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RESEARCH ARTICLE

Application of Pulse Width Modulation to Boron-Doped Diamond Wastewater and Water Treatment

Chaeyun Kim

Fairview High School, 1515 Greenbriar Blvd, Boulder, CO, 80305, USA; boomaboom0818@gmail.com

ABSTRACT: Wastewater and water treatment using boron-doped diamond (BDD) electrodes has garnered significant attention due to their distinguishing properties. In this study, we describe the application of a pulse width module (PWM) technique to a wastewater and water treatment system utilizing BDD electrodes prepared via hot-filament chemical vapor deposition (HFCVD). To investigate the efficiency of PWM, PWM square waves with a 50% duty cycle and a frequency of between 1 Hz and 500 Hz were applied to the BDD electrodes in 600 ml of tap water, and the resulting ozone concentrations were measured. Specifically, at frequencies above 10 Hz, the PWM technique generated higher ozone concentrations than the continuous DC voltage method while using only 50% of the electrical energy. The resulting treatment efficiency was 14.3 ppm/mW in DC mode and 34.9 ppm/mW in PWM mode, highlighting that PWM application significantly enhances ozone generation efficiency. These results demonstrate that the PWM technique not only reduces energy consumption but also enhances the treatment efficiency of BDD-based wastewater and water treatment systems.

KEYWORDS: Chemistry, Environmental Chemistry, Wastewater Treatment Using Boron-doped Diamond, Pulse width Module.

Introduction

Wastewater and water treatment using boron-doped diamond (BDD) electrodes, grown using the hot-filament chemical vapor deposition (HFCVD) method, is well-known for its efficiency and has been extensively studied.[1,2] BDD electrodes possess exceptional properties, including excellent corrosion resistance, chemical stability, high wear resistance, and outstanding electrical conductivity. Additionally, they exhibit unique electrochemical characteristics, such as low surface reactivity toward generated reactive chemical species.[1]

Numerous studies have focused on enhancing the efficiency of the treatment using BDD electrodes. Key factors influencing this efficiency include the thickness of the BDD thin films, the electrical conductivity of the electrodes, the properties of the electrolyte solution, and its temperature. However, there are still limitations to further improving efficiency, showing the need for new technological breakthroughs.

In this study, the application of the pulse width modulation (PWM) technique to a BDD wastewater and water treatment system is investigated. This is a new approach to enhancing the energy efficiency and performance of BDD treatment systems. PWM is a switching technique that controls analog devices with digital circuits.[3] A PWM switching controller was implemented in the BDD treatment system to evaluate the approach. Its effectiveness was evaluated by measuring the dissolved ozone concentrations in the treated water. Experimental results demonstrate that PWM can reduce energy consumption and enhance the treatment performance of the BDD treatment system.

Methods

BDD electrodes were prepared by depositing BDD films onto the surface of a silicon (Si) electrode body using an HFCVD at Pusan National University. HFCVD is widely known as an effective technique for depositing diamond films on substrate surfaces. Figure 1 presents a schematic illustration of the HFCVD system used in this study. A gas mixture of CH_4/H_2 was used for diamond film deposition on the Si substrate. B_2H_6 was introduced into the vacuum chamber during the deposition process, resulting in the doping of boron into the diamond films.[4] Hot filaments were heated to 2000 ˚C using an electrical power supply, and the temperature of the Si electrode body was raised to 750 ˚C by the heated filaments. The chamber pressure was maintained at 5.3 kPa (refer to Ref. 5 for more detailed conditions). The deposition time for the BDD films was 15 hours.

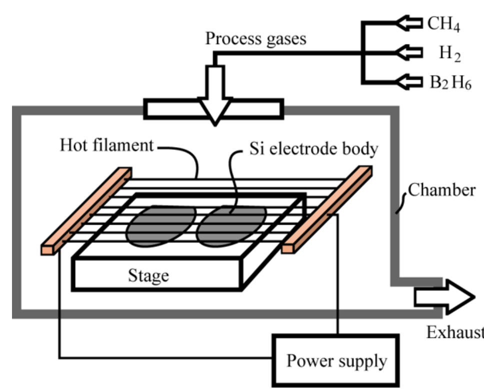

Figure 1: A schematic illustration of a hot-filament chemical vapor deposition (HFCVD) system used for the preparation of boron-doped diamond (BDD) electrodes. A gas mixture of CH_4 and H_2 was introduced for diamond film growth on a Si electrode body. B_2H_6 was added to achieve boron doping into the growing diamond film. The hot filaments were electrically heated to 2000 ˚C, raising the substrate temperature to 750 ˚C. The growth of diamond films was carried out at a chamber pressure of 5.3 kPa.

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Figure 2 (a) and (b) show a picture and a schematic illustration of the water treatment system with a PMW switching controller, respectively. The water treatment system has a 1000 ml glass beaker as the reactor container, a set of BDD electrodes consisting of cathode and anode electrodes, an ion exchange membrane (Nafion^{TM} #117 membrane film) placed between them, a DC power supply, and components for PWM switching. The distance between BDD electrodes is fixed at 3 mm. The PWM switching controller is composed of two devices: a PWM signal generator and a MOSFET (Metal oxide semiconductor field effect transistor) module. The PWM signal generator provides a square wave pulse of 50% duty cycle with a frequency range between 1 Hz and 20 kHz, with a DC of less than 30 mA. The generated square wave pulse is input to the MOSFET module. The MOSFET module (Operating voltage: DC 5 V-36 V, Max current: 15 A) acts as a switch by continuously turning on and off according to the input square wave pulses. The DC voltages supplied by the DC power supply to the MOSFET module are converted into DC square waves based on the input PWM signal and are then supplied to the BDD electrodes. 600 ml of tap water in the glass beaker was used for experiments without any added electrolyte, except when treating water contaminated with water-based ink. BDD electrodes have been reported to facilitate ozone generation without the use of any electrolytes.[6] After the treatment, the ozone concentration in the treated water was measured using an ozone colorimeter (EUTECH instruments, C105) within 1 minute. To estimate the efficiency of applying the PWM technique to the BDD water treatment system, tap water in the glass beaker was treated with a DC voltage of 20 V and DC square waves with a 50% duty cycle and a frequency range of 1 to 500 Hz.

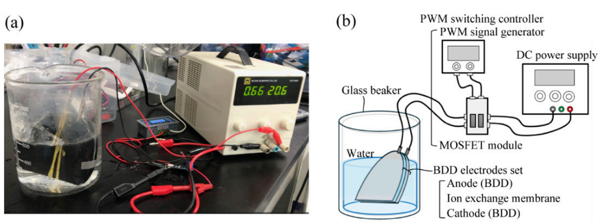

Figure 2: (a) Photograph and (b) schematic illustration of boron-doped diamond (BDD) water treatment system equipped with a pulse width modulation (PWM) switching controller. The system includes a gas beaker filled with tap water, BDD electrodes set (anode and cathode) with an ion exchange membrane in between, a DC power supply, and a PWM controller consisting of a signal generator and a MOSFET module. The PWM signal generator outputs a square wave signal, which is used to control the MOSFET module, converting the supplied DC voltage into a square wave. This modulated voltage is applied to the BDD electrode.

Results and Discussion

Figure 3 (a), (b), and (c) show a picture of a BDD electrode prepared by an HFCVD, a scanning electron microscope (SEM) image of a BDD surface, and a cross-sectional SEM image of BDD, respectively. The SEM images show that polycrystalline diamond films with a grain size of around 7 μm and a thickness of 14 μm were deposited on the Si electrode body. It is well known that CVD-grown diamonds without any doping have a high electrical resistance. Boron doping in diamond enhances the electrical conductivity by making it a conductor.[7] The sheet resistance of the prepared BDD electrodes in this work, measured using a 4-point probe method, is around 4.3 Ω/sq.[5]

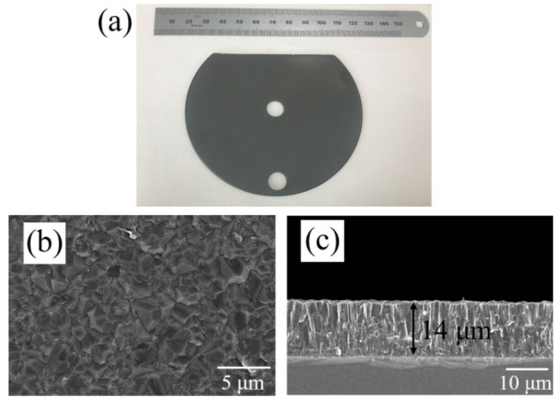

Figure 3: Characterization of a boron-doped diamond (BDD) electrode prepared by hot-filament chemical vapor deposition (HFCVD). (a) Photograph of the BDD electrode. (b) SEM image of a BDD surface, displaying polycrystalline diamond films. (c) Cross-sectional SEM image of a BDD electrode. The BDD electrode exhibits enhanced conductivity due to boron doping.

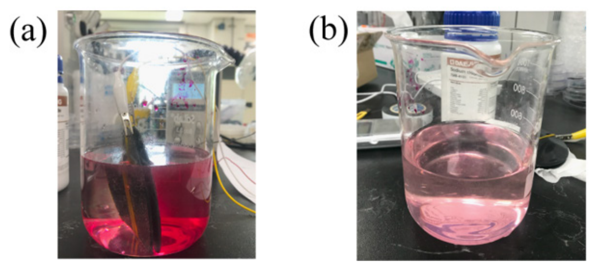

Figure 4: Photographs of ink wastewater (a) before and (b) 5 minutes after the electrochemical treatment using boron-doped diamond (BDD) under DC voltage. The discoloration results from the oxidative degradation via direct anodic oxidation and indirect oxidation by reactive oxygen species such as OH and O_3. Gas bubble formation on the electrode surface indicates oxygen and hydrogen evolution.

The BDD treatment system prepared in this work has been successfully operated, as confirmed by the treatment of water-based ink wastewater. When DC voltage was applied to BDD electrodes, bubbles formed on the surfaces of the electrodes, and the wastewater became gradually colorless and transparent, as shown in Figure 4. Figure 4 (a) and (b) show pictures of ink wastewater before treatment and 5 minutes after treatment began, respectively. Electrochemical wastewater and water treatment using BDD electrodes is governed by a combination of direct and indirect oxidation mechanisms.[8] Direct anodic oxidation involves an outer-sphere electron transfer at the surface of the electrode, does not involve adsorbed intermediates, and typically proceeds in a quasi-reversible manner.[8,9] Hydroxyl radicals (OH), hydrogen peroxide (H_2O_2), and ozone (O_3) can also be formed at the BDD anode surface.[9] The primary mechanism for organic degradation shifts from a direct to an indirect oxidation under appropriate electrochemical conditions.[8] The colored components in ink wastewater are broken down by hydroxyl radicals and ozone through oxidative reactions. During the treatment, bubbles are observed on the electrode surfaces, most likely due to the evolution of oxygen at the anode and hydrogen at the cathode.[8]

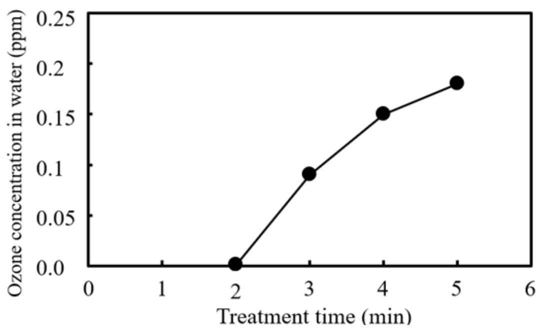

Figure 5: Ozone concentration in water as a function of treatment time using boron-doped diamond (BDD) electrodes under a constant 20 V DC. The ozone level increased steadily with treatment time, reaching 0.18 ppm after 5 minutes in 600 mL of water.

Figure 5 shows the ozone concentrations in water treated using the BDD treatment system, where a DC power supply was directly connected to the BDD electrodes. A 20-V DC voltage was applied between the electrodes. Ozone concentrations in 600 ml of water treated for 2 to 5 minutes were measured. As shown in Figure 5, the ozone concentration in water treated for 2 minutes was 0.001 ppm. The ozone concentration was increased with the treatment time. It was 0.18 ppm in water treated for 5 minutes.

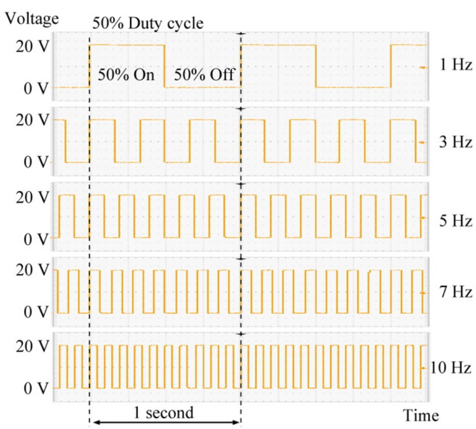

Figure 6: Oscilloscope measurements of pulse width modulation (PWM) with square wave voltages generated at 1, 3, 5, 7, and 10 Hz with 50% duty cycle. Each signal alternates between 0 V (off) and 20 V (on) for equal durations. As frequency increases, the number of on-off cycles per second increases. With a 50% duty cycle, the average voltage is 10 V, reducing the average power input to the electrodes by half compared to continuous DC voltage.

Next, the voltage shapes generated by the PWM switching controller shown in Figure 2 were measured using an oscilloscope (Tektronix, TBS1064). Figure 6 shows voltage shapes of PWM square waves with a 50% duty cycle with a frequency of 1 Hz, 3 Hz, 5 Hz, 7 Hz, and 10 Hz. As shown in Figure 6, a PWM square wave is on for half of the time and off for the other half. The number of times per second of a PWM signal is increased as the frequency of the PWM signal increases, where the frequency of a PWM signal is the number of times per second that the on-and-off cycle is repeated. When the 20 V DC voltage is supplied on the BDD electrodes with a duty cycle of 50%, then the average voltage over time would be 10 V, resulting in the reduction of average power wasted in a resistive load by half.

Finally, experiments were carried out to investigate the efficiency of the application of a PWM system to a BDD water treatment. A 600 ml of water in a glass beaker was treated by applying the PWM signals, shown in Figure 6, to the BDD electrodes for 5 minutes, and the ozone concentrations in the treated water were measured. The dependence of ozone concentration on the frequency of PWM signals is shown in Figure 7 (a). Ozone concentration was 0.05 ppm at 1 Hz. Ozone concentration gradually increased with the increase in the frequency of the PWM signal. It was 0.08 ppm, 0.09 ppm, and 0.11 ppm at 3 Hz, 5 Hz, and 7 Hz, respectively. As the frequency increased further to 10 Hz, ozone concentration was doubled, 0.22 ppm, which is higher than the value in water treated with a continuous DC voltage shown in Figure 5. Next, the change of ozone concentration in treated water was investigated when the frequency was further increased from 10 Hz to 500 Hz as shown in Figure 7 (b). As the frequency increases further than 10 Hz, ozone concentration tends to saturate at around 0.22 ppm.

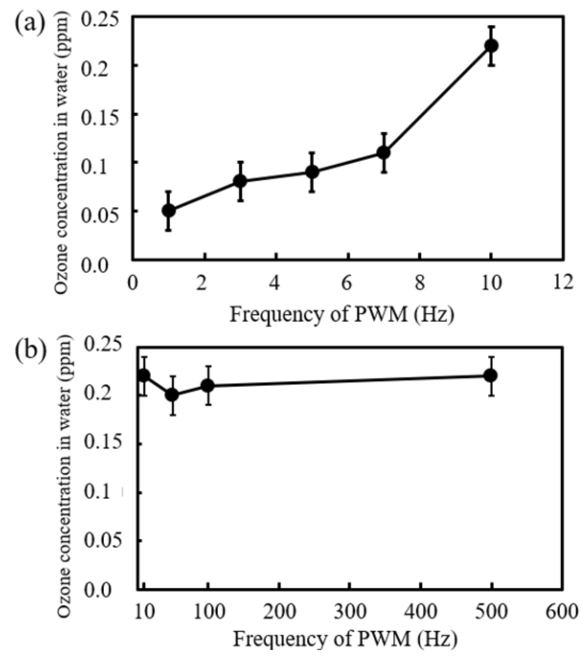

Figure 7: Ozone concentration in water as a function of pulse width modulation (PWM) signal frequency applied to boron-doped diamond (BDD) electrodes during 5-minute treatments. (a) At low frequencies (1-10 Hz), ozone concentration increases with frequency, reaching 0.22 ppm at 10 Hz. (b) At higher frequencies (100-500 Hz), ozone concentration plateaus near 0.22 ppm. In both DC and PWM modes, the current was approximately 0.63 A at a voltage of 20 V; however, due to the 50% duty cycle in PWM mode, the power consumption was halved compared to DC mode. The resulting treatment efficiency was 14.3 ppm/mW in DC mode and 34.9 ppm/mW in PWM mode, highlighting that PWM application significantly enhances ozone generation efficiency while reducing energy consumption.

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In the experiments, the current flowing through both electrodes was approximately 0.63 A in both DC mode and PWM mode. The electrical power, calculated using the formula P=V×I, is 12.6 W in DC mode. On the other hand, when applying PWM with a 50% duty cycle, the power is 6.3 W, as calculated using the formula P= V×I_{peak}×Duty cycle. Treatment efficiency is 14.3 ppm/mW in DC mode and 34.9 ppm/mW in PWM mode at 50% duty cycle and 10 Hz, respectively. This indicates that the use of PWM can reduce energy consumption and significantly improve treatment efficiency in electrochemical water treatment technology.

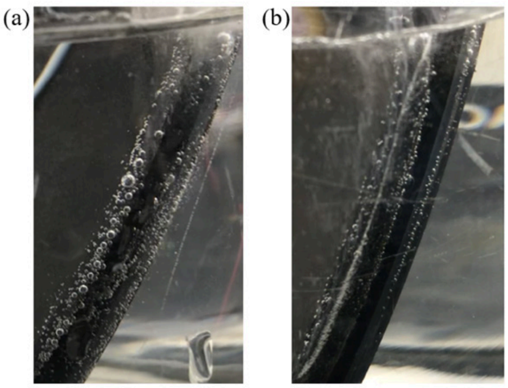

Figure 8: Pictures of BDD electrode surfaces during water treatment: (a) under conventional DC mode, and (b) under PWM mode. Compared to DC mode, PWM results in the formation of smaller bubbles that detach more rapidly from the electrode surface, which can contribute to reduced activation, ohmic, and concentration overpotentials, thereby enhancing overall energy efficiency.

In addition, in the experiments, it is observed with the naked eye that bubbles produced on the surface of BDD electrodes are smaller and quickly fall away from the electrode surfaces when a PWM switching controller is used (Figure 8). Bubbles can affect the energy efficiency of electrode processes, detailing the bubble's impact on activation, ohmic, and concentration overpotentials.[2] Persistent bubbles on the electrode surface can hinder electrochemical reactions, disrupt ionic conduction paths in the electrolyte, and obscure mass transport phenomena. This shows that the application of the PWM technique can influence the formation of bubbles and allow the reaction efficiency on the electrode surfaces. Further research into that is needed to better understand its mechanism as future work. Additionally, investigating a wider range of duty cycles could offer deeper insights into PWM behavior. Unfortunately, further experiments were not feasible due to limited access to the laboratory at the time. Future work may involve exploring additional duty cycles to provide a more comprehensive understanding of how PWM parameters influence performance.

Conclusions

This study investigated the application of the PWM technique in a BDD water treatment system. PWM square waves with a 50% duty cycle, generated by a PWM switching controller, were applied to the BDD electrodes, achieving ozone concentrations higher than those produced with continuous DC voltage. The results demonstrate that this new approach is an effective technology for reducing energy consumption and improving treatment efficiency in BDD-based wastewater and water treatment systems.

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Author

Chaeyun Kim is a senior at Fairview High School in Boulder, Colorado. He plans to study chemical engineering, combining his love for creating, discovering, and sharing new ideas. He is particularly interested in sustainable technology and community-focused projects that address global challenges.