



Destination of organic pollutants during electrochemical oxidation of biologically-pretreated dye wastewater using boron-doped diamond anode

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ABSTRACT

Electrochemical oxidation of biologically-pretreated dye wastewater was performed in a boron-doped diamond (BDD) anode system. After electrolysis of 12 h, the COD was decreased from 532 to 99 mg L⁻¹ (<100 mg L⁻¹, the National Discharge Standard of China). More importantly, the destination of organic pollutants during electrochemical oxidation process was carefully investigated by molecular weight distribution measurement, resin fractionation, ultraviolet-visible spectroscopy, HPLC and GC-MS analysis, and toxicity test. As results, most organic pollutants were completely removed by electrochemical oxidation and the rest was primarily degraded to simpler compounds (e.g., carboxylic acids and short-chain alkanes) with less toxicity, which demonstrated that electrochemical oxidation of biologically-pretreated dye wastewater with BDD anode was very effective and safe. Especially, the performance of BDD anode system in degradation of large molecular organics such as humic substances makes it very promising in practical applications as an advanced treatment of biologically-pretreated wastewaters.

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1. Introduction

Dyes are organic colorants extensively used in textile, cosmetic, pharmaceutical, food and other industries for imparting colors [1]. Global annual production of dyes is estimated at more than 7×10^5 tons [2]. The dye manufacturers release a large number of wastewaters containing lost dyes, dissolved inorganic salts and organics washed out from the materials. In China, above 1.6×10^9 m³ of dye wastewater are generated annually [3]. The discharge without meeting required standard would result in deterioration of soil and water resources.

However, dye wastewaters are usually difficult to be treated to meet the National Discharge Standard of China (COD < 100 mg L⁻¹) only by biological processes [4–6]. Thus, some physicochemical methods (e.g., coagulation, adsorption, chemical oxidation and ultrafiltration) have been examined as advanced treatment, but they are found to be ineffectual due to inherent disadvantages in terms of efficiency, cost, regeneration, or secondary pollution [7–10].

Electrochemical oxidation systems have been proved to be very effective to treat bio-refractory organic wastewaters, of which boron-doped diamond (BDD) anode system is of particular use because of its robust oxidation capacity, high current efficiency, strong corrosion stability, long service life and weak electrode foul-

ing [11–15]. Most organic pollutants in landfill leachate [16,17], olive oil mill waste [18] and coking wastewater [19] could be completely removed using the BDD anode system. Hitherto, few studies have been reported on electrochemical oxidation of a real dye wastewater using BDD anode.

Real wastewater treatment is intricate owing to complex compositions of various organic pollutants and inorganic salts. During electrochemical oxidation, part of organics may be completely mineralized to CO₂, while some may be degraded to other organic compounds with higher or lower toxicity [20–24]. Therefore, investigation on the evolution of organic pollutants is of significance to deeper understanding of electrochemical oxidation process. However, few studies were focused on changes of organic compounds in a real wastewater during electrochemical oxidation. In this study, electrochemical oxidation of biologically-pretreated dye wastewater was performed in a BDD anode system with particular attention to the destination of organic pollutants.

2. Materials and methods

2.1. Bulk electrolysis

Electrochemical oxidation of dye wastewater was performed in a BDD anode reactor under galvanostatic condition (20 mA cm⁻²). The anode was the Nb/BDD electrode with a working area of 2904 cm², which was bought from CONDIAS GmbH, Germany. A piece of stainless steel with the same size was used as the cathode. The gap between electrodes was set to be 1.55 cm. Details about

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Table 1
Characteristics of dye wastewater used in this study.

Parameter	Unit	Value
Chemical oxygen demand, COD	mg L ⁻¹	532
Total organic carbon, TOC	mg L ⁻¹	138
Biochemical oxygen demand, BOD ₅	mg L ⁻¹	80
pH		7.76
Color	Dilution times	200
Sulfate	mg L ⁻¹	1940
Chloride	mg L ⁻¹	3000
Salinity	mg L ⁻¹	6146
Conductivity	mS cm ⁻¹	5.53

this electrochemical system and its optimization are referred to our previous study [25]. Dye wastewater was stored in a tank of 30 L volume and circulated through the electrochemical reactor at a flow rate of 4 L min⁻¹ by a peristaltic pump. At various intervals, samples were withdrawn from the tank for chemical analysis.

The dye wastewater was collected from a dye manufactory in Henan Province of China, which mainly produce 4,4'-diaminostilbene-2,2'-disulfonic acid (DSD acid, CAS No: 81-11-8, Formula: C₁₄H₁₄N₂O₆S₂, Molecular weight: 370.4). A process composed of pretreatment (zero-valent iron and coagulation) and UASB (up-flow anaerobic sludge blanket) has been applied to treat this wastewater on site. The COD was decreased about from 7000 mg L⁻¹ to 532 mg L⁻¹, but it is difficult to be further effectively reduced by following biological and chemical processes. Therefore, the dye wastewater used in this study was the effluent of the "pretreatment + UASB" process. The characteristics of the dye wastewater are shown in Table 1. Note that no DSD acid is detected in the dye wastewater, which might be that it has been degraded by "pretreatment + UASB" process.

2.2. Analytical methods

Chemical oxygen demand (COD) was measured by titrimetric method using dichromate as the oxidant in acidic solution at 150 °C for 2 h (Hach, USA). Total organic carbon (TOC) was monitored using multi TOC/TN analyzer (Analytik Jena AG, Germany). Biochemical oxygen demand (BOD₅) was determined by the respirometric method using OxiTop IS 6 respirometer system (WTW, Germany). The pH and conductivity were detected with the pH-201 pH meter (Hanna, Italy) and the DDS-307 conductivity meter (Leici, China), respectively. Color was monitored by dilution method. Sulfate was measured by precipitation analysis with barium chloride. Chloride was detected by titrimetric method using silver nitrate. Salinity was determined by gravimetric method.

Molecular weight distribution (MWD) was analyzed by membrane separation method [26,27]. A pressure of 0.2 MPa was provided by a steady supply of highly pure N₂ (99.999%). The sample was first filtered through the 0.45 μm cellulose acetate membrane and then through different polyethersulfone ultrafiltration membranes with a molecular weight cut-off (MWCO) of 3000–30,000 Da. The membranes were steeped and washed with deionized water before use.

The fractionation procedure of humic acid (HA), fulvic acid (FA) and hydrophilic (HyI) compounds by XAD-8 resin were used similarly to the other researches [28–30]. First, the sample was filtered by the 0.45 μm cellulose acetate membrane. Then, the filtered solution (COD₁) was acidified to pH 2 and precipitated for 24 h. Finally, the supernatant liquor (COD₂) was slowly pumped through the Amberlite XAD-8 resin. The COD of the permeated solution was COD₃. According to the procedure, different COD values for the fractions of HA, FA and HyI could be calculated as follows: COD_{HA} = COD₁ – COD₂, COD_{FA} = COD₂ – COD₃, COD_{HyI} = COD₃.

Ultraviolet–visible absorption spectra were recorded using a SPECORD200 spectrophotometer. The samples were diluted by 42 times.

Agilent HP1100 HPLC was used to identify the organic compounds with a ZORBAX SB-C18 column and a diode array detector. The composition of the mobile phase was 99% 10 mM KH₂PO₄ (pH 2.75 adjusted by H₃PO₄) and 1% acetonitrile. The flow rate was 0.8 mL min⁻¹. The UV detector was set at 210 nm.

Agilent 6890N/5973 GC–MS was used for the analysis of organic compounds after liquid–liquid extraction pretreatment using CH₂Cl₂ [27,31]. The extraction procedures were conducted using a 250 mL sample under acidic, neutral and alkaline conditions. Then, 1 mL pretreated sample was analyzed by the GC–MS system. Pure He gas (99.999%) was employed as the carrier gas at a flow rate of 1 mL min⁻¹. A DB-35MS capillary column was adopted in the separation system. The temperature in the oven was maintained at 280 °C. The temperature control program was as follows: 40 °C was maintained for 3 min and then increased to 280 °C at a rate of 3 °C min⁻¹. The electron energy and the electron double voltage were set at 70 eV and 1400 V, respectively. Organic compound analysis was undertaken with reference to the NIST02 mass spectral library database.

2.3. Toxicity test

The whole acute toxicity of dye wastewater including toxic organic and inorganic pollutants was assessed by growth inhibition test using the luminescent bacteria *Photobacterium phosphoreum* (T3 spp.) [19,32,33]. The difference in luminescence intensities of tested samples (diluted by 25 times) and reference with 10 μL *P. phosphoreum* suspension at 15 min exposure was determined by a photometer (DXY-2), which was used to calculate the inhibition ratio of luminescence (R_I) by:

$$R_I = 1 - \frac{L_S}{L_R} \quad (1)$$

where L_S and L_R are the luminescence intensities of the sample and the reference (DI water), respectively. Before determination, NaCl was added into each water sample or reference to a 3% concentration (w/w) to keep the ionic strength consistent with that of the nutrient medium.

3. Results and discussion

3.1. General change of organic pollutants

Fig. 1 shows the evolution of color, COD and TOC as a function of electrolysis time during electrochemical oxidation of dye wastewater. They all followed the pseudo-first-order kinetics with high correlation coefficient ($R^2 > 0.9$). The apparent pseudo-first-order kinetic constants for color, COD and TOC removal were 0.4220 h⁻¹, 0.1209 h⁻¹ and 0.0876 h⁻¹, respectively. The color removal was faster than the COD and TOC removals, which implied that chromophoric groups were easily damaged by electrochemical oxidation. This indicated effective decoloration ability of electrochemical oxidation, which was in agreement with other studies [34–36]. After electrolysis of 12 h, the color of wastewater almost vanished. During electrochemical oxidation process, it was observed that the dark brown dye wastewater was gradually changed to light yellow and finally colorless. The COD reduction was also very effectual. After treatment, the COD was decreased from 532 mg L⁻¹ to 99 mg L⁻¹ (<100 mg L⁻¹, the National Discharge Standard of China). The average current efficiency was 6.17% and the specific energy consumption was 199 kWh m⁻³, which was similar to some comparable literatures [18,37,38]. The TOC removal rate was slightly smaller than that of COD, which implied that a

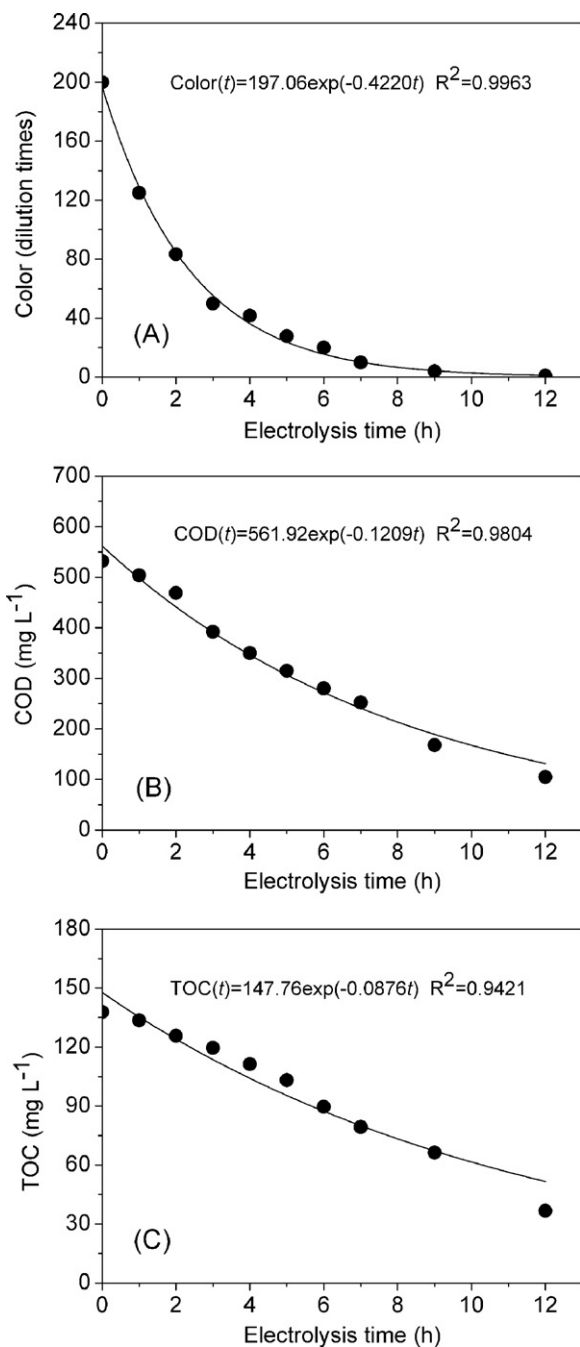


Fig. 1. Evolution of color (A), COD (B) and TOC (C) as a function of electrolysis time during electrochemical oxidation of dye wastewater using BDD anode.

small part of organic compounds was degraded to other organics rather than completely mineralized to CO_2 . The evolution of organic pollutant types during the electrochemical oxidation process will be carefully discussed in the following section.

3.2. Destination of organic pollutants

In order to investigate the destination of organic pollutants during the electrochemical process, organic pollutants in dye wastewater before and after electrochemical treatment were tried to be distinguished by molecular weight distribution (MWD) measurement, resin fractionation, ultraviolet–visible (UV–vis) spectroscopy, HPLC and GC–MS analysis.

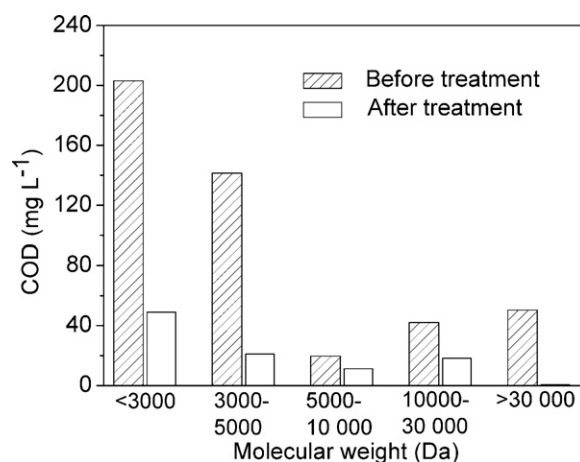


Fig. 2. Molecular weight distribution of dye wastewater in terms of COD before and after electrochemical treatment using BDD anode.

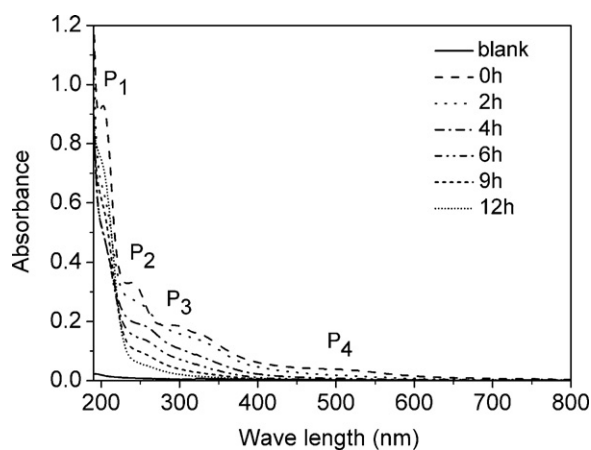


Fig. 3. UV–vis spectra of dye wastewater at different electrolysis time (0 h, 2 h, 4 h, 6 h, 9 h and 12 h) during electrochemical oxidation using BDD anode.

First, the molecular weight distribution of organic pollutants (COD) in dye wastewater before and after treatment was analyzed by membrane separation method (Fig. 2). The original dye wastewater was mainly composed of organic pollutants with molecular weight (MW) less than 5000 Da, which were significantly decreased after treatment. Moreover, it was found that the organics with MW larger than 5000 Da were also greatly degraded. Especially, the compounds (MW > 30,000 Da) were completely removed. These results demonstrated that electrochemical oxidation with BDD anode was very effective for organics degradation in real wastewater, even for the elimination of organic pollutants with very large MW.

The large MW compounds might be humic substances including humic acid (HA) and fulvic acid (FA), which were formed during foregoing biological treatment [27,29,30]. The corresponding COD concentrations of HA, FA and Hyl (hydrophilic) compounds in dye wastewater before and after treatment were distinguished by resin fractionation (Table 2). For the original dye wastewater, Hyl

Table 2

COD values for the fractions of HA, FA and Hyl in dye wastewater before and after electrochemical treatment with BDD anode.

Component	Before	After
COD_{HA} (mg L^{-1})	1.4	0
COD_{FA} (mg L^{-1})	145.6	0
COD_{Hyl} (mg L^{-1})	309.4	99.4

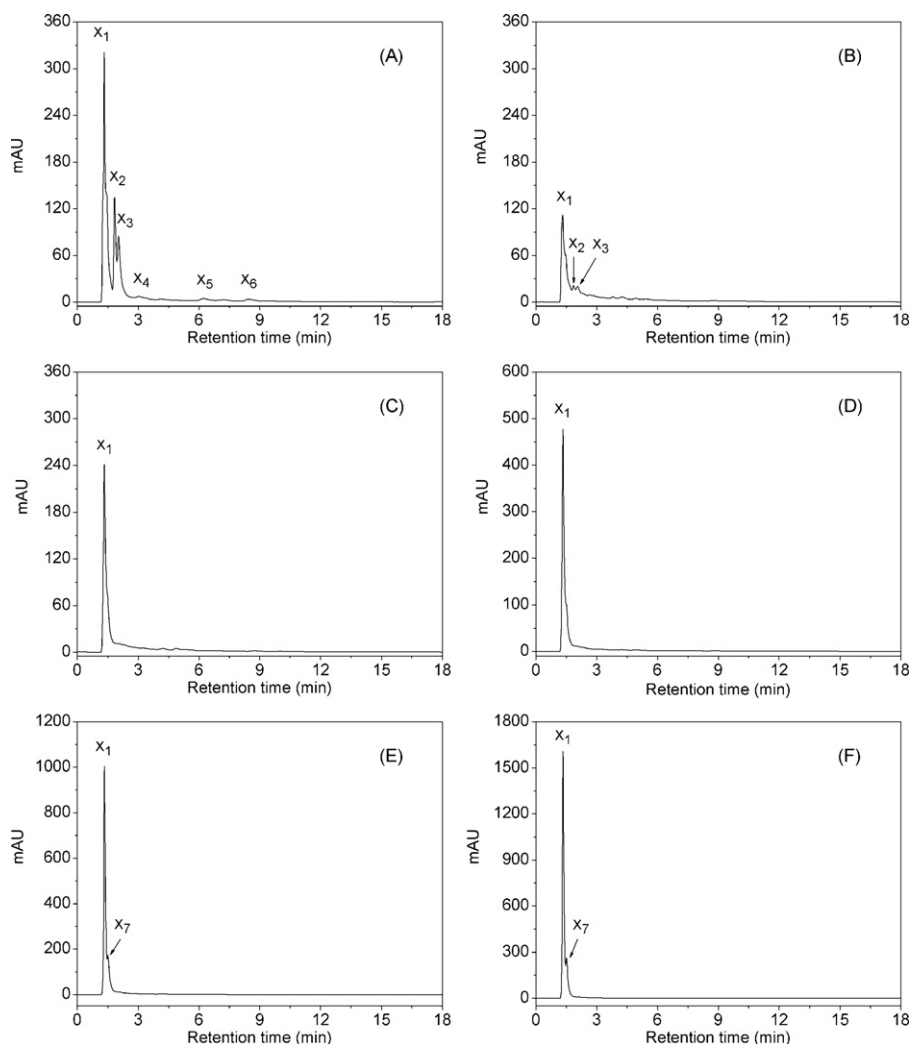


Fig. 4. HPLC chromatograms of dye wastewater during electrochemical oxidation using BDD anode at different electrolysis time: (A) 0 h, (B) 2 h, (C) 4 h, (D) 6 h, (E) 9 h, (F) 12 h. Peaks: X₁ oxalic acid, X₂ malonic acid, X₃ maleic acid, X₄ succinic acid, X₅ hydroquinone and X₆ resorcin.

compounds were the main composition (309.4 mg L^{-1}). The humic substances were chiefly fulvic acid (145.6 mg L^{-1}) only with a little of humic acid (1.4 mg L^{-1}), which was due to the higher water-solubility of fulvic acid [29,30]. After treatment, Hyl compounds were significantly decreased to 99.7 mg L^{-1} and humic substances were completely eliminated, which indicated that electrochemical oxidation using BDD anode was powerful for complex organic pollutants, such as humic substances.

Then, the hydrophilic compounds were analyzed by UV–vis spectroscopy, HPLC and GC–MS analysis. Fig. 3 shows the UV–vis spectra of dye wastewater during the electrochemical oxidation process. For the original wastewater, four absorption peaks appeared at 203 nm (P₁), 240 nm (P₂), 291 nm (P₃) and 500 nm (P₄). P₁ might be attributed to carboxylic acid, such as oxalic acid, acetic acid and butenoic acid [39]. P₂ and P₃ might correspond to aromatic compounds (e.g., nitrophenol, chlorophenol and cresol) [39,40]. P₄ might be the absorption peak of azo compounds, which resulted in the wastewater color [2,39]. As the increase of electrolysis time, P₂, P₃ and P₄ decreased and finally almost disappeared, indicating that the corresponding compounds were totally removed. P₁ first declined and then rose after electrolysis of 4 h, which might be attributed to the accumulation of carboxylic acids. Some organic pollutants might be degraded to carboxyl acids instead of complete mineralization to CO₂ [23,40,41].

Thus, HPLC was mainly used to detect the organic acids in the dye wastewater. Fig. 4 shows the HPLC chromatograms of dye wastewater at different electrolysis time. In the original wastewater, six substances were detected at 1.33 min (X₁), 1.84 min (X₂), 2.03 min (X₃), 3.01 min (X₄), 6.23 min (X₅) and 8.45 min (X₆). Their retention times were close to those of following compounds orderly: oxalic acid, malonic acid, maleic acid, succinic acid, hydroquinone and resorcin (see Supplementary data Fig. S1). Hence, it was considered that they were these organics or similar compounds. After electrolysis of 2 h, the peak areas of X₁, X₂ and X₃ significantly decreased, indicating that they were greatly degraded. The X₄, X₅ and X₆ disappeared, which implied that they were completely removed. After electrolysis of 4 h, X₂ and X₃ were finally eliminated, while the peak area of X₁ increased, which indicated the formation of X₁ during electrochemical oxidation process. After electrolysis of 6 h, the X₁ continuously rose until the end of treatment. After electrolysis of 9 h, a new substance (X₇) appeared at 1.51 min very closed to the peak of X₁, which might be formic acid of the similar retention time (see Supplementary data Fig. S1). It was obvious that part of organic pollutants were degraded to simple carboxyl acids (e.g., oxalic acid and formic acid) rather than mineralized to CO₂. Because degradation of these carboxylic acids was relative slow, accumulation of them occurred.

GC–MS was mainly used to identify the more complex organic pollutants in dye wastewater except for organic acids. The

Table 3
Main organic compounds in dye wastewater before and after electrochemical treatment with BDD anode analyzed by GC–MS.

Organic compounds	Before	After	Organic compounds	Before	After
Hexatriacontane	✓	✓	Hexadecane	✓	–
Tetratriacontane	✓	✓	10-Methylnonadecane	✓	–
Octacosane	✓	✓	Ethanone, 1-(9-anthracenyl)-	✓	–
Pentacosane	✓	✓	Octadecane	✓	–
Dodecane, 2,6,10-trimethyl-	✓	✓	Decane, 3-ethyl-3-methyl-	✓	–
Heptadecane	✓	✓	Decane, 2,3,5-trimethyl-	✓	–
Pentadecane	✓	✓	1,2-Benzenedicarboxylic acid, mono(2-ethylhexyl) ester	✓	–
Heneicosane	✓	✓	n-Hexadecanoic acid	✓	–
Heptadecane, 9-octyl-	✓	✓	Heptacosane, 1-chloro-	✓	–
Heptacosane	✓	✓	Tributyl phosphate	✓	–
Pentadecane, 8-heptyl-	✓	✓	Decane, 3-methyl-	–	✓
Docosane	✓	✓	Dodecane, 1-iodo-	–	✓
Pentatriacontane	✓	–	Octane, 2,3,6,7-tetramethyl-	–	✓
1,3,5-Triazine,	✓	–	Heptane, 4,4-dimethyl-	–	✓
2-allylamino-4,6-bis(4-morpholyl)-	–	–	Heptane, 2,4-dimethyl-	–	✓
Naphthalene,	✓	–	Trifluoroacetic acid, 4-methylpentyl ester	–	✓
1,2,3,4-tetrahydro-1-methoxy-	–	–	Decane, 2,3,6-trimethyl-	–	✓
Thiophene-2-carboxylic acid	✓	–	Cyclohexane, 1,2,4-trimethyl-	–	✓
[2-(5-methoxy-2-methyl-1H-indol-3-yl)-ethyl]-amide	–	–	1,4-Bis(trimethylsilyl)-1,3-butadiyne	–	✓
Hexane, 3,3-dimethyl-	✓	–	Hexadecane, 2-methyl-	–	✓
Heptadecane, 2,6,10,15-tetramethyl-	✓	–			
Benzoic acid,	✓	–			
3-[(1,2-dihydro-2-oxo-4-pyrimidinyl)amino]-, methyl ester	–	–			
Eicosane	✓	–			

"✓" Detected.

"–" Not detected.

analysis results were given in Table 3. The original wastewater contained many complex compounds, such as long-chain alkanes (hexatriacontane, pentatriacontane, tetratriacontane, octacosane, heptacosane, etc.), 2-allylamino-4,6-bis(4-morpholyl)-1,3,5-triazine, 1,2,3,4-tetrahydro-1-methoxy-naphthalene, thiophene-2-carboxylic acid [2-(5-methoxy-2-methyl-1H-indol-3-yl)-ethyl]-amide, and so on. Some were completely eliminated and not detected after electrochemical treatment. Some of them (generally alkanes) were partly degraded and remained a little after electrolysis of 12 h. Simultaneously, some simple organic compounds (mostly short-chain alkanes) were formed, e.g., methyl-substituted decane, octane and heptanes. These results demonstrated that most toxic and complex organic pollutants in dye wastewater were effectively removed and the compositions of dye wastewater became simpler (mainly short-chain alkanes) after electrochemical oxidation.

Although not all organic pollutants were distinguished in this study due to the limitations of used analytical methods and relatively low concentration of some organic compounds, it can still be concluded that electrochemical oxidation using BDD anode is very effective to organic pollutants degradation,

even for those with very large MW, such as humic substances, which can be completely removed. The compositions of wastewater became simpler after electrochemical treatment. Most organic pollutants were completely mineralized to CO₂, while some were degraded to simpler compounds, such as carboxyl acids and alkanes.

The strong oxidation ability of BDD anode system was attributed to the generation of free hydroxyl radicals, which are very effective to oxidize organic compounds [11,42–44]. At BDD anodes, water was decomposed to hydroxyl radicals. Due to the weak adsorption property of BDD electrodes, the produced hydroxyl radicals mainly existed as free ones. This type of hydroxyl radicals transferred to the vicinity of the electrode surface and moreover was difficult to combine with each other to produce oxygen (side reaction), and thus this type of hydroxyl radicals reacted with organic compounds effectively. Therefore, BDD anodes showed strong oxidation ability.

3.3. Toxicity of wastewater

Although the 12 h electrolysis of dye wastewater could considerably reduce COD to meet the National Discharge Standard

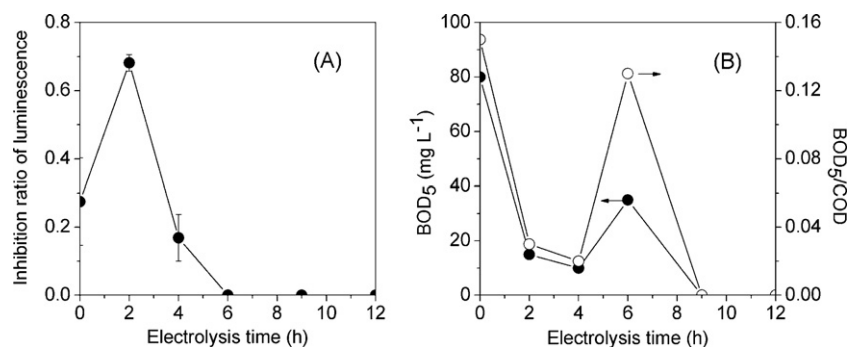


Fig. 5. Evolution of the toxicity (A), BOD₅ (B, solid symbols) and BOD₅/COD (B, open symbols) as a function of electrolysis time during electrochemical oxidation of dye wastewater using BDD anode.

of China ($<100 \text{ mg L}^{-1}$), there were still some organic compounds (such as carboxylic acids and alkanes) existed in the treated wastewater. Therefore, the toxicity of wastewater should be monitored. Fig. 5A shows the evolution of wastewater toxicity with electrolysis time. The original wastewater displayed certain toxicity. The inhibition ratio of luminescence (R_i) was about 27%. After electrolysis of 2 h, the R_i increased to ca. 68% indicating the increase of wastewater toxicity, which might be due to the generation of chlorinated organic compounds [1,17,45]. However, the toxicity of wastewater decreased after electrolysis of 4 h, which might be attributed to the degradation of chlorinated organic compounds or their precursors. After electrolysis of 6 h, the toxicity of wastewater was almost negligible.

The evolution of BOD_5 and BOD_5/COD (biodegradability index) also indicated these changes (Fig. 5B). The BOD_5 of original wastewater was 80 mg L^{-1} ($\text{BOD}_5/\text{COD}=0.15$). After electrolysis of 2 h and 4 h, BOD_5 greatly declined to 15 mg L^{-1} ($\text{BOD}_5/\text{COD}=0.03$) and 10 mg L^{-1} ($\text{BOD}_5/\text{COD}=0.02$), indicating the increase of wastewater toxicity. However, BOD_5 increased to 35 mg L^{-1} ($\text{BOD}_5/\text{COD}=0.13$) after electrolysis of 6 h possibly due to the elimination of toxic organics. The BOD_5 almost decreased to zero after electrolysis of 9 h with decreasing concentration of organics. Thus, it was considered that electrochemical oxidation of biologically-pretreated dye wastewater with BDD anode was safe.

4. Conclusions

Electrochemical oxidation of biologically-pretreated dye wastewater using BDD anode is very effective and safe. After electrolysis of 12 h, the COD of dye wastewater was reduced from 532 mg L^{-1} to 99 mg L^{-1} meeting the National Discharge Standard of China. Most organic pollutants were completely eliminated, even for those with very large MW, such as humic substances. Some was degraded to simpler compounds (e.g., carboxyl acids and alkanes) with less toxicity. The application of electrochemical oxidation with BDD anode is very promising as an advanced treatment of biologically-pretreated wastewaters.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2011.02.008.

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