Electrochemical degradation of diclofenac for pharmaceutical wastewater treatment

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Pharmaceutical compounds are potential bioactive chemicals in the environment, and their removal from water has aroused increasing concern. Novel electrochemical techniques have demonstrated potential application in the treatment of wastewater containing pharmaceuticals. In this study, the degradation of diclofenac in aqueous solution was carried out by an electrooxidation method with boron-doped diamond (BDD) and Ta/PbO_2 anodes. The influence of various operating parameters, such as the applied current density, temperature, initial concentration of diclofenac and pH value, on the degradation efficiency of diclofenac with the Ta/PbO_2 anode was systematically investigated. In comparison with the BDD anode, the Ta/PbO_2 anode possessed a higher oxidation rate and current efficiency.

1. INTRODUCTION

Pharmaceuticals, as potential bioactive chemicals in the environment, have aroused increasing concern over the last 15 years. Owing to their imperfect management system, pharmaceuticals are emerging pollutants in most urban wastewater, which seriously affect the quality of water. In addition, medicinal compounds in water pose potential threats to human health and ecosystems in the long run [1]. Until now, high concentrations of drugs in rivers, groundwater, lakes and urban wastewater plants around the world have been verified by various studies [2-14].

Conventional wastewater treatment processes appear to be ineffective for the removal of many pharmaceutical compounds. Owing to the various advantages in comparison with many chemical and

photochemical processes, advanced oxidation processes with conductive diamond anodes have been widely studied for the degradation of pharmaceutical compounds [4, 15-17]. As shown by many reports, wastewater contaminated with drugs can be successfully treated with an anodic oxidation process with a BDD anode. In this degradation process, the contaminants in water were oxidized by a large quantity of hydroxyl radicals, which were produced from the electrolysis of water on the diamond surface.

Diclofenac (ethyl 2-[2-(2,6-dichlorophenyl)aminophenyl]), a standard drug for renal monitoring and a basic component in various pharmaceutical formulations [18], has become a persistent toxic substance in bodies of water, owing to its extraordinary resistance towards biodegradation. Diclofenac has been detected in surface waters in various countries (e.g., United States, Pakistan, Austria and Germany), and the highest concentration detected was 4.4 μg/L [19]. As seen from many important studies, advanced oxidation processes are effective for the removal of diclofenac from water. Zhao et al. showed that approximately 72% mineralization could be obtained for 30 mg/L diclofenac contained in a mixed solution of Na_2SO_4 (0.1 M) and NaCl (0.1 M) during an anodic oxidative degradation process with BDD [8]. The degradation of diclofenac is mediated by hydroxyl radicals generated on the BDD anode, while certain species, such as O_2, H_2O_2 and active chlorine, are electro-generated at the same time. In addition, the anodic oxidative degradation performance of the BDD anode for 175 mg/L diclofenac in a Na_2SO_4 solution (0.05 M) was compared with that of a Pt anode [9]. More byproducts were observed on the Pt anode than on the BDD anode. It was verified that the degradation of diclofenac was mediated by peroxodisulphates, which were generated from the oxidation of sulphates on both the BDD and Pt anodes.

Novel electrochemical techniques with boron-doped diamond (BDD) electrodes have demonstrated potential applications in the determination of certain compounds that are critical to agriculture, food chemistry, the environment, and the defence of human health. Owing to various advantages, such as an inert surface with a poor adsorption property, extremely wide potential window (up to 3.5 V) in aqueous solution, good repeatability and reproducibility, and outstanding corrosion stability (even in strong acidic media), BDD electrodes have been employed as excellent alternatives to many other conventional anodes (e.g., Pt, doped SnO_2, IrO_2 and PbO_2) for the generation of HO$^\bullet$ [20-22].

The remarkable oxidation ability of BDD anodes for the electrochemical treatment of organic compounds in wastewaters has been verified by many important studies [23-25]. In addition, owing to the chemical and electrochemical stability of PbO_2, a Ta/PbO_2 anode that was prepared by the direct electrodeposition of PbO_2 on a tantalum substrate has also been used [26]. In this work, the degradation of diclofenac by an electrochemical method with both BDD and Ta/PbO_2 anodes was studied.

2. EXPERIMENTS

To increase the adhesion of the deposited PbO_2, the surface of the tantalum plate (70 mm × 10 mm × 1 mm) was first mechanically roughened by sand blasting with grains of an

average diameter of 0.3 mm at a pressure of 5 bar (Brasfanta 037/320 Bremor, Switzerland). Subsequently, the tantalum substrate was washed with distilled water under ultrasonic treatment for 10 min to remove the sand particles from the surface. The average loss per unit area was 0.55 mg/cm^2 during the sand blasting process. To remove the layer of tantalum oxide that formed spontaneously in air, the tantalum substrate was chemically stripped in 40% hydrofluoric acid for 30 s at 25 °C. Then, the tantalum substrate was rinsed with distilled water. The loss was calculated as 0.2 mg/cm^2 from the chemical stripping.

A two-compartment cell ($V = 200$ cm^3) with a lead nitrate solution (1 M) as the anolyte and a sulphuric acid solution (1 M) as the catholyte was employed for the deposition of lead dioxide on the tantalum substrate. A porous ceramic separator was used for preventing short circuits, which were caused by the formation of lead dendrites on the cathode. The deposition experiments were carried out at 65 °C for 2.5 h with a constant anodic current density of 20 mA/cm^2. The obtained Ta/PbO$_2$ sample was mat grey and uniform, and the coverage density of PbO$_2$ was 0.25 mg/cm^2.

Electrooxidation of diclofenac was performed at different current density values (10, 15 and 20 mA/cm^2) in an FM01-LC cell. As shown by the microelectrolysis studies, the range of mean linear flow velocities should be approximately 14.6~58.4 cm/s to keep the electrode potential in the range of 2.2 ~2.7 V *vs*. SHE, where the generation of hydroxyl radicals was favoured. The degree of electrooxidation was evaluated by the COD values of the samples that was determined by a closed reflux dichromate titration method. In addition, the concentration of diclofenac during electrooxidation was measured by UV-visible spectroscopy (λ=276 nm).

## 3. RESULTS AND DISCUSSION

Table 1. Effect of the applied current density (j_{app}) on the mass transfer coefficient (k_m) and initial limiting current density ($j_{lim}(0)$).

J_{app} (mA/cm^2)	$k_m \times 10^5$ (m/s)	$J_{lim}(0)$ (mA/cm^2)
50	1.21	19.52
70	2.58	36.44
100	3.65	54.23

As demonstrated in several studies, the applied current density is critical to the electrolysis kinetics of an electrochemical process. Fig. 1 shows the COD removal efficiency as a function of the applied current density during the electrooxidation of diclofenac at the Ta/PO$_2$ anode. The degradation of diclofenac greatly depended on the applied current density (j_{app}). The degradation rate increased with an increasing current density, which is ascribed to the increased amount of hydroxyl radicals. The results must be carefully interpreted, as the literature [27] indicates that some of these metabolites may be hydrolysed and converted to the parent compound. For instance, the COD removal increased from 52 to 88% over an electrolysis time of 270 min when the applied current density increased from 50 to 100 mA/cm^2. The COD concentration decayed exponentially with the applied current, indicating that the electrooxidation process followed first-order reaction kinetics. The concentration of hydroxyl

radicals remained basically unchanged with the galvanostatic conditions. Since the j_{app} values were higher than the $j_{lim}(0)$ (limiting current density) values (Table 1) and since the current efficiency was less than 100% (inset of Fig. 1), the degradation of diclofenac was controlled by mass transfer in the tested current density range. In addition, the diffusion flux of diclofenac towards the surface of the anode increased when the applied current density increased, resulting in a decrease in the thickness of the diffusion layer and thus an increase of the overall mass transfer coefficient (k_m).
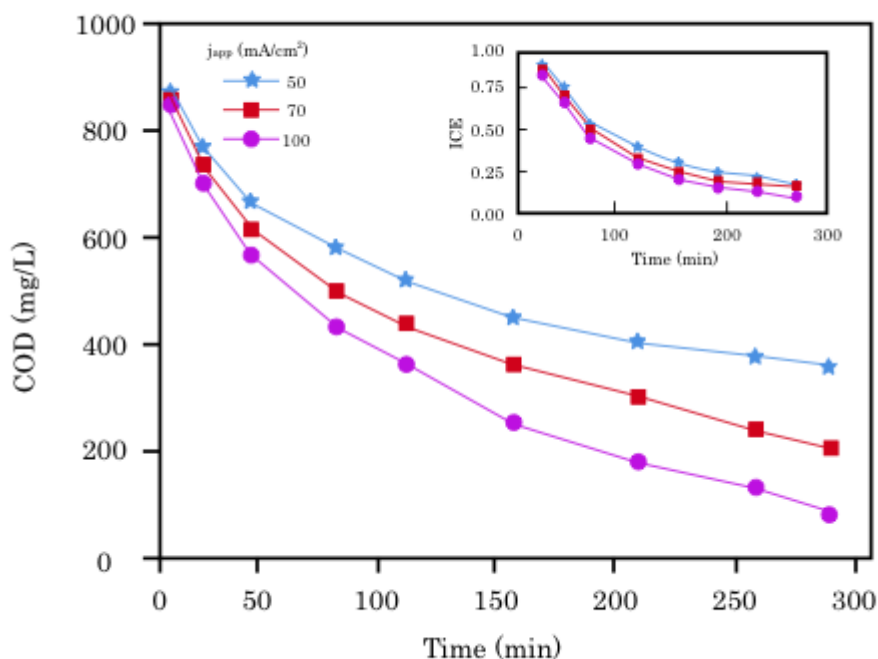

Figure 1. COD removal efficiency as a function of the applied current density during the electrooxidation of diclofenac on the Ta/PO$_2$ anode. Electrolyte: 2 g/L N$_{a2}$SO$_4$; pH=3.0; T=25 °C.

The initial concentration of a pesticide is of great importance to the treatment efficiency of that substance in wastewater. Therefore, the effect of the initial concentration of diclofenac on the COD removal efficiency was investigated. The other experimental parameters were set as follows: pH of 3.0, temperature of 25 °C and applied current density of 100 mA/cm^2. As shown in Fig. 2, the COD removal efficiency decreased with an increasing initial concentration of diclofenac. For instance, the COD removal efficiency decreased from 98 to 90% with an electrolysis time of 270 min when the initial concentration of diclofenac increased from 278 to 950 mg/L. Moreover, in a previous study on the treatability with conventional technologies, it was found that, after treatment in a pilot-scale sewage plant [28], approximately 95% of diclofenac was not eliminated. As seen from the influence of the instantaneous current efficiency (ICE) on the diclofenac degradation with an applied current density of 100 mA/cm^2 (inset of Fig. 2), the ICE value decreased exponentially with time, which is ascribed to the reaction between HO$^{\bullet}$ radicals and small amounts of organics around the anode.

Fig. 3 shows the effect of the temperature ranging from 25 to 65 °C on the COD removal efficiency during the electrolysis of diclofenac on the Ta/PO$_2$ anode with an applied current density of 100 mA/cm^2. It was observed that the degradation rate of diclofenac at 65 °C was higher than that at 25 °C, indicating the positive effect of temperature on kinetic rate of diclofenac degradation.
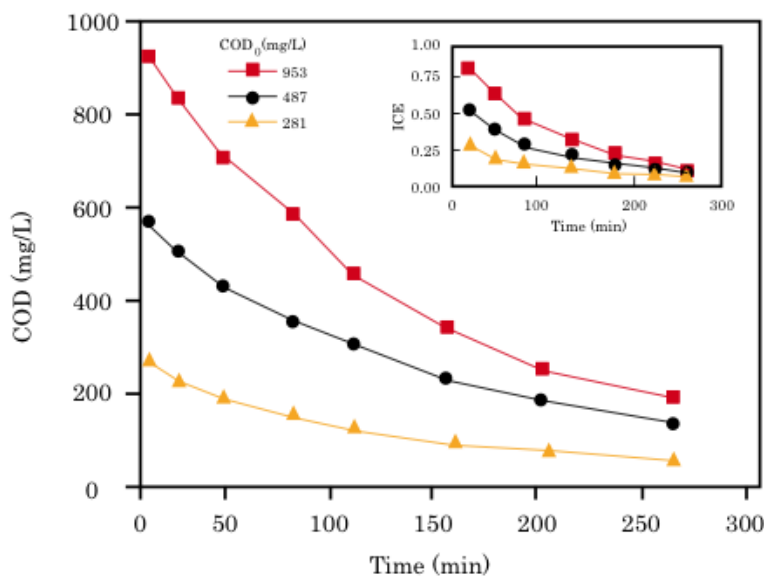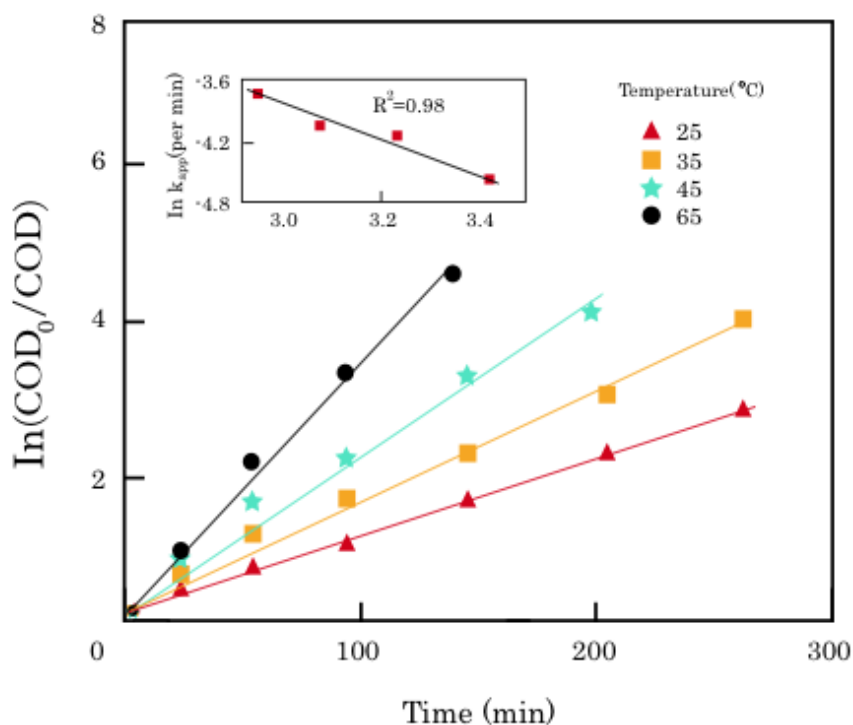

Figure 2. Influence of the initial concentration of diclofenac on the COD removal efficiency during electrolysis of diclofenac on the Ta/PO$_2$ anode. Electrolyte: 2 g/L Na$_2$SO$_4$; j$_{app}$=100 mA/cm^2; pH=3.0; T=25 °C.
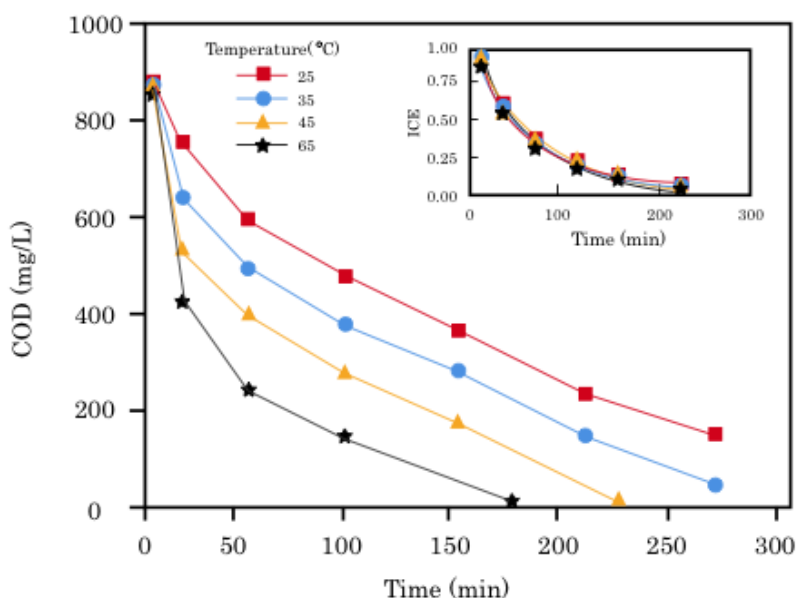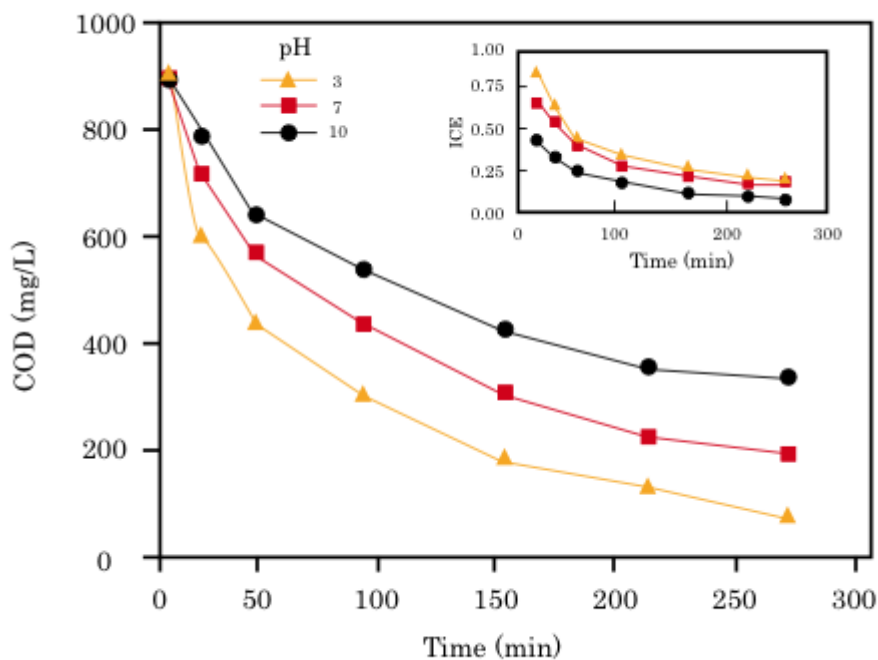

Figure 3. Influence of temperature on the COD removal efficiency during electrolysis of diclofenac on the Ta/PO$_2$ anode. Electrolyte: 2 g/L Na$_2$SO$_4$; j$_{app}$=100 mA/cm^2; pH=3.0.

As shown in Fig. 4, the COD removal efficiency followed pseudo-first-order kinetics, and the value increased from 75% to 96% over an electrolysis time of 150 min when the temperature increased from 25 to 65 °C. In addition, k_{app} increased from 1.52×10^{-4} to 4.86×10^{-4} with an increasing temperature. It was observed that peroxodisulphates were formed in the sulphate-containing solution. Therefore, the increased COD removal efficiency with temperature is ascribed to the electro-generation of inorganic oxidizing agents.


Figure 4. Linear regression of the COD removal efficiency over time at different temperatures during the electrolysis of diclofenac on the Ta/PO_2 anode. Inset: Arrhenius-type plot of the apparent first-order kinetic constants. Electrolyte: 2 g/L Na_2SO_4; $j_{app}=100$ mA/cm^2; pH=3.0.

The initial pH value of the solution greatly affects the electrooxidation of a pesticide as well. According to previous research findings, either acidic media or alkaline media can be beneficial to the efficiency of an oxidation process. It was affirmed that the effect of pH strongly depends on the nature of the investigated compound. Here, the diclofenac solutions with pH values ranging from 3.0 to 10.0 were used to study the effect of pH on the degradation rate of diclofenac. As seen from Fig. 5, an acidic medium was more favourable for diclofenac degradation than alkaline and neutral media. Chiang et al. [29] explained that the indirect electrochemical oxidation of organic compounds occurs mainly via electrolytically generated chlorine/hypochlorite. However, the production rate of chlorine/hypochlorite was not affected by the initial pH value in the range of 4.0–10.0 during the electrochemical oxidation. At an electrolysis time of 270 min, the COD removal efficiency increased from 51 to 84% with a decreasing pH value from 10.0 to 3.0. Therefore, a pH value of 3.0 was chosen for all the following electrochemical experiments

Figure 5. Influence of the initial pH value of the diclofenac solution on the COD removal efficiency during electrolysis of diclofenac on the Ta/PO_2 anode. Electrolyte: 2 g/L Na_2SO_4; j_{app}=100 mA/cm^2; T=25 °C.
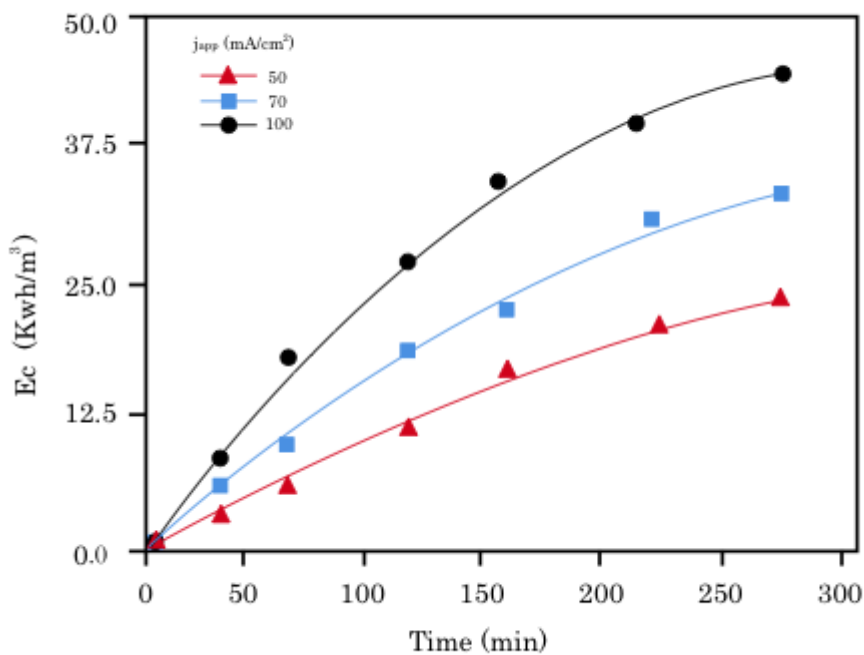
Figure 6. Evolution of the energy consumption during the electrolysis of diclofenac on the Ta/PO_2 anode at different applied current densities. Electrolyte: 2 g/L Na_2SO_4; pH=3.0; T=25 °C.

The efficiency of the electrolysis system, as one of the most crucial factors to the economics of the electrolysis process, can be expressed as the energy consumption for the reduction of 1 kg of organic matter during the electrochemical treatment of an organic-containing effluent. Fig. 6 shows the electrical energy consumption (Ec) during the degradation process of diclofenac at different applied current densities. The energy consumption increased with an increasing applied current density, which is attributed to a decrease of the organic content in the solution and the formation of less oxidizable intermediates, such as carboxylic acids, by an increase of the oxygen evolution side reaction [30, 31].

The current efficiency and COD removal trends during the degradation of diclofenac obtained on the Ta/PbO_2 anode was compared with that obtained on a BDD anode, and the results are shown in Fig. 7. Obviously, the COD removal efficiency obtained on the Ta/PbO_2 anode (97%) was higher than that obtained on the BDD anode (71%) after 2.5 hours of treatment, suggesting that the oxidation rate and current efficiency of the Ta/PbO_2 anode were higher than those of the BDD anode. The degradation reaction involves different oxidant species, such as hydroxyl radicals and other strong oxidizing species, produced *in situ* in the reaction media. Hydroxyl radicals produced via hydrogen peroxide, leaving the "green" byproducts oxygen gas and water, has a high standard reduction potential. In addition, the ICE during the electrooxidation process of diclofenac obtained on the Ta/PbO_2 anode was higher than that obtained on the BDD anode, which was greatly related to the adsorption property of Ta/PbO_2. Owing to the weak adsorption property of the Ta/PbO_2 anode, the generated hydroxyl radicals at the Ta/PbO_2 anode were very active and thus reacted very quickly with the organic species delivered to the anode surface. Table 2 lists a comparison of the rate constant (k') and respective r^2 values for various COD removal processes.
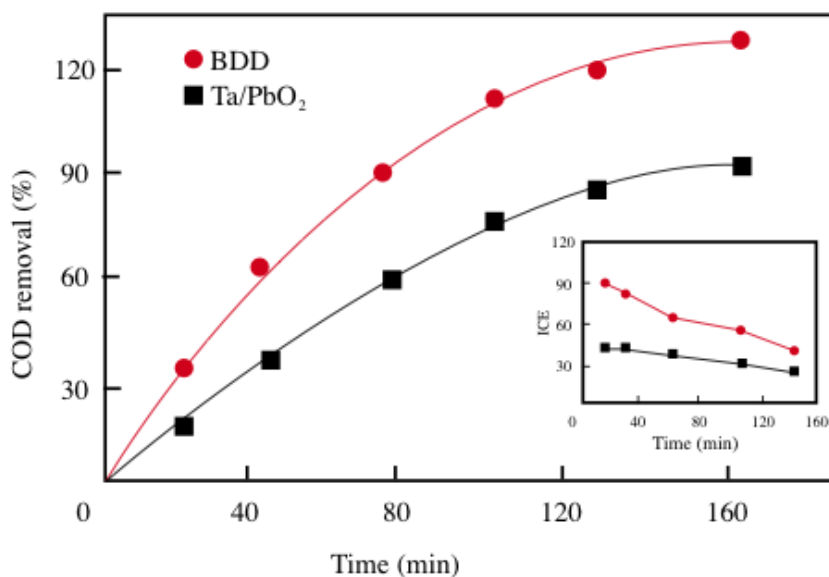
Figure 7. Comparison of current efficiency and COD removal trends during the electrochemical oxidation of diclofenac on the BDD and Ta/PbO_2 anodes. Electrolyte: 2 g/L Na_2SO_4; j_{app}=100 mA/cm^2; pH=3.0; T=25 °C.

Table 2. Comparison of the BDD and Ta/PbO$_2$ anode electrochemical treatments of pharmaceutical wastewater with other reports.

Wastewater type	Electrode	Kinetics (per min)	Current efficiency	Reference
Phenol–formaldehyde resin manufacture	BDD	1.5×10^{-3}	0.98	[32]
Oil refinery	BDD	1.6×10^{-3}	0.97	[32]
Bulk drug manufacture	BDD	1.1×10^{-3}	0.95	[32]
Diclofenac	BDD	1.1×10^{-3}	0.89	This work
Diclofenac	Ta/PbO$_2$	1.8×10^{-3}	0.98	This work

4. CONCLUSIONS

In conclusion, the electrochemical degradation of diclofenac was achieved employing BDD and Ta/PbO$_2$ anodes. Specifically, the oxidation of diclofenac was promoted by hydroxyl radicals generated via the oxidation of water on the surface of BDD and Ta/PbO$_2$. The degradation efficiency of diclofenac on the Ta/PbO$_2$ anode increased with an increasing current density and temperature. In addition, the degradation efficiency of diclofenac decreased with an increasing initial concentration of diclofenac and pH value of the solution. Under the optimized conditions, mass transport was the limiting step of the entire electrooxidation process, and the COD removal was well described by pseudo-first-order kinetics. The oxidation rate and current efficiency of the diclofenac degradation obtained on the Ta/PbO$_2$ anode was higher than that obtained on the BDD anode, indicating that the anodic oxidation with the Ta/PbO$_2$ electrode is a promising method for the treatment of pharmaceutical effluents.

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