

Advanced electrochemical treatment of real biotreated petrochemical wastewater by boron doped diamond anode: performance, kinetics, and degradation mechanism

Hao Li, Xinmou Kuang, Congping Qiu, Xiaolan Shen, Botao Zhang and Hua Li

ABSTRACT

Petrochemical wastewater is difficult to process because of various types of pollutants with high toxicity. With the improvement in the national discharge standard, traditional biochemical treatment methods may not meet the standards and further advanced treatment techniques would be required. In this study, electrochemical oxidation with boron doped diamond (BDD) anode as post-treatment was carried out for the treatment of real biotreated petrochemical wastewater. The effects of current density, pH value, agitation rate, and anode materials on COD removal and current efficiency were studied. The results revealed the appropriate conditions to be a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, a pH value of 3, and an agitation rate of 400 rpm. Moreover, as compared with the graphite electrode, the BDD electrode had a higher oxidation efficiency and COD removal efficiency. Furthermore, GC-MS was used to analyze the final degradation products, in which ammonium chloride, formic acid, acetic acid, and malonic acid were detected. Finally, the energy consumption was estimated to be $6.24 \text{ kWh}\cdot\text{m}^{-3}$ with a final COD of $30.2 \text{ mg}\cdot\text{L}^{-1}$ at a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$ without the addition of extra substances. This study provides an alternative for the upgrading of petrochemical wastewater treatment plants.

Key words | anodic oxidation, boron doped diamond electrode, COD removal, energy consumption, petrochemical wastewater

HIGHLIGHTS

- Electro-oxidation of real biotreated petrochemical wastewater with a boron doped diamond anode.
- Possible degradation pathways were established.
- Energy consumption was estimated to be $6.24 \text{ kWh}\cdot\text{m}^{-3}$ with a COD of $30.2 \text{ mg}\cdot\text{L}^{-1}$.
- Application of BDD anode in upgrading of petrochemical wastewater treatment plants.

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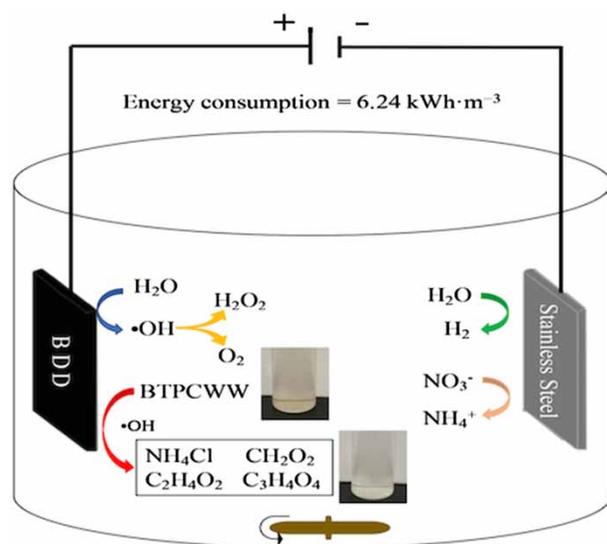
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GRAPHICAL ABSTRACT



INTRODUCTION

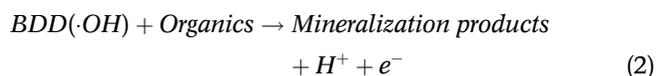
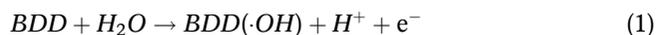
Petrochemical wastewater (PCWW) refers to the wastewater discharged by petrochemical plants. It is produced in large quantities, including not only produced wastewater, but also cooling water and water for other uses. Because of the variety of petrochemical products, as well as the complex reaction processes and unit operations involved, the composition and nature of PCWW is complex and changeable. Generally, PCWW is very difficult to treat because of the high content of organic compounds, especially aromatic and aliphatic hydrocarbons, including their derivatives, and a large number of heavy metals (Jia *et al.* 2019).

At present, biochemical treatment technology, which is economical in investment, low in operation cost, convenient in management, and stable in treatment effect, is commonly used to treat PCWW in practice (Huang *et al.* 2017). Liang *et al.* (2019) reported on a super-sized industrial-scale plant with an expanded granular sludge bed bioreactor and aerobic-activated sludge to treat PCWW containing $4,649 \pm 651 \text{ mg}\cdot\text{L}^{-1}$ COD and more than $50 \text{ mg}\cdot\text{L}^{-1}$ of petrochemicals with removal efficiencies of $85.6 \pm 2.5\%$ and $81.5 \pm 4.8\%$, respectively. Yang *et al.* (Yang *et al.* 2015) developed a microaerobic hydrolysis–acidification–anoxic/oxic process that had an overall COD removal efficiency of 72–79% with an influent COD of $348 \pm 59 \text{ mg}\cdot\text{L}^{-1}$.

Although biochemical treatments have high efficiency and are the most widely used in industrial wastewater treatment, their effluent CODs are still high. With the improvement in the emission standards for industrial sewage effluent in China (especially when the effluent COD is required to be less than $50 \text{ mg}\cdot\text{L}^{-1}$ to meet the 1A effluent discharge standard), simple biochemical treatment technology may have difficulty in meeting these standards, so coupling with other advanced treatment technologies to further reduce COD is required.

Typically, membrane technology, advanced oxidation, adsorption, coagulation, and combined systems are considered as the appropriate technologies (dos Santos *et al.* 2014a). Among them, the electrochemical advanced oxidation processes (EAOPs) take ‘electrons’ as the reaction reagent, which has strong oxidation ability, good treatment effect, strong reaction controllability, simple equipment, small space area, low cost, and high energy efficiency, making it widely used in the treatment of refractory effluents (Brillas & Martínez-Huitle 2015; Martínez-Huitle & Panizza 2018). The degradation efficiency of EAOPs depends mainly on the performance of the electrode materials, among which the boron doped diamond (BDD) electrode appears to be one of the best candidates

for the mineralization of organic compounds, as it has a wide potential window, low background current, and high stability (Woisetschläger *et al.* 2013), that allow the electrogeneration of large numbers of hydroxyl radicals ($\cdot\text{OH}$) on its surface. Generated $\cdot\text{OH}$ is considered to be one of the most powerful oxidizing agents and can mineralize all organic compounds into CO_2 unselectively as follows (Kapalka *et al.* 2008):



At present, there are already several reports on the BDD anodic oxidation of biochemically treated industrial wastewaters. Martin de Vidales *et al.* (Martin de Vidales *et al.* 2015) reported the application of a BDD electrode in the electrochemical oxidation of caffeine-intensified biologically treated urban wastewater to obtain almost complete mineralization. Garcia-Segura *et al.* (Garcia-Segura *et al.* 2015) reported the use of the BDD anode to treat secondary effluent from a municipal sewage treatment plant containing 29 target pharmaceuticals and pesticides and achieved almost complete mineralization. However, compared with these wastewaters, the composition of PCWW is more complex and the treatment is more difficult. Moreover, most of the reported electrochemical treatments of PCWW are direct oxidation, which always suffer from high effluent COD or high energy consumption (Rocha *et al.* 2012; dos Santos *et al.* 2014b), making them unsuitable for practical application. There are few reports focusing on the combining of biochemical treatment and BDD anodic oxidation technology for the treatment of PCWW to produce ultra-low COD effluent.

In this study, the electrochemical degradation of real biotreated petrochemical wastewater (BTPCWW) by a BDD anode was conducted to achieve an effluent COD lower than $50 \text{ mg}\cdot\text{L}^{-1}$. The effects of the applied current density, pH of the solution, agitation rate, and type of anode materials were investigated. The main contaminants in the influent and the oxidation intermediates were determined by gas chromatography coupled to mass spectrometry (GC-MS). Moreover, the possible degradation mechanism was proposed according to the results of the GC-MS analysis. Finally, the energy consumption of the whole process was also estimated.

METHODS

Description of wastewater

A real BTPCWW sample was derived from the effluent of an industrial sewage treatment plant in Ningbo, China. The influent contained dyestuff wastewater, paint wastewater, organic phosphorus wastewater, organic cyanide wastewater, halogenated organic wastewater, ether-containing wastewater, and organic resin wastewater produced by companies in a chemical industrial district in Ningbo. The wastewater had strong toxicity and a complex composition, which may have contained oil, cyanide, phenols, sulfur, arsenic, aromatic hydrocarbons, ketones, and other pollutants. The wastewater was treated first by an anaerobic-aerobic biochemical technique in the industrial sewage treatment plant. The pH of the secondary effluent was about 7.4 and the COD was about $120 \text{ mg}\cdot\text{L}^{-1}$. It should be noted that the wastewater used in this study was the raw effluent without any additional treatment.

Materials

The BDD electrode was supplied by Condias (Germany). The coatings were double-sized deposited on an Nb plate ($20 \times 20 \times 2 \text{ mm}$) by hot filament chemical vapor deposition. A graphite plate electrode was purchased from Chuxi Industrial Co., Ltd, China. All chemicals at the analytical grade were purchased from Aladdin Industrial Inc., China, and used without further purification. All aqueous solutions were prepared with ultrapure water (resistivity $>18 \text{ M}\Omega\cdot\text{cm}$) at room temperature.

Electrochemical experiment

The degradation of the BTPCWW was conducted in batch within an undivided electrochemical cell with a capacity of 300 mL. The solution was stirred by a magnetic stirrer. Of the real BTPCWW, 200 mL was stored in the electrochemical cell each time and the electrolysis was conducted under galvanostatic condition by a DC power supply (MS-305D, Maisheng, China). A BDD or graphite electrode with a surface area of 8 cm^2 was used as the anode while a same-sized stainless-steel plate was used as the cathode. In all conditions, the distance between the anode and cathode was maintained at 2 cm and the solution was kept at 25°C by a thermostat water bath. The adjustment of the pH value was conducted using $1 \text{ mol}\cdot\text{L}^{-1}$

H₂SO₄ or 1 mol·L⁻¹ NaOH solution. The applied current was 40–120 mA, pH value was 3–10, and agitation rate was 200–600 rpm.

Analytical method

The COD value of the solution was determined by rapid digestion spectrophotometry. The sample was dissolved in K₂Cr₂O₇ solution with Ag₂SO₄ as the catalyst in a strong sulfuric acid medium. After sealed digestion at 165 °C in a digestion instrument (Gelin Kairui GL-12 K, China) for 15 min, the COD value was determined by an ultraviolet spectrophotometer (Shimadzu UV-2550, Japan). The COD removal efficiency was calculated with the following equation:

$$\text{COD removal efficiency} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \times 100\% \quad (3)$$

where COD_0 and COD_t are the COD values (mg·L⁻¹) at times $t = 0$ (initial) and t , respectively.

The instantaneous current efficiency (ICE) for the anodic oxidation was derived from the COD value as expressed by the following equation:

$$\text{ICE} = FV \left(\frac{\text{COD}_t - \text{COD}_{t+\Delta t}}{8I\Delta t} \right) \quad (4)$$

where F is the Faraday constant (96,485 C·mol⁻¹), COD_t and $\text{COD}_{t+\Delta t}$ are the COD values (g O₂·L⁻¹) at times $t = t$ and $t + \Delta t$, respectively, V is the solution's volume (L), 8 is the oxygen equivalent mass (g·eq⁻¹), I is the applied current (A), and Δt is the degradation time (s).

The initial limiting current density was given by the following equation:

$$j_{lim0} = 4Fk_m\text{COD}_0 \quad (5)$$

where k_m is the average mass transport coefficient (m·s⁻¹).

The energy consumption per volume (kWh·m⁻³) was also estimated by the following equation:

$$\text{Energy consumption} = \frac{\Delta E \times I \times t}{1000 \times V} \quad (6)$$

where ΔE is the average voltage (V) during electrolysis.

The compounds in BTPCWW and corresponding intermediates in the degradation process were determined by GC-MS (Shimadzu QP2010 SE, Japan) coupled with an

Agilent DB-1 column (30 m × 0.25 mm, 1 μm film thickness). The injection volume was 1 μL. The temperatures of the detector and the ion source were both 250 °C.

The concentration of chloride ion was determined by titrimetry with K₂CrO₄ solution as the indicator and AgNO₃ solution as the titrator.

RESULTS AND DISCUSSION

Effect of the applied current density

As a key variable affecting anodic oxidation performance and energy consumption, applied current density has been reported to be the most important factor governing the production of •OH at a BDD anode and determining the degradation rate and effectiveness. Therefore, the effect of the current density on the anodic oxidation of BTPCWW was analyzed. As shown in Figure 1(a), the COD removal efficiency increased with the current density from 5 to 15 mA·cm⁻², which was mainly due to the larger amount of •OH produced by the BDD anode under a higher applied current. However, COD could not be completely removed under all applied currents. After 3 h of electrolysis, the final COD removal efficiencies were 70.6%, 71.7%, 74.9%, 76.8%, and 82.6% at the current densities of 5, 7.5, 10, 12.5, and 15 mA·cm⁻², respectively. Moreover, the inset of Figure 1(a) shows the pseudo-first-order kinetics ($\ln \frac{C_0}{C} = k_{obs} \cdot t$) for all applied current densities. The observed pseudo-first-order kinetic rate constant (k_{obs}) increased from 0.412 to 0.636 h⁻¹ when the current density increased from 5 to 15 mA·cm⁻², further proving that the increase in current density could accelerate the BDD anodic oxidation of BTPCWW.

It has been reported that k_m could be calculated from k_{obs} (Ammar et al. 2016):

$$k_m = \frac{V}{A} k_{obs} \quad (7)$$

where V is the solution's volume (m³) and A is the electrode area (m²).

Therefore, k_m and related j_{lim0} under different current densities were calculated and listed in Table 1. Under all conditions, the j_{lim0} values were lower than the applied current densities, signifying that the electrolysis was under diffusion control. However, diffusion control leads to the usage of part of the current for side reactions, such as

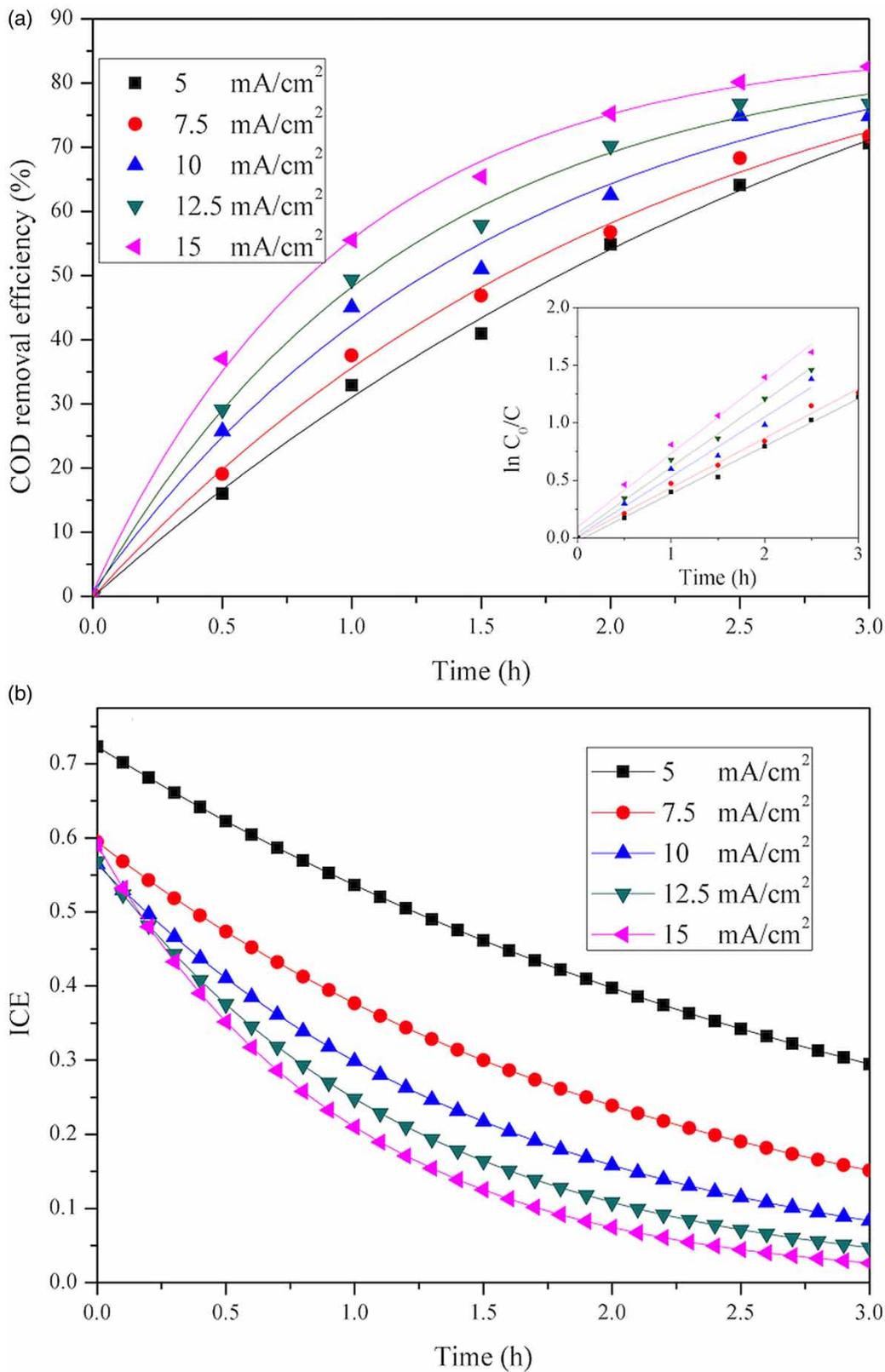
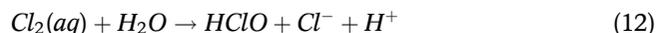
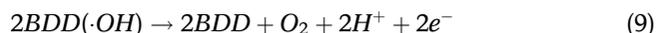
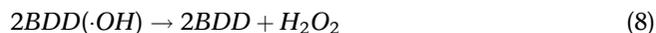


Figure 1 | Effect of current density on anodic oxidation of 200 mL BTPCWW with BDD electrode: (a) variation of COD removal efficiency; (b) variation of ICE. (pH = 7.4 and agitation rate = 400 rpm).

Table 1 | List of calculated k_{obs} , k_m , and j_{limo} under different applied current densities

Applied current density (mA·cm ⁻²)	k_{obs} (h ⁻¹)	k_m (m·h ⁻¹)	j_{limo} (mA·cm ⁻²)
5	0.412	0.103	4.14
7.5	0.431	0.108	4.33
10	0.518	0.129	5.21
12.5	0.576	0.144	5.79
15	0.636	0.159	6.39

dimerization to H₂O₂, O₂ evolution, and formation of other oxidants (i.e. peroxodisulfuric acid and hypochlorous acid) (Ennouri *et al.* 2017):



Unlike generated H₂O₂ and O₂, the generated S₂O₈²⁻ and ClO⁻ are helpful, and can also contribute to the electrochemical degradation of organic compounds through indirect oxidation (Cotillas *et al.* 2018a).

The occurrences of side reactions can be further confirmed by the ICE values (shown in Figure 1(b)), which were below 1 under all applied current densities. Moreover, ICE decreased with increasing electrolysis time, which is a typical electrochemical mass transfer control process (Cotillas *et al.* 2018b). However, the highest initial ICE value was obtained at the lowest applied current. For current densities of 5, 7.5, 10, 12.5, and 15 mA·cm⁻², the corresponding initial ICE values were 0.723, 0.595, 0.564, 0.568, and 0.590, respectively, mainly because the increasing current was used in parasitic reactions at the anode rather than in the degradation of the organic compounds.

Overall, the degradation of BTPCWW followed the pseudo-first-order kinetic. With the increase in current density, a higher degradation rate and higher COD removal efficiency were obtained, whereas the corresponding current efficiency decreased because of the occurrence of the side reactions.

Effect of pH value

The effect of pH on the anodic oxidation of organic compounds was contradictory, since it is closely related to the chemical properties of the treated organic compounds. Therefore, the effect of pH on the anodic oxidation of BTPCWW with a BDD anode was studied. The results are shown in Figure 2. The fastest degradation rate was observed at a pH of 3 ($k_{obs} = 0.591 \text{ h}^{-1}$) with a final COD removal efficiency of 83.5% (COD = 19.7 mg·L⁻¹). At a pH of 10, k_{obs} decreased to 0.382 h⁻¹ with a final COD removal efficiency of only 65.8%. The pH can affect the rate of the electro-generation of ·OH (Kouskouki *et al.* 2019), therefore, it can be inferred that a large amount of physisorbed ·OH's being produced at low pH values. On the other hand, increasing the pH value will reduce the O₂ over-potential, leading to the promotion of the oxygen evolution reaction and reduction of the degradation's performance (Ammar *et al.* 2016). It is noteworthy that after 3 h of electrolysis in the alkaline medium, the solution became a bit turbid with a white flocculent. This may have been due to the formation of polymer intermediates, which make the degradation process more difficult (Saad *et al.* 2016).

The variation of the ICE values under different pH values was also examined. The results are displayed in Figure 2(b). Similar to COD removal efficiency, the highest ICE value was obtained at a pH of 3. For pH of 3, 7.4, and 10, the initial ICE values were 0.670, 0.564, and 0.489, respectively. Typically, ICE at pH of 3 is 1.37 times of that at pH of 10.

Accordingly, an acidic medium not only increased COD removal efficiency, but also had higher current efficiency, as compared with the neutral and alkaline media.

Effect of the agitation rate

To verify the role of the mass transfer process in the electrochemical oxidation of BTPCWW with the BDD anode, the effect of the agitation rate, which ranged from 200 to 600 rpm, was studied. As shown in Figure 3(a), the agitation rate had a significant impact on the COD removal efficiency, when the agitation rate was below 400 rpm, the COD removal efficiency increased with the agitation rate. Under a low agitation rate, mass transportation would be limited and would lead to low COD removal efficiency (de Oliveira Marcionilio *et al.* 2019). However, at an agitation rate of 600 rpm, an unexpected performance of the COD removal was seen. In the first 1.5 h, the COD removal rate at 600 rpm was faster than that at 400 rpm.

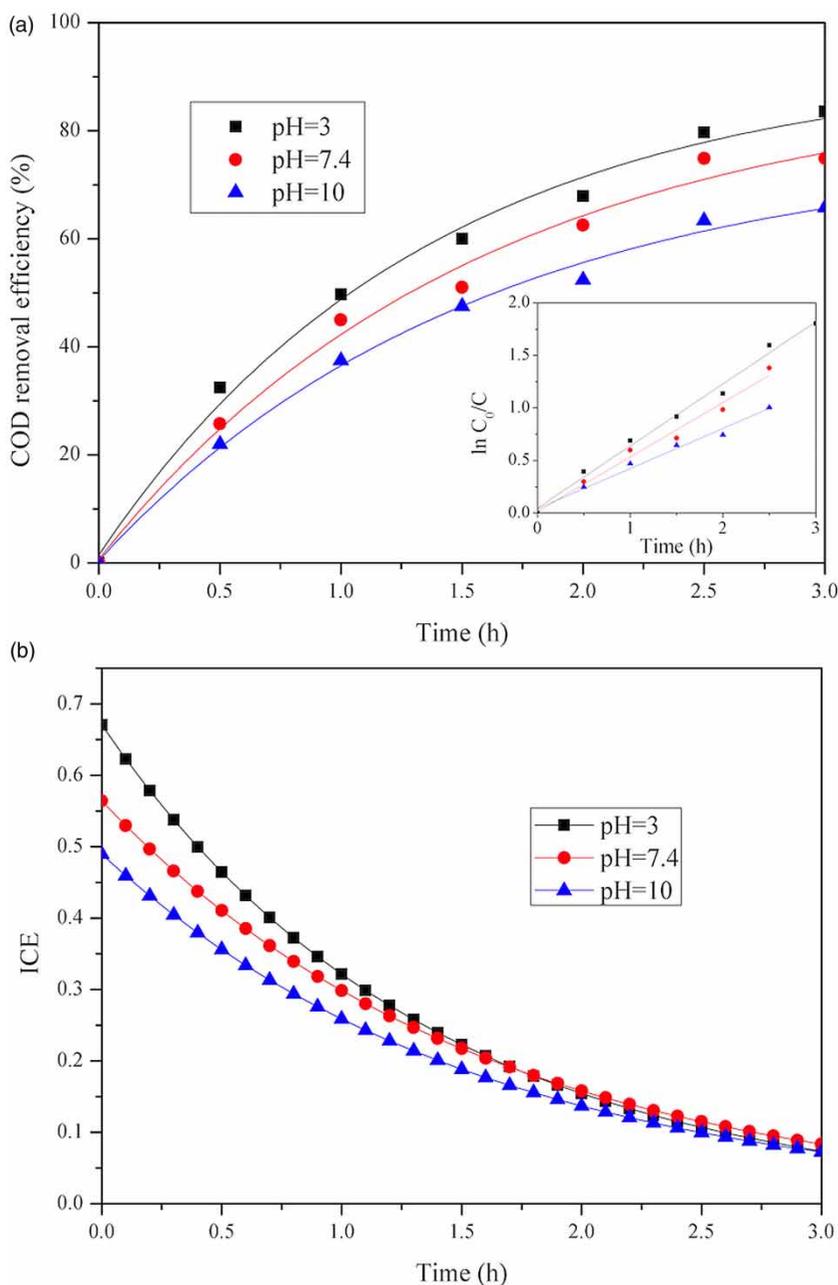


Figure 2 | Effect of pH value on anodic oxidation of 200 mL BTPCW with BDD electrode: (a) variation of COD removal efficiency; (b) variation of ICE. (Current density = $10 \text{ mA}\cdot\text{cm}^{-2}$ and agitation rate = 400 rpm).

Afterward, the rate increased extremely slowly until the final COD removal efficiency was only 65.3%, which was much lower than that at 400 rpm (74.9%). This result may have been due to the electro-oxidation with the BDD anode's having been controlled mainly by direct oxidation rather than indirect oxidation with the other oxidants (Moreira *et al.* 2015). Under such a mechanism and with the decrease in the concentrations of the pollutants in the

solution, the amount of adsorbed pollutants on the surface of the electrode decreased dramatically when the agitation rate was too fast, resulting in a significant decrease in the COD removal efficiency.

The variation of the ICE values also shows a similar trend (shown in Figure 3(b)). The highest initial ICE value of 0.879 was obtained at an agitation rate of 600 rpm, which was 1.56 times that at 400 rpm. But the value decreased very rapidly

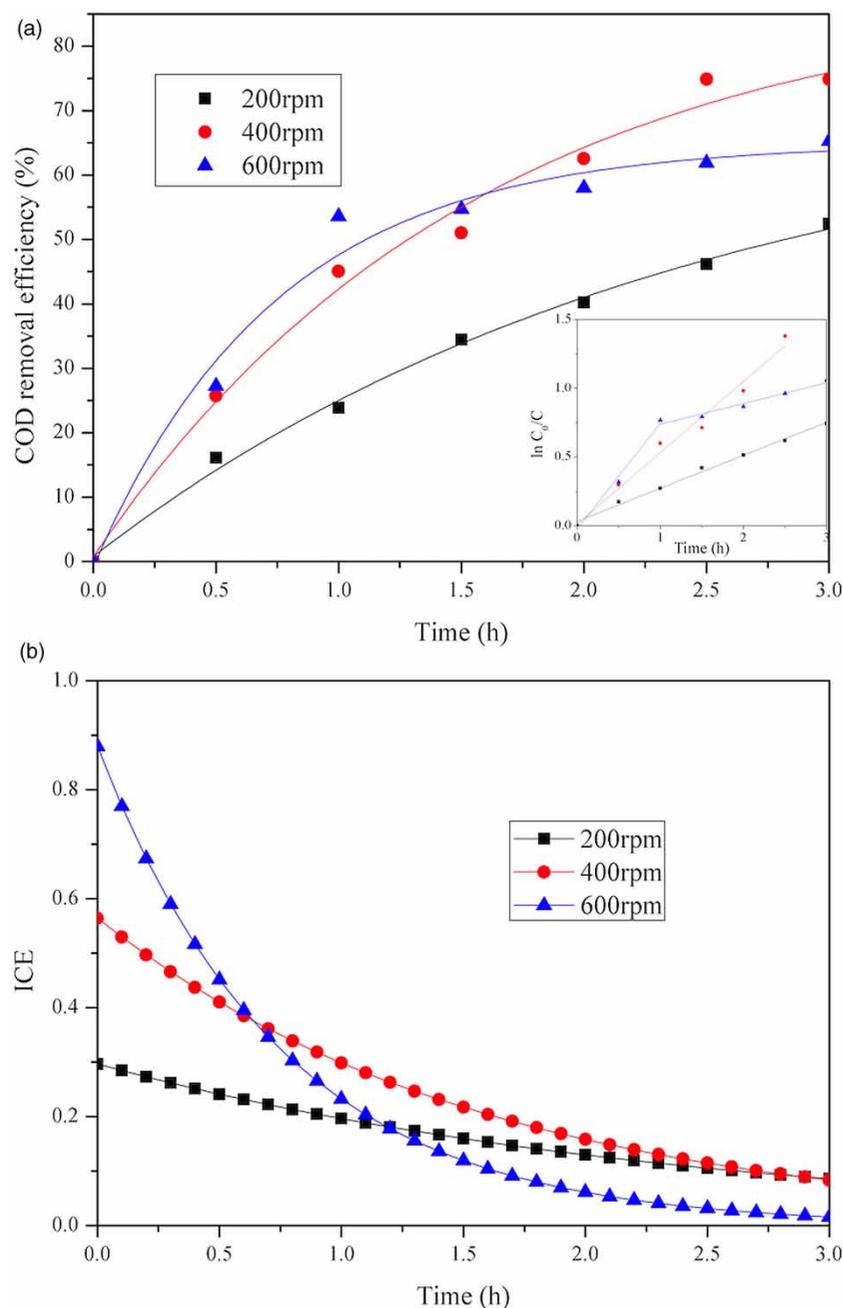


Figure 3 | Effect of agitation rate on anodic oxidation of 200 mL BTPCWW with BDD electrode: (a) variation of COD removal efficiency; (b) variation of ICE. (Current density = 10 mA·cm⁻² and pH = 7.4).

and became lower than that at 400 rpm after about 0.7 h and reached 0.016 after 3 h of electrolysis, which was only 19.1% of that at 400 rpm, signifying that the side reactions, including O₂ evolution, had become serious at 600 rpm as a result of the low quantities of adsorbed organic pollutants on the surfaces of the electrode.

Accordingly, too fast or too slow agitation rate was detrimental to the degradation of BTPCWW. In this study,

agitation rate of 400 rpm is considered as the most appropriate value.

Comparison of the anode materials

The anode plays an important role in electrochemical oxidation, since it has a great influence on the oxidation efficiency and reaction mechanism. This study

comparatively analyzed the electrochemical degradation of BTPCWW on the BDD and graphite electrodes. As shown in Figure 4(a), the COD removal efficiency on the BDD electrode was significantly higher than that on the graphite electrode. After 3 h of electrolysis, COD removal efficiencies of 74.9% and 49.6% were obtained from the BDD and graphite electrodes, respectively. Moreover, the inset of Figure 4(a) shows the pseudo-first-order kinetic with k_{obs}

of 0.518 h^{-1} and 0.217 h^{-1} for the BDD and graphite electrodes, respectively. The higher oxidation efficiency of the BDD electrode could be explained by a large amount of electrogenerated $\cdot\text{OH}$. The BDD electrode was classified as an inert electrode. Therefore, a large amount of $\cdot\text{OH}$ was physisorbed on the surface of the electrode, resulting in a higher degradation rate and efficiency. On the contrary, the $\cdot\text{OH}$ produced on the graphite electrode was less and

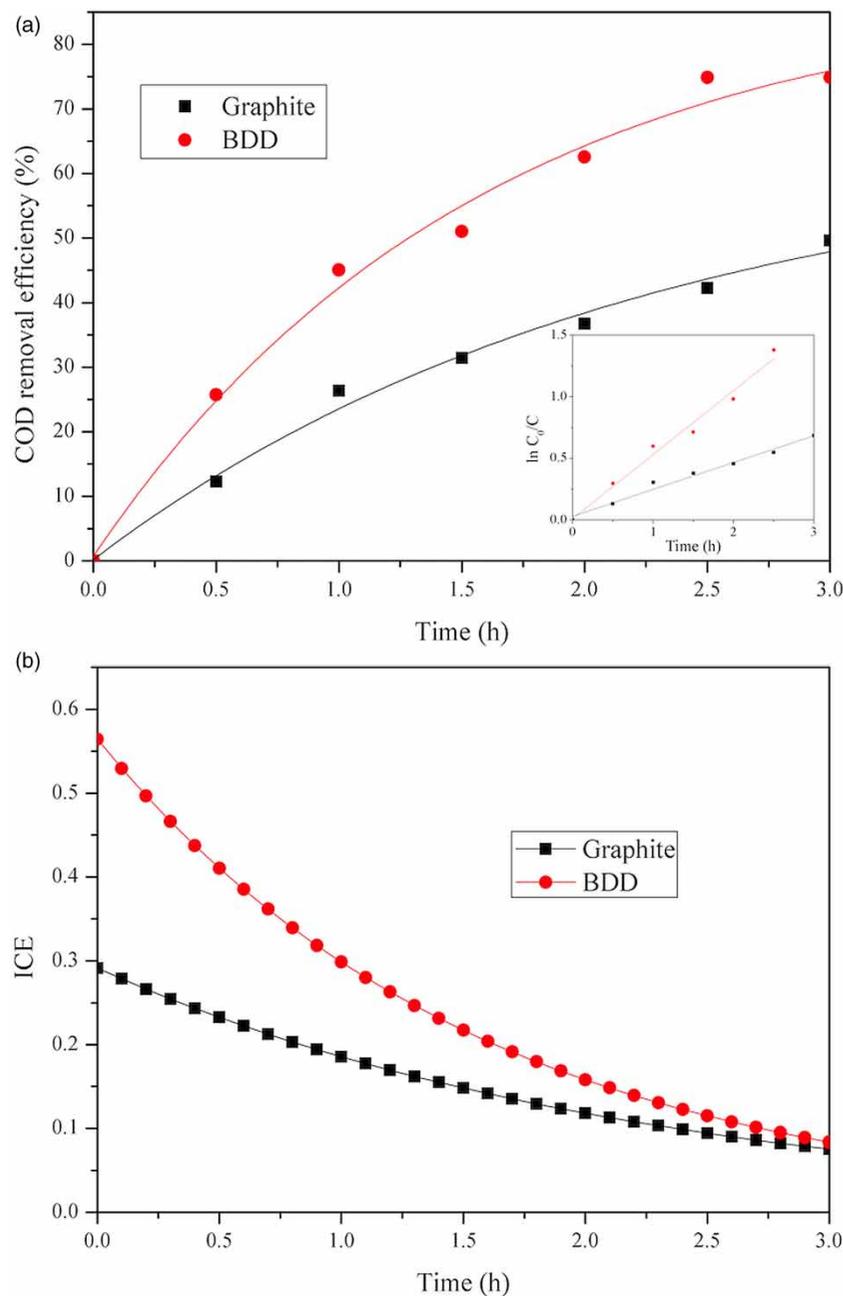


Figure 4 | Effect of anode materials on anodic oxidation of 200 mL BTPCWW: (a) variation of COD removal efficiency; (b) variation of ICE. (Current density = $10 \text{ mA}\cdot\text{cm}^{-2}$, pH = 7.4, and agitation rate = 400 rpm).

its oxidation depended mainly on the chemisorbed 'active oxygen' (oxygen in the oxide lattice, MO_{x+1}) and other strong oxidants (ClO^- and $\text{S}_2\text{O}_8^{2-}$) (Fil et al. 2014). However, $\bullet\text{OH}$ had the strongest oxidation ability, so the BDD electrode was more efficient for the anodic oxidation of BTPCWW.

The variation of ICE also shows a similar trend (shown in Figure 4(b)). The initial ICE values were 56.4% and 29.1% for the BDD and graphite electrodes, respectively, with the former's being 1.94 times larger than the latter, signifying that most of the applied current had been used to oxidize organic pollutants on the surface of the BDD electrode instead of creating side reactions, as compared with the graphite electrode.

Possible degradation mechanism

To investigate the possible electrochemical degradation pathway of BTPCWW on the BDD electrode, the electrolysis of 200 mL of wastewater was conducted under a current density of $10 \text{ mA}\cdot\text{cm}^{-2}$, pH of 7.4, and agitation rate of 400 rpm. The corresponding intermediates and main products were determined by GC-MS analysis.

Firstly, the GC-MS analysis of the raw wastewater revealed that it was mainly composed of biochemical refractory compounds, including nitrous oxide, sulfonates (i.e. aminomethanesulfonic acid), alcohol, ammonium chloride, chloroalkanes, benzenes (i.e. p-methylaminoethyl phenol,

nitrobenzene, nitrophenyl sulfonate etc), and small amounts of formic acid and acetic acid. During electrolysis, the main intermediates detected included benzoquinone, methylphenylethylamine, methylsulfonyl acetic acid, cyclohexylethylamine, pyruvic acid, ethanol, ammonium chloride, chloramines, malonic acid, formic acid, acetic acid, and carbon dioxide. After 3 h of electrolysis, the main products in the effluent were ammonium chloride, formic acid, acetic acid, and malonic acid.

After consideration of the peak heights, as well as the components of the final products, carbon dioxide, malonic acid, ammonium chloride, formic acid, and acetic acid were selected for quantitative analysis. The results are shown in Figure 5. The concentration of CO_2 increased rapidly to $33.3 \text{ mg}\cdot\text{L}^{-1}$ in the first half-hour, then began to decline gradually until no CO_2 was detected after 3 h of electrolysis, indicating that the mineralization of the organic compounds had been achieved during the electrochemical oxidation of BTPCWW. In the initial stage of the reaction, the current efficiency is relatively high and the mineralization of the organic compounds dominated with only a few side reactions having occurred. Thus, a large amount of CO_2 was generated. As the reaction proceeded, the concentrations of the organic compounds declined continuously, the occurrences of the side reactions increased, and the generation of CO_2 by the mineralization of the organic compounds decreased. The variation of NH_4Cl behaved oppositely by decreasing rapidly from 66.9 to $14.5 \text{ mg}\cdot\text{L}^{-1}$

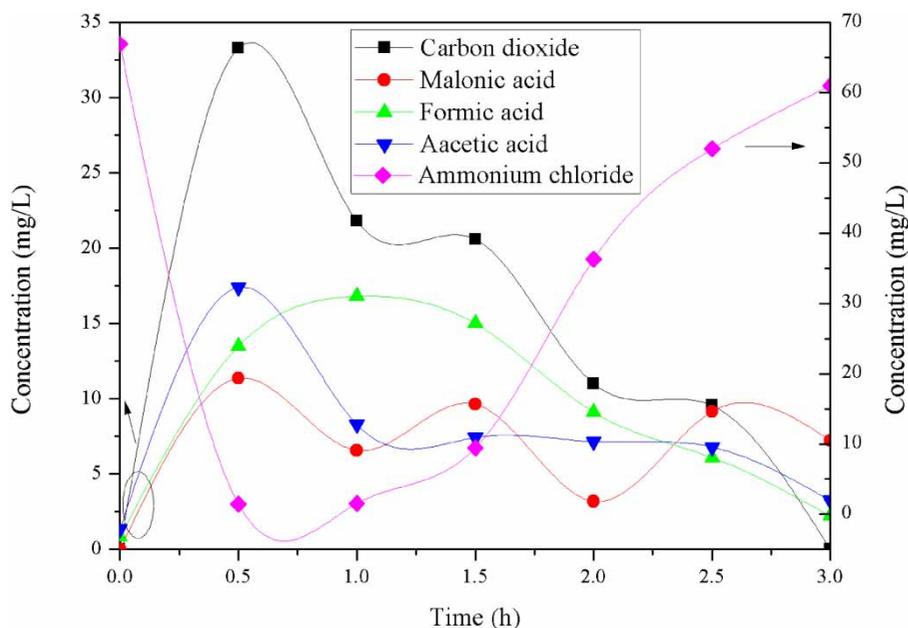


Figure 5 | Evolution of main compounds during anodic oxidation of 200 mL BTPCWW with BDD electrode. (Current density = $10 \text{ mA}\cdot\text{cm}^{-2}$, pH = 7.4, and agitation rate = 400 rpm).

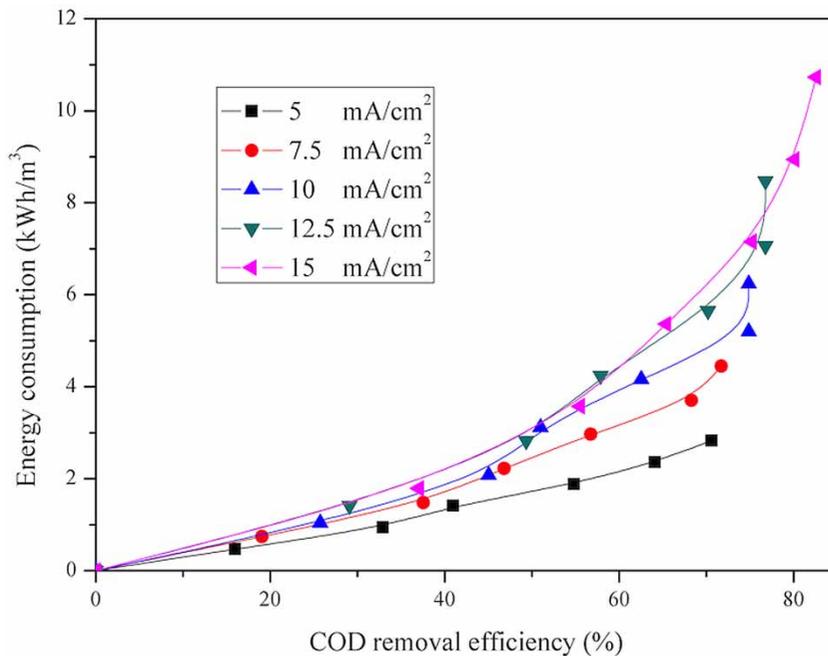


Figure 7 | Evolution of energy consumption against COD removal efficiency under different current densities during anodic oxidation of 200 mL BTPCWW with BDD electrode. (pH = 7.4 and agitation rate = 400 rpm).

Furthermore, the concentration of Cl^- was also determined, because the presence of chloride compounds had been detected by GC-MS, and chloride ions were also considered to be one of the main oxidants in electrochemical oxidation (Li et al. 2017). In this study, the detected initial and final concentrations of Cl^- were 221.7 and 162.4 $\text{mg}\cdot\text{L}^{-1}$, respectively, signifying that a part of Cl^- may have been oxidized to active chlorine, chlorate, and perchlorate, proving that indirect oxidation also occurred. In addition, the degradation of the chemicals on the graphite anode may have depended mainly on Cl^- in wastewater. CH_2O_2 , $\text{C}_2\text{H}_4\text{O}_2$, and $\text{C}_3\text{H}_4\text{O}_4$ were the main organic compounds in the final effluent. During the whole electrolysis process, they exhibited a similar evolution, which increased in the first few hours but then decreased gradually. However, their concentration peaks appeared at different times. $\text{C}_2\text{H}_4\text{O}_2$ and $\text{C}_3\text{H}_4\text{O}_4$ reached their peaks at 0.5 h, while CH_2O_2 reached its peak in 1 h, confirming that CH_2O_2 , $\text{C}_2\text{H}_4\text{O}_2$, and $\text{C}_3\text{H}_4\text{O}_4$ were intermediates from the oxidation of the other organic compounds. Accordingly, the possible degradation pathways of the anodic oxidation of BTPCWW with the BDD electrode are displayed in Figure 6.

Energy consumption

Since the treated wastewater in this study was real industrial wastewater, it was particularly important to estimate the

cost. The evolution of energy consumption against COD removal efficiency under different current densities was calculated. The results are displayed in Figure 7. Generally, the energy consumption increased with the current density under the same COD removal efficiency and the variation was more significant at higher COD removal efficiency. When the current density was 5, 7.5, 10, 12.5, and 15 $\text{mA}\cdot\text{cm}^{-2}$, the corresponding average voltage was 4.71, 4.94, 5.20, 5.65, and 5.96 V, respectively. The voltage growth was faster than the increase in COD removal efficiency caused by the increasing applied current. Thus, the result was higher energy consumption at high current density. However, it should be noted that the COD removal rate and efficiency was relatively deficient at low current density. Therefore, it was necessary to select an appropriate applied current (i.e. an applied current density of 10 $\text{mA}\cdot\text{cm}^{-2}$ was used).

Some researchers have also studied the energy consumption in the treatment of real wastewater with BDD electrodes. The results are listed in Table 2. The direct electrochemical oxidation of PCWW was difficult, the reported energy consumption in Rocha's study was as high as 109 $\text{kWh}\cdot\text{dm}^{-3}$, signifying that this treatment was unsuitable for industrial application. Although, in Gargouri's study, the energy consumption was much lower than that of Rocha, it was still too high for practical application, and the most important thing is that the effluent COD was still

Table 2 | Comparison of energy consumption of electrochemical oxidation of different wastewaters using BDD anode

Wastewater	Method	Volume (mL)	Electrode area (cm ²)	COD ₀ (mg·L ⁻¹)	Effluent COD (mg·L ⁻¹)	Energy consumption (kWh·m ⁻³)	Ref.
PCWW	Direct	500	10	1588	32	109000	Rocha <i>et al.</i> (2012)
PCWW	Direct	200	7	19842	794	38	Gargouri <i>et al.</i> (2014)
Biotreated coking wastewater	Post-treatment	3000	202.8	220	30.5	25.5	Wang <i>et al.</i> (2015)
Biotreated winery wastewater	Post-treatment	1500	10	120	38.4	5.5	Moreira <i>et al.</i> (2015)
BTPCWW	Post-treatment	200	8	120	30.2	6.24	this work

as high as 794 mg·L⁻¹. However, the treatment of biotreated wastewaters (both coking and winery wastewater) showed a significant reduction of energy consumption with low effluent COD. In this study, on the basis of the existing biochemical process, electrochemical oxidation with BDD anode was considered to treat the BTPCWW, in order to reduce the effluent COD and improve the effluent quality. Without chemical supplements and pH adjustment, the energy consumption was only 6.24 kWh·m⁻³ with a final COD of 30.2 mg·L⁻¹ at a current density of 10 mA·cm⁻², which was basically the same as that of treatment of biotreated winery wastewater. These results indicate that BDD anodic oxidation has a relatively low cost and it has good potential applications for existing biochemically treated industrial petrochemical wastewater treatment plants, which would need to further improve the effects of their treatments.

CONCLUSIONS

The electrochemical degradation of real BTPCWW with a BDD anode was conducted. The results showed that the degradation process followed the pseudo-first-order kinetic. With the increase in the applied current density, a higher degradation rate and higher COD removal efficiency were obtained, whereas the corresponding current efficiency decreased during degradation. An analysis of the effect of the pH value revealed that the degradation of BTPCWW favored an acidic medium by faster COD removal efficiency and higher current efficiency. The effect of the agitation rate was variable. The highest COD removal efficiency was achieved under 400 rpm and a further increase in the agitation rate would only increase COD removal in the first few hours but lower the total COD removal efficiency. In addition, a comparative study of the degradation effect of

the BDD and graphite anodes was conducted and a better COD removal efficiency was obtained with the BDD electrode. A GC-MS analysis revealed that after 3 h of electrolysis with the BDD electrode, the main products were ammonium chloride, formic acid, acetic acid, and malonic acid. Finally, an estimation of the energy consumption was 6.24 kWh·m⁻³ with a final COD of 30.2 mg·L⁻¹ at a current density of 10 mA·cm⁻² without the need for a chemical supplement.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

REFERENCES

- Ammar, H. B., Brahim, M. B., Abdelhédi, R. & Samet, Y. 2016 Green electrochemical process for metronidazole degradation at BDD anode in aqueous solutions via direct and indirect oxidation. *Separation and Purification Technology* **157**, 9–16.
- Brillas, E. & Martinez-Huitle, C. A. 2015 Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review. *Applied Catalysis B: Environmental* **166**, 603–643.
- Cotillas, S., Clematis, D., Cañizares, P., Carpanese, M. P., Rodrigo, M. A. & Panizza, M. 2018a Degradation of dye Procion Red

- MX-5B by electrolytic and electro-irradiated technologies using diamond electrodes. *Chemosphere* **199**, 445–452.
- Cotillas, S., Llanos, J., Cañizares, P., Clematis, D., Cerisola, G., Rodrigo, M. A. & Panizza, M. 2018b Removal of Procion Red MX-5B dye from wastewater by conductive-diamond electrochemical oxidation. *Electrochimica Acta* **263**, 1–7.
- de Oliveira Marcionilio, S. M. L., Crisafulli, R., Medeiros, G. A., Tonha, M. d. S., Garnier, J., Neto, B. A. D. & Linares, J. J. 2019 Influence of hydrodynamic conditions on the degradation of 1-butyl-3-methylimidazolium chloride solutions on boron-doped diamond anodes. *Chemosphere* **224**, 343–350.
- dos Santos, E. V., Rocha, J. H. B., de Araujo, D. M., de Moura, D. C. & Martinez-Huitle, C. A. 2014a Decontamination of produced water containing petroleum hydrocarbons by electrochemical methods: a minireview. *Environmental Science and Pollution Research* **21** (14), 8432–8441.
- dos Santos, E. V., Sena, S. F. M., da Silva, D. R., Ferro, S., De Battisti, A. & Martinez-Huitle, C. A. 2014b Scale-up of electrochemical oxidation system for treatment of produced water generated by Brazilian petrochemical industry. *Environmental Science and Pollution Research* **21** (14), 8466–8475.
- Ennouri, R., Kchaw, M., Panizza, M. & Elaoud, S. C. 2017 Electrochemical degradation of vanillic acid on a BDD anode. *Journal of The Electrochemical Society* **164** (9), E213–E216.
- Fil, B. A., Boncukcuoglu, R., Yilmaz, A. E. & Bayar, S. 2014 Electro-oxidation of pistachio processing industry wastewater using graphite anode. *Clean-Soil Air Water* **42** (9), 1232–1238.
- Garcia-Segura, S., Keller, J., Brillas, E. & Radjenovic, J. 2015 Removal of organic contaminants from secondary effluent by anodic oxidation with a boron-doped diamond anode as tertiary treatment. *Journal of Hazardous Materials* **283**, 551–557.
- Gargouri, B., Gargouri, O. D., Gargouri, B., Trabelsi, S. K., Abdelhedi, R. & Bouaziz, M. 2014 Application of electrochemical technology for removing petroleum hydrocarbons from produced water using lead dioxide and boron-doped diamond electrodes. *Chemosphere* **117**, 309–315.
- Huang, C., Luo, M. T., Chen, X. F., Xiong, L., Li, X. M. & Chen, X. D. 2017 Recent advances and industrial viewpoint for biological treatment of wastewaters by oleaginous microorganisms. *Bioresource Technology* **232**, 398–407.
- Jia, X., Jin, D., Li, C. & Lu, W. 2019 Characterization and analysis of petrochemical wastewater through particle size distribution, biodegradability, and chemical composition. *Chinese Journal of Chemical Engineering* **27** (2), 444–451.
- Kapalka, A., Lanova, B., Baltruschat, H., Fóti, G. & Comninellis, C. 2008 Electrochemically induced mineralization of organics by molecular oxygen on boron-doped diamond electrode. *Electrochemistry Communications* **10** (9), 1215–1218.
- Kouskouki, A., Chatzisyseon, E., Mantzavinos, D. & Frontistis, Z. 2019 Electrochemical degradation of piroxicam on a boron doped diamond anode: investigation of operating parameters and ultrasound synergy. *ChemElectroChem* **6** (3), 841–847.
- Li, H., Long, Y., Zhu, X., Tian, Y. & Ye, J. 2017 Influencing factors and chlorinated byproducts in electrochemical oxidation of bisphenol A with boron-doped diamond anodes. *Electrochimica Acta* **246**, 1121–1130.
- Liang, J., Mai, W., Tang, J. & Wei, Y. 2019 Highly effective treatment of petrochemical wastewater by a super-sized industrial scale plant with expanded granular sludge bed bioreactor and aerobic activated sludge. *Chemical Engineering Journal* **360**, 15–23.
- Martin de Vidales, M. J., Millan, M., Saez, C. & Perez, J. F. 2015 Conductive diamond electrochemical oxidation of caffeine-intensified biologically treated urban wastewater. *Chemosphere* **136**, 281–288.
- Martínez-Huitle, C. A. & Panizza, M. 2018 Electrochemical oxidation of organic pollutants for wastewater treatment. *Current Opinion in Electrochemistry* **11**, 62–71.
- Moreira, F. C., Boaventura, R. A. R., Brillas, E. & Vilar, V. J. P. 2015 Remediation of a winery wastewater combining aerobic biological oxidation and electrochemical advanced oxidation processes. *Water Research* **75**, 95–108.
- Rocha, J. H. B., Gomes, M. M. S., Fernandes, N. S., Silva, D. R. d. & Martínez-Huitle, C. A. 2012 Application of electrochemical oxidation as alternative treatment of produced water generated by Brazilian petrochemical industry. *Fuel Processing Technology* **96**, 80–87.
- Saad, M. E. K., Rabaoui, N., Elaloui, E. & Moussaoui, Y. 2016 Mineralization of p-methylphenol in aqueous medium by anodic oxidation with a boron-doped diamond electrode. *Separation and Purification Technology* **171**, 157–163.
- Wang, C., Zhang, M., Liu, W., Ye, M. & Su, F. 2015 Effluent characteristics of advanced treatment for biotreated coking wastewater by electrochemical technology using BDD anodes. *Environmental Science and Pollution Research* **22** (9), 6827–6834.
- Woisetschlager, D., Humpl, B., Koncar, M. & Siebenhofer, M. 2013 Electrochemical oxidation of wastewater – opportunities and drawbacks. *Water Science and Technology* **68** (5), 1173–1179.
- Yang, Q., Xiong, P., Ding, P., Chu, L. & Wang, J. 2015 Treatment of petrochemical wastewater by microaerobic hydrolysis and anoxic/oxic processes and analysis of bacterial diversity. *Bioresource Technology* **196**, 169–175.

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