Expanding the Application of Boron-Doped Modified Diamond Electrodes in the Treatment of Recalcitrant Organic Pollutants

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ABSTRACT Wastewater from textile, leather, pharmaceutical, and chemical industries contains high concentrations of recalcitrant organic pollutants, which are difficult to mineralize completely using conventional biological or chemical processes and pose persistent ecological risks. Boron-doped diamond (BDD) electrodes, with a wide electrochemical potential window, high oxygen evolution overpotential, strong hydroxyl radical generation ability, and excellent chemical stability, provide an effective electric-field-driven route for advanced oxidation treatment. This paper systematically reviews the preparation processes, structural optimization, and electrochemical performance of BDD electrodes, and analyzes the roles of boron doping, substrate selection, surface termination, and functional modification in regulating conductivity, interfacial activity, and long-term stability. The degradation mechanism of recalcitrant organics is discussed from the perspectives of quasi-free hydroxyl radical oxidation, direct electron transfer, adsorption-controlled interfacial reactions, and mineralization pathways. Potential applications in textile dyeing wastewater, pharmaceutical wastewater, emerging pollutant degradation, and wastewater reuse are further examined. In addition, the synergistic coupling of BDD electrochemical oxidation with biological treatment, membrane separation, photocatalysis, and ultrasonic enhancement is evaluated for improving mass transfer, energy efficiency, and process stability. The analysis shows that BDD electrodes have strong engineering potential for high-COD and chromatic industrial wastewater treatment, while future scale-up requires lower-cost electrode fabrication, optimized flow-field design, and intelligent control of electrochemical parameters.

INDEX TERMS boron-doped diamond electrode, electrochemical oxidation, electric-field-driven treatment, textile wastewater, hydroxyl radicals

I. INTRODUCTION

With the continuous advancement of industrialization, the emissions of recalcitrant organic pollutants from industries such as textiles, dyeing and printing, pharmaceuticals, and chemicals are increasing. These pollutants are structurally stable and highly toxic, making it difficult for conventional biological and chemical treatment methods to completely mineralize them, thus becoming a major problem in water pollution control. Electrochemical advanced oxidation (BDD) technology has attracted attention due to its advantages such as flexible operation, no need for external chemical reagents, and ability to deeply mineralize pollutants. Boron-doped diamond electrodes (BDD electrodes) are the main material in this field, possessing a very wide electrochemical stability window, very low background current, and highly efficient hydroxyl radical generation capability, demonstrating excellent performance in the degradation of various recalcitrant organic pollutants. This article evaluates the fabrication performance and degradation mechanisms of BDD electrodes, specifically highlighting their industrial potential for the sustainable electrochemical treatment of complex textile dyeing wastewater.

II. PREPARATION AND PERFORMANCE CHARACTERISTICS OF BORON-DOPED MODIFIED DIAMOND ELECTRODES

A. FABRICATION PROCESS AND STRUCTURAL OPTIMIZATION OF BORON-DOPED DIAMOND ELECTRODES

Boron-doped diamond electrodes are generally prepared by chemical vapor deposition, which deposits a boron-

doped diamond film on a conductive substrate under high temperature and low pressure using a mixture of boron-containing gas source and carbon source. The boron doping concentration is the key factor that determines the conductivity of the electrode. Appropriately increasing the boron doping amount can significantly improve the conductivity of the film, making the film change from an insulator to a semiconductor or even a quasi-metallic conductor [1]. However, it should be noted that a trade-off exists; excessively high doping levels may lead to a narrowing of the electrochemical potential window due to the increase in metallic-like states, which can slightly reduce the overpotential for oxygen evolution. The choice of substrate material is also very important. Silicon wafers, titanium wafers, niobium wafers, etc. are all used as supporting substrates. Different substrates have a great influence on the adhesion and thermal stability of the film. By adjusting the process parameters such as deposition temperature, gas flow ratio, and deposition time, BDD electrode materials with uniform structure and stable performance can be obtained [2].

B. ANALYSIS OF ELECTROCHEMICAL PERFORMANCE AND WIDE POTENTIAL WINDOW CHARACTERISTICS

BDD electrodes have a wide electrochemical stability window in aqueous systems and can reach more than 3.2V in acidic media, approximately 2.8V in neutral solutions, and remains significantly wider than traditional materials even in alkaline media (above 2.3V), which is much higher than traditional electrode materials such as platinum and graphite. Therefore, BDD electrodes can remain stable at high potentials without substrate oxidation or electrode corrosion, providing a favorable potential operating space for the deep oxidation of recalcitrant organic matter [3]. BDD electrodes have low background current and low capacitive current interference, which is beneficial to improving the accuracy of electrochemical detection and oxidation processes. In addition, it has a high overpotential for redox reactions, effectively suppressing oxygen evolution side reactions, and using electrical energy preferentially to oxidize and degrade target pollutants, thereby improving the overall current efficiency [4].

C. MECHANISM OF THE EFFECT OF SURFACE MODIFICATION ON CATALYTIC ACTIVITY

The chemical state of the BDD electrode surface plays an important role in regulating its catalytic performance. Through anodic oxidation, the electrode surface can have more oxygen-containing functional groups, exhibiting hydrophilic characteristics, which is conducive to the adsorption and activation of water molecules on the electrode surface, thereby promoting the effective generation of hydroxyl radicals [5]. Conversely, hydrogen terminal treatment makes the surface hydrophobic, thus affecting the interfacial contact state between the electrode and the aqueous solution. In addition to the adjustment of terminal groups, metal oxide nanoparticles, conductive polymers or other functional materials can be used to modify the BDD surface [6].

III. MECHANISM OF ACTION OF BORON-DOPED DIAMOND ELECTRODES IN TREATING RECALCITRANT ORGANIC POLLUTANTS

A. HYDROXYL RADICAL GENERATION AND ADVANCED OXIDATIVE DEGRADATION PATHWAYS

The main mechanism of BDD electrode treatment of recalcitrant organic pollutants is the efficient generation of hydroxyl radicals on the electrode surface. When water molecules are at a level higher than the oxygen evolution potential on the BDD electrode surface, they will undergo oxidative decomposition and generate adsorbed hydroxyl radicals. Since the adsorption capacity of BDD electrode for ·OH is weak, the generated ·OH is in a quasi-free state and has strong oxidative activity. While the degradation primarily occurs via these quasi-free radicals in the reaction zone near the electrode surface, the process is simultaneously governed by the adsorption of organic molecules onto the electrode; thus, the overall reaction rate is a synergistic result of both surface-adsorbed species and bulk-solution mediated oxidation. The redox potential is as high as 2.80V, which can non-selectively attack almost all organic chemical bonds [7]. Under the continuous action of ·OH, the benzene ring of recalcitrant organic pollutants is opened, the long chain is broken, and they gradually become small molecule organic acids. Finally, they are mineralized into carbon dioxide and water, achieving the purpose of completely detoxifying the pollutants. Compared with traditional advanced oxidation technologies such as Fenton and ozone, BDD electrode electrochemical oxidation does not require the addition of external oxidants. The process is clean and efficient, the degradation path is more thorough, and it has a good degradation ability for a variety of complex recalcitrant pollutants. It is an important technical means to achieve deep mineralization of organic pollutants [8]. To more intuitively demonstrate the differences between BDD electrodes and common advanced oxidation technologies in terms of hydroxyl radical oxidation capabilities, Table 1 compares the core parameters of various technologies.

TABLE 1. Comparison of hydroxyl radical performance of different advanced oxidation technologies

Technology type	·OH redox potential (V)	Do we need to add external reagents?	Applicable pH range	Completeness of mineralization
BDD electrochemical oxidation	2.80	No	Width (2–12)	High
Fenton oxidation	2.76	Yes (H_2O_2/Fe^{2+})	Acidic (2–4)	Middle
Ozone oxidation	2.07	Yes (O_3)	Better alkalinity	Middle
Photocatalytic oxidation	2.80	Light source required	Neutral to slightly acidic	Medium and high
Wet air oxidation	–	No	Width	Middle

B. ELECTRON TRANSFER MECHANISM AND ORGANIC MINERALIZATION PROCESS

In addition to indirect oxidation, BDD electrodes can also oxidize and degrade organic pollutants by direct electron

transfer. When organic molecules lose electrons directly on the electrode surface, anodization occurs, producing free radical cation intermediates. These intermediates are highly chemically active and can quickly trigger subsequent chain reactions, causing organic matter to degrade gradually. Direct oxidation and indirect oxidation occur simultaneously in the BDD electrode system. The proportion of the two is affected by the combined effects of solution pH, electrolyte type, current density, and organic matter concentration [9]. During organic matter mineralization, pollutants first undergo functional group oxidation modification and carbon chain breakage and recombination, generating short-chain organic acid intermediates such as oxalic acid, acetic acid, and formic acid. These intermediates are continuously converted into CO_2 and H_2O under continuous electro-oxidation. The total organic carbon (TOC) concentration decreases continuously with the extension of electrolysis time, and the mineralization rate increases continuously, eventually reaching the level of complete mineralization of organic pollutants [10]. Different operating parameters have a significant impact on the rate of mineralization. Table 2 summarizes the main influencing factors and their effects.

TABLE 2. Main factors affecting the organic mineralization process of BDD electrodes

Influencing factors	Direction of change	Impact on TOC removal rate	Main mechanism of action
Current density	Increase	Initially increased and subsequently plateaued	Increasing the ·OH generation rate; too much will increase energy consumption.
Solution pH	Neutral to slightly acidic	Superior	Effects on the stability of ·OH and the adsorption state of organic matter
Electrolyte concentration	Appropriately increase	Improve	Improve solution conductivity and reduce tank voltage
Initial pollutant concentration	Increase	Removal rate exhibits a threshold effect	At lower concentrations, increasing the pollutant load improves mass transfer and current efficiency; however, beyond a critical threshold, the relative removal rate may decrease as ·OH generation becomes the limiting factor.
Electrolysis time	Continuous extend	Mineralization improvement	Mineralization intermediates are gradually oxidized

C. THE IMPACT OF ELECTRODE STABILITY ON THE CONTINUOUS DEGRADATION OF POLLUTANTS

The long-term stability of the electrode is one of the important factors affecting the practical application efficiency of BDD electrochemical oxidation technology. BDD electrodes have strong chemical inertness and will not undergo significant corrosion and dissolution in strong acid, strong alkali and highly oxidizing media, and the surface active sites can be maintained. However, during long-term electrolysis, the degradation intermediates of organic pollutants will polymerize and adsorb on the electrode surface, forming a passivation layer, which will cause the electrode activity to gradually decrease and the degradation efficiency to decline [11]. For the problem of electrode passivation, the activity of the electrode can be effectively restored and the service life extended by using methods such as periodic polarity reversal of the anode and cathode, ultrasonic-assisted cleaning or electrochemical regeneration treatment. In addition, the bonding strength between the BDD film and the substrate affects the durability of the electrode under high current density [12]. Table 3 systematically compares the effects and applicable conditions of common electrode regeneration methods to provide a basis for the selection of maintenance strategies in practical applications.

TABLE 3. Comparison of Commonly Used Regeneration Methods for BDD Electrodes

Regeneration method	Operating conditions	Active recovery effect	Electrode damage	Applicable Scenarios
Polarity reversal	Periodically switch the direction of current	Better	Low	Continuous operation system
Ultrasonic Assisted Cleaning	Ultrasonic frequency 20–40 kHz	Good	Lower	Intermittent operation system
Electrochemical regeneration	High potential anodic polarization	Good	Medium	Severe passivation
Chemical soaking cleaning	Immersion in acid/alkali solutions	Generally	Low	Mild pollution
High-temperature heat treatment	Calcination at 300–500°C	Better	Higher	Offline maintenance

IV. APPLICATION EXPANSION AND PROSPECTS OF BORON-DOPED MODIFIED DIAMOND ELECTRODES

Due to its strong oxidation capabilities, BDD electrodes have been widely used in the treatment of highly recalcitrant organic wastewater in industries such as textile printing and dyeing, pharmaceuticals, and chemicals. The core treatment process is as follows.

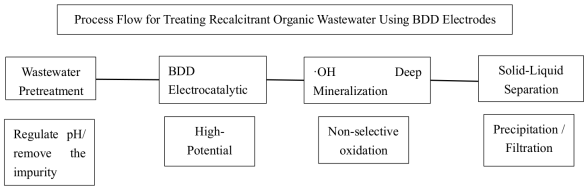

FIGURE 1. Process flow of BDD electrode for treating recalcitrant organic wastewater

A. APPLICATION IN THE DEGRADATION OF EMERGING POLLUTANTS IN INDUSTRIAL WASTEWATER

With the continuous expansion of industrial production scale and the increasing complexity of product structure, many new recalcitrant organic pollutants that cannot be effectively removed by traditional treatment processes have appeared in industrial wastewater. These mainly include antibiotic drug residues, endocrine disruptors, perfluorinated compounds and synthetic dyes. These pollutants have high persistence in

the natural environment and can also bring obvious ecotoxicological effects to organisms even at low concentrations. BDD electrodes have strong oxidizing properties and a wide applicable pH range, and show good degradation effects on the abovementioned new pollutants. While the generation of hydroxyl radicals is inherently nonselective, the "selective" removal observed in industrial wastewater often stems from the high oxidation potential of BDD, which allows it to attack recalcitrant functional groups in emerging pollutants that remain untouched by less powerful, more selective oxidants. In the treatment of textile printing and dyeing wastewater, BDD electrodes have a good oxidative degradation effect on structurally stable colored organics such as reactive dyes and azo dyes, and can achieve the effects of decolorization and COD reduction. The effluent quality is better than that of traditional treatment processes [13]. BDD electrodes can completely mineralize antibiotic molecules such as tetracycline and sulfonamides, eliminating their biological activity and the risk of drug resistance transmission. Compared with biological treatment units, BDD electrochemical treatment is not limited by the biological toxicity of organic matter. It can be used as a pretreatment or deep treatment unit for biochemical treatment and can be flexibly embedded into the existing wastewater treatment process, which greatly improves the overall treatment effect and broadens the application scope of electrochemical technology in industrial wastewater treatment [14].

B. SYNERGISTIC ENHANCEMENT EFFECT OF COUPLING WITH OTHER PROCESSING TECHNOLOGIES

BDD electrochemical oxidation technology with other treatment technologies is a current research focus. The synergy of multiple technologies can overcome the efficiency limitations of individual treatment processes, achieving complementary advantages. Combining BDD electrochemical oxidation with photocatalysis, under the combined action of electric and light fields, can significantly accelerate the generation of ·OH, speeding up the oxidative degradation process of organic matter. This is particularly effective for treating high-concentration, highly toxic, and recalcitrant wastewater. The combination of BDD electrochemical technology and biological treatment has also attracted attention. Electrochemical pretreatment can convert recalcitrant organic matter into readily biodegradable small-molecule intermediates, greatly improving the biodegradability index of wastewater (BOD5/COD), creating favorable conditions for subsequent biological treatment units, thereby improving overall degradation efficiency. Furthermore, the coupling of BDD electrochemical oxidation with membrane separation technology is significant for wastewater reuse. Electrochemical treatment can inhibit membrane fouling, extend the service life of membrane modules, and achieve the dual goals of improving treatment efficiency and operational stability. The ultrasonic electrochemical coupling system utilizes the ultrasonic cavitation effect to enhance the mass transfer process, thereby improving the mass transfer rate and reactivity of the electrode surface, providing a new technical approach for BDD electrode treatment of complex wastewater systems. The development of multi-technology coupling strategies will enable BDD electrode technology to be more widely applied in various application scenarios [15]. The coupling of BDD electrode with biological, membrane separation, photocatalysis and other technologies can solve the bottleneck of a single process and improve the treatment efficiency and economy. The comparative advantages are as follows.

TABLE 4. Comparison of BDD electrode coupling technology and single process

Coupling technology	Core advantages	Applicable Scenarios	Improved processing effect
BDD + Biological Treatment	Improve biodegradability and reduce energy consumption	High-concentration pharmaceutical/chemical wastewater	COD removal rate increased by 20%–30%.
BDD + Membrane Separation	Retaining contaminants and extending electrode lifespan	Dyeing/Papermaking Wastewater	Color removal rate reaches over 95%.

C. TECHNICAL CHALLENGES AND OPTIMIZATION DIRECTIONS FOR LARGE-SCALE APPLICATION

Although BDD electrodes have demonstrated excellent performance in treating recalcitrant organic compounds in laboratory studies, several significant technical challenges remain in their transition from small-scale research to large-scale engineering applications, limiting their widespread adoption and industrialization. Firstly, the high cost of BDD electrode fabrication, coupled with the stringent equipment requirements of chemical vapor deposition (CVD) processes, low film deposition rates, and the technical difficulties in preparing large-area, uniform BDD films, directly increases the initial investment cost of electrode materials. Secondly, the structural design and flow field optimization of large-scale electrolyzers are critical engineering factors affecting treatment efficiency. Reducing system energy consumption while maintaining mass transfer efficiency is a key challenge to address during scale-up. Furthermore, the complex composition of industrial wastewater, with significant fluctuations in the concentrations of coexisting ions, suspended solids, and organic matter, can impact the degradation efficiency and stability of BDD electrodes. Further evaluation of the long-term performance of electrodes under actual wastewater conditions requires further accumulation of experience. To address the above issues, future optimization directions mainly include the following: developing new low-cost, high-efficiency BDD thin film preparation technologies to promote the large-scale production of electrode materials; improving the hydrodynamic design of electrolyzers to create reactor structures with high mass transfer efficiency; and relying on artificial

intelligence and process control technologies to achieve intelligent dynamic adjustment of electrolysis parameters.

V. CONCLUSION

Boron-doped diamond (BDD) electrodes exhibit significant advantages in treating recalcitrant organic pollutants, specifically addressing the high chemical oxygen demand (COD) and complex coloration inherent in textile dyeing effluents through their unique electrochemical properties. This paper reviews the research progress of BDD electrodes from three aspects: preparation process, degradation mechanism, and application expansion. It concludes that BDD electrodes show promising application prospects in the advanced treatment of industrial wastewater such as textile dyeing and printing wastewater and pharmaceutical wastewater. Future research will further reduce fabrication costs and deepen multi-technology integration. By optimizing energy efficiency through multi-technology coupling (as shown in Table 4) to offset initial capital expenditure, BDD electrodes are positioned as essential components for large-scale textile wastewater reclamation, providing more efficient, cleaner technical support for industrial water pollution control.

AUTHOR CONTRIBUTIONS

Conceptualization – Beibei Kang, Kai Shang, Yang Lou and Piaoying Gao; methodology – Beibei Kang, Yang Lou and Piaoying Gao; investigation – Beibei Kang, Kai Shang, Yang Lou and Piaoying Gao; writing-original draft preparation – Beibei Kang, Kai Shang, Yang Lou and Piaoying Gao. All authors have read and agreed to the published version of the manuscript.

CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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