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Research Article

Investigation of Caffeine Degradation by Anodic Oxidation Using Boron-Doped Diamond Electrode

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ABSTRACT

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In this study, the purification of caffeine by electrochemical oxidation, one of the advanced oxidation processes, was systematically investigated. A boron-doped diamond electrode was used as the anode, which has a high potential for the production of large amounts of hydroxyl radicals. The effects of applied current density, initial pH, supporting electrolyte concentration, cathode type, anode-cathode distance, and initial caffeine concentration were evaluated. The results showed that the electrochemical degradation rates of caffeine follow pseudo-first-order kinetics. with rate constants ranging from 0.0154 to 0.0496 min⁻¹ depending on the operating parameters. The applied current density and the electrolysis time proved to be the most important parameters influencing both caffeine degradation and energy consumption. However, varying the initial caffeine concentration and the concentration of the supporting electrolyte also influenced the caffeine degradation rates. Changing the anode-cathode distance and the type of cathode has no effect on the rate of caffeine degradation, but it does have an effect on energy consumption. A current density of 20 mA cm⁻², a supporting electrolyte concentration of 50 mM K₂SO₄, an anode-cathode distance of 2 mm, a cathode type of stainless steel, and an initial solution pH of 3 were found to be optimal values for the degradation of a solution containing 25 mg L⁻¹ caffeine in 45 minutes using a boron-doped diamond anode. Finally, it was found that the pH value of the solution tended to increase during electrolysis.

1. Introduction

The pollution of surface waters such as rivers and lakes with organic pollutants is a growing concern today. Protecting surface waters from potential contamination is of great importance as they are the main source of drinking water in many countries around the world. Pharmaceuticals and personal care products, endocrine-disrupting compounds, and pesticides are the primary pollutants of concern [1-3]. Pharmaceuticals and personal care products have become a primary concern for scientists and regulators as they have been shown to negatively impact freshwater fish and invertebrates and contribute to the development of antibioticresistant bacteria [4-6].

Caffeine is one of the most widely consumed food ingredients in the world and has been used for thousands of years. Caffeine is a methylxanthine alkaloid found in varying amounts in the beans, leaves, and fruits of more than 60 plants, including coffee beans, tea leaves, kola nuts, and cocoa beans [7, 8]. It is found in coffee, tea, chocolate, and some soft drinks, as well as in medicines and dietary supplements [9]. Coffee in particular, with 2.25 billion cups consumed every day, is the world's most traded beverage after oil [10].

Caffeine is also an important compound used in the pharmaceutical industry. Therefore, large amounts of caffeine are needed for the

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production of various beverages, foods, and medicines. In line with increasing consumption, caffeine is continuously discharged into water bodies worldwide. Caffeine was detected at 8.5-50 µg L⁻¹ in effluent from hospital wastewater treatment plants in Spain [11], 2.9-83 µg L⁻¹ in wastewater in the Czech Republic [12], 0.23-20.7 µg L⁻¹ in wastewater in Saudi Arabia [13], 5.64-6.20 µg L⁻¹ in wastewater in Pakistan [14], 27.8-642 µg L⁻¹ in wastewater in China [15], and 20.8-159 µg L⁻¹ in wastewater and 62.6 to 129.3 µg L⁻¹ in hospital wastewater in Türkiye [16].

After the discharge of caffeine into the aquatic environment, it is extremely stable due to its high solubility in water and a half-life reported to be 100-240 days [16, 17]. Conventional wastewater treatment processes cannot completely remove caffeine, which leads to its presence in surface waters, groundwater, oceans, and other water bodies and thus has a negative impact on ecosystems and the environment [18, 19]. Caffeine can also have negative effects, such as neurological damage and reproductive effects, and can even affect the survival of aquatic organisms [20]. Therefore, wastewater containing caffeine must be treated before discharge into the receiving environment to avoid environmental problems caused by the excessive use of caffeine and the low removal efficiency of conventional wastewater treatment.

Conventional wastewater treatment systems for domestic and industrial wastewater are insufficient to remove some persistent organic pollutants. Other treatment systems are required to remove these persistent pollutants [21]. Advanced oxidation processes (AOPs) are used to remove various persistent organic pollutants in wastewater. AOPs such as sonophotocatalysis [22], UV/chlorine [23], ozonation [24], and UV/H₂O₂ [25] have been applied for caffeine removal. In recent years, new AOPs based on electrochemical technology, so-called electrochemical advanced oxidation processes (EAOPs), have been developed for the treatment of various wastewater containing refractory pollutants [26-28]. EAOPs are based on the direct or indirect oxidation of organic materials using an insoluble anode material (Ti, Ti/Pt, Ti/RuO₂, graphite, boron-doped Ti/IrO₂, BDD diamond) [29-31]. electrodes have

technologically important properties such as an inert surface with low adsorption properties, remarkable stability against corrosion even in strong acids, and extremely high overpotentials for oxygen evolution. Due to these properties, BDD electrodes are known to have a high potential for producing large amounts of hydroxyl radicals, which are strong oxidising agents capable of mineralizing any class of organic pollutants, making it an effective application for water purification [3, 32].

In this study, the degradation of caffeine was investigated in a batch reactor operated in galvanostatic mode using a BDD anode. The effects of different current densities, initial solution pH, supporting electrolyte concentration, cathode type, inter-electrode distance, and initial caffeine concentration on caffeine degradation were investigated. Based on the experimental data obtained, the degradation kinetics were analyzed using the pseudo-firstorder rate equation, and the energy consumption was also evaluated.

2. Materials and Methods

2.1. Chemicals

Caffeine ($C_8H_{10}N_4O_2$, >98.5%), sulfuric acid (H_2SO_4 , 95-98%), sodium hydroxide (NaOH, >99%), and potassium sulfate (K_2SO_4 , >99%) were purchased from Merck. All solutions were prepared with distilled water at room temperature.

2.2. Analytical procedures

A standard caffeine stock solution was prepared and diluted with distilled water to obtain known caffeine concentrations of 2, 5, 10, 20, 30, 40, and 50 mg L^{-1} . The absorbance values of these caffeine concentrations were measured in a UV-Vis spectrophotometer (DR 6000, HachLange) at a specific wavelength of 273 nm, and the calibration curve was plotted. The absorbance was found to be linearly related to the caffeine and coefficient concentration, the of determination for the experimental data was R^2 = 0.9997. The degradation efficiency and energy consumption were calculated using Equation 1 and Equation 2, respectively:

Removal, $(\%) = (1 - C_t / C_0) \times 100$ (1)

$$Ec, (kWh m-3) = V \times I \times t/V_s$$
(2)

where C_0 is the initial caffeine concentration (mg L⁻¹), C_t is the caffeine concentration at time *t* (mg L⁻¹), *V* is mean cell voltage (V), *I* is electrolysis current (A), *t* is electrolysis duration (h), and V_S is solution volume (L).

2.3. Experimental setup

The electrolysis experiments were carried out in an undivided cylindrical electrochemical cell (Figure 1) made of glass with a diameter of 7.5 cm and a capacity of 400 mL of aqueous solution. A single boron-doped diamond electrode (BDD) with an area of 50 cm² (5 cm x 10 cm) was used as the anode. The BDD electrode with a 12 μ m thick diamond layer on niobium was purchased from DiaCCon GmbH (Germany). Stainless steel (SS), graphite, and BDD electrodes with an area of 50 cm² (5 cm x 10 cm) were used as cathodes. The anode and cathode electrodes were immersed 7 cm deep in the solution. Therefore, 35 cm² was used as the anode area.

The temperature of the solution was kept constant at 25°C using a temperature-controlled cooling/heating circulator (LABO, C200-H13). Potassium sulfate (K₂SO₄) was added to the reactor as a supporting electrolyte to improve the conductivity of the solution. The caffeinecontaining solution was stirred continuously at 600 rpm using a magnetic stirrer (IKA, RCT basic) to improve mass transfer. The electrolysis experiments were performed with a constant current power supply (GW Instek, PSW 80-40.5). This device also displayed the cell voltage during the entire process. Experiments were performed at the natural pH of the caffeine solution, 5.8, unless otherwise stated. Without adding a buffer solution, the pH of the solution was adjusted to the desired value only once at the beginning of the experiment with 1 M H₂SO₄ or 1 M NaOH and was not changed during the experimental run. At each sampling time, the change in the pH value of the solution was monitored using the portable WTW MultiLine® Multi 3620 IDS meter (Xylem Analytics, Germany).



Figure 1. Diagram of the experimental setup

2.4. Kinetic analysis

The removal of organic compounds by the electrooxidation process follows pseudo-firstorder kinetics [27, 33, 34]. The reaction rate constant (k_1) can, to a certain extent, indicate the rate of the overall reaction. Therefore, the nonlinear form of the pseudo-first-order kinetic model shown in Equation 3 is used in this study to understand the degradation kinetics of caffeine under different reaction conditions:

$$dC/dt = -k_1 t \tag{3}$$

where k_1 is the rate constant (min⁻¹) for the pseudo-first-order kinetic model, *t* is the reaction time, and C_0 and C_t are the caffeine concentrations (mg L⁻¹) in the initial sample and in the sample at any time, respectively. The Microsoft Excel solver add-in tool was used to estimate the parameters of the kinetic model.

3. Results and Discussion

The effects of applied current density (5-20 mA cm⁻²), supporting electrolyte concentration (10-50 mM), initial solution pH (3-10), initial caffeine concentration (25-75 mg L⁻¹), cathode type (SS, graphite, BDD), and anode-cathode distance (2-14 mm) on caffeine degradation in the electrooxidation system were systematically analyzed.

3.1. Effect of applied current density

The applied current density is the most important parameter affecting both the degradation kinetics and the treatment costs, as it influences the amount of oxidizing species produced [35]. The effect of the applied current density on caffeine degradation is shown in Figure 2. The experimental conditions were an initial pH of 5.8, a supporting electrolyte concentration of 50 mM, an initial caffeine concentration of 25 mg L⁻¹, an anode-cathode distance of 2 mm, and cathode type of SS. Figure 2(a) shows that caffeine removal varies at different current densities. At the end of the electrolysis time (120 min), caffeine removal was 75.2%, 92.7%, and 96.3% at current densities of 5, 10, and 20 mA cm⁻², respectively.

After 60 minutes of electrolysis, the efficiency of caffeine degradation was 59.1%, 75.0%, and 96.0% at current densities of 5, 10, and 20 mA cm⁻², respectively. Increasing the applied current density increases the rate and amount of hydroxyl radical production on the BDD surface according to Equation 4 [28, 35], and thus increases the efficiency of caffeine degradation. As the current density increases, the caffeine degradation time decreases. Li et al. reported the electrochemical degradation of ciprofloxacin with a BDD anode and found that ciprofloxacin was completely degraded in about 10 minutes at a current density of 40 mA cm⁻² [36]. The pseudo-first-order reaction rate constant calculated by the nonlinear method is 0.0154, 0.0238, and 0.0438 min⁻ ¹ for current densities of 5, 10, and 20 mA cm⁻², respectively. These results indicate that the rate of caffeine degradation depends significantly on the current density. The pseudo-first-order rate constant showed a linear correlation with the increase in applied current density $(k_1 =$ $0.0019 \times J + 0.0051$; $R^2 = 0.9988$). Similar results were obtained in the ibuprofen removal study [37].

The effect of applied current density on energy consumption in electrolysis experiments conducted at different current densities was calculated using Equation 2 and shown in Figure 2(b). As the current density of the system increases, the energy consumption increases along with the voltage increase. The energy consumption for current densities of 5, 10, and 20 mA cm⁻² is calculated as 3.80, 8.44, and 18.75 kWh m⁻³, respectively. With increasing current density, the amount of oxidizing species produced according to Equation 4 increases [35], which can lead to chemical changes on the electrode surface and reduce the lifetime of the electrode [38]. Although a high current density increases caffeine removal, it can lead to a decrease in current efficiency above a certain value [31, 39]. The decrease in current efficiency can be attributed to the degradation of caffeine by BDD('OH) and the formation of less degradable reactions by-products and parasitic of BDD('OH). The most important of these parasitic reactions is the oxidation of BDD('OH) to O_2 at the anode, according to Equation 5. However, it can also occur by dimerization of BDD('OH) to H₂O₂ according to Equation 6 and formation of hydroperoxyl radicals, which have a low oxidation capacity of BDD('OH) and H₂O₂ according to Equation 7. Increasing the speed of these reactions means that less oxidizing BDD('OH) is formed, and thus the degradation of organic pollutants is reduced [31, 40-42]. For these reasons, higher current densities were not investigated.



Figure 2. Variation of caffeine degradation efficiency (a) and energy consumption (b) over time with applied current density

$$BDD(H_2O) \to BDD(^{\bullet}OH) + H^+ + e^-$$
(4)

$$BDD(^{\bullet}OH) \rightarrow BDD + 1/2O_2 + H^+ + e^-$$
(5)

$$BDD(^{\bullet}OH) \rightarrow BDD + 1/2 H_2 O_2 \tag{6}$$

$$BDD(^{\bullet}OH) + H_2O_2 \rightarrow BDD(HO_2^{\bullet}) + H_2O \quad (7)$$

3.2. Effect of supporting electrolyte concentration

Supporting electrolytes (SEs) are one of the important parameters that influence the electrochemical degradation process [43]. Increasing the SE concentration plays an important role in increasing the conductivity of the solution and accelerating electron transfer [44]. In this study, K_2SO_4 was used as SE, and the effect of different SE concentrations (10, 25, and 50 mM K₂SO₄) on caffeine degradation was investigated (Figure 3). The experimental conditions were an initial pH of 5.8, a current density of 20 mA cm⁻², an initial caffeine concentration of 25 mg L⁻¹, an anode-cathode distance of 2 mm, and cathode type SS. SE has a major influence on the degradation of caffeine in the BDD-SS system. Figure 3(a) shows that the efficiency of caffeine degradation varies with the different SE concentrations.

The efficiency of caffeine degradation at 60 min of electrolysis time is 67.7%, 87.7%, and 96.0% at 10, 25, and 50 mM SE concentrations, respectively. After 120 minutes of electrolysis, caffeine removal was 93.4 %, 98.7 %, and 96.7 % for 10, 25, and 50 mM SE concentrations, respectively. These results show that the caffeine removal rate depends on the SE concentration and that the caffeine removal time decreases with increasing SE concentration. The pseudo-firstorder reaction rate constants are 0.0196, 0.0308, and 0.0438 min⁻¹ for supporting electrolyte concentrations of 10, 25, and 50 mM. respectively. The pseudo-first-order reaction rate constant showed a linear correlation with the concentration of the supporting electrolyte (k_1 = $0.0006 \times [K_2 SO_4]_0 + 0.0145; R^2 = 9901).$

The required voltage decreases as the SE concentration increases. By increasing the SE concentration to 10, 25, and 50 mM, the average voltage decreased to 6.0, 5.5, and 5.4 V, respectively. The energy consumption was calculated as 21.11, 19.17, and 18.75 kWh m⁻³ with increasing SE concentration (Figure 3(b)). Therefore, considering the electrical energy consumption, a higher SE concentration would be more suitable for the operation of the system. However, if the salt concentration (i.e., the SE concentration) exceeds a certain threshold value,

a salt film may form on the electrode surface, which reduces the number of active sites on the electrode or causes a change in the chemistry of the active sites, leading to a reduction in the pollutant degradation rate [45, 46].



Figure 3. Variation of caffeine degradation efficiency (a) and energy consumption (b) over time with SE concentration

3.3. Effect of anode-cathode distance

Various studies on the electrooxidation process have reported that the distance between the anode and cathode influences the rate of decomposition and the electrical energy consumption [47-49]. The effects of different anode-cathode distances (2, 8, and 14 mm) on caffeine degradation were investigated; the results are shown in Figure 4. In the experiments, the initial pH was 5.8, the current density was 20 mA cm⁻², the supporting electrolyte concentration was 50 mM, the initial caffeine concentration was 25 mg L⁻¹, and the cathode type was SS. After 120 minutes of electrolysis, the degradation efficiencies are almost the same regardless of the distance between the anode and cathode (Figure 4(a)).

Examination of the pseudo-first-order reaction rate constants shows that the degradation of caffeine is faster with smaller anode-cathode distances. The caffeine degradation rates for 2, 8, and 14 mm distances are 0.0438, 0.0403, and 0.0392 min⁻¹, respectively. In studies where coking wastewater, sulfamethoxazole, and

perfluorooctanoic acid were removed, it was reported that electrolysis proceeds at higher reaction rates under shorter distances between the anode and cathode [47, 49, 50]. By increasing the anode-cathode distance to 2, 8, and 14 mm, the average voltage increased to 5.4, 5.7, and 6.6 V, respectively. Since the electrolysis system was operated at a constant current, the energy consumption increased with the increase in voltage. By increasing the anode-cathode distance to 2, 8, and 14 mm, the energy consumption was calculated to be 18.75, 19.94, and 22.99 kWh m⁻³, respectively (Figure 4(b)). Therefore, considering the electrical energy consumption, a shorter distance would be more suitable for the operation of the system.



Figure 4. Variation of caffeine degradation efficiency (a) and energy consumption (b) over time with anode-cathode distance

3.4. Effect of initial caffeine concentration

To determine the effects of the initial concentration of caffeine, several experiments were performed with initial concentrations of 25, 50, and 75 mg L⁻¹ using 50 mM K₂SO₄ solutions as the supporting electrolyte (Figure 5). Further experimental parameters were an initial pH value of 5.8, a current density of 20 mA cm⁻², an anode-cathode distance of 2 mm, and a cathode SS. At an electrolysis time of 60 minutes, the efficiency of caffeine degradation was 96.0%, 86.2%, and 77.8% for initial caffeine concentrations of 25,

50, and 75 mg L^{-1} , respectively. After 105 minutes of electrolysis time, the change in initial caffeine concentration had no significant effect caffeine degradation. As the caffeine on concentration was increased from 25 to 75 mg L⁻ the absolute caffeine removal amounts increased from about 24 mg L⁻¹ to 58 mg L⁻¹ at the end of the 60 minutes electrolysis time. The total amount of caffeine removed by electrolysis was higher with increasing initial caffeine concentration. One possible reason for this was that increasing the initial caffeine concentration increased the concentration gradient and mass transfer through the diffusion layer, which in turn increased degradation at the electrode [51, 52].



efficiency over time with initial caffeine concentration

The rate of caffeine degradation decreased with increasing initial caffeine concentration. The pseudo-first-order reaction rate constants were 0.0438, 0.0297, and 0.0251 min⁻¹ for initial caffeine concentrations of 25, 50, and 75 mg L^{-1} , respectively. The results were similar to the electrochemical oxidation of ciprofloxacin and the decolorization of reactive orange 122 by the UV/H_2O_2 process [52, 53]. The decrease in the reaction rate constant at higher caffeine concentrations can be attributed to the formation of a larger amount of by-products that can compete with the caffeine itself. The energy consumption was calculated to be 18.75, 17.79, 17.59 kWh m⁻³ for initial caffeine and concentrations of 25, 50, and 75 mg L⁻¹, respectively. It can be concluded that the energy consumption was not significantly affected by changing the initial caffeine concentration.

3.5. Effect of different cathodes

Figure 6 shows the effects of cathode type on caffeine degradation during the electrolysis of caffeine. The experiments were performed with stainless steel (SS), graphite, and boron-doped diamond (BDD) cathodes and a BDD anode. The experiments were carried out at the natural pH of the solution (5.8). The initial caffeine concentration was 25 mg L⁻¹, the current density was 20 mA cm⁻², the anode-cathode distance was 2 mm and the concentration of the supporting electrolyte was 50 mM K₂SO₄.



Figure 6. Variation of caffeine degradation efficiency (a) and energy consumption (b) over time with different cathodes

The results showed that the type of cathode used had no significant effect on the degradation efficiency of caffeine as a function of electrolysis time (Figure 6(a)). However, in a study conducted on the removal of tetracycline, it was reported that the use of carbon felt as a cathode was more efficient than stainless steel [54]. The pseudo-first-order reaction rate constants calculated with the non-linear method are 0.0438, 0.0422, and 0.420 min⁻¹ for SS, graphite, and BDD, respectively. The estimated removal rate is slightly higher when SS is used as a cathode.

When analyzing the energy consumption, 18.75, 19.66, and 21.09 kWh m^{-3} were calculated for

SS, graphite, and BDD, respectively (Figure 6(b)). From this, it can be seen that the cathode type affects the energy consumption, and SS is the cathode type with the lowest energy consumption. It should also be noted that SS as a cathode is less expensive than graphite and BDD [55, 56]. Therefore, SS was chosen as the cathode material.

3.6. Effect of initial solution pH

The results of the experiments to investigate the influence of initial solution pH on caffeine degradation are shown in Figure 7. Without the addition of buffer solution, the pH value of the solution was adjusted to the desired value only once at the beginning of the experiment with 1 M H₂SO₄ or 1 M NaOH and was not changed during the experiment. In the experiments, the applied current density was 20 mA cm⁻², the initial caffeine concentration was 25 mg L⁻¹, the anodecathode distance was 2 mm, the cathode type was SS, and the supporting electrolyte concentration was 50 mM. At an electrolysis time of 45 minutes, the efficiency of caffeine degradation was 98.5%, 90.8%, and 92.2% at an initial pH of 3, 5.8, and 10, respectively.

At an electrolysis time of 120 minutes, the change in initial pH had no significant effect on the degradation of caffeine. This shows that a wide range of initial pH values can be applied in the degradation of caffeine at the BDD anode (Figure 7(a)). The rate constants of the pseudofirst-order reaction calculated by the non-linear method were 0.0496, 0.0438, and 0.0483 min⁻¹ for initial pH 3, 5.8, and 10, respectively. The degradation of caffeine was faster at an initial pH of 3 than at a higher initial pH. The difference in the degradation rate of organic matter at different pH values is often attributed to the higher redox potential of hydroxyl radicals under acidic conditions compared to alkaline conditions [57]. Similar results obtained were in the electrochemical oxidation of 2.4dichlorophenoxyacetic acid and sulfamerazine [58, 59]. The energy consumption was calculated to be 18.25, 18.75, and 18.17 kWh $m^{\text{-}3}$ for an initial pH of 3, 5.8, and 10, respectively. It can be concluded that changing the initial pH of the solution has no effect on energy consumption.



Figure 7. Variation of caffeine degradation efficiency (a) and solution pH (b) over time with initial pH value

The change in pH of the solution with time during electrolysis is shown in Figure 7(b). In the experiment conducted at an initial solution pH of 3, an increase in pH with electrolysis time was observed. After 60 minutes of electrolysis, the pH value of the solution reached 3.8. The pH value of the solution then increased rapidly and reached 9.1 after 120 minutes. With an initial pH value of the solution of 5.8, the pH value of the solution increased to 9.4 after 20 minutes of electrolysis. Thereafter, the pH of the solution slowly increased and reached 10.2 at the end of 120 minutes. With an initial solution pH of 10, the solution pH value first decreased to 9.8 and then increased to 10.6. Therefore, it can be said that the pH value tends to increase during the electrochemical degradation of caffeine using a BDD anode and an SS cathode.

The oxidation reaction at the anode decreases the pH of the solution, while the reduction reaction at the cathode causes an increase in the pH of the solution (Equations 4 and 5) [46]. The oxidation reaction of the water on the cathodic surface (Equation 8) and the resulting release of hydroxyl ions, which are formed during this process, into the aqueous environment can lead to an increase in the pH value with the electrolysis time [57, 60, 61]. In addition, the increase in the pH of the solution may also be related to the scavenging of

the hydroxyl radical in the presence of sulfate, according to Equation 9 [62].

$$2H_20 + 2e^- \to H_2 + 20H^-$$
 (8)

$$SO_4^{2-} + {}^{\bullet}OH \to SO_4^{\bullet-} + OH^-$$
(9)

4. Conclusion

This study demonstrates the efficient degradation of caffeine by anodic oxidation using a BDD electrode. From a kinetic point of view, it was found that the degradation of caffeine follows the pseudo-first-order kinetics, while the reaction rate constant increases with increasing current density and concentration of the supporting electrolyte and decreases with increasing initial caffeine concentration. It was found that the influence of the anode-cathode distance, the cathode type, and the initial pH of the solution on the reaction rate constant was not very significant. When analyzing the energy consumption, the applied current density and the electrolysis time were found to be the most effective parameters.

It was found that the supporting electrolyte concentration, the anode-cathode distance, and the cathode type have a minor influence on energy consumption. A current density of 20 mA cm⁻², a supporting electrolyte concentration of 50 mM K₂SO₄, an anode-cathode distance of 2 mm, a cathode type of SS, and an initial solution pH of 3 were found to be the optimum values for degrading a solution containing 25 mg L⁻¹ caffeine in 45 minutes using a BDD anode. It was found that the pH of the solution tended to increase during electrolysis.

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References

- M. Ghosh, K. Manoli, X. Shen, J. Wang, A. K. Ray, "Solar photocatalytic degradation of caffeine with titanium dioxide and zinc oxide nanoparticles," Journal of Photochemistry and Photobiology A: Chemistry, vol. 377, pp. 1-7, May 2019.
- [2] L. Cizmas, V. K. Sharma, C. M. Gray, T. J. McDonald, "Pharmaceuticals and personal care products in waters: occurrence, toxicity, and risk," Environmental Chemistry Letters, vol. 13, no. 4, pp. 381-394, Aug. 2015.
- [3] S. W. da Silva, E. M. O. Navarro, M. A. S. Rodrigues, A. M. Bernardes, V. Pérez-Herranz, "Using p-Si/BDD anode for the electrochemical oxidation of norfloxacin," Journal of Electroanalytical Chemistry, vol. 832, pp. 112-120, Jan. 2019.
- [4] T. S. Oliveira, M. Murphy, N. Mendola, V. Wong, D. Carlson, L. Waring, "Characterization of Pharmaceuticals and Personal Care products in hospital effluent and waste water influent/effluent by direct-

injection LC-MS-MS," Science of the Total Environment, vol. 518-519, pp. 459-478, Jun. 2015.

- [5] A. Pal, K. Y. H. Gin, A. Y. C. Lin, M. Reinhard, "Impacts of emerging organic contaminants on freshwater resources: Review of recent occurrences, sources, fate and effects," Science of the Total Environment, vol. 408, no. 24, pp. 6062-6069, Nov. 2010.
- [6] L. Guardabassi, A. Petersen, J. E. Olsen, A. Dalsgaard, "Antibiotic resistance in *Acinetobacter* spp. isolated from sewers receiving waste effluent from a hospital and a pharmaceutical plant," Applied and Environmental Microbiology, vol. 64, no. 9, pp. 3499-3502, Sep. 1998.
- [7] A. Rajkamal, H. Kim, "Theoretical verification on adsorptive removal of caffeine by carbon and nitrogen-based surfaces: Role of charge transfer, π electron occupancy, and temperature," Chemosphere, vol. 339, p. 139667, Oct. 2023.
- [8] M. A. Heckman, J. Weil, E. G. de Mejia, "Caffeine (1, 3, 7-trimethylxanthine) in foods: A comprehensive review on consumption, functionality, safety, and regulatory matters," Journal of Food Science, vol. 75, no. 3, pp. 77-87, Apr. 2010.
- [9] T. H. Pham, N. M. Viet, P. T. T. Hoai, N. H. Tung, H. M. Tran, M. G. Mapari, T. Kim, "Synthesis of solar-driven Cu-doped graphitic carbon nitride photocatalyst for enhanced removal of caffeine in wastewater," Environmental Research, vol. 233, p. 116483, Sep. 2023.
- [10] S. Mayson, I. D. Williams, "Applying a circular economy approach to valorize spent coffee grounds," Resources Conservation and Recycling, vol. 172, p. 105659, Sep. 2021.
- [11] M. Fernández, M. Fernández, A. Laca, A. Laca, M. Díaz, "Seasonal occurrence and

removal of pharmaceutical products in municipal wastewaters," Journal of Environmental Chemical Engineering, vol. 2, no. 1, pp. 495-502, Mar. 2014.

- [12] J. Vymazal, T. D. Březinová, M. Koželuh, L. Kule, "Occurrence and removal of pharmaceuticals in four full-scale constructed wetlands in the Czech Republic-the first year of monitoring," Ecological Engineering, vol. 98, pp. 354-364, Jan. 2017.
- [13] Y. Picó, R. Alvarez-Ruiz, A. H. Alfarhan, M. A. El-Sheikh, H. O. Alshahrani, D. Barceló, "Pharmaceuticals, pesticides, personal care products and microplastics contamination assessment of Al-Hassa irrigation network (Saudi Arabia) and its shallow lakes," Science of The Total Environment, vol. 701, p. 135021, Jan. 2020.
- [14] M. Ashfaq, Y. Li, M. S. U. Rehman, M. Zubair, G. Mustafa, M. F. Nazar, C. P. Yu, Q. Sun, "Occurrence, spatial variation and risk assessment of pharmaceuticals and products personal care in urban wastewater, canal surface water, and their sediments: A case study of Lahore, Pakistan." Science of the Total Environment, vol. 688, pp. 653-663, Oct. 2019.
- [15] L. Bo, L. Feng, J. Fu, X. Li, P. Li, Y. Zhang, "The fate of typical pharmaceuticals in wastewater treatment plants of Xi'an city in China," Journal of Environmental Chemical Engineering, vol. 3, no. 3, pp. 2203-2211, Sep. 2015.
- [16] Z. Ayman, M. Işik, "Pharmaceutically active compounds in water, Aksaray, Turkey," Clean-Soil Air Water, vol. 43, no. 10, pp. 1381-1388, Oct. 2015.
- [17] O. Hillebrand, K. Nödler, T. Licha, M. Sauter, T. Geyer, "Caffeine as an indicator for the quantification of untreated wastewater in karst systems," Water Research, vol. 46, no. 2, pp. 395-402, Feb. 2012.

- [18] F. Comeau, C. Surette, G. L. Brun, R. Losier, "The occurrence of acidic drugs and caffeine in sewage effluents and receiving waters from three coastal watersheds in Atlantic Canada," Science of the Total Environment, vol. 396, no. 2-3, pp. 132-146, Jun. 2008.
- [19] H. B. Quesada, T. P. de Araújo, L. F. Cusioli, M. A. S. D. de Barros, R. G. Gomes, R. Bergamasco, "Caffeine removal by chitosan/activated carbon composite beads: Adsorption in tap water and synthetic hospital wastewater," Chemical Engineering Research and Design, vol. 184, pp. 1-12, Aug. 2022.
- [20] J. Tejedor, R. Álvarez-Briceño, V. H. Guerrero, C. A. Villamar-Ayala, "Removal of caffeine using agro-industrial residues in fixed-bed columns: Improving the adsorption capacity and efficiency by selecting adequate physical and operational parameters," Journal of Water Process Engineering, vol. 53, p. 103778, Jul. 2023.
- [21] K. K. Beltrame, A. L. Cazetta, P. S. C. de Souza, L. Spessato, T. L. Silva, V. C. Almeida, "Adsorption of caffeine on mesoporous activated carbon fibers prepared from pineapple plant leaves," Ecotoxicology and Environmental Safety, vol. 147, pp. 64-71, Jan. 2018.
- [22] A. Moghaddasfar, M. Darbandi, Z. A. Li, "Mesoporous cobalt oxide nanoparticles synthesized by a sonochemical method in the presence of a deep eutectic solvent for oxidative sonophotocatalytic decomposition of caffeine," Journal of Water Process Engineering, vol. 54, p. 104056, Aug. 2023.
- [23] S. Cheng, X. Zhang, X. Yang, C. Shang, W. Song, J. Fang, Y. Pan, "The Multiple Role of Bromide Ion in PPCPs Degradation under UV/Chlorine Treatment," Environmental Science and Technology, vol. 52, no. 4, pp. 1806-1816, Feb. 2018.

- [24] F. S. Souza, L. A. Féris, "Degradation of caffeine by advanced oxidative processes:
 O₃ and O₃/UV," Ozone: Science and Engineering, vol. 37, no. 4, pp. 379-384, Jan. 2015.
- [25] K. Guo, Z. Wu, S. Yan, B. Yao, W. Song, Z. Hua, X. Zhang, X. Kong, X. Li, J. Fong, "Comparison of the UV/chlorine and UV/H₂O₂ processes in the degradation of PPCPs in simulated drinking water and wastewater: Kinetics, radical mechanism and energy requirements," Water Research, vol. 147, pp. 184-194, Dec. 2018.
- [26] N. Tran, P. Drogui, L. Nguyen, S. K. Brar, "Optimization of sono-electrochemical oxidation of ibuprofen in wastewater," Journal of Environmental Chemical Engineering, vol. 3, no. 4, pp. 2637-2646, Dec. 2015.
- [27] R. J. A. Felisardo, E. Brillas, E. Bezerra Cavalcanti, S. Garcia-Segura, "Revealing degradation of organic constituents of urine during the electrochemical oxidation of ciprofloxacin via boron-doped diamond anode," Separation and Purification Technology, vol. 331, p. 125655, Mar. 2024.
- [28] H. Hai, X. Xing, S. Li, S. Xia, J. Xia, "Electrochemical oxidation of sulfamethoxazole in BDD anode system: Degradation kinetics, mechanisms and toxicity evaluation," Science of The Total Environment, vol. 738, p. 139909, Oct. 2020.
- [29] G. D. Değermenci, "Removal of reactive azo dye using platinum-coated titanium electrodes with the electro-oxidation process," Desalination and Water Treatment, vol. 218, pp. 436-443, Apr. 2021.
- [30] B. A. Fil, S. Günaslan, "Treatment of Slaughterhouse Wastewaters with Ti/IrO₂/RuO₂ Anode and Investigation of Energy Consumption," Arabian Journal for

Science and Engineering, vol. 48, no. 1, pp. 457-466, Jan. 2023.

- [31] E. Brillas, A. Thiam, S. Garcia-Segura, "Incineration of acidic aqueous solutions of dopamine by electrochemical advanced oxidation processes with Pt and BDD anodes," Journal of Electroanalytical Chemistry, vol. 775, pp. 189-197, Aug. 2016.
- [32] A. Kapałka, G. Fóti, C. Comninellis, "The importance of electrode material in environmental electrochemistry. Formation and reactivity of free hydroxyl radicals on boron-doped diamond electrodes," Electrochimica Acta, vol. 54, no. 7, pp. 2018-2023, Feb. 2009.
- [33] B. Boye, E. Brillas, B. Marselli, P. A. Michaud, C. Comninellis, M. M. Dieng, "Electrochemical decontamination of waters by advanced oxidation processes (AOPS): Case of the mineralization of 2,4,5-T on BDD electrode," Bulletin of the Chemical Society of Ethiopia, vol. 18, no. 2, pp. 205-214, Dec. 2004.
- [34] J. E. L. Santos, D. R. da Silva, C. A. Martínez-Huitle, E. V. dos Santos, M. A. Quiroz, "Cathodic hydrogen production by simultaneous oxidation of methyl red and 2,4-dichlorophenoxyacetate aqueous solutions using Pb/PbO₂, Ti/Sb-doped SnO₂ and Si/BDD anodes. Part 1: Electrochemical oxidation," RSC Advances, vol. 10, no. 62, pp. 37695-37706, Oct. 2020.
- [35] B. Marselli, J. Garcia-Gomez, P.-A. Michaud, M. A. Rodrigo, C. Comninellis, "Electrogeneration of Hydroxyl Radicals on Boron-Doped Diamond Electrodes," Journal ofThe Electrochemical Society, vol. 150, no. 3, pp. 79-83, Feb. 2003.
- [36] G. Li, S. Zhou, Z. Shi, X. Meng, L. Li, B. Liu, "Electrochemical degradation of ciprofloxacin on BDD anode using a differential column batch reactor: mechanisms, kinetics and pathways," Environmental Science and Pollution

Research, vol. 26, no. 17, pp. 17740-17750, Jun. 2019.

- [37] S. Cho, C. Kim, I. Hwang, "Electrochemical degradation of ibuprofen using an activated-carbon-based continuous-flow three-dimensional electrode reactor (3DER)," Chemosphere, vol. 259, p. 127382, Nov. 2020.
- [38] E. GilPavas, P. Arbeláez-Castaño, J. Medina, D. A. Acosta, "Combined electrocoagulation and electro-oxidation of industrial textile wastewater treatment in a continuous multi-stage reactor," Water Science and Technology, vol. 76, no. 9, pp. 2515-2525, Nov. 2017.
- [39] N. Flores, I. Sirés, R. M. Rodríguez, F. Centellas, P. L. Cabot, J. A. Garrido, E. Brillas "Removal of 4hydroxyphenylacetic acid from aqueous medium by electrochemical oxidation with a BDD anode: Mineralization, kinetics and oxidation products," Journal of Electroanalytical Chemistry, vol. 793, pp. 58-65, May 2017.
- [40] E. B. Cavalcanti, S. Garcia-Segura, F. Centellas, E. Brillas, "Electrochemical incineration of omeprazole in neutral aqueous medium using a platinum or boron-doped diamond anode: Degradation kinetics and oxidation products," Water Research, vol. 47, no. 5, pp. 1803-1815, Apr. 2013.
- [41] M. Panizza, G. Cerisola, "Application of diamond electrodes to electrochemical processes," Electrochimica Acta, vol. 51, no. 2, pp. 191-199, Oct. 2005.
- [42] I. Sirés, E. Brillas, M. A. Oturan, M. A. Rodrigo, M. Panizza, "Electrochemical advanced oxidation processes: Today and tomorrow. A review," Environmental Science and Pollution Research, vol. 21, no. 14, pp. 8336-8367, Apr. 2014.
- [43] S. Kul, R. Boncukcuoğlu, F. Ekmekyapar Torun, Z. Reçber, O. Sözüdoğru, E. Aladağ, "Investigation of the Treatment of

Olive Mill Wastewater by Electrooxidation," Water Air Soil and Pollution, vol. 233, no. 10, p. 421, Oct. 2022.

- [44] A. Dargahi, D. Nematollahi, G. Asgari, R. Shokoohi, A. Ansari, M. R. Samarghandi, "Electrodegradation of 2,4-dichlorophenoxyacetic acid herbicide from aqueous solution using three-dimensional electrode reactor with G/β-PbO₂ anode: Taguchi optimization and degradation mechanism determination," RSC Advances, vol. 8, no. 69, pp. 39256-39268, Nov. 2018.
- [45] M. R. Samarghandi, A. Dargahi, A. Shabanloo, H. Z. Nasab, Y. Vaziri, A. Ansari, "Electrochemical degradation of methylene blue dye using a graphite doped PbO₂ anode: Optimization of operational parameters, degradation pathway and improving the biodegradability of textile wastewater," Arabian Journal of Chemistry, vol. 13, no. 8, pp. 6847-6864, Aug. 2020.
- [46] I. Ali, A. B. de Souza, S. D. Laet, K. V. Eyck, R. Dewil, "Anodic oxidation of sulfamethoxazole paired to cathodic hydrogen peroxide production," Chemosphere, vol. 319, p. 137984, Apr. 2023.
- [47] H. Lin, J. Niu, S. Ding, L. Zhang, "Electrochemical degradation of perfluorooctanoic acid (PFOA) by Ti/SnO₂-Sb/PbO₂ Ti/SnO₂-Sb. and Ti/SnO₂-Sb/MnO₂ anodes," Water Research, vol. 46, no. 7, pp. 2281-2289, May 2012.
- [48] J. G. Kim, H. B. Kim, S. Lee, E. E. Kwon, K. Baek, "Mechanistic investigation into flow-through electrochemical oxidation of sulfanilamide for groundwater using a graphite anode," Chemosphere, vol. 307, p. 136106, Nov. 2022.
- [49] H. Lin, J. Niu, J. Xu, Y. Li, Y. Pan, "Electrochemical mineralization of sulfamethoxazole by Ti/SnO 2-Sb/Ce-

PbO₂ anode: Kinetics, reaction pathways, and energy cost evolution," Electrochimica Acta, vol. 97, pp. 167-174, May 2013.

- [50] D. Zhi, J. Zhang, J. Wang, L. Luo, Y. Zhou, Y. Zhou, "Electrochemical treatments of coking wastewater and coal gasification wastewater with Ti/Ti₄O₇ and Ti/RuO₂– IrO₂ anodes," Journal of Environmental Management, vol. 265, p. 110571, Jul. 2020.
- [51] T. S. Chen, Y. M. Kuo, J. L. Chen, K. L. Huang, "Anodic degradation of ofloxacin on a boron-doped diamond electrode," International Journal of Electrochemical Science, vol. 8, no. 6, pp. 7625-7633, Jun. 2013.
- [52] Y. Wang, C. Shen, M. Zhang, B. T. Zhang, Y. G. Yu, "The electrochemical degradation of ciprofloxacin using a SnO₂-Sb/Ti anode: Influencing factors, reaction pathways and energy demand," Chemical Engineering Journal, vol. 296, pp. 79-89, Jul. 2016.
- [53] K. Çobanoğlu, N. Değermenci, "Comparison of reactive azo dye removal with UV/H₂O₂, UV/S₂O₈²⁻ and UV/HSO₅⁻ processes in aqueous solutions," Environmental Monitoring and Assessment, vol. 194, no. 4, p. 302, Apr. 2022.
- [54] N. Oturan, J. Wu, H. Zhang, V. K. Sharma, M. A. Oturan, "Electrocatalytic destruction of the antibiotic tetracycline in aqueous medium by electrochemical advanced oxidation processes: Effect of electrode materials," Applied Catalysis B: Environmental, vol. 140-141, pp. 92-97, Aug. 2013.
- [55] M. R. Samarghandi, D. Nemattollahi, G. Asgari, R. Shokoohi, A. Ansari, A. Dargahi, "Electrochemical process for 2,4-D herbicide removal from aqueous solutions using stainless steel 316 and graphite Anodes: optimization using response surface methodology,"

Separation Science and Technology, vol. 54, no. 4, pp. 478-493, Mar. 2019.

- [56] T. Muddemann, R. Neuber, D. Haupt, T. Graßl, M. Issa, F. Bienen, M. Enstrup, J. Möller, T. Matthée, M. Sievers, U. Kunz, "Improving the treatment efficiency and lowering the operating costs of electrochemical advanced oxidation processes," Processes, vol. 9, no. 9, p. 1482, Sep. 2021.
- [57] A. Pieczyńska, T. Ossowski, R. Bogdanowicz, E. Siedlecka, "Electrochemical degradation of textile dyes in a flow reactor: effect of operating conditions and dyes chemical structure," International Journal of Environmental Science and Technology, vol. 16, no. 2, pp. 929-942, Feb. 2019.
- [58] A. Fabiańska, A. Białk-Bielińska, P. Stepnowski, S. Stolte, E. M. Siedlecka, "Electrochemical degradation of sulfonamides at BDD electrode: Kinetics, reaction pathway and eco-toxicity Journal evaluation." of Hazardous Materials, vol. 280, pp. 579-587, Sep. 2014.
- [59] J. Cai, M. Zhou, Y. Pan, X. Lu, "Degradation of 2,4dichlorophenoxyacetic acid by anodic oxidation and electro-Fenton using BDD anode: Influencing factors and mechanism," Separation and Purification Technology, vol. 230, p. 115867, Jan. 2020.
- [60] S. Vasilie, F. Manea, A. Baciu, A. Pop, "Dual use of boron-doped diamond electrode in antibiotics-containing water treatment and process control," Process Safety and Environmental Protection, vol. 117, pp. 446-453, Jul. 2018.
- [61] P. V. Nidheesh, A. Kumar, D. Syam Babu, J. Scaria, M. Suresh Kumar, "Treatment of mixed industrial wastewater by electrocoagulation and indirect electrochemical oxidation," Chemosphere, vol. 251, p. 126437, Jul. 2020.

Gökçe Didar Değermenci

[62] F. C. Moreira, R. A. R. Boaventura, E. Brillas, V. J. P. Vilar, "Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters," Applied Catalysis B: Environmental, vol. 202, pp. 217-261, Mar. 2017.