



Applicability of boron-doped diamond electrode to the degradation of chloride-mediated and chloride-free wastewaters

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ABSTRACT

The electrochemical degradation of chloride-mediated and chloride-free dye wastewaters was investigated on a boron-doped diamond (BDD) electrode in comparison with that on a dimensionally stable anode (DSA), and the applicability of BDD electrode to the degradation of these two kinds of wastewaters was explored. In chloride-free wastewater, the electrochemical degradation efficiency of dye on BDD electrode was much higher than that on DSA, with a chemical oxygen demand (COD) removal of 100% and 26% for BDD and DSA, respectively. In chloride-mediated dye wastewater, COD removal was faster than that in chloride-free wastewater on both BDD and DSA electrodes with COD removal efficiencies higher than 95%, whereas the rate of COD removal on DSA was faster than that on BDD electrode. The investigation indicates that DSA is more suitable than BDD electrode in degradation of originally chloride contained dye wastewaters for the sake of energy and time saving. However, for chloride-free dye wastewaters, with the aim of environmental protection, BDD electrode is more appropriate to realize complete mineralization. At the same time, the secondary pollution can be avoided.

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1. Introduction

Electrochemical oxidation techniques have been applied to the treatment of effluents from industrial plants. These techniques have various advantages, for instance, easy control, mild operation conditions, amenability to automation, environmental compatibility, high efficiency, and low cost [1–4]. As a high performance material with many excellent electrochemical features as wide potential, low background current, high oxygen evolution potential, and stable dimension and mechanical properties, boron-doped diamond (BDD) electrode has been arousing a lot of research interests, and is extensively used to electrochemical degradation of organic pollutants. Many of the biorefractory pollutants were decontaminated completely using BDD electrode [5–8]. The electrochemical oxidations for naphthalenesulfonates [9], sodium dodecylbenzenesulfonate, and hexadecyltrimethyl ammonium chloride [10] were studied, and these surfactants were mineralized completely. Alizarin red, eriochrome black T [11], indigo carmine [6], and other dye wastewaters [12,13] were degraded by BDD electrode, and the chemical oxygen demand (COD) removal efficiency was higher than 95%. Highly toxic herbicide or pesticide, such

as 4-chloro-2-methylphenoxyacetic acid, 2-(4-chlorophenoxy)-2-methylpropionic acid, 2-(4-chloro-2-methylphenoxy)propionic acid [14], diuron, and 3,4-dichloroaniline [5], were also mineralized completely by BDD electrode.

Electrochemical methods for wastewater treatment mainly involve the direct and indirect electrochemical oxidation. The direct electrolysis is a process that organic pollutants are directly oxidized on the anode electrochemically with no intermediates. By indirect electrolysis, organic pollutants can be degraded by generating in situ strong oxidative intermediates that convert these pollutants into less hazardous products. The main oxidizing agent is active chlorine compounds, such as gaseous chlorine, hypochlorous acid, and hypochlorite ions, which are anodically produced from original chlorides present in the wastewater [15]. The active chlorine compounds can electrochemically oxidize organic molecules quickly. This process is irreversible due to the intense oxidative activity of active chlorine compounds. It is obvious that a much faster COD removal will be obtained by indirect oxidation owing to strong oxidative chlorine compounds formed during electrolysis. However, gaseous chlorine, hypochlorous acid, and hypochlorite ions produced during the indirect electrolysis are highly toxic and caustic. Moreover, gaseous chlorine can be easily interacted with organic molecules and form carcinogenic, mutagenic, and teratogenic halogen compounds. Therefore, we hope that pollutants can be mineralized during the direct oxidations in solutions without the formation of active chlorine compounds to avoid this secondary pollution.

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As far as is known, the efficiency of electrochemical oxidation is pertinent to electrode materials and supporting medium, and some studies have been performed in wastewaters containing low concentration of organic pollutants [15,16]. The experimental results have indicated that the efficiency of electrochemical oxidation in chloride-mediated wastewaters is higher than that in chloride-free wastewaters for most of electrodes. However, whether BDD electrode can present its electrochemical excellence over other electrode materials under various conditions is rarely reported.

The color and low light transmissivity of high concentration dye wastewater restrain a possible application of photocatalytic decomposition. Therefore, in this work, a study on the electrochemical oxidation behavior and degradation process of a synthetic solution containing high concentration methylene blue (MB), a dye widely used in many fields, in supporting electrolytes with and without chloride ions will be conducted on BDD electrode. And the comparative research of electrochemical degradation efficiency on BDD electrode and a dimensionally stable anode (DSA) will be performed to assess the applicability of BDD to degrade a dye in chloride containing and chloride-free model wastewater.

2. Experimental

2.1. Chemicals and materials

All chemicals used in the experiments were of analytical pure grade and used without further purification. The concentration of MB in wastewater for these experiments was 1000 mg/L with a corresponding COD value of 1371 mg/L. 0.05 mol/L Na_2SO_4 solution was used as supporting electrolyte, and NaOH or H_2SO_4 in proper amounts was used to get suitable pH value.

BDD electrode was deposited on Si wafers by microwave plasma chemical vapor deposition (MWCVD) [17]. DSA electrodes were made of a titanium base covered by metal oxides (iridium and ruthenium oxides in our case).

2.2. Electrolytic system

Galvanostatic electrolyses with imposed current density of 20 mA cm^{-2} were performed in an undivided three-electrode cell. 50 ml solution was degraded in each experiment and stirred at constant temperature (25°C). The anode was a square plate of BDD electrode or DSA with effective surface area of 5 cm^2 , whereas the cathode was a Ti square plate of 5 cm^2 , and the gap between electrodes was 10 mm. A saturated calomel electrode (SCE) was used as reference.

2.3. Analytical procedure

The electrochemical behavior of wastewater was studied using CHI660A electrochemical working station (CHI, USA) by linear sweep voltammetry (LSV) using a conventional three-electrode cell at 25°C . The working electrode was a BDD electrode or DSA, the counter electrode was a Pt wire, and the reference electrode was SCE. LSV was performed with unstirred solutions at scan rates (v) of 100 mV s^{-1} . All potentials are referred vs. SCE unless otherwise stated.

The UV–vis spectra of dye were recorded in 200–800 nm range using a UV–vis spectrophotometer (Agilent 8453) with a spectrometric quartz cell (1 cm path length).

COD of the same solutions was monitored by dichromate titrimetric method as described in standard methods.

3. Results and discussion

3.1. Electrochemical oxidation behavior of dye wastewater on BDD electrode

The electrochemical oxidation behavior of MB during the electrochemical degradation on BDD was studied; and the results obtained in electrolytes with and without Cl^- are shown in Figs. 1 and 2, respectively. Three oxidation peaks at 0, +0.25, and +1.46 V are observed in both Cl^- -mediated and Cl^- -free wastewaters before electrochemical degradation, which indicates a multistep oxidation process of MB on BDD. Thus, MB can be electrochemically degraded on BDD under both conditions. The dependence of oxidation current on degradation time at peak potential is shown in Figs. 1B and 2B. It can be observed that the oxidation peak at 0 and +0.25 V decreases quickly with the electrolysis time, whereas the oxidation peak at +1.46 V decreases more slowly. The largest difference between the direct electrolysis and indirect electrolysis is proved by the different electrochemical behavior of oxidation peak at +0.85 V. No oxidation peaks is observed at +0.85 V before degradation. There is still no oxidation peak at +0.85 V during direct electrolysis. Although the current at +0.85 V increases at first and then decreases, it maintains at low value during electrolysis. However, the oxidation peak is observed at +0.85 V and reaches the highest value in 30 min during indirect electrolysis. As the electrolysis time increases, the peak current decreases gradually. It may be assumed that some electroactive chlorine compound is formed during the indirect electrolysis. Further, the concentration of chloride ions in wastewater solutions decreased gradually, and then the

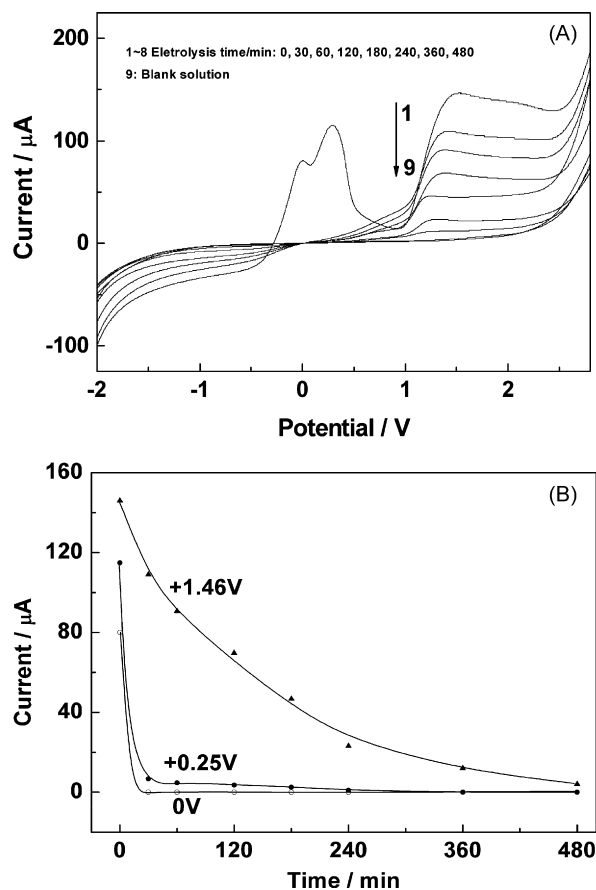


Fig. 1. (A) Linear sweep voltammogram of MB in electrolytes without chloride on BDD during electrolysis; (B) dependence of oxidation current at 0, +0.25, and +1.46 V on electrolysis time.

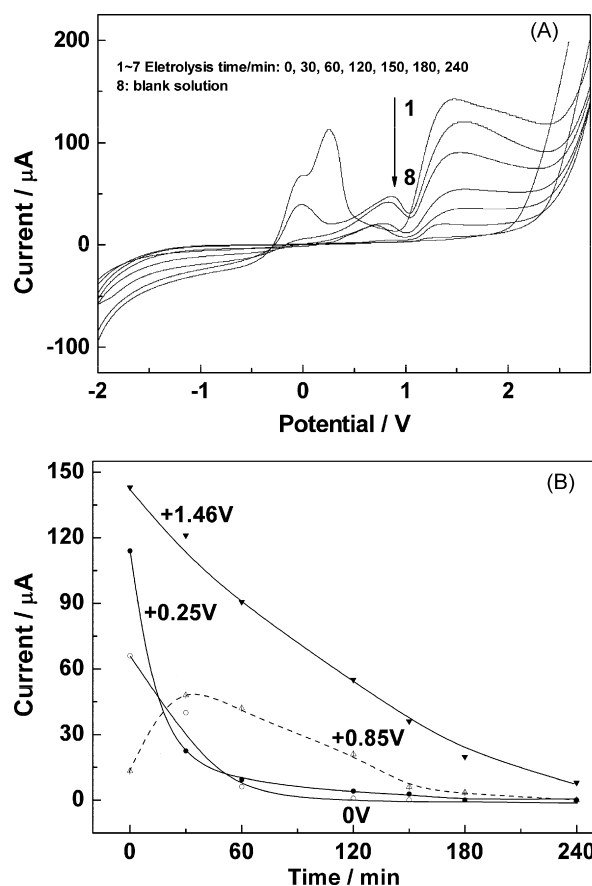


Fig. 2. (A) Linear sweep voltammogram of MB in chloride-mediated electrolytes on BDD during electrolysis; (B) dependence of oxidation current at 0, +0.25, +0.85, and +1.46 V on electrolysis time.

intermediate decayed completely. The chlorine compound was not formed during the direct electrolysis.

For the concentrated MB wastewater, the oxidation peaks on BDD disappeared completely after 8 h of electrolysis, indicating that MB and electroactive intermediates can be degraded on BDD electrode.

The effect of pH on the electrochemical degradation of MB on BDD was also investigated. The dependence of COD value and cell potential on pH in electrochemical degradation is shown in Fig. 3. Lissens et al. [10] confirmed that the initial electrolyte pH had great effect on the electrochemical oxidation of organic pollutants. However, as can be observed in Fig. 3A, during the galvanostatic electrolysis of MB, there is no considerable effect of initial pH on degradation of MB and the cell potential when the initial electrolyte pH is ranged from 2 to 12; only small fluctuations of that can be detected within certain ranges. As is known to us, for most organic compounds, their redox potentials will be greatly affected by the variation of electrolyte pH value. Usually, the oxidation potential in acidic medium is higher than that in alkaline medium. Therefore, the electrochemical oxidation degradation of most pollutants will be influenced by the change of the initial electrolyte pH value. However, as from the linear voltammograms of MB obtained in electrolytes of pH 4, 8, and 10 (Fig. 3C), we can see that there is nearly no dependence between the number and the shape of the oxidation peaks for MB and the pH value of electrolyte. Few changes occur to both the oxidation peak potential and current with the change of the acidity of electrolyte. It indicated that the redox behavior of MB is not easily affected by the electrolyte pH value. The reason may be that MB is a kind of conjugated azo compounds containing

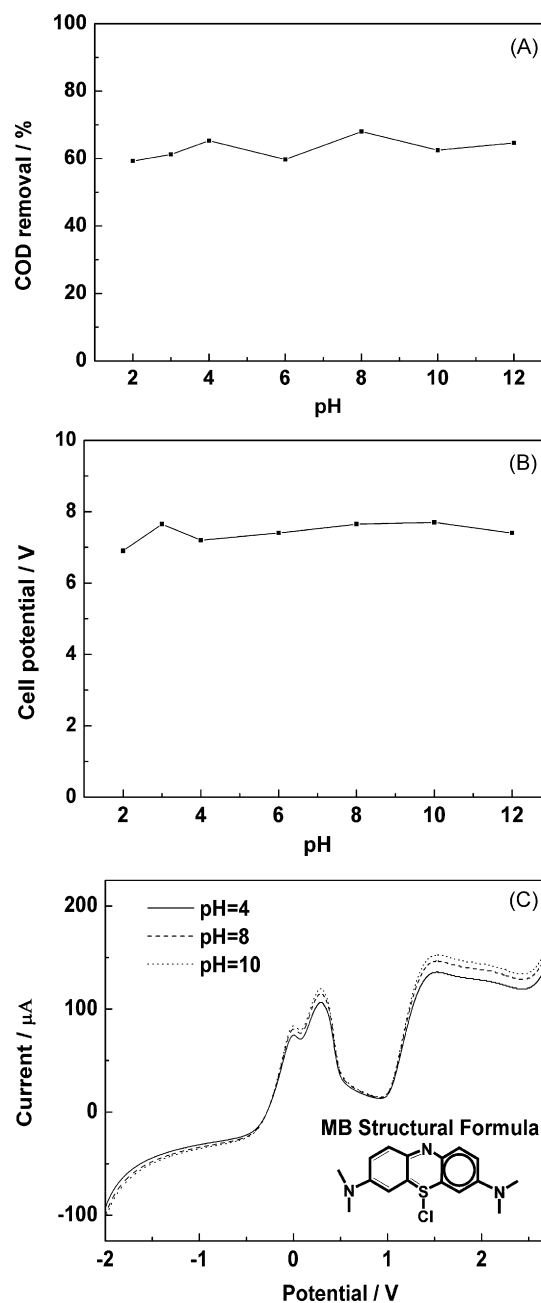


Fig. 3. Effect of initial electrolyte pH on (A) COD removal (after 2 h electrochemical degradation) and (B) cell potential (in chloride-free wastewaters), and (C) the linear voltammograms of MB obtained on BDD electrode in electrolytes of pH 4, 8, and 10.

benzene ring (see the structural formula of MB in Fig. 3C). This may be the same reason which leads to little dependence between electrochemical oxidation of MB and the pH value of the medium. It means that the initial pH has no appreciable effect on electrolysis energy consumption. Therefore, lower cost and higher efficiency may be obtained simultaneously since the adjustment for pH is not required in practical applications. In the following investigation, aqueous solutions of Na_2SO_4 and NaCl are selected as supporting electrolytes.

3.2. Inspection of MB degradation process on BDD electrode

As the spectral features of MB are very manifest, UV-vis spectral analysis was used to monitor the electrochemical degradation

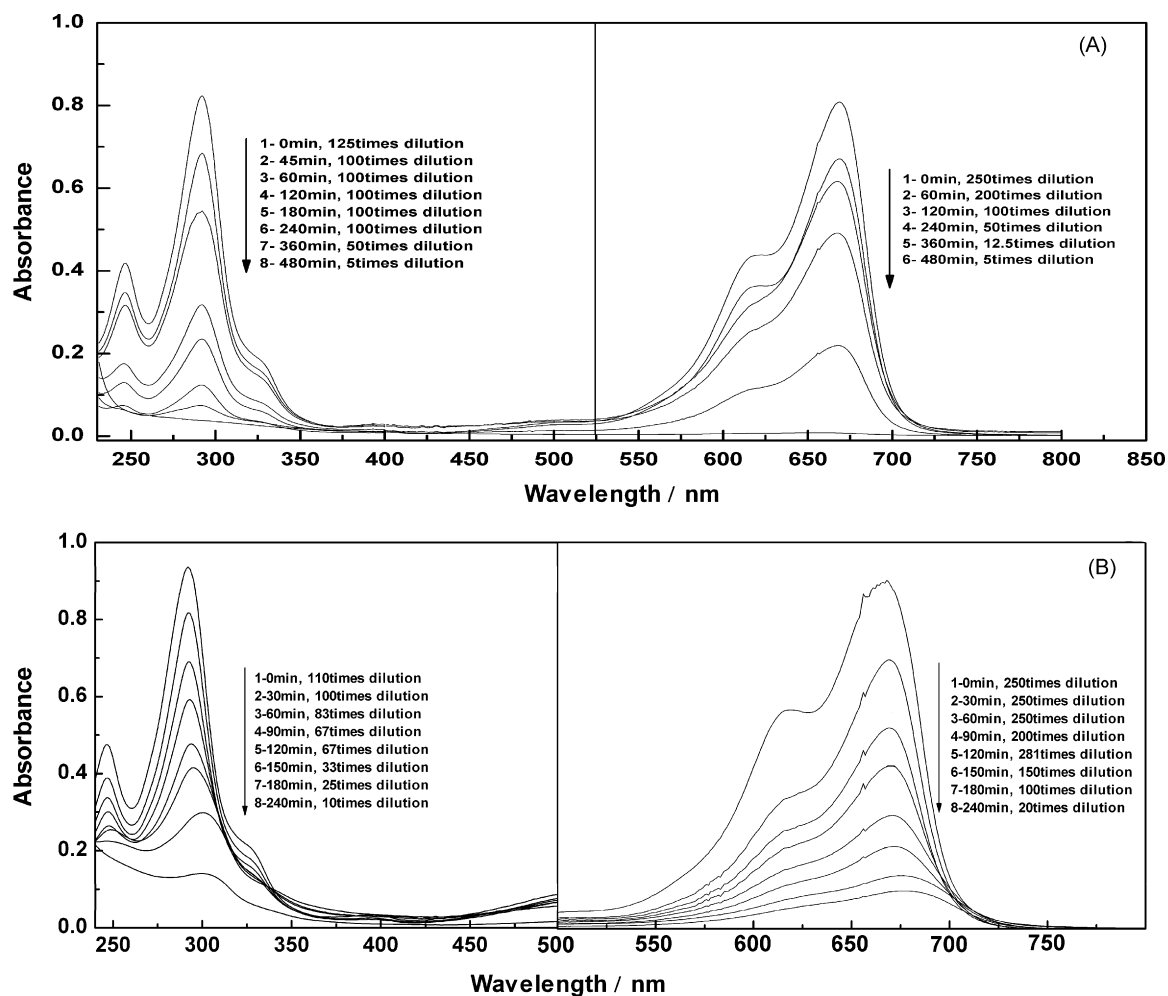


Fig. 4. UV-vis absorbance in the degradation process of MB wastewater without chloride (A) and with chloride ions (B).

process of MB wastewaters. A typical UV-vis spectral of MB as a function of electrolysis time was investigated (Fig. 4). The peak at 246 and 292 nm are assigned to aromatic rings and other unsaturated groups in dye molecules. The peak at 670 nm is attributed to electron transition of hyperconjugation formed by aromatic ring and hetero ring. These three absorbance peaks decrease significantly after the direct and indirect electrolysis on BDD, so we may conclude that the conjugated and unsaturated bonds in MB are destroyed, and the molecules are broken into small ones under both conditions.

From Fig. 4, a linear relationship between $\ln A_0/A$ and electrolysis time (t) is obtained, indicating that the color removal process of MB is a pseudo first order reaction. As shown in Table 1, during the direct electrolysis, the kinetic rate constants of color removal are 0.01045, 0.00895, and 0.00863 min^{-1} at the wavelength of 670, 290, and 246 nm, respectively. In indirect electrolysis, they are 0.01347, 0.01251, and 0.01092 min^{-1} at corresponding

wave length. It is observed that the color removal rate for indirect electrolysis is slightly higher than that for direct electrolysis. The rate constants of the color removal process at 670, 290, and 246 nm are close to each other in both chloride-free and chloride-mediated wastewaters. It suggests that color removal of MB is a process in which bond dissociation of the conjugated and unsaturated bonds in MB occurs simultaneously, rather than the process in which some functional groups are oxidized faster than others.

Combined with the electrochemical behavior, the above results indicate that some electroactive compound is formed during the indirect electrolysis in comparison with direct electrolysis, although this electroactive compound has no obvious spectral absorbance.

3.3. Comparative study of electrochemical degradation efficiency on BDD and DSA electrode

Fig. 5A shows the decay of COD value for chloride-free MB wastewaters. It is seen that high concentration MB with COD value of 1371 mg L^{-1} is easily decomposed on BDD surface, so that the dye wastewater is oxidized completely. The COD approaches to zero as the electrolysis time increases to 8 h, and the COD removal efficiency is almost 100%. However, the COD removal of dye wastewater only reaches 26% on DSA electrode and does not change anymore afterwards. The relationship between current efficiency for elec-

Table 1

Color removal rate constant (min^{-1}) on BDD electrode at the early stage of electrolysis

Wavelength (nm)	Chloride-free wastewaters	Chloride-mediated wastewaters
670	0.01045	0.01347
290	0.00895	0.01251
246	0.00863	0.01092

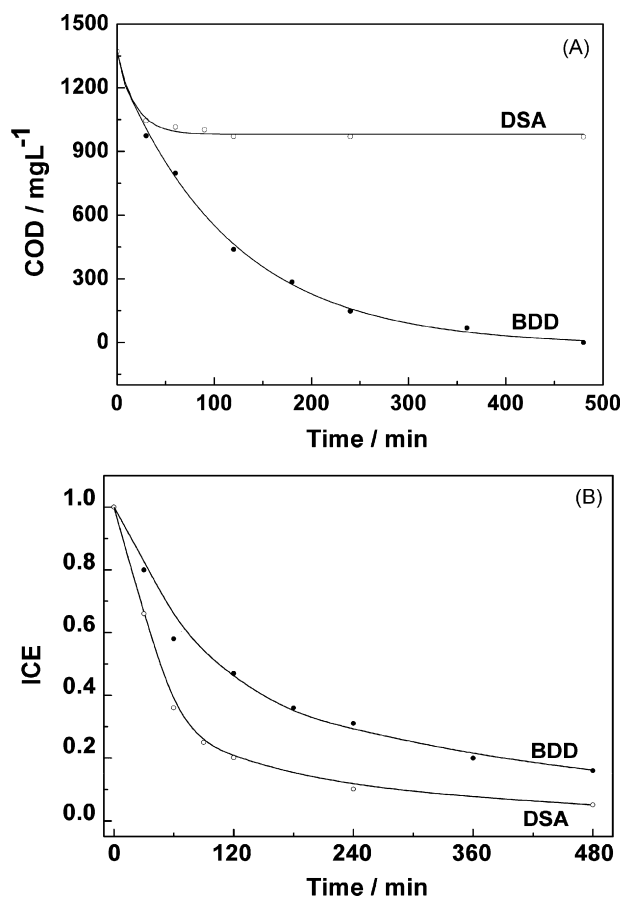


Fig. 5. COD (A) and ICE (B) in MB degradation in chloride-free wastewater.

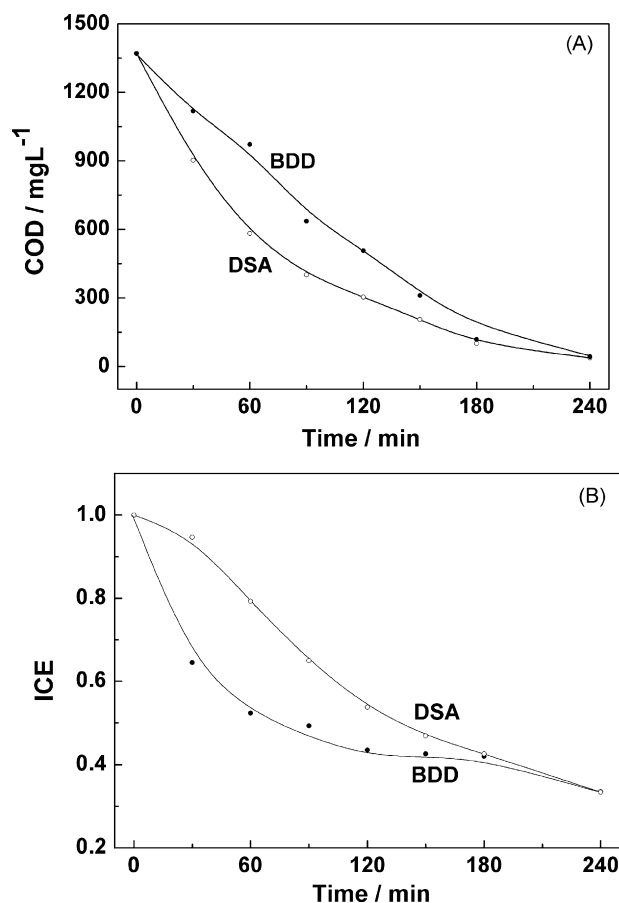


Fig. 6. COD (A) and ICE (B) in MB degradation in chloride-mediated wastewater.

trochemical degradation of MB and electrolysis time is obtained by the following formula:

$$\text{ICE} = FV \frac{[(\text{COD})_t - (\text{COD})_{t+\Delta t}]}{8I \Delta t} \quad (1)$$

where ICE is the instantaneous current efficiency, which is the current efficiency measured at a particular time or at constant time intervals during the electrochemical treatment of wastewater. $(\text{COD})_t$ and $(\text{COD})_{t+\Delta t}$ are the COD values at electrolysis times t and $t + \Delta t$ ($\text{gO}_2 \text{ dm}^{-3}$), respectively, I is the applied current (A), F is the Faraday constant ($96,487 \text{ C mol}^{-1}$), and V is the volume of electrolyte (dm^3). Thus the variation of ICE during the degradation of chloride-free MB wastewaters can be obtained (Fig. 5B).

From Fig. 5B, it is observed that the current efficiency on BDD is much higher than that on DSA electrode. When the electrochemical treatment time was extended to 120 min, ICE on BDD electrode is 0.467, more than two times of that on DSA, 0.212. The phenomena appeared in Fig. 5 indicates that DSA is unsuitable to the direct electrochemical degradation of MB while BDD electrode shows high direct electrolysis efficiency for MB wastewater and can mineralize it completely.

The comparative study of electrochemical degradation for MB in chloride-mediated wastewaters was also performed on BDD and DSA electrodes, respectively, by measuring the decay of COD (Fig. 6A). It is observed that a faster degradation could be obtained on DSA instead of on BDD electrode. The COD removal of MB on BDD is only of 54% while that on DSA electrode reaches 71% for 90 min treatment of wastewater; the COD removal on DSA is 1.3 times higher than that on BDD. The COD removal reaches 95% on both anodes as electrolysis time increases to 240 min. Fig. 6B shows

the evolution of the corresponding ICE value with electrolysis time. Here we see that ICE on DSA is always higher than that on BDD during the whole degradation time, especially the initiatory period of the degradation. For example, ICE on DSA is 0.795 on the degradation time of 60 min. It is much higher than that of 0.526 on BDD. Thus, for the degradation of chloride containing wastewaters, DSA is more favorable than BDD.

The results in Fig. 6 indicate that MB dye wastewater can be decomposed completely on both BDD and DSA electrodes in electrolytes containing chloride, with the COD removal rate higher than 95%. Moreover, by comparing Figs. 5 and 6, it can be seen that the speed of MB degradation in chloride-mediated wastewaters is significantly higher than that in chloride-free wastewaters. To reach 95% of COD removal rate in chloride-mediated wastewaters on BDD electrode or DSA takes only 240 min, while that in chloride-free wastewaters on BDD will spend more than 400 min. This indicates that the degradation of MB will be time and energy saving through the addition of chloride into supporting electrolytes.

From the above-mentioned results, it is seen that the electrochemical degradation efficiency of MB on BDD is much higher than that on DSA in chloride-free wastewaters. In chloride-mediated wastewaters, a faster degradation process occurs on DSA in comparison to BDD. To make this clear, the chlorine and oxygen evolution potential on BDD and DSA electrodes were measured by LSV in electrolytes with and without chloride ions. The experimental results show that the chlorine and oxygen evolution potential on BDD electrode are of 1.9 and 2.4 V, while that on DSA are of 1.0 and 1.2 V, respectively. It demonstrates that both chlorine and oxygen evolution potential on BDD are much higher than that on DSA. It is known that a lower oxygen evolution potential on anodes decreases

the current efficiency of electrochemical degradation and increases the energy consumption due to byproducts, oxygen being produced easily. The high oxygen evolution potential on BDD prevents the side reaction of oxygen evolution, and greatly improves the current efficiency. In Cl^- -free wastewaters, the degradation efficiency on BDD is therefore much higher than that on DSA. On the other hand, in Cl^- -mediated wastewater the high chlorine evolution potential may cause the difficulty in the formation of active chlorine from wastewater and decrease the rate of electrochemical degradation of organic compounds, leading to a slower electrochemical degradation process on BDD. The lower chlorine evolution potential of 1.0 V on DSA probably makes the formation of active chlorine on DSA surface much easier, so that the oxidation rate of MB on DSA is greatly higher than that on BDD due to the strong oxidative feature of active chlorine. As the electrolysis takes place, the concentration of chloride in electrolyte decreases gradually, and the amount of active chlorine on electrode surface decreases, so that the rate of electrochemical decontamination of wastewater is lowered. However, this electrochemical treatment of chloride containing wastewater will introduce strong toxic halogen compounds, and requires a second step to remove this chlorinated organic compound, e.g. by adsorption on activated carbon [18]. In view of a concern for environmental protection, the strongpoint of BDD, the high oxygen evolution potential and low chlorine evolution potential, will make it take precedence over other electrodes in the degradation of chloride-free dye wastewater.

Therefore, in practical applications, the degradation of chloride-free wastewaters, especially the degradation of that in water supply and drainage system, should be performed on BDD electrode rather than DSA for the sake of environmental protection in spite of high energy and time consuming. However, for effluents from industries and domestic sewage, which originally containing Cl^- ions, its electrochemically degradation should be carried out on DSA, because the required energy may be higher and the rate may be lower by using BDD.

4. Conclusions

The electrochemical degradation of high concentration MB in chloride-mediated and chloride-free wastewater at a BDD electrode was investigated in comparison with that on DSA. In chloride-free wastewater, the electrochemical degradation efficiency of dye on BDD electrode was much greater than that on DSA with a COD removal of 100% and 26% on BDD and DSA, respectively, and the degradation cost and electrolysis time on BDD electrode is much lower than that on DSA. In chloride-mediated dye wastewater, a faster COD removal than that in chloride-free wastewater could be obtained on both BDD electrode and DSA with COD removal efficiencies higher than 95%, with the rate of COD removal on DSA higher than that on BDD electrode ascribed by a lower chlorine evolution potential of 1.0 V on DSA. The degradation of chloride-mediated dye wastewater on DSA can be time and cost saving. However, this electrochemical treatment of chloride containing wastewater requires a second step to remove toxic chlorinated organic compounds.

The research in this work indicates that originally chloride-mediated dye wastewaters could be degraded quickly using DSA for the sake of energy and time saving. For dye wastewaters without chloride, it can be electrolyzed directly on BDD to realize complete mineralization for environmental protection and avoidance of secondary pollution.

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