

# Electrochemical Determination of Chemical Oxygen Demand Based on Boron-Doped Diamond Electrode

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## ABSTRACT

A rapid and environment-friendly electrochemical sensor to determine the chemical oxygen demand (COD) has been developed. The boron-doped diamond (BDD) thin-film electrode is employed as the anode, which fully oxidizes organic pollutants and provides a current response in proportion to the COD values of the sample solution. The BDD-based amperometric COD sensor is optimized in terms of the applied potential and the solution pH. At the optimized conditions, the COD sensor exhibits a linear range of 0 to 80 mg/L and the detection limit of 1.1 mg/L. Using a set of model organic compounds, the electrochemical COD sensor is compared with the conventional dichromate COD method. The result shows an excellent correlation between the two methods.

**Keywords :** Chemical oxygen demand, Amperometric detection, Boron-doped diamond, Environmental analysis, Electrochemical sensor

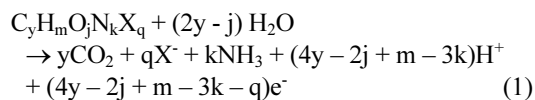
Received : 5 January 2023, Accepted : 2 February 2023

## 1. Introduction

Chemical oxygen demand (COD) is a critical parameter to evaluate water quality. COD is defined as the oxygen equivalents required to decompose the organic compound using a strong oxidizing agent [1]. The conventional COD methods involve the digestion of organic compound by dichromate or permanganate followed by the colorimetric detection of the oxidant consumption. This procedure is time consuming, taking 2–4 hours to achieve a complete oxidation of the sample [2,3]. Furthermore, the use of toxic reagents, such as chromium and mercury [4,5], provokes health and safety concerns. Therefore, efforts have been made to overcome these disadvantages by developing a fast and environment-friendly analytical method that can replace the conventional method.

Electrochemical advanced oxidation process (EAOP) has acquired high relevance for water reme-

diation technology [6,7]. EAOP can proceed in either direct or indirect pathway [8]. Whereas the direct oxidation involves a direct electron transfer between electrode and organic compounds, the indirect oxidation is mediated by hydroxyl radicals and other active intermediates produced on the anode surface by the discharge of water or electrolyte [9]. Hydroxyl radical is a powerful oxidant [10] possessing a high standard potential ( $E^\circ(\cdot\text{OH}/\text{H}_2\text{O}) = 2.38 \text{ V vs. SHE}$ ) [11–13], thus  $\cdot\text{OH}$  can fully oxidize the organic compound into carbon dioxide [14]:



Here  $\text{C}_y\text{H}_m\text{O}_j\text{N}_k\text{X}_q$  is the organic compound to be oxidized, in which X is a halogen atom. The number of electrons  $n$  that is required for complete oxidation of an organic molecule is  $4y - 2j + m - 3k - q$ . Note that the oxidation product of nitrogen atoms is  $\text{NH}_3$  not  $\text{NO}_2$ , as the standard COD method using dichromate will not oxidize the  $\text{NH}_3$  in strong acid solution [15].

In EAOP, electrode materials play a vital role,

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DOI: <https://doi.org/10.33961/jecst.2023.00017>

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directly influencing the reaction mechanism [16], process and energy efficiency [17]. Traditional anode materials, such as graphite and platinum, have been primarily employed for organics oxidation. However, the materials can be gradually deactivated due to the formation of an adsorbed layer on the electrode surface [18]. The  $\text{TiO}_2$  has also been studied as non-toxic, inexpensive, and photosensitive electrocatalyst for amperometric COD determination. The main disadvantage of  $\text{TiO}_2$  is that it requires a UV light source [16] to generate electron/hole pairs. However, the high recombination rate of the active species results in a lower photocatalytic activity, working range, and irreproducibility [19].

Boron-doped diamond (BDD) has been suggested as the promising anode material for electrochemical incineration. It can produce and accumulate a high density of hydroxyl radical and other active intermediates on its surface [20,21]. Its wide potential window in an aqueous medium [22] enables the material to exhibit high over-potential for oxygen evolution [6,23], which is beneficial for organic oxidation. BDD electrodes also offer excellent stability over prolonged periods due to their chemical and physical robustness [24], high anodic stability, and good conductivity for electrochemical purposes [25]. BDD electrodes are very effective for the degradation of organic pollutants, such as phenols [26], aromatic amines [27], textile dyes [28], and refractory herbicides [29].

Previously, the feasibility of the COD determination based on the BDD electrodes was demonstrated [30,31]. However, more research is needed on mechanistic aspect of the electrochemistry on the BDD electrode. In this work, we provide a theoretical explanation for the electrochemical COD determination based on the mass-transfer-limited reaction. In addition, the effect of essential parameters was investigated to achieve optimum analytical performance. Especially, as the applied potential and solution pH mainly determine the kinetics of organics oxidation thus the efficiency of electrochemical COD measurements, the optimization of the applied potential and solution pH is important. Sensor behavior was evaluated using a set of model organic compounds. Finally, the novel E-COD sensor was validated toward the conventional dichromate method.

## 2. Experimental

### 2.1 Chemicals

All chemicals were used as received (Daejung Chemicals) and solutions were prepared with ultrapure water (resistivity =  $18 \text{ MW}\cdot\text{cm}$ ).

### 2.2 Devices and Equipment

The electrochemical measurements were performed with a potentiostat (BioLogic SP-150) in a three-electrode cell configuration at ambient temperature. Experiments were conducted in an undivided electrochemical cell (PECC-2 Cells, Zahner) with a solution volume of  $\sim 7 \text{ cm}^3$ . A pre-treated BDD electrode with an exposed area of  $2.54 \text{ cm}^2$  ( $d=18 \text{ mm}$ ) was employed as the working electrode. A Pt coil and a saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively.

### 2.3 Electrode preparation

The anode was the BDD thin film grown on a thick monocrystalline Si substrate via the hot filament chemical vapor deposition method (NeoCoat). The boron doping level was 5000 ppm, while the film thickness and resistivity were  $3 \mu\text{m}$  and  $100 \text{ m}\Omega\cdot\text{cm}$ , respectively. Before loading, the BDD electrode was cleaned by sonication in acetone, isopropyl alcohol, and deionized water for 10 minutes. The degreased BDD was then treated in  $1.0 \text{ M HNO}_3$  for an hour to remove any impurities on the surface, rinsed by ultrapure water and dried with  $\text{N}_2$  gas.

### 2.4 Standard COD method

For comparison, the standard COD methods using the dichromate digestion were performed following the previous procedure [32]. In short, a digestion solution was prepared containing  $5.0 \text{ g/L K}_2\text{Cr}_2\text{O}_7 + 16.0 \text{ g/L Hg}_2\text{SO}_4$  in conc.  $\text{H}_2\text{SO}_4$ . A catalyst solution was separately prepared by dissolving  $0.22 \text{ g Ag}_2\text{SO}_4$  in  $40 \text{ mL conc. H}_2\text{SO}_4$ . For digestion of organic compounds,  $2.5 \text{ mL}$  sample solution was mixed with  $1.5 \text{ mL}$  digestion solution and  $3.5 \text{ mL}$  catalyst solution. The mixture was heated at  $150^\circ\text{C}$  for 2 hours. After cooling down to room temperature, the absorbance of the digested solution at  $440 \text{ nm}$  was measured in a UV-VIS spectrometer.

### 2.5 Electrochemical procedures

The amperometric detection under well-stirred conditions was used to determine the COD value.

Before each E-COD measurement, potential cycling was conducted for 20 cycles to pre-condition the BDD electrode in blank 0.1 M  $\text{KNO}_3$ . The solution pH was adjusted by adding a proper amount of 1.0 M  $\text{HNO}_3$  or 1.0 M  $\text{KOH}$ . A proper potential was applied to allow the background current to reach a steady. Subsequently, aliquots of organic compounds were injected to obtain a current increase, which was measured as the response current.

### 3. Results and Discussion

#### 3.1 Electrochemical characterization

Electrochemical characterizations were carried out to evaluate the anodic behavior of the BDD electrode toward organic compounds. As shown in Fig. 1(a), in a blank electrolyte (0.1 M  $\text{KNO}_3$ ), a very low background current is observed between +1.1 V and +2.2 V (vs. SHE), which is typical of the BDD electrode with a low double layer capacitance. The anodic current begins to rise at  $\sim 2.3$  V, marking the onset of water oxidation at the BDD electrode. This onset potential is close to the theoretical potential for hydroxyl radical generation ( $E^\circ(\cdot\text{OH}/\text{H}_2\text{O}) = 2.38$  V), so it is expected that hydroxyl radical is generated by the BDD above the onset potential [3].

When malonic acid is added as a sample organic compound, an additional current is observed above the background, as shown by the red line in Fig. 1(a). We note that the oxidation of the organic compound occurred at the potential region for  $\cdot\text{OH}$  generation. (2.2–2.5 V) This indicates that the oxidation of malonic acid is mainly via reaction with hydroxyl radical rather than direct oxidation on the BDD electrode. The additional current in the presence of organic

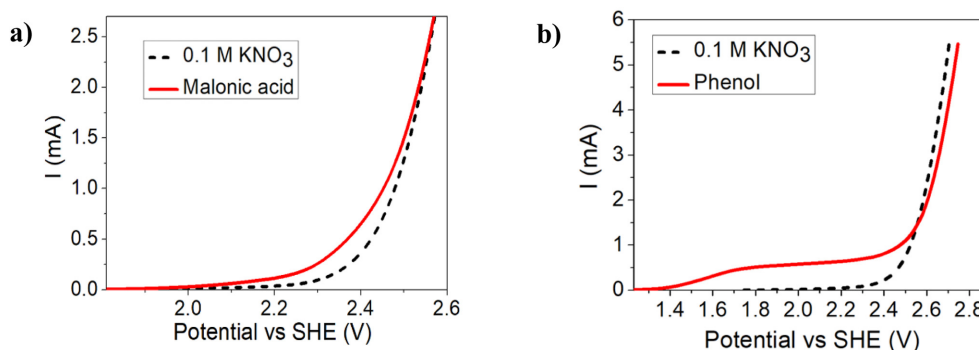
compound is the basis for E-COD measurements.

On the other hand, the voltammetry for phenol on the BDD in Fig. 1(b) exhibits a different behavior. The onset potential ( $\sim 1.3$  V) for phenol is much more negative than that for malonic acid, which can be attributed to the direct oxidation of the aromatic phenol on the BDD electrode [26]. However, at positive potentials ( $>2.3$  V), where the BDD electrode begins to produce hydroxyl radicals, indirect oxidation (via hydroxyl radical) should accompany the direct oxidation. Again, the current difference between the sample and the background offers the basis for the E-COD measurements.

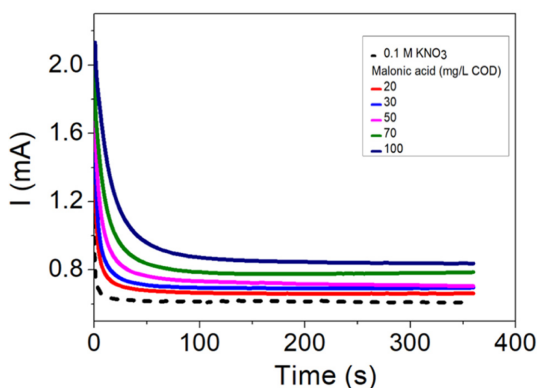
#### 3.2 Chronoamperometry of organic compounds

Fig. 2 shows the chronoamperometry of different concentrations of malonic acid at anodic potential where hydroxyl radical is generated and organic compound is oxidized. Note that the electrolyte solution is stirred so that mass transfer is both diffusive and convective. As long as a constant stirring is applied to the solution, the measurement gives a consistent and stable responses for extended time regime. After the initial current spike, the current approaches steady-state values. The background current (dotted line) is from pure water oxidation, while the sample current in the presence of organic compound has additional current due to oxidation of organic compound [33]. A linear increase of the steady-state current is observed with the increase of the malonic acid concentration.

The linear increase of the steady-state current with organic concentration can be understood as follows: We assume that i) organic compounds are fully oxidized at the electrode surface; ii) the overall reaction



**Fig. 1.** Cyclic voltammograms on the BDD electrode for (a) malonic acid (COD=100 mg/L) and (b) phenol (COD=100 mg/L). Supporting electrolyte: 0.1 M  $\text{KNO}_3$ . Scan rate: 100 mV/s.



**Fig. 2.** Chronoamperometric responses recorded in 0 to 100 mg/L COD of malonic acid (solid line). Supporting electrolyte: 0.1 M KNO<sub>3</sub> (dashed line). Applied potential: 2.5 V (vs SHE); pH: 5.

rate is determined by the mass transfer of the organic compound (mass-transfer limited process); iii) the bulk concentration of organic compounds remains unchanged within the time scale of the experiment. Then, the steady-state current can be represented as [34]:

$$i_{ss} = \frac{nFAD}{\delta} C_b \quad (2)$$

where  $i_{ss}$  is the steady-state current,  $n$  the number of electrons,  $F$  the Faraday current,  $A$  the electrode area,  $D$  the diffusion coefficient,  $d$  the thickness of diffusion layer,  $C_b$  the bulk concentration of organic compounds [3]. Eq. 2 states that the steady-state current  $i_{ss}$  is proportional to the bulk concentration of the organic compound. Note that the molar concentration can be converted to the equivalent COD value (mg/L of O<sub>2</sub>) using:

$$[\text{COD}] = 8000n \cdot C_b \quad (3)$$

Substitute Eq. 3 into Eq. 2 to get:

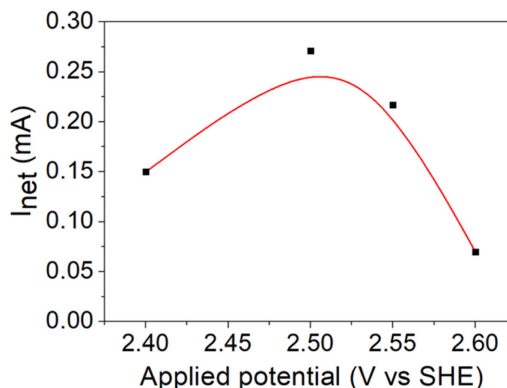
$$i_{ss} = \frac{FAD}{\delta} \times \frac{[\text{COD}]}{8000} \quad (4)$$

If we assume that  $D$  and  $d$  are relatively constant for different organic compounds, we conclude that  $i_{ss}$  is solely determined by  $[\text{COD}]$ .

### 3.3 Optimization of the experimental parameters

#### 3.3.1 Effect of applied potential

In order to optimize the potential with respect to



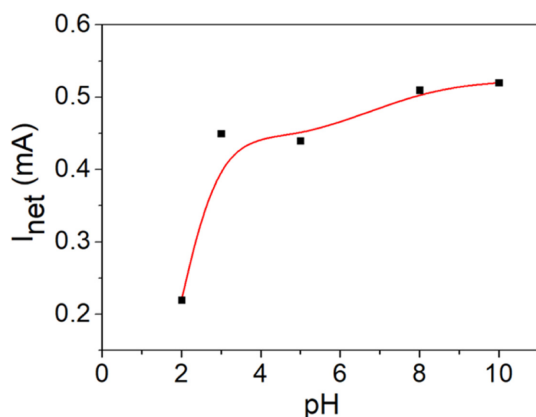
**Fig. 3.** Effect of applied potential on the  $I_{net}$  value of 100 mg/L COD of malonic acid. Supporting electrolyte: 0.1 M KNO<sub>3</sub>.

the sensor response, chronoamperometric measurements were repeated at a range applied potentials. As shown in Fig. 3,  $I_{net}$ , which is the difference between the sample and the background currents, was highest at 2.5 V. At lower potential,  $I_{net}$  was lower because the oxidation of organic compounds was slower. At higher potentials,  $I_{net}$  was lower probably due to the excessive oxygen evolution which reduces the active electrode area. Furthermore, vigorous oxygen evolution at positive potential resulted in an unstable and irreproducible responses. Consequently, 2.5 V was selected for carrying the following experiments owing to sensitive current response and stability.

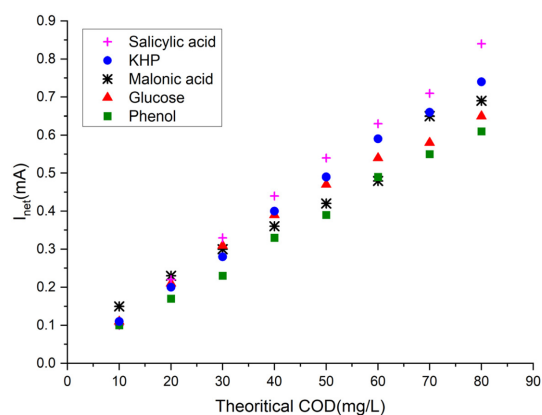
#### 3.3.2 Effect of solution pH

The influence of pH on the analytical performance was then investigated. Fig. 4 shows the  $I_{net}$  values as function of solution pH. At low pH (pH=1~2), the  $I_{net}$  value is small because the onset potential of hydroxyl radical generation ( $E^{\cdot}\text{OH}/\text{H}_2\text{O}$ ) becomes more positive.

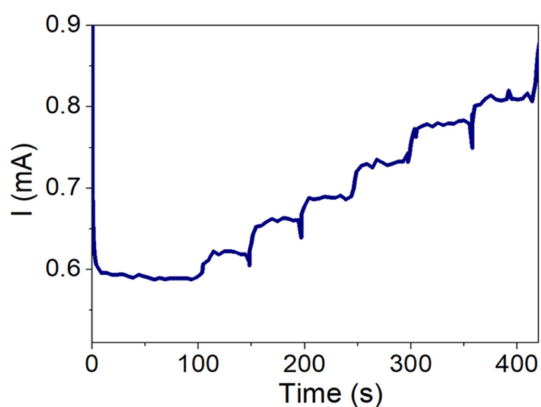
When pH was adjusted to a higher value,  $I_{net}$  value was relatively independent of pH in the pH range of 3 to 10. At a higher pH, water molecules are readily oxidized to generate hydroxyl radicals, which leads to oxidation of organic compounds and higher  $I_{net}$ . However, in a strong alkaline condition (pH >10), the main reaction will turn into oxygen evolution and a vigorous generation of oxygen bubbles is observed on the BDD surface, which results in irreproducible results. Accordingly, pH in the neutral range was employed for the subsequent experiments.



**Fig. 4.** Effect of solution pH on the  $i_{\text{net}}$  value of 100 mg/L COD of malonic acid. Supporting electrolyte: 0.1 M  $\text{KNO}_3$ . Applied potential: 2.5 V (vs. SHE).



**Fig. 6.** A linear increase of  $I_{\text{net}}$  in response to the COD of model organic compounds. ( $E_{\text{applied}}$ : 2.50 V vs. SHE, pH: 5).



**Fig. 5.** Current-time response of the BDD electrode to the addition of malonic acid (+4 mg/L COD per addition) at 2.5 V (vs. SHE). Supporting electrolyte: 0.1 M  $\text{KNO}_3$ .

### 3.4 Linear response of the BDD electrode

A typical current response toward organic compounds under the optimized conditions is shown in Fig. 5. Initially a stable background current is observed when the appropriate potential bias was applied. The injection of an organic compound causes a sharp increase of the anodic current, and a steady-state current can be reached quickly within ~10 seconds. As expected from Eq. 4, the steady-state current is increased linearly with the concentration of the organic compound.

### 3.5 Measurement of model organic compounds

The applicability of the BDD sensor was evalu-

ated through the E-COD determination of various organic compounds. A list of organic compounds was selected as model organics samples. First type was organic pollutants often contained in wastewater: malonic acid, salicylic acid, and phenol, while second type was the ones often used as standards for COD analysis: glucose and potassium hydrogen phthalate (KHP). The measurement results of  $I_{\text{net}}$  and theoretical COD (mg/L of  $\text{O}_2$ ) of the various organic compounds are presented in Fig. 6. As previously defined,  $I_{\text{net}}$  is the difference between the sample and the background currents, as demonstrated in Fig. 5, and the theoretical COD is obtained by converting molar concentration of individual organic compound into COD equivalent using Eqs. 1 and 3. A strong linear relationship is found between  $I_{\text{net}}$  and the theoretical COD for various organic compounds (the correlation coefficient  $R^2=0.97$ ). The strong linearity for different organic compounds indicates that our assumption of relatively constant  $D/d$  values for different organic compounds in Eq. 4 is valid. From the measurements, the linear range for the E-COD measurements were found to be up to ~80 mg/L and detection limit to be 1.1 mg/L ( $S/N=5$ ). This compares with the previous report, which claims a linear range of 20 to 9000 mg/L and a detection limit of 7.5 mg/L [31].

In the conventional COD measurements, KHP is commonly used as standard materials for calibration. So, the E-COD sensor response for KHP in Fig. 6 is used for calibration to get the calibration equation: E-COD (mg/L) =  $123 \times I_{\text{net}}$  (mA). From the obtained

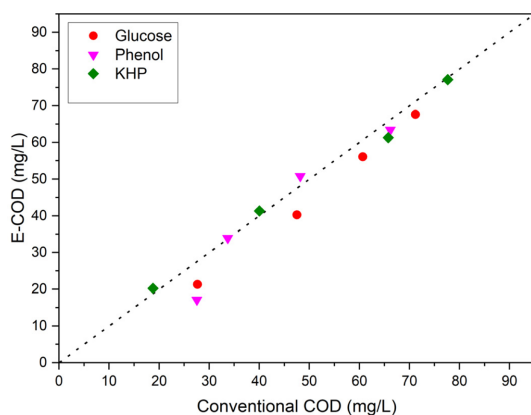


Fig. 7. Strong correlation between the E-COD and the conventional COD using dichromate oxidant.

calibration equation, the  $I_{\text{net}}$  values in Fig. 6 is converted into E-COD, as shown in Fig. S1.

Finally, in order to confirm that the novel E-COD sensor is compatible with the conventional COD methods, the conventional COD measurements (using dichromate) of the model organic compounds are conducted. The model organic compounds are digested by dichromate in a strong acid solution and the COD values are measured through colorimetry following the well-established procedure (KHP is used as standard material for calibration). Fig. 7 shows the comparison of the E-COD and the conventional COD results for the model organic samples. A strong correlation is found between the two methods (slope = 1.0067, correlation coefficient  $R^2=0.96$ ). The average difference between the COD values from the two methods is ~7%. This indicates that the novel E-COD sensor produces measurement results that are compatible with the conventional COD method using strong oxidant.

#### 4. Conclusions

As an alternative method to measure COD in a faster and more environment-friendly way, an electrochemical method for COD determination is developed. The novel E-COD sensor is based on the conductive diamond electrode, which exhibits a wide potential window and a high stability even in extreme anodic potential. Sample organic compounds are completely oxidized on the BDD electrode, which produces a mass-transfer-limited current. Thus, the

steady-state current is proportional to the bulk concentration of organic compounds, as demonstrated by the linear amperometric response of the E-COD sensor. The compatibility of the novel E-COD sensor with the conventional dichromate method is demonstrated. Providing a faster, safer, and more compact COD device, the E-COD sensor has a potential to replace the conventional lab-based time-consuming COD method.

#### Acknowledgments

This research was supported by the academic research fund from the Kumoh National Institute of Technology (2019104143).

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