

Article

Hydrogen Production from Wastewater Degradation on a Rotating Hole-Arranged Boron-Doped Diamond Anode

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Abstract: An electrochemical system using a rotating hole-arranged boron-doped diamond (HABDD) film anode was designed for wastewater degradation. Meanwhile, in a reciprocal process, a foam nickel (FNI) cathode was employed for hydrogen evolution using the ions liberated from the HABDD. The HABDD was custom-made using an MWCVD device and characterized by SEM, Raman and electrochemical measurement. Some wastewater was tested on the HABDD anode to examine its electrochemical performance. The efficiency of the electrochemical system was evaluated by COD removal rate and hydrogen production yields. The influence of the rotating and flowing rates of the electrolyte on electrochemical performance was discussed. The rotating HABDD with dynamic three-dimensional flowing paths provided a high mass transfer, which promoted the overall performance of the wastewater mineralization. Meanwhile, the ions released from the anode to the cathode improved the hydrogen generation performance on the cathode. The hydrogen production efficiency in relation to the electrochemical oxidation process was studied in terms of the COD change and treatment time.

Keywords: hole-arranged boron-doped diamond; wastewater degradation; hydrogen production



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1. Introduction

Every year, a significant amount of wastewater, mainly composed of industrial effluent and municipal drainage water, is released into the environment, which has disastrous consequences. There is an urgent need to develop a facile and green wastewater treatment system with high performance that can be made available to varied areas and fields. On the one hand, as an alternative treatment method, the electrochemical oxidation (EO) process shows high efficiency for waste organic degradation owing to its environmental compatibility and versatility. It provides an ideal solution to wastewater treatment. On the other hand, hydrogen energy has been regarded as having strategic status due to its clean and effectively reproducible advantages, which can also be produced by electrochemical methods. In this circumstance, the development of a binary electrochemical system combined with EO treatment and hydrogen gas generation simultaneously has significant economic and sustainable potential [1,2]. In addition, the combination of hydrogen production and electrochemical wastewater degradation can partly offset the cost of energy consumption.

Currently, a variety of materials, such as glass carbon, platinum, graphite, titanium, and metal oxides, are used as electrodes in the EO industries [3–7]. Among them, boron-doped diamond (BDD) film electrodes have attracted attention since they are promising anodes in wastewater treatment due to the lower adsorption surface, high anti-corrosion performance, low background current, and wide potential window [8,9]. In comparison to many traditional electrode materials, BDD films can be used as both anodes and cathodes in environmental electrochemistry [10]. Hydroxy radicals (OH^{*}) generated at the BDD surface at high anodic potentials are highly efficient oxidants to decompose organics in the electrolyte, finally forming smaller molecules such as CO₂ and H₂O [11]. This unique property makes BDD suitable for the degradation of toxic but stable materials, such as nitrophenol and multiwall carbon nanotubes [12].

Meanwhile, a large number of small molecules and ion species, including hydrogen ions, are generated at the anode surface, which will arrive at the cathode and transform into H_2 in the reduction process. However, sufficient active sites or reaction pathways cannot be provided on common BDD electrodes to satisfy the reaction requirements of mass transfer rate. In addition, polymerization often takes place on the BDD surface for many kinds of organics, which will decrease the degradation efficiency since they cover the active sites of the electrode. The existing problems limit the further improvement of BDD's electrochemical efficiency. One of the solutions to these limitations is using a dynamic electrode with special structures providing more active sites and ion channels to improve the electrochemical property.

In this study, we proposed an electrochemical system with dual functions for simultaneous wastewater EO treatment and hydrogen production using a rotating hole-arrayed boron-doped diamond (HABDD). The reaction areas on the rotating HABDD electrode are expanded from the plane surface to the sectional depth, which forms a flowing three-dimensional reaction zone [13] and exposes more active sites in the electrolyte [14]. The kinetics process of the 3D holey framework in HABDD enables the ions to be efficiently transported to active sites buried deeply in the electrode [15]. The fast flowing through the holes will disperse through a dynamic three-dimensional structure, improving the mass transfer rate on the HABDD electrode surface and in the electrode space [16]. The EO efficiency of the HABDD was studied using the chemical oxygen demand (COD) removal rate. The liberated protons (H^+ ions) from the HABDD are diffused and discharged at a foam Nickel (FNi) cathode to generate hydrogen gas. Since the 2000s, researchers have reported the use of diamond electrodes for electrochemical oxidation processes and water splitting to produce hydrogen [1,17,18]. However, BDD electrodes with channeled structures for wastewater treatment combined with hydrogen production in a single system have rarely been explored. Therefore, this study aims to investigate the properties of rotating 3D-BDD electrodes and the reciprocal effect of hydrogen evolution during wastewater degradation.

2. Experimental

2.1. Preparation

The HABDD was custom-made by Zhengyinghao Metal Co.(Hefei, China), and was prepared using a microwave plasma-assisted chemical vapor deposition (MPCVD, 2.45 GHz) device. A tantalum (Ta) plate with arrayed holes was designed and fabricated by laser processing, which was then used as the deposition substrate for the diamond growth. Acetone and hydrogen gas mixture was used as the carbon source in the deposition, and B_2O_3 was used as the boron source. Both sides of the Ta substrate were exposed for the diamond growth. A flat BDD with the same size as the HABDD, only without the holes, was also prepared under the same conditions for performance comparison.

2.2. Electrochemical Setup

The electrochemical system for the simultaneous EO treatment and hydrogen production is shown in Figure 1, which was custom-made of transparent organic glass. This setup was composed of two sub-cells (each with a 500 mL volume) that were separated by an ion membrane (Sx-2301 DH, Zhongren Int. Co. Ltd. Shanghai, China), which allowed hydrogen ions to pass through. The distance between the anode and the cathode was 20 mm. The HABDD electrode was used as the anode, and a foam nickel (FNi, Dekun Electronic Co. Ltd. Shenzhen, China) electrode was used as the cathode. The electrochemical experiment was carried out under magnetic stirring conditions for electrolytes and mechanical stirring conditions for HABDD. In the electrochemical process, the HABDD was rotated at 100 rpm against the magnetic stirring direction, forming a strong flowing convection of the electrolyte ions. The anodic cell had a water inlet and a gas outlet, as did the cathodic cell. The wastewater samples from the polluted zones were used as the electrolytes in the anodic cell, which was circulated for the EO treatment from an outside water tank by a pump. The circulation flowing rate could be controlled at 20–300 mL/min.

0.5 M H₂SO₄ aqueous solution was used as the cathodic electrolyte for performance testing. Water was periodically supplied into the cathodic sub-cell through a valve during the electrolysis process. A custom-made electric source (Gaohu Co. Ltd. Suzhou, China) was used as the power supply. After each circulation, the ion membrane was replaced with a new one. The hydrogen yielding was quantified by drainage of solution in a glass-scaled tube connected to the cathodic cell. The COD values from the anodic cell were monitored at the scheduled time in the EO process [1]. The waste removal efficiency was measured using a UV–Vis spectrometer (UV-3600, Shimadzu, Japan). The UV peaks were the super-imposed responses of the various species present in the complex wastewater matrix. All electrochemical experiments were performed in batch mode at room temperature.

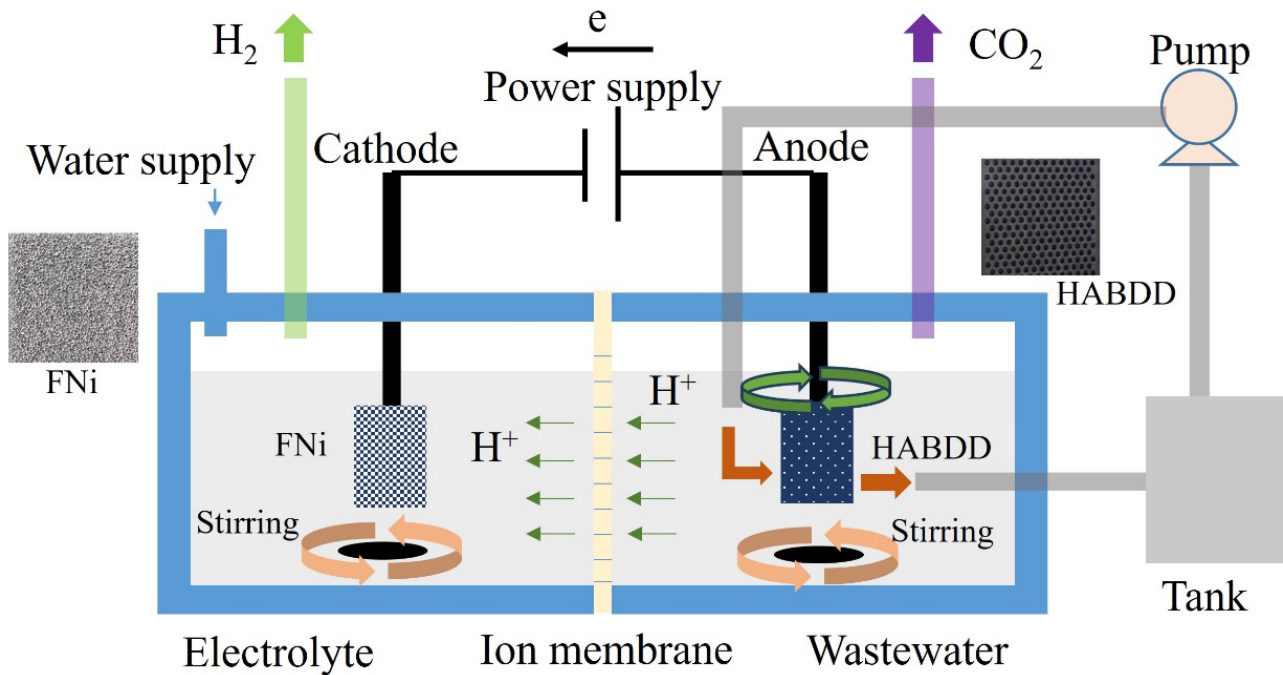


Figure 1. Schematic illustration of the electrochemical system consisting of the rotating HABDD anode and the FNi cathode. The EO process takes place on the HABDD anode. The hydrogen ions generated from the HABDD surface diffuse to the FNi cathode through the ion membrane to form hydrogen gas.

The current efficiency for wastewater mineralization E_w is calculated by:

$$E_w = F \cdot V \cdot \Delta COD / (8 \cdot I \cdot \Delta t) \quad (1)$$

where F is the Faradaic constant (96,485 C/mol), V is the wastewater volume, I is the applied current, and ΔCOD is the change of COD value in the treatment time (Δt). The current efficiency of E_w for wastewater degradation depended on the electrocatalytic activity of the HABDD electrode, which was evaluated by the COD removal efficiency. The hydrogen production efficiency (E_h) was determined by electronic hoarding, which was indicated by the ratio of real production to theoretical production.

The E_h value is calculated by:

$$E_h = m / (I \cdot t \cdot m_0 / F) \quad (2)$$

where m is the practical hydrogen production, I is the current, t is the time, m_0 is the hydrogen production from 1 mol of electron, and F is the Faraday constant. The decrease in the COD values was referenced as the organic removal efficiency.

2.3. Characterization

The surface morphology of the HABDD was examined by scanning electron microscope (SEM, JSM-5400, JEOL, Tokyo, Japan). The composition of the sample was examined using the Raman spectrum (LabRAM HR, Horiba, Longjumeau, France). The hydrogen yield was measured by timing the gas volume changing in the glass-scaled tube, and the concentration was measured by a gas chromatograph (GC, Agilent 7890B, Santa Clara, CA, USA). The COD value was monitored by a table COD detector (QCOD-3M, Changhong, Shenzhen, China), which was calibrated by an experimental device (MI-80K Pro, Massinno, Tianjin, China).

2.4. Wastewater Sampling and Storage

The wastewater was collected in the pipe or channel where the flow was straight and stable to ensure the representativeness of the sample, and floating grease species or solid deposition should be avoided from entering the sampling device. The sampling sites were located at the wastewater discharge outlet before flowing into the treatment workshops. Before introduction into the system, the wastewater was physically filtered by a stainless steel mesh filter and a sand filter. Several clean and dried containers made of organic glass were used to sample and store the wastewater. The sampled wastewater was stored without air contact and light illumination at room temperature.

3. Results and Discussion

3.1. Structural and Composition Characterization

The SEM images of the HABDD surface and its inner structure are shown in Figure 2a. Each hole had a diameter of approximately 0.5 mm (500 μm) with a depth of 1.5 mm, which is the same as the HABDD thickness. All the substrate surfaces, including the planar surface on both sides and along the hole depth, were covered with diamond phase. The HABDD had a uniformly rough surface compacted with diamond microcrystals, as shown in Figure 2b. Polycrystalline film and diamond crystallites sized at approximately 5 μm can be observed with good reproducibility. Raman spectrum was used to examine the crystalline quality of the HABDD (Figure 2c). The sharp peak at 1332 cm^{-1} indicated the presence of sp^3 carbon as the main component in the HABDD. Besides, there was a small amount of sp^2 carbon in the film, characterized by the peak at 1550 cm^{-1} . The boron concentration in the HABDD was estimated as 1000 ppm according to the resistivity at $300\ \Omega\text{ cm}$ with 10 μm of thickness, which was measured by the four-probe method with a conductivity meter (DDSJ-318T, Shanghai, China).

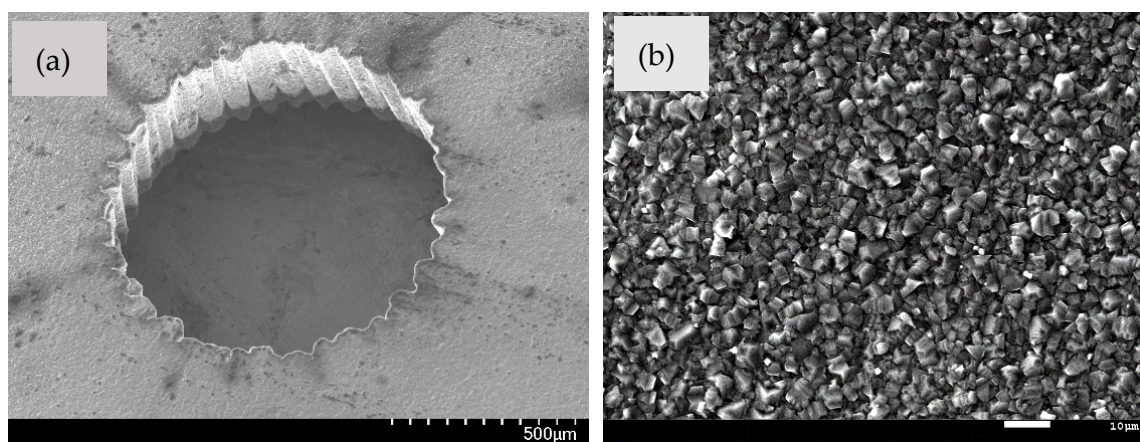


Figure 2. Cont.

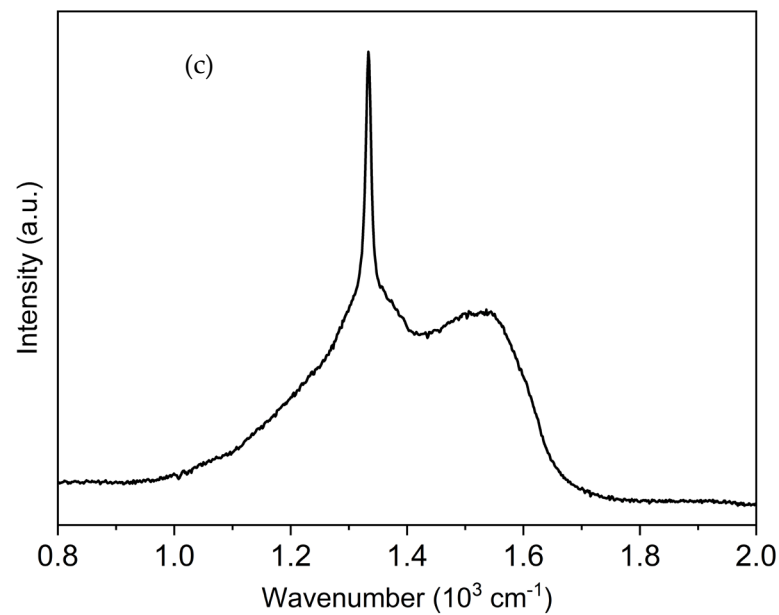


Figure 2. SEM images of (a) a hole in the HABDD, (b) the HABDD surface from the top view, and (c) Raman of the HABDD surface.

3.2. Electrochemical Characterization

The potential window of the HABDD in 0.5 M H_2SO_4 solution by cyclic voltammetry (CV) measurement is illustrated in Figure 3. It can be seen the HABDD was an excellent anode for wastewater degradation since it had a wide potential window ($-1.8 \sim 2.5 \text{ V}$), low-background current, and remarkable anti-corrosion stability due to almost no changes of the potential window after two weeks of the wastewater treatment. The wide potential window guaranteed high yields of hydroxy radicals (OH^*) as the anode, which afforded it high performance for organic decomposition. In addition, free active radicals, such as O_2^* and HO_2^* , could be generated by the overpotential at the diamond anode [19]. In addition, hydrogen and oxygen evolution could be avoided due to the wide potential window [11].

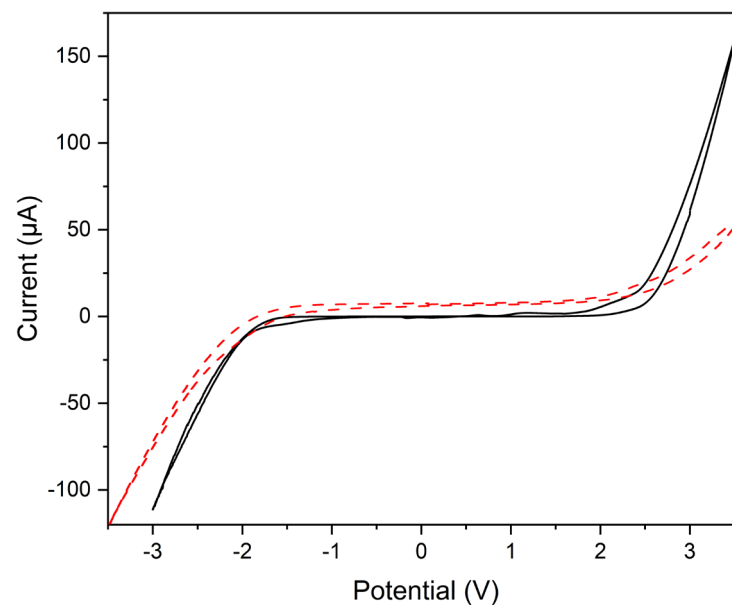


Figure 3. CV curve of the potential window of the HABDD in 0.5 M H_2SO_4 solution at a scan rate of 50 mV/min (black line, initial state; red dot, after two weeks).

3.3. Electrolyte Current

The feasibility of the wastewater as the electrolyte was first examined. The cathodic current at a voltage of 5.0 V in the wastewater sampled from municipal drain and tapwater was compared in Figure 4. A stable current with an increasing tendency could be obtained on the HABDD when the wastewater was used as the electrolyte, both in the anodic and the cathodic cells, demonstrating the feasibility of wastewater as the electrolyte. In comparison, there was almost no response when tapwater was used as the electrolyte on both sides. It showed that the wastewater could be directly used as an electrolyte without additives.

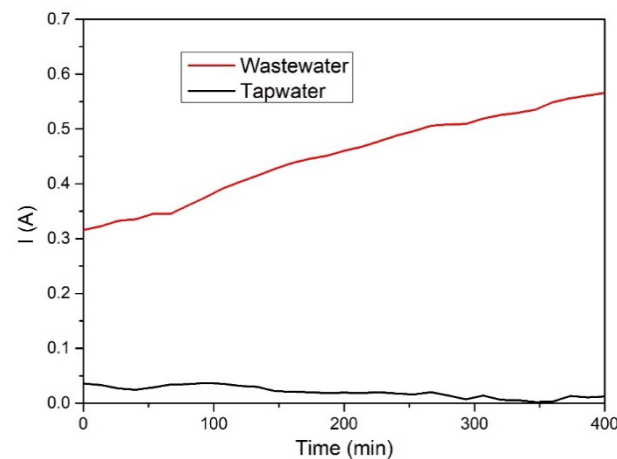
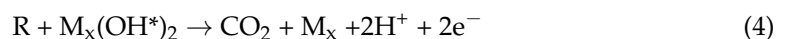
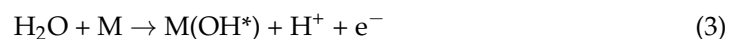


Figure 4. Comparison of the current vs. time between the electrolyte using wastewater (municipal drain) and tapwater at the voltage of 5.0 V.

Diamond electrodes can continuously work in harsh environments for a long period due to their high stability and anti-corrosion properties. The HABDD, with a hierarchical hole-arrayed structure like some microchannel arrays [20], may facilitate the deionization of organics in the electrolyte [21]. Microfluidic diffusion can be formed through these arrayed holes, promoting the EO reaction rate [22]. The reaction species generated in the degradation process are quickly exchanged under a high-convection flow condition because the arranged holes create three-dimensional diffusion channels and accelerate the mass transfer of the electrolyte [17,23]. The FNi electrode with a mesh structure can improve the reaction rate.

The pollutant species can be oxidized on the HABDD surface as the following equations [8]:



M represents the anode active sites producing adsorbed hydroxyl radicals (OH^*). CO_2 and other smaller molecules are generated when the organics are deeply decomposed in the presence of a large amount of OH^* species. The EO reaction on HABDD is an indirect oxidation process, and the reaction rate is determined by the mass transfer rate [11].

3.4. Rotating Effect

The rotating effect was evaluated by the COD decreasing measurements in a phenol aqueous solution with NaCl as the electrolyte, and the result is shown in Figure 5. The rotating HABDD decreased the COD values faster compared to the stationary HABDD within 60 min, indicating the increased efficiency of the dynamic HABDD. The rotating electrode is an innovative electrochemical technique enabling high-speed, high flux of minute electron transfer reactions, thereby facilitating the reaction processing at material surfaces. The mass transport was improved due to the turbulence formed in the system, thus enhancing the overall performance of the electrolytic cell [24].

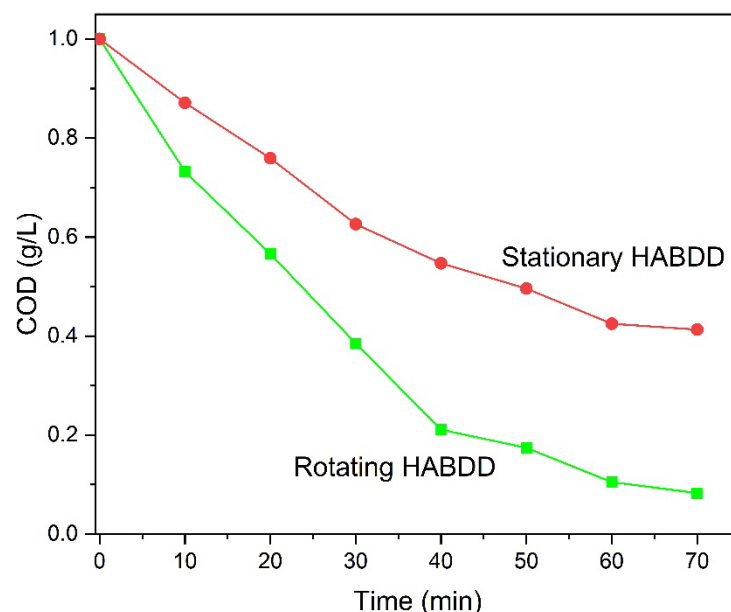


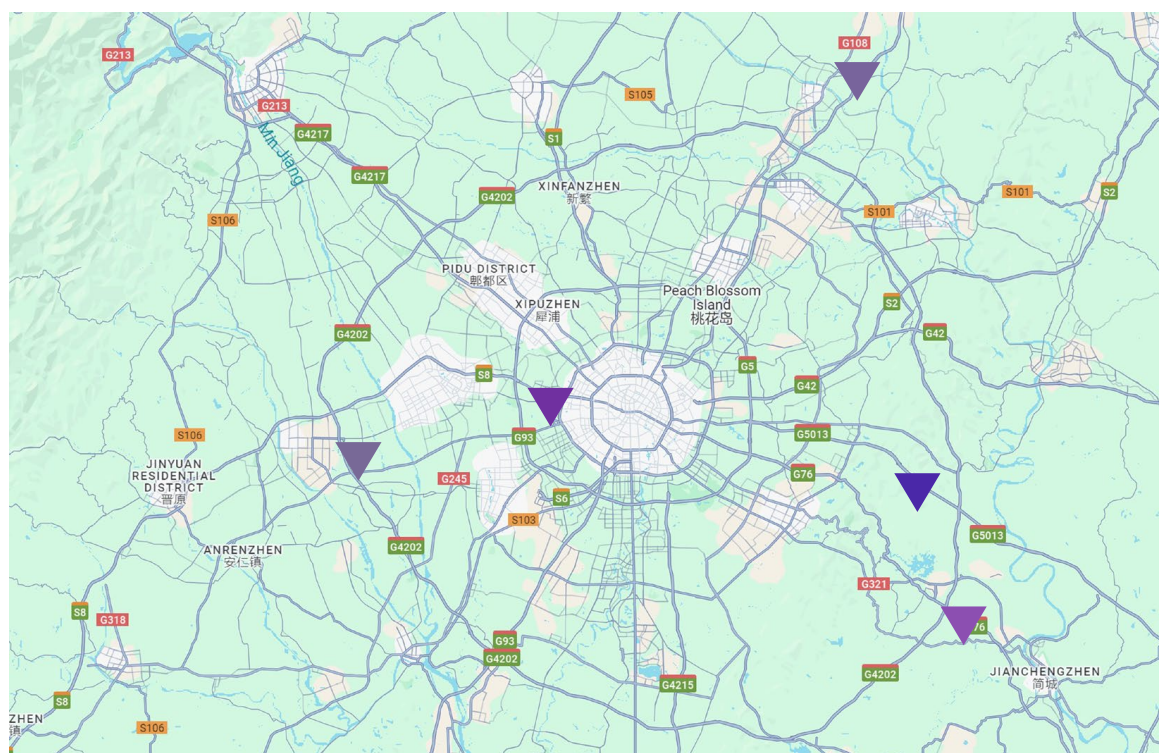
Figure 5. COD changes on the rotating HABDD (green line) and stationary HABDD (red line) via treatment time.

The HABDD had a total area of 48 cm² (both sides), which could load a current density of up to 40 mA/cm² in an H₂SO₄ aqueous solution. The electrolyte ions flowed through the holes from one side to the other side of the HABDD. The mass transfer rate on the HABDD was higher than that on a normal flat BDD electrode (of the same size) in high convectional flowing conditions. Meanwhile, the possible polymerization of the organics in the electrolyte was reduced partly due to the fast flowing through the holes. The high potential and mass transfer could increase the degradation efficiency before possible polymerization reactions occur. After a period of degradation, most of the original organics and intermediate products were decomposed into H₂O and CO₂ on the HABDD anode.

3.5. Applied Cases

Several types of wastewater from a pharmaceutical plant, municipal drain, chemical plant, vehicle maintenance, and a farm were sampled for the test. The sampling sites are indicated on the map in Figure 6. The sampled wastewater, composed of certain concentrations of organic compounds, inorganic salts, and other contaminants, were filtrated before the electrochemical degradation. The range of wastewater that can be treated had a pH range of 3.8~6.5. The wastewater that can be degraded had main contents included 1,2,4-triazole, toluene, sulfamide, isopropyl acetate, tert-butyl alcohol, phosphoric acid, and alcohols with salt content below 5%. The wastewater was a mixture of these contents, which resulted in superposing responses for the removal efficiency.

The hydrogen evolution in acidic electrolytes is better than that in the alkaline medium in this electrochemical system [9]. The wastewater samples tested in this experiment were conductive due to their acidic properties. The generated hydrogen had a high purity (>85%) by GC measurement. An accelerated reaction rate on the HABDD anode could promote the reaction rate on the FNi cathode [25]. The performances for the COD removal rate and hydrogen production efficiency of the electrochemical system are listed in Table 1. The typical treatment times for the wastewater with the initial COD and pH values are provided for the prediction estimation of the practical running time [26]. The acid species in the wastewater could play an electrolyte role. However, the pH value should not be too low; otherwise, the ion exchange membrane might be destroyed by the high concentration of acidic ions.



pH 3.8 6.5

Figure 6. Sampling sites in Chengdu urban and suburb areas (Google map) as chemical plant, municipal drain, pharmaceutical plant, vehicle maintenance, and farm from the top to the bottom indicated as triangle shape associated with the pH range.

Table 1. Performance of wastewater degradation and hydrogen production of the HABDD-FNi system.

Wastewater	Initial COD (g/L)	Initial pH	COD Removal Rate (%)	Treatment Time (h)	Hydrogen Concentration (%)	Energy Efficiency E_h/E_w (%)
Pharmaceutical plant	6.52	4.26	83.4	7.2	85.5	81.8
Municipal drain	4.66	6.22	85.2	5.4	90.3	88.4
Chemical plant	5.87	5.11	78.1	6.5	92.1	77.6
Vehicle maintenance	3.85	5.47	93.3	3.8	88.1	86.5
Farm	2.28	5.84	91.3	3.5	92.5	85.2

Note: The wastewater was sampled from the sites indicated on the map.

The electrochemical-generated radicals from the HABDD surface contribute to the EO process for wastewater. A typical EO process on the HABDD surface is determined by the mass transfer steps [11,27]. After each EO circulation, the color in the anodic cell changed from light yellow to almost colorless, indicating the decomposition of the waste organics on the HABDD. Small amounts of foam formed on the anode surface were observed during the treatment process, but they might disappear in the fast-flowing solution. The sampled wastewater for treatment was less than 50 L for each sample due to the design's capacity. The maximum COD of this system was normally lower than 8.0 g/L since much more time would be required. The E_h/E_w values were located between 81~89% because of the complex content of the organic materials and the rotating power needed. The hydrogen production efficiency was normally higher than 80% due to the higher electrochemical performance of the FNi electrode. The decolorization of the wastewater occurred quickly on the rotating HABDD, which can be attributed to the higher mass transportation on the dynamic structure. Referenced from previous reports, the typical wastewater with COD values between 3~9 g/L treated by flat BDD electrodes would cost 6~20 h [9,28]. The

3D-BDD electrodes show advantages of higher mass transfer efficiency and higher removal rates than the flat BDD electrodes by approximately 90% [17], which was confirmed by our results.

The higher applied voltages facilitate the promotion of wastewater degradation efficiency, but the lower voltages decrease the energy consumption of hydrogen evolution. Hence, a moderate voltage applied on the HABDD-FNi electrodes should be carefully chosen. In this study, we chose an operating voltage of 5.0 V in electrolysis because most waste species could be efficiently degraded at this voltage while not consuming much energy. The mass transfer effect was affected by the flow of the ions generated at the HABDD surface, which became more efficient with an increasing flow rate.

The EO process's effect on mass transfer ability must be critically evaluated. A comparison of the COD removal ability for municipal wastewater on the HABDD and the BDD (with the same size) was illustrated in Figure 7a. The highest removal performance was located at the flowing rate of 150 mL/min in this system. This was because, on the one hand, under a lower flowing rate, the EO rate in the local area was increased while the total EO rate was decreased due to a lower contact surface area between the electrode surface and the electrolyte. On the other hand, at a higher flow rate, the wastewater could not sufficiently contact the electrode surface before it flowed out. Hence, the flow rate of the wastewater should be selected at a moderate value. In addition, the influence of the flowing rate on the HABDD was much higher than that on the flat BDD. The flow on the flat surface will maintain a low turbulence state like the laminar flow state. Meanwhile, in the HABDD, the cross-flow velocity and turbulence of the flow are generated by a higher turbulent kinetic energy [13]. The COD removal rate on the HABDD was higher than on the flat BDD, demonstrating the promotion effect from the dynamic holed structure.

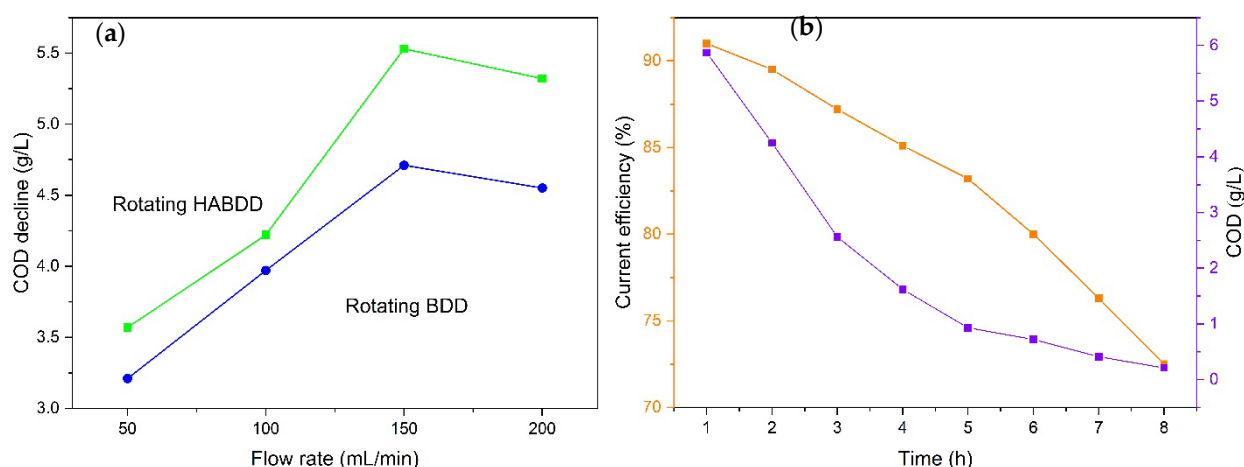


Figure 7. (a) The dependence of COD remove ability of HABDD (green line) and BDD (blue line) on flowing rate; (b) Current efficiency of hydrogen generation (orange line) on FNi, and COD decline (phenol aqueous solution, purple line) versus the working time on the rotating HABDD.

The correlation between the E_h and COD removal rate on the HABDD electrode was studied. As shown in Figure 7b, after 8 h of treatment time for the phenol wastewater, the E_h for the hydrogen production decreased from 92% to 75%, while the COD value decreased with the current efficiency, meaning the waste species were consumed. In the treatment process, the current efficiency decreased less than the decreasing COD values. The electrolyte flowing resistance from the anode to the cathode due to the presence of complex contents in the cell might increase the extra power consumption. This whole system is currently under continuous development in our lab.

4. Conclusions

A dual-functional electrochemical system based on the HABDD and FNi electrodes was used simultaneously for wastewater degradation and hydrogen generation. The HABDD film electrode was custom-made and prepared on the patterned template using the MWCVD method. It was characterized by SEM and Raman, which showed the details of the HABDD microstructures. The HABDD was used as the anode for fast degradation of wastewater and generation of H^+ ions for the hydrogen evolution on the FNi cathode. A fast liquid-solid convection with relative stirring was formed during the degradation process, making the flow state change from stagnation to turbulence near the electrode surface. Different kinds of wastewater were chosen to test the electrochemical performance of this system. The relationship between wastewater degradation and hydrogen evolution was evaluated in terms of the COD decline and the hydrogen yields. The electrochemical efficiency was discussed, and the advantages of this electrochemical system were mainly caused by the diffusion path structure created by the arranged holes of the HABDD. The HABDD had a faster effective mass transfer in comparison to the flat BDD, which promoted the COD removal rate due to the holed structure. The hydrogen production efficiency was evaluated in correlation to the COD decline. This electrochemical system based on the HABDD and FNi electrodes showed its advantages in environmental protection and energy generation. Future development should focus on efficiently coupling this system with regenerative energy to reduce energy consumption.

Author Contributions: D.L. proposed the conceptualization, performed the electrochemical experiments and wrote the article. Y.L. collected the wastewater samples and performed the characterization. D.M. performed data collection and computation. All authors have read and agreed to the published version of the manuscript.

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