DC power supply to initiate the reaction. Depth of the anode immersed in the solution was manually adjusted to make the current to 100 mA.

Absorbance of PBB solution was measured by a UV-2450 spectrophotometer (Shimadzu) at a wavelength of 524 nm, with the solution without PBB as the background. The chemical oxygen demand (COD) was determined by a dichromate method. Total organic carbon (TOC) was determined by a TOC analyzer (TOC-VCSH, Shimadzu). Organic acids and inorganic ions were analyzed by a Dx–500 ionic chromatography. The separation was performed on an Ion Pac AS–14 column, with an aqueous solution of Na_2CO_3 as the mobile phase at a flow rate of 0.25 mL/min. H_2O_2 and NH_4^+ formed in the solution during the electrical discharge were determined by a titanyl reagent [9] and a Nessler's reagent [14], respectively. It should be mentioned that the sample should be decolorized by a little amount of activated carbon before the measurement of H_2O_2 and NH_4^+ in order to avoid the color interference from PBB and its degraded by-products.

3. Results and discussion

3.1. PBB discoloration under different applied voltages

In this experiment, the applied voltage was investigated from 350 V to 550 V. Fig. 3 shows the PBB discoloration under different applied voltages.

It can be seen from Fig. 3 that the applied voltage imposed an apparent effect on the discoloration of PBB. For example, at 350 V, less than 20% of color was removed after 60 min of treat-
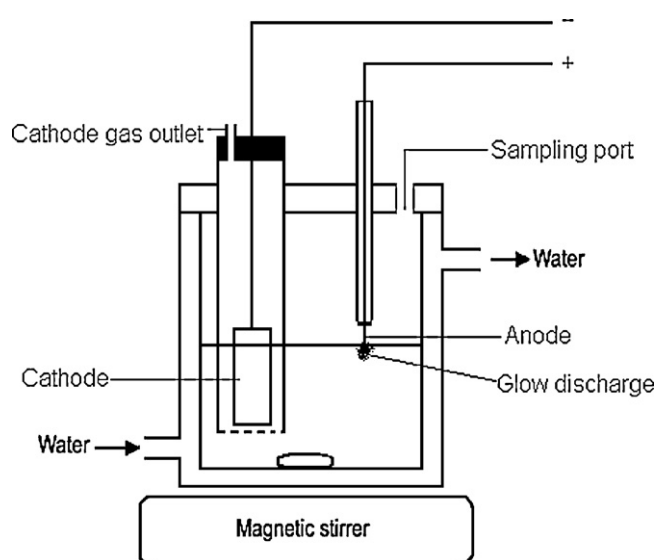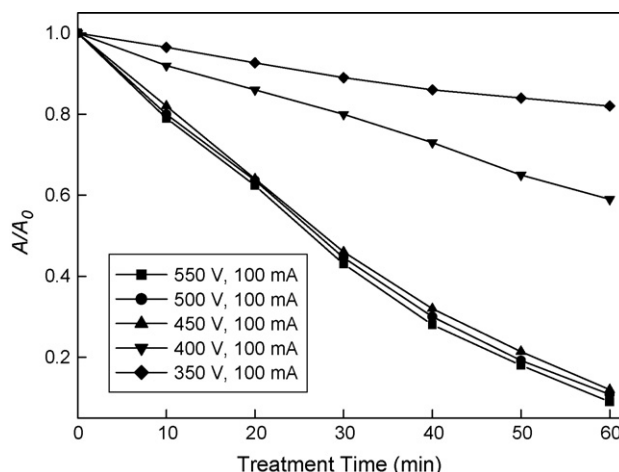

Fig. 3. PBB discoloration under different applied voltages (solution volume 150 mL, conductivity 6.4 mS/cm, pH_0 6.5, electrolyte Na_2SO_4).

ment, whereas at 550 V, more than 90% of color was removed with the same treatment time. The phenomena can be explained by the fact that when the voltage is lower than 400 V, plasma is not fully formed and the amount of reactive species produced in the solution was trace and the color removal was fairly low [2]. This phenomenon indirectly demonstrated that the contribution of electrolysis for the PBB discoloration was minor. It can also be observed from Fig. 3 that the difference in color removals is not obvious between 450 V and 550 V, which is different with those reported previously [12]. This can be understood that when CGDE fully develops, its cathode-fall did not increase with the rising applied voltage. When the applied voltage increases, more energy was consumed for the decomposition of water in the plasma area, producing oxygen and hydrogen gas [2]. As the oxygen and hydrogen gas did not contribute the PBB discoloration, increasing the applied voltage did not lead to the increase in color removal. When the applied voltage is over 550 V, the anode would be melted. 500 V is chosen as the operating voltage in the subsequent study.

3.2. PBB discoloration under different electrolytes

Fig. 4 shows the PBB discoloration in different electrolytic solutions. As shown in Fig. 4, the PBB discoloration proceeded faster in sodium chloride solution than in sulfate or phosphate solutions. The
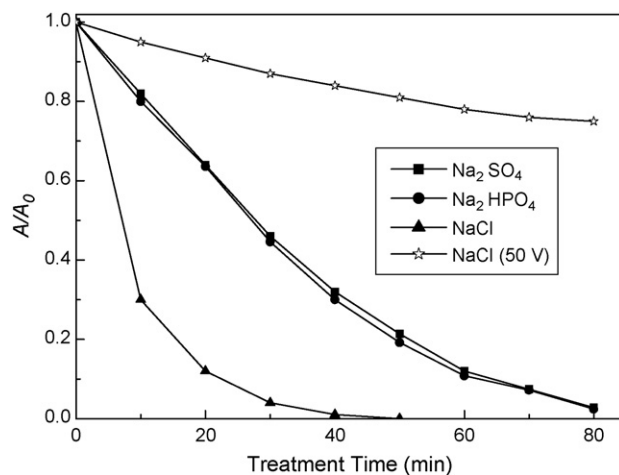

Fig. 2. Schematic diagram of the CGDE reactor.

Fig. 4. PBB discoloration in different electrolytes (voltage 500 V, current 100 mA, solution volume 150 mL, conductivity 6.4 mS/cm, pH_0 6.5, $[PBB]_0$ 50 mg/L).
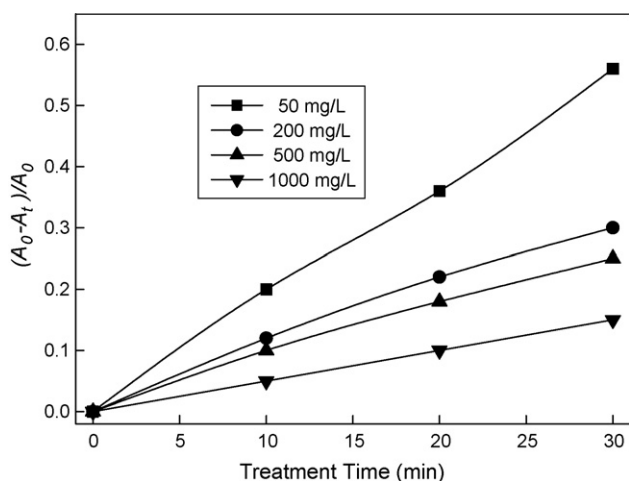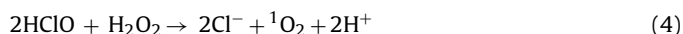
Fig. 5. Effect of initial concentration on PBB discoloration (voltage 500 V, current, 100 mA, solution volume 150 mL, conductivity 6.4 mS/cm, pH_0 6.5, electrolyte Na_2SO_4).

discoloration rate in phosphate solution equaled to that in sulfate solution.

Generally, when CGDE occurs in inert solution, hydroxyl radicals and hydrogen peroxide are produced ([2] and c.f. 3.3). Hydroxyl radicals are reactive and can induce the discoloration of PBB. However, when CGDE was performed in chloride solution, chloride ions would be transformed to chlorine atom. The chorine atoms react with each other to form molecular chlorine (Cl_2), which ultimately reacts with the H_2O_2 formed in the solution to give singlet oxygen [15,16]:

$$\bullet OH + Cl^- \rightarrow Cl^\bullet + OH^- \tag{1}$$

$$Cl^\bullet + Cl^\bullet \rightarrow Cl_2 \tag{2}$$

$$Cl_2 + H_2O \rightarrow HCl + HClO \tag{3}$$

$$2HClO + H_2O_2 \rightarrow 2Cl^- + {}^1O_2 + 2H^+ \tag{4}$$

The singlet oxygen thus produced is strongly oxidizing and can oxidize the PBB [16]. As a result, PBB discoloration rate was higher in chloride solutions than in other solutions. Fig. 4 shows that the electrolysis at 50 V can also decolorize the PBB. However, the discoloration efficiency at 50 V is much lower than 500 V with the same magnitude of current, indicating that Cl_2 (from electrolysis) contributes little to the PBB discoloration in CGDE [17]. It has been reported that the presence of chloride ions inhibits the H_2O_2 formation and pollutants removal in pulsed corona discharge discharges [15]. The present study showed that the presence of chloride ions was favorable for PBB discoloration, which will be of great importance in practice, since most of the advance oxidation processes did not perform well in the presence of chloride ions. It should be mentioned that there is a little chlorine gas liberated from the reactor during the treatment, which is not beneficial to the environment.

3.3. Effects of initial concentration on PBB discoloration

Previous studies deemed that the discoloration followed the first-order kinetics, which means the color removal efficiency is invariant with the initial concentration. In this study, the effect of initial concentration of PBB (50–1000 mg/L) on its color removal is shown in Fig. 5.

It is seen from Fig. 5 that higher initial concentration results in lower color removal. For example, when the initial PBB concentration is 50 mg/L, 56% of color can be removed within 30 min of treatment, whereas only about 15% can be removed in the case of 1000 mg/L within the same treatment time. This means that the PBB

discoloration is not first-order as reported in the previous studies [12,13]. The phenomenon can be explained as follows.

When CGDE occurs in inert electrolytes, the hydroxyl radicals are produced. The hydroxyl radicals react with PBB or dimerize to hydrogen peroxide:

$$\bullet OH + PBB \rightarrow Products \tag{5}$$

$$\bullet OH + \bullet OH \rightarrow H_2O_2 \tag{6}$$
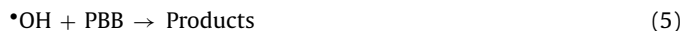
The PBB degradation/discoloration can be described by:

$$\frac{d[PBB]}{dt} = -k_{PBB}[PBB][\bullet OH] \tag{7}$$

where k_{PBB} is the reaction rate constant of hydroxyl radicals with PBB. It can be seen from Eq. (7) that if PBB discoloration is first-order, the concentration of hydroxyl radicals should be kept constant when the concentration of PBB varies.

However, as hydroxyl radicals are very reactive, a steady state will be maintained:

$$\frac{d[\bullet OH]}{dt} = a - 2k_{H_2O_2}[\bullet OH]^2 - k_{PBB}[PBB][\bullet OH] = 0 \tag{8}$$

where a is the production rate of hydroxyl radicals in the solution, the $k_{H_2O_2}$ is the rate constant of coupling to hydrogen peroxide. From Eq. (8), we get the following equation:

$$[\bullet OH] = \frac{\sqrt{k_{PBB}^2[PBB]^2 + 8ak_{H_2O_2}} - k_{PBB}[PBB]}{4k_{H_2O_2}} \tag{9}$$

It can be seen from Eq. (9) that the concentration of hydroxyl radicals reduces as the PBB concentration increases. Therefore, the discoloration of PBB did not obey the first-order reaction kinetics. When $[PBB] \ll \sqrt{8ak_{H_2O_2}/k_{PBB}}$, the Eq. (9) becomes

$$[\bullet OH] = \frac{a}{2k_{H_2O_2}} \tag{10}$$

Therefore, when the initial PBB concentration was very low, the discoloration is first-order, consistent with the previous reports [7,12,13].

3.4. Effects of radical scavengers on PBB discoloration

In practice, wastewater often contains various other organics that consume the radicals. Here, methanol was chosen the typical hydroxyl radical scavenger [18]:

$$\bullet OH + CH_3OH \rightarrow H_2O + \bullet CH_2OH \qquad k_{11} = 8.4 \times 10^8 \, M^{-1} \, s^{-1} \tag{11}$$

The PBB color removals after 30 min of treatment in the presence of various concentrations of methanol are presented in Fig. 6. As shown in Fig. 6, the PBB discoloration decreased with the increase in methanol concentration. This further indicated that the hydroxyl radicals were the primary species for PBB discoloration. However, as the concentration of methanol increased further, the PBB discoloration increases with the increase of methanol concentration. Such phenomena may be explained that when the concentration of methanol increased, methanol molecules enter the plasma area, where they undergo pyrolysis to produce additional hydroxymethyl radical ($\bullet CH_2OH$) and hydrogen atoms:

$$CH_3OH \rightarrow \bullet CH_2OH + \bullet H \tag{12}$$

The produced $\bullet CH_2OH$ and $\bullet H$ radicals can also react with PBB, leading to its decolorizing [19,20].

3.5. Effect of iron salts on PBB discoloration

It is demonstrated that a lot of H_2O_2 formed during the CGDE treatment [c.f. 3.6]. Therefore, it is useful to add iron salts to enhance
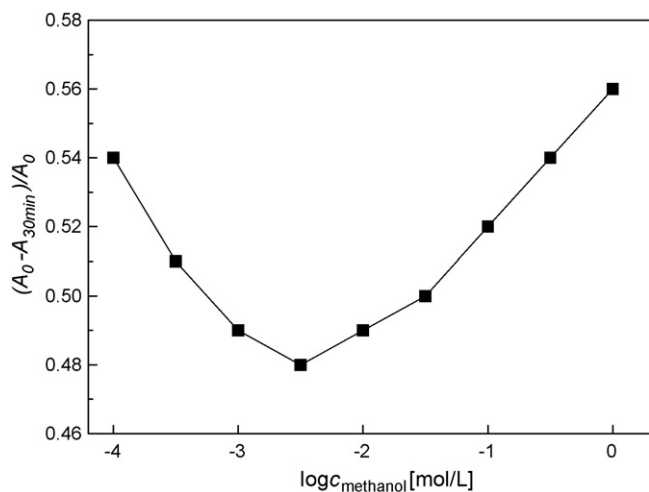
Fig. 6. Effect methanol on PBB degradation (voltage 500 V, current 100 mA, solution volume 150 mL, conductivity 6.4 mS/cm, pH_0 6.5, electrolyte Na_2SO_4, $[PBB]_0$ 50 mg/L).

hydroxyl radical formation and increase the efficiency of PBB discoloration through the Fenton's reaction. Here, effects of ferric and ferrous ions were both examined. PBB discolorations at 2 min of treatment under different concentrations of Fe^{2+} or Fe^{3+} are shown in Fig. 7.

It can be observed from Fig. 7 that Fe^{2+} ion showed apparent catalytic effect on the color removal of PBB solution. This is because the additional hydroxyl radicals were produced through the following reaction:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \tag{13}$$

However, the color removal decreases when the concentration of Fe^{2+} ion is over 80 mg/L. This is because of the following reaction:

$${}^\bullet OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \tag{14}$$

The discoloration rate increases with Fe^{3+} concentration, presumably due to the following reaction:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2{}^\bullet + H^+ \tag{15}$$
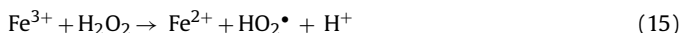
However, when the concentration of Fe^{3+} ion is over 120 mg/L, its catalytic effect is better than that of Fe^{2+} ion. This phenomenon cannot be explained by reaction (7) since the rate constant of Fe^{3+}
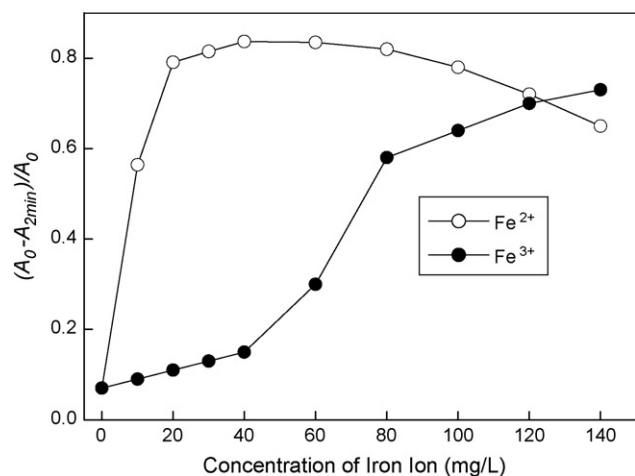

Fig. 7. Effect of iron salts on PBB discoloration (voltage 500 V, current 100 mA, solution volume 150 mL, conductivity 6.4 mS/cm, pH_0 2.5, electrolyte Na_2SO_4, $[PBB]_0$ 50 mg/L).
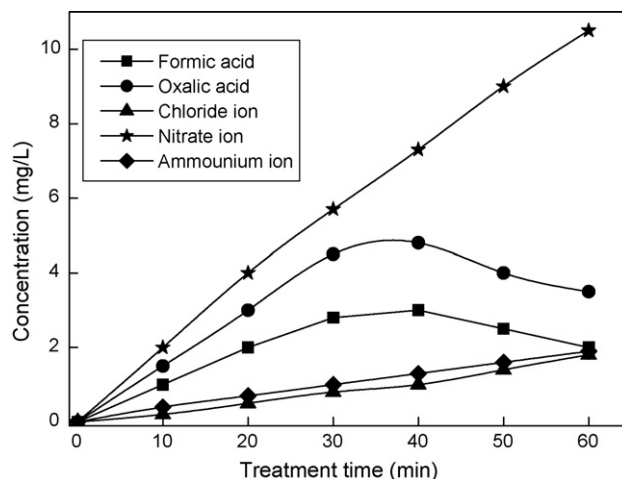

Fig. 8. Intermediate products formed during PBB degradation (voltage 500 V, current 100 mA, solution volume 150 mL, conductivity 6.4 mS/cm, pH_0 6.5, electrolyte Na_2SO_4, $[PBB]_0$ 50 mg/L).

ion with H_2O_2 ($0.01\,M^{-1}\,s^{-1}$) is almost four orders of magnitude smaller than that of Fe^{2+} ion with H_2O_2 ($76\,M^{-1}\,s^{-1}$). The following reactions may explain the above phenomenon:

$${}^\bullet OH + RH \rightarrow R^\bullet + H_2O \tag{16}$$

$$R^\bullet + Fe^{3+} \rightarrow R^+ + Fe^{2+} \tag{17}$$

Here, the RH denotes PBB. Previous reports showed that the catalytic effect of Fe^{3+} ion is much better than that of Fe^{2+} ion in phenol removal by CGDE [11]. However, the present study showed a little difference. The possible explanation may be that the mechanism in color removal is different with the other aromatics.

### 3.6. Degradation products

As PBB is very soluble in water, it and its byproducts are hardly retained by reversed phase column. Therefore, ionic chromatography and Nessler's reagent were used to identify the major intermediate products. Formic acid, oxalic acid, nitric acid, chloride ions and ammonium ions were identified as the main intermediates shown in Fig. 8.

It can be seen from Fig. 8 that the formic acids was about one half of the oxalic acid during the whole process. These acid intermediates eventually disappeared with longer discharge time. During the treatment, the pH of the solution containing PBB gradually decreased, further indicating the formation of organic acids. The major inorganic nitrogen is nitrate and the concentration of ammonium ions is very low, indicating the reductive degradation of PBB was minor.

3.7. COD and TOC changes

COD and TOC are important indicators of water contamination. The COD variations and H_2O_2 formation during the treatment are shown in Fig. 9a.

It is observed from Fig. 9a that the COD of the solution increased with treatment time. The reason maybe that the H_2O_2 formed in the solution interferes the COD measurement through the reaction [21]:

$$3H_2O_2 + Cr_2O_7{}^{2-} + 8H^+ \rightarrow 3O_2 + 2Cr^{3+} + 7H_2O \tag{18}$$
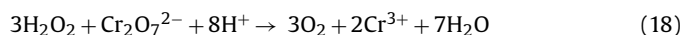
Control experiment without PBB present in the solution also supports the above assumption. TOC changes during the PBB degradation are shown in Fig. 9b. From therein, it can be seen that the
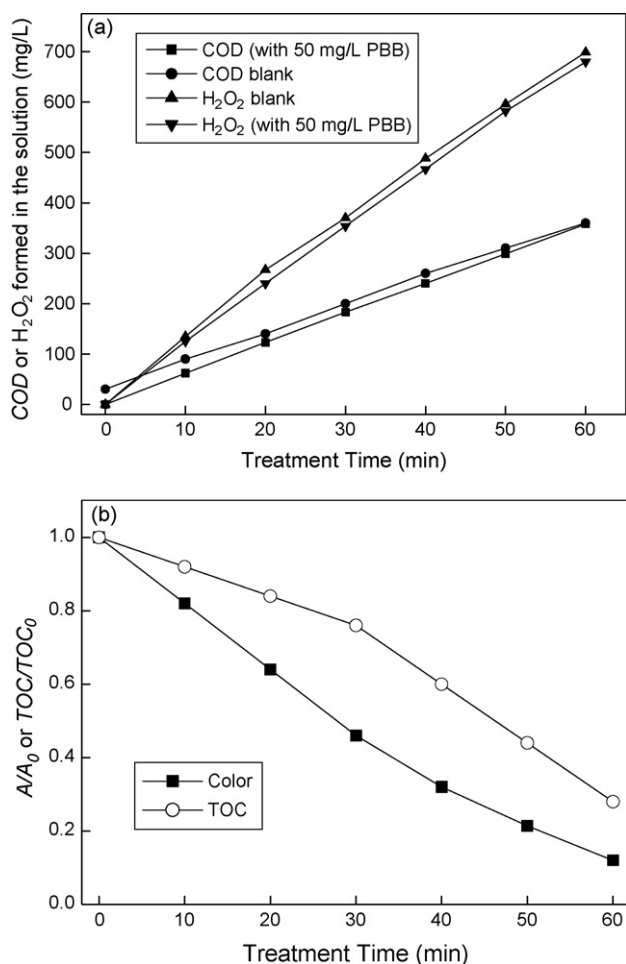
Fig. 9. COD variation and H_2O_2 formation (a) and TOC changes and (b) during CGDE treatment (voltage 500 V, current 100 mA, solution volume 150 mL, electrolyte Na_2SO_4, initial conductivity 6.4 mS/cm, pH_0 3.0, $[PBB]_0$ 50 mg/L).

TOC of the solution gradually reduced with the treatment time. However, the reduction rate of TOC is lower than the PBB discoloration rate. This indicated that there are some intermediate products present in the solution.

4. Conclusions

The following conclusions can be drawn from the present study: PBB can be efficiently decolorized by CGDE. The PBB discoloration proceeded faster in chloride solution than in phosphate or sulfate solutions. The applied voltage did not have appreciable influence on the discoloration in the range of 450–550 V. The discoloration did not comply with the first-order reaction kinetics in inert solutions. Ferrous and ferric ions enhanced the discoloration. During the treatment, TOC of the solution smoothly decreased whereas COD of the solution gradually increased because H_2O_2 was produced during the treatment.

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