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The degradation of glyphosate through the electrocatalytic oxidation of a boron-doped diamond electrode

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ABSTRACT: Electrochemical oxidation has received increasing attention for organic wastewater treatment due to its many advantages, such as simple equipment, ease of operation, no additional chemicals, low energy consumption, and no secondary pollution. Boron-doped diamond (BDD) thin films are a new electrode material that has been reported to have excellent characteristics, such as a wide electrochemical potential window, low background electricity, chemical stability, and strong surface anti-fouling ability. In this study, water contaminated with glyphosate was employed as sample wastewater. It was observed that BDD effectively functioned as an anode in electrochemical oxidation and led to adjustment of water parameters, such as pH and temperature. In addition, the performances of PbO_2 and BDD as anodes were compared, and their respective efficiencies were evaluated. The degradation products of glyphosate generated due to the electrochemical treatment of the model wastewater have been analyzed and probable pathways for their formation are proposed.

KEYWORDS: glyphosate, electrocatalytic oxidation, BDD thin film electrode, wastewater treatment

INTRODUCTION

Organophosphorus pesticides are widely applied in agriculture due to their high efficiency and low cost [1, 2]. However, the wastewater produced from activities associated with these pesticides has an abundance of complex toxic substances that cause severe environmental and health problems if they are not properly disposed of. Due to economic and technological factors, a large portion of wastewater influenced by organophosphorus pesticides is discharged directly into natural waterbodies resulting in severe environmental pollution, making its disposal a serious issue in the pesticide industry [3].

Due to the high concentrations of toxic compounds with poor biodegradability in pesticide-influenced wastewater, large amounts of uncontaminated water, which may be dozens or even hundreds of times as much as the wastewater, are required for dilution. This results in biochemical treatment plants with low load capacities but high energy consumption. To improve this situation and create more efficient treatment plants, it is necessary to carry out in-depth studies of the technicalities behind biochemical pretreatment. Major pretreatments currently employed across the world include activated carbon adsorption, hydrolysis, extraction, wet oxidation, ultrasonic flotation, Fenton, photocatalytic methods, etc. [4–6].

In recent years, the use of electrocatalytic oxidation to treat organophosphorus pesticides before their discharge into major ecosystems has been a popular research subject [7–9]. The fundamental principle of electrocatalytic oxidation is to oxidize organic matter on the surface of a suitable electrode under the action of free radicals produced by an electric field. In such a setup, the reaction rate of the oxidative process can be controlled by regulating the external voltage. Although electrocatalytic oxidation can effectively degrade organophosphorus pesticides in wastewater, its application is restricted due to the difficulty in choosing suitable electrode material, the short life of commonly available electrodes, and the large energy consumption [10].

Diamond has become a very popular electrode material due to its excellent mechanical, electrical, thermal, acoustic, and optical properties. Research has demonstrated that there is a very weak interaction between boron-doped diamond (BDD) material and hydroxyl radicals; therefore, their interaction can produce active free radicals that can completely mineralize organic matter, allowing BDD to have a very high oxidation potential, and thus, making it a suitable candidate for biochemical treatment of wastewater [11].

Herein, we studied the degradation of glyphosate wastewater through electrochemical anodic oxidation, using the BDD electrode, which presented excellent physicochemical properties. This study explores the different parameters to optimize electrolysis and an-

alyzes the degradation products of glyphosate.

MATERIALS AND METHODS

Reagents

BDD was provided by CONDlAS GmbH (Dortmund, Germany) and produced through microplasma chemical deposition (MPCVD). Glyphosate [N-(phosphonomethyl) glycine] (95%) was provided by Suzhou Jiahui Chemicals (Suzhou, Jiangsu, China). Chemical reagents, such as perchloric acid, sulfuric acid, hydrogen bromide, sodium nitrite, ammonium molybdate, ascorbic acid, sodium sulfate, and sodium chloride, were all analytically pure and were purchased from China National Medicines Corporation Ltd. (Shanghai, China). They were used without further purification. Sulfuric acid and sodium hydroxide were used to adjust the pH. Water used in the experiment was prepared using the Millipore Milli-Q water purification system (Millipore, USA) (M-Q purified water > 18 MΩ·cm).

Experimental installation

Using a 500-ml flask as the reservoir, the reaction was driven by a peristaltic pump at a rate of 120 r/min in a sealed reactor. We used BBD or PbO_2 as the anode, and Pt was the cathode (with an effective area of 77.44 cm^2). The electrode separation was maintained at 0.8 cm. The reactor is illustrated in Fig. 1.

Experimental equipment and method

The absorbance of the solution was determined using a Shimadzu UV-2450 UV–Vis spectrophotometer, (Shimadzu, Japan). We used a 1010 total organic carbon (TOC) analyzer (OI Analytical, USA) to quantify the TOC before and after the reaction. A Merck Nova 60 spectroquant (Merck, Germany) was used to analyze the COD of the solution. The electrochemical measurements were performed using the CHI660c electrochemical analyzer from the Shanghai Chenhua Instruments Co., Ltd., China. The experiment used a three-electrode electrochemical cell with a working-electrode area of 0.07 cm^2. The counter and reference electrodes were Pt and $Hg/HgCl_2$ (saturated KCl solution), respectively.

Determination of glyphosate degradation

As the atomic structure of glyphosate contains no chromophore, it must undergo chemical derivation before it can be analyzed using photometry. Glyphosate is a secondary amine that can easily be nitrated under acidic conditions as illustrated in Eqs. (1)–(3) and Fig. 2. Here, NOBr was used as a catalyst. The nitroso compounds thus produced present absorption peaks at 242 nm, allowing the glyphosate derivatives to be analyzed with UV-spectrophotometry.

$$2\,NaNO_2 + H_2SO_4 \rightarrow 2\,HNO_2 + Na_2SO_4 \quad (1)$$

$$H_2SO_4 + 2\,KBr \rightarrow 2\,HBr + K_2SO_4 \quad (2)$$

$$HBr + HNO_2 \rightarrow NOBr + H_2O \quad (3)$$

Determination of the degree of glyphosate mineralization

The following reaction equation shows that PO_4^{3-} is a product of the full degradation of glyphosate.

$$C_3H_8O_5NP + 8\,H_2O \rightarrow 3\,CO_2 + PO_4^{3-} + NO_3^- + 24\,H^+ + 20\,e^- \quad (4)$$

Molybdenum blue colorimetry is commonly used to determine trace amounts of phosphorus in acidic test solutions. In this test, phosphate reacts with ammonium to produce yellow molybdenum phosphate. The reaction is as follows:

$$PO_4^{3-} + 12\,MoO_4^{2-} + 27\,H^+ \rightarrow H_3[P(Mo_3O_{10})_4] + 12\,H_2O \quad (5)$$

The yellow compound thus produced is further reduced to a molybdenum blue complex, when it encounters a reducing agent, such as ascorbic acid or $SnCl_2$, yielding a dark blue product. The intensity of the blue color of the product is proportional to its phosphorus content. Based on these optical properties, we used a spectrophotometer to determine and discover the largest absorption peaks at 730 nm.

RESULTS AND DISCUSSION

Variation in voltage

In this experiment, electrolysis was conducted at a constant current. Voltage was recorded throughout the experiment and the various readings are shown in Fig. 3(a), where the voltage remains constant. This lack of change implies that during the reaction, no polymer membrane was generated upon the oxidation of the organic matter attached to the surface of the BDD because of the high electrode potential of BDD. In the voltage range that is typical of water decomposition, strong hydroxyl-free radicals that are capable of further oxidizing the polymer membrane prevent the surface of the electrode from deactivation.

Glyphosate standard curve

Glyphosate ($C_3H_8NO_5P$; MW: 169.07 Da) was the model compound used in this study. UV–Vis spectrophotometry experiments on sample wastewater containing glyphosate showed that there is a correlation between concentration and absorbance. After the complete nitration of the standard glyphosate solution, the absorbance of different sample solutions was measured separately at 242 nm.

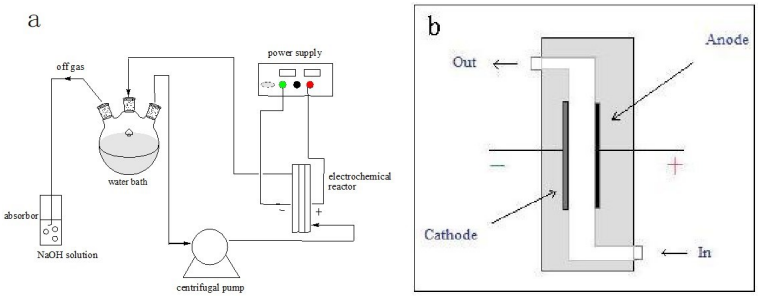

Fig. 1 Experimental device (a) and the partial enlargement of the electrolytic reactor (b).

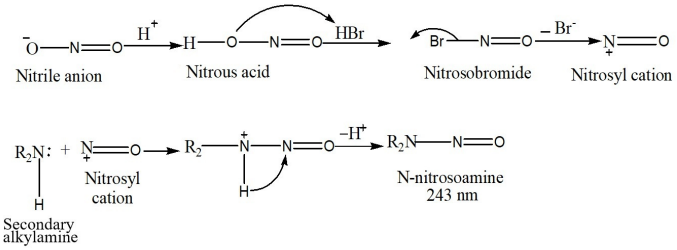

Fig. 2 Under acidic conditions, the secondary amine is converted to the nitrite compound.

As shown in Fig. 3(b), the concentration of glyphosate decreased from 80 to 0 mg/l with excellent linear correlation. The regression equation was $y = 0.03698x - 0.04267$ and linear correlation coefficient (R^2) was 0.9993.

Phosphorus standard curve

The standard solution of phosphorus was prepared using KDP (potassium dihydrogen phosphate); the solution was first subjected to molybdenum blue colorimetry and the product was analyzed with UV–Vis spectrophotometry. The characteristic absorption peaks at 730 nm were used to build a correlation between concentration and absorbance. When the concentration of PO_4^{3-}-trapped P fell between 0.6 and 4 mg/l, the correlation was linear and the regression equation was $y = 0.24764x - 0.13987$ with an R^2 of 0.994 (Fig. 4(a)); however, when $C_{glp} < 0.6$ mg/l, unstable peaks were detected, and the absorbance tended to vary frequently over time.

Influence of experimental parameters

Fig. 4(b) shows the influence of temperature on the rate of degradation of glyphosate. When temperature increases, the rate of degradation also increases because the mass transfer rate is directly proportional to temperature. The chance of generating polymerization products was rather low in these conditions. Instead, organic matter became relatively unstable, and thus, its degradation accelerated.

The pH of the solution was adjusted to be acidic, alkaline, or neutral. Fig. 5(a) illustrates the differences in TOC removal rate in glyphosate solutions with different pH values 3 h into the electrolysis. The oxidation efficiency of glyphosate was relatively high in the acidic medium. A previous study has reported that glyphosate shows electrochemical oxidation characteristics at low pH (acidic conditions) [12]. Other

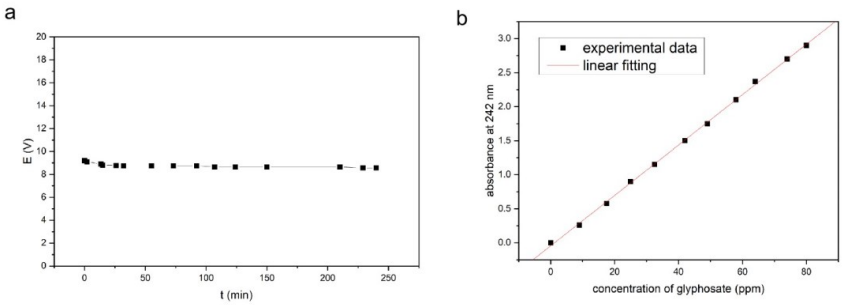

Fig. 3 (a) The voltage curve, i.e., trends of variation in voltage, during electrolysis conducted at a constant current. (b) Glyphosate standard curve: a linear-fitting curve between concentration and absorbance.

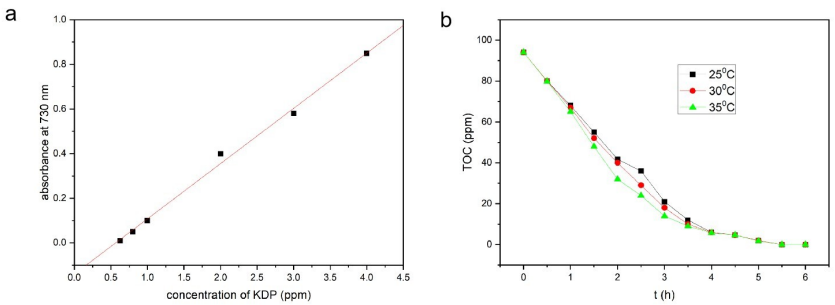

Fig. 4 (a) Phosphorus standard curve (KDP, potassium dihydrogen phosphate). (b) The influence of temperature on the removal of TOC: 50 mM Na_2SO_4 as the electrolyte, 500 mg/l GLP (glyphosate) solution, (▲) 35 °C; (●) 30 °C; (■) 25 °C, current with a density of 6.4 mA/cm^2.

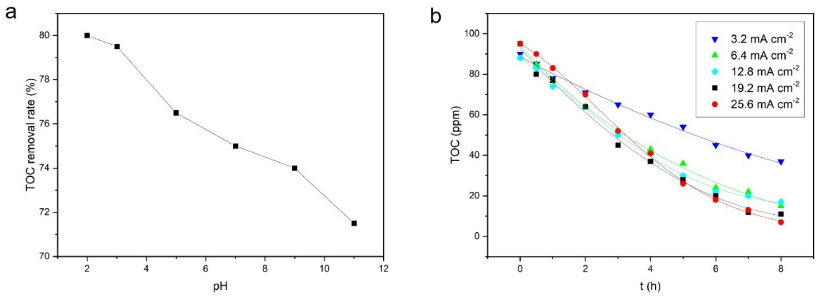

Fig. 5 (a) The influence of pH on the removal rates of TOC: 50 mM Na_2SO_4 as the electrolyte, 500 mg/l GLP (glyphosate) solution, time elapsed = 4 h, current = 6.4 mA/cm^2. (b) The influence of current density on the degradation of TOC: PbO_2 as the anode, 50 mM Na_2SO_4 as the electrolyte, 500 mg/l GLP solution, current densities: (▼) 3.2; (▲) 6.4; (♦) 12.8; (■) 19.2; (●) 25.6 mA/cm^2.

research studies have revealed that it is easier for the oxygen evolution side reaction to occur in an alkaline medium [13]. Therefore, at low-pH conditions, the oxygen evolution reaction reduces, while the oxidation efficiency is expected to increase.

Comparison of BDD and PbO_2 electrodes

Unlike common electrodes, such as Pt, graphite, or oxygen, which are slow in transmission and consume a lot of current, PbO_2 or BDD electrodes use high oxygen overpotential, and thus, can accelerate the degradation of organic matter, while suffering from lower loss of energy [14]. Previous studies have compared these two kinds of electrodes to assess them as so-called inactive electrodes, i.e., electrodes with no high-grade oxidation. In simpler words, both these electrodes oxidize effectively and can produce large amounts of active free radicals that are physically absorbed on their surfaces through reactions (6) and (7). Overall, these properties result in the mineralization of organic matter.

$$PbO_2 + H_2O \rightarrow PbO_2(\cdot OH) + H^+ + e^- \quad (6)$$

$$BDD + H_2O \rightarrow BDD(\cdot OH) + H^+ + e^- \quad (7)$$

PbO_2 is a common metal-oxide electrode. It is widely used for industrial purposes due to its low cost, convenient preparation, low resistance, chemical stability, and large surface area.

Fig. 5(b) depicts the rate of degradation of the mixed solution of 50 mM Na_2SO_4 and 500 mg/l GLP at different current densities. It was found that when the current density was below 3.2 mA/cm^2, the TOC removal rate was also relatively low. Contrarily, when the current density was higher than or equal to 6.4 mA/cm^2, the TOC removal rate greatly increased. Later, even if the current value was increased, the removal rate did not vary strongly, which was largely attributed to the transfer rate of the solution.

According to previous research, if the oxidation reaction is regulated by diffusion, a theoretical model of the electrochemical reaction can be achieved [15]. With this model, the ultimate current value can be estimated according to the COD.

$$i_{\text{lim}}(t) = 4Fk_m\text{COD}(t) \quad (8)$$

In this model, i_{lim} is the ultimate current value (A/cm^2) for a given period, t; '4' is the number of electrons exchanged per mole of oxygen; F stands for the Faraday constant (C/mol); k_m refers to the average mass transfer coefficient (m/s) of the electrochemical reactor. COD (t) is the chemical oxygen demand at a given time (mol O_2/m^3).

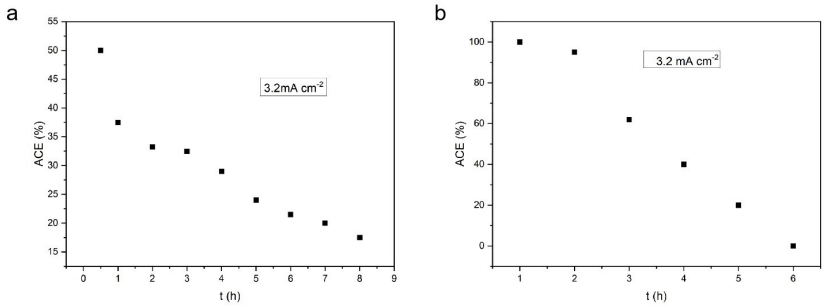

Fig. 6 The differences in average current efficiency (ACE) for the degradation of glyphosate using PbO_2 (a) and BDD (b) as the anodes; the experimental conditions were the same.

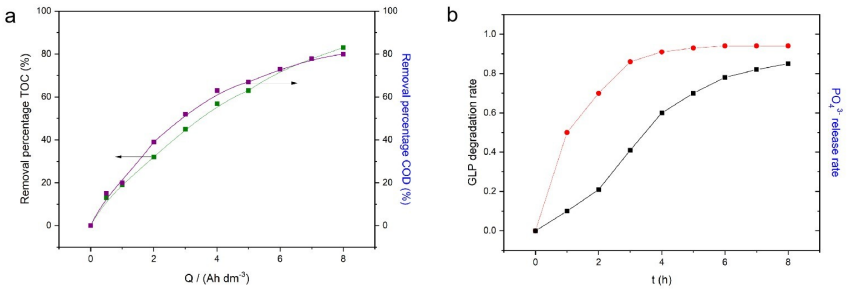

Fig. 7 (a) Change in the removal rate of glyphosate (•) TOC and (■) COD with the same power consumption. Experimental conditions: 6.4 mA/cm^2, 500 mg/l GLP solution using 50 mM Na_2SO_4 as the electrolyte. (b) The electrolysis efficiency of glyphosate: (•) the glyphosate (GLP) degradation rate and (■) the rate of release of PO_4^{3-}. Experimental conditions: 6.4 mA/cm^2, 500 mg/l GLP solution using 50 mM Na_2SO_4 as the electrolyte.

When the initial COD of 500 mg/l GLP was 232 g/l, and the mass transfer coefficient (k) was 0.6×10^{-5} m/s (the rate of the peristaltic pump was 120 r/min), the initial ultimate current density ($i_{\text{lim}}(0)$) was calculated to be 6 mA/cm^2. Thus, when the actual current density was smaller than 6 mA/cm^2, i.e., 3.2 mA/cm^2, the free radicals on the surface of the electrodes were not fully effective. However, when it was $>$ 6 mA/cm^2, the transmission was complete, and thus, the oxidation took place effectively on the surface of the BDD. However, afterwards, as the current density continued to increase, the free radicals generated on the surface of the electrode became insufficient for the organic matter transmitted. In this situation, a lot of current energy was released in the form of heat.

Fig. 6 depicts the change in the average current efficiency with time for the degradation of glyphosate using PbO_2/BDD as the electrodes. The current density was controlled at a value less than the ultimate current density. According to the current efficiency formula:

$$\text{ACE} = \frac{[\text{COD}_0 - \text{COD}_t]FV}{8It} \tag{9}$$

The average current efficiency is supposed to reach 100% at the beginning of the reaction. However, virtually, only the BDD electrode conformed to this theoretical model. When PbO_2 was used as the anode, the average current efficiency was only 50% of that recorded at the very beginning, which is attributable to the better absorption of hydroxyl-free radicals by PbO_2 compared to BDD. Free radicals are not prone to reacting with organic matter. Reactions with the electrode are more likely to occur and generate oxygen. When PbO_2 is used as the anode, although the current density is set at less than the ultimate value, the oxygen evolution reaction is unavoidable.

Analysis of the degradation products of glyphosate

Fig. 7(a) illustrates the difference between the removal rates of the TOC and the COD after degradation during different periods. They never present strong differences in their removal patterns. The COD removal rate was always higher than the TOC removal rate; this gap was especially prominent in the middle of the experiment, suggesting the existence of intermediate products.

The rate of release of PO_4^{3-} is an indicator of the full degradation of glyphosate. As per Fig. 7(b), when glyphosate is oxidized, its molecules separate much faster than the release of PO_4^{3-}. These observations are consistent with the comparative results of TOC and COD.

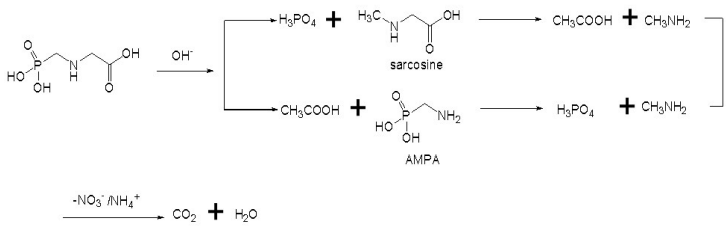

Fig. 8 The route for the degradation of glyphosate.

Considering the reliability and sensitivity of the four ways, we can infer that by-products, other than CO_2 and PO_4^{3-}, were generated during the oxidation reaction. According to previous research using microorganisms, the major intermediate products are AMPA ((Aminomethyl) phosphonic acid) and sarcosine [16].

Fig. 8 depicts the route by which the degradation of glyphosate takes place. The formation of these products explains the phenomenon that takes place during electrolysis. In addition, the trends of degradation and mineralization justify the production of non-degradable products in this system.

CONCLUSION

The voltage remained stable during the experiment, with no polymer film formed on the BDD electrode. Higher temperature and acidic conditions accelerated glyphosate degradation by improving mass transfer and inhibiting oxygen evolution. Within the limiting current density, raising current density boosted electrolysis efficiency; beyond this value, efficiency dropped sharply with little rate improvement. Compared with PbO_2, BDD showed higher current efficiency due to weaker hydroxyl radical adsorption and stronger reactivity with organics. During electrolysis, glyphosate was degraded into intermediates such as AMPA and sarcosine, and finally fully mineralized into CO_2 and water.

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REFERENCES

1. Yaah VBK, Ahmadi S, Quimbayo MJ, Morales-Torres S, Ojala S (2024) Recent technologies for glyphosate removal from aqueous environment: A critical review. *Environ Res* **240**, 117477.
2. Thompson M, Chauhan BS (2022) History and perspective of herbicide use in Australia and New Zealand. *Adv Weed Sci* **40**, e20210075.
3. Dechakiatkrai C, Kaewtheta O, Phanichphant S (2023) Potential effectiveness of visible-light-driven Fe/TiO_2 photocatalysts for degradation of dyes contaminated wastewater and their antibacterial activity. *ScienceAsia* **49**, 454–461.
4. Ahmad S, Chandrasekaran M, Ahmad HW (2023) Investigation of the persistence, toxicological effects, and ecological issues of S-triazine herbicides and their biodegradation using emerging technologies: A review. *Microorganisms* **11**, 2558.
5. Guimarães T, de Aguiar A, da Silva E, Mielke K, da Costa M, da Silva A, Teixeira APC, Lopes RP (2023) Dicamba degradation by Fenton-like process using iron/biochar composites. *J Brazilian Chem Soc* **34**, 1753–1761.
6. Mohanty SS, Das AP (2021) A systematic study on the microbial degradation of glyphosate: A review. *Geomicrobiol J* **39**, 316–327.
7. Brdarić TP, Aćimović DD, Savić Rosić BG, Simić MD, Stojanović KD, Vranješ ZM, Anićijević DV (2024) Bibliometric analysis of nanostructured anodes for electro-oxidative wastewater treatment. *Sustainability* **16**, 3982.
8. Wan Y, Liu J, Pi F, Wang J (2023) Advances on removal of organophosphorus pesticides with electrochemical technology. *Crit Rev Food Sci Nutr* **63**, 8850–8867.
9. Magdaleno AL, Brillas E, Garcia-Segura S, dos Santos AJ (2024) Comparison of electrochemical advanced oxidation processes for the treatment of complex synthetic dye mixtures. *Sep Purif Technol* **345**, 127295.
10. Kangkamano T, Kongsune P, Suwanraksa K, Charoenlapa T, Khaophonga S, Intachai S (2025) Effect of temperature of boric acid-doped porous activated carbon preparation on the electrochemical capacitor performance. *ScienceAsia* **51**, 2025031.
11. 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. *J Hazard Mater* **283**, 551–557.
12. Chen S, Liu Y (2007) Study on the photocatalytic degradation of glyphosate by TiO_2 photocatalyst. *Chemosphere* **67**, 1010–1017.
13. Nylén L, Behm M, Cornell A, Lindbergh G (2007) Investigation of the oxygen evolving electrode in pH-neutral electrolytes. *Electrochimica Acta* **52**, 4513–4524.
14. Sirés I, Brillas E, Cerisola G, Panizza M (2008) Comparative depollution of mecoprop aqueous solutions by electrochemical incineration using BDD and PbO_2 as high oxidation power anodes. *J Electroanal Chem* **613**, 151–159.
15. Rodrigo MA, Michaud PA, Duo I, Panizza M, Cerisola G, Comninellis C (2001) Oxidation of 4-chlorophenol at boron-doped diamond electrode for wastewater treatment. *J Electrochem Soc* **148**, D60–D64.
16. Dick RE, Quinn JP (1995) Glyphosate-degrading isolates from environmental samples: Occurrence and pathways of degradation. *Appl Microbiol Biotechnol* **43**, 545–550.