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# Electrooxidation of 2-nitrobenzaldehyde: A comparative study of $SnO_2$ and boron doped diamond anodes

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**ABSTRACT**

*This study compared the electrochemical degradation of 2-nitrobenzaldehyde (2-NBA) on the bored-doped diamond (BDD) and $SnO_2$ electrode. The effect of several parameters such as current density, electrolyte type, initial 2-NBA concentration and temperature, were investigation in terms of degradation. The 2-nitrobenzaldehyde demonstrated different behaviors upon operative parameters on these two electrodes. Compared to the degradation on BDD, it performed better on $SnO_2$ in wide operating conditions, and was proved to be more cost-effective and more suitable for 2-NBA mineralization. The presence of NaCl promoted that the 2-NBA degradation on both electrodes, which decreased on $SnO_2$ but significantly improved on the BDD electrode.*

**Keywords**: 2-nitrobenzaldehyde (2-NBA); Electro-oxidation; Boron doped diamond, $SnO_2$

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## INTRODUCTION

Water is essential for life. It plays a vital role in the proper functioning of the earth's ecosystems. Only about 0.01% of the total water on earth is fresh water that can be utilized in the daily life of human beings and other creatures. Therefore, the pollution of the fresh water has a serious impact on all living creatures, and can negatively affect the use of water for drinking, household needs, recreation, fishing, transportation and commerce. Pollutants in water can be classified into three categories: organics, inorganics and microorganisms. The high chemical oxygen demand (COD) of the wastewater is mainly due to organic pollutants. Various wastewater treatment methods, including common physical, chemical and biological technologies have been attempted, but verified to be either non-destructive or ineffective for the efficient removal of dye compounds. In recent years, electrochemical oxidation has been proposed as an efficient and emerging alternative for the treatment of wastewater containing toxic or refractory organic pollutants. Many processes such as Fenton oxidation, ozonation, wet air oxidation, electrochemical oxidation and their combined processes have been investigated [1–3]. Among these electrochemical oxidation, has attracted ever-increasing interests for refractory pollutants abatement due to its high efficiency and environmental compatibility [4–6]. It has been shown that the anode material plays an important role on the electrochemical degradation of organic pollutants. The requirements for an ideal anode material include satisfactory efficiency, cost-effectiveness and stability even in extreme conditions. Various anodes have been tested and assessed for dye wastewater treatment, including ACF [7], Pt [8, 9], boron-doped diamond (BDD) [10–14] and $SnO_2$, among which, BDD dimensionally stable is of particular interest. This paper discusses the treatment of 2-Nitrobenzaldehyde (2-NBA) by an electrochemical method, in laboratory scale plant using an $SnO_2$ and boron-doped diamond (BDD) electrode as anode.

## MATERIALS AND METHODS

### Chemicals

2-Nitrobenzaldehyde is an organic aromatic compound containing a nitro group ortho to formyl. 2-Nitrobenzaldehyde once was produced as an intermediate in the synthesis of the popular dye Indigo [15]. 2-Nitrobenzaldehyde is an intermediate in an early route to Indigo, a water-insoluble dye commonly used to dye jeans and other fabrics. Fig. 1 shows the chemical structure of 2-Nitrobenzaldehyde (2-NBA).

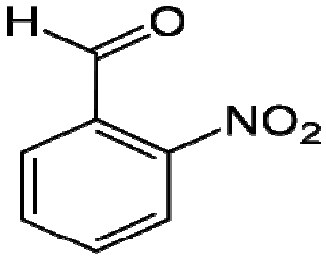


**Figure 1. Chemical structure of 2-Nitrobenzaldehyde (2-NBA).**

### Electrolytic system

Electrochemical measurements were performed using a computer controlled by Potentiostat/Galvanostat model PGZ 100 associated to "Volta-Master 4" software. A conventional three electrodes cell (100 $cm^3$) thermoregulated glass cell was used (Tacussel Standard CEC/TH). The anode was a square plate of $SnO_2$ and boron-doped diamond (BDD) electrode with effective surface area of 1 $cm^2$, whereas the cathode was a platinum electrode, and the gap between electrodes was 1cm. A saturated calomel electrode (SCE) was used as a reference. Galvanostatic electrolysis was carried out with a volume of 80 $cm^3$ aqueous solution of 0.01 mg/L. The range of applied current density was 40 to 80 $mA/cm^2$ and samples were taken at predetermined intervals during the experiment and submitted for analysis. The chemical oxygen demand (COD) is measured according to the standard methods for examination of water and wastewater [16]. All measurements were repeated in triplicate and all results were observed to be repeatable within a 5% margin of experimental error.

## RESULTS AND DISCUSSION

### Effect of supporting electrolytes

Electrolytes of chloride ions concentration on the destruction of 2-NBA has been performed in the range 1 to 3% for NaCl and were studied by BDD and $SnO_2$ electrode (Figs. 2 & 3).

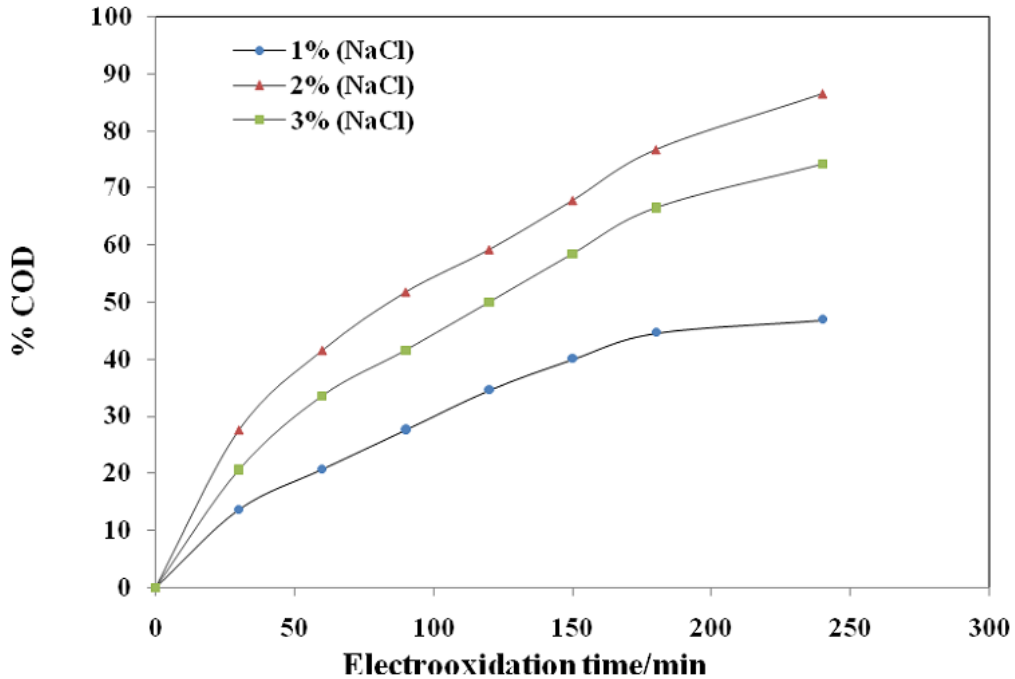


**Figure 2. Electrooxidation at BDD anode: effect of NaCl concentration on the % COD (10 $mg.L^{-1}$ 2-NBA solution, 80 $mA/cm^2$ and T=25°C)**

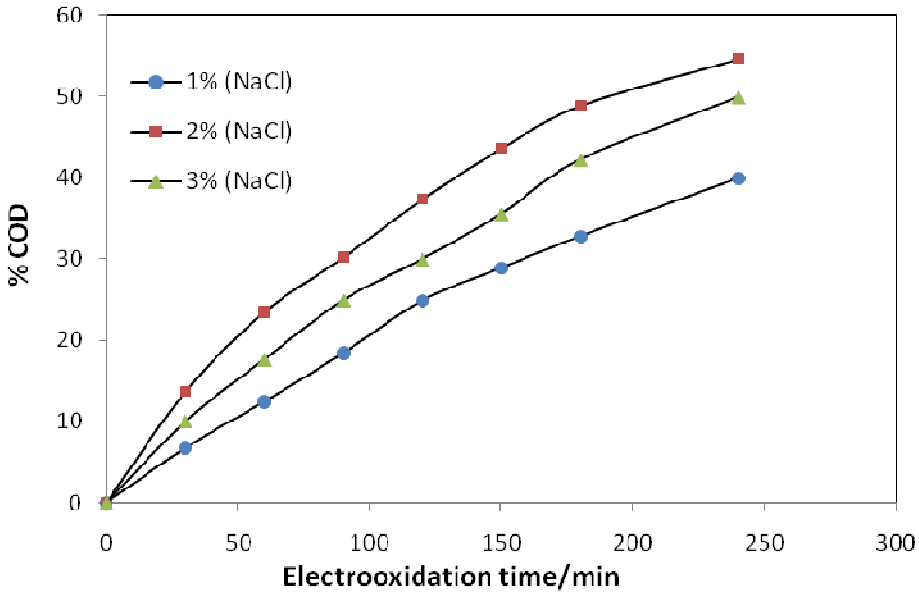


**Figure 3. Electrooxidation at $SnO_2$ anode: effect of NaCl concentration on the % COD (10 mg.L$^{-1}$ 2-NBA solution, 80 mA.cm $^{-2}$ and T=25°C)**

We observed that the application of electrolysis in this compound have the ability to reduce considerably the COD [17-19]. As appears that the NaCl were the most effective conductive electrolyte for the electrocatalytic degradation of the investigated 2-NBA and COD removal while 1% NaCl electrolytes show poor results. As shown in thie Figs 2 & 3, the % COD increases with the increase of electrooxidation time but decreases with the amount of NaCl in the solution. This indicates that at low concentration of NaCl, the 2-NBA removal ratios increased with time. The presence of a low concentration of chloride ions (2% NaCl) allows inhibiting the water discharge into oxygen, and promotes hydroxyl, chloride, and oxycloride radicals formation [20]. The increase of the NaCl concentration ( > 3%) could cause a "potentiostatic buffering" by the chlorine redox system and, consequently, a decrease of the anode potential. It is also possible that the presence of competitive reactions, in particular oxygen and chloride evolution due to recombination of radicals that becomes bigger with the increasing of NaCl concentration. The balance of all of these phenomena results in an optimum of NaCl concentration, which is 2% mass of NaCl for the degradation of 2-NBA. Further increase, above this limit, causes and inversion of the trend. Possibly, when the chloride concentration becomes sufficiently high, a decrease of the anode potential takes place, due to the potentiostatic buffering by the chlorine evolution reaction. The balance of all of these phenomena results in an optimum of NaCl concentration, which is 2% mass of NaCl for the degradation of 2-NBA. The achieved reduction was 92% and 74% for 2% NaCl and 3% NaCl respectively, while for 1% NaCl was 57%. The mechanism of electrochemical mineralization can be direct, in this case there is oxidation of 2-NBA on the electrode or indirect via some mediators like chlorinated species or other radicals [20-22]. The effect of supporting electrolyte on the rate constant increased with decreasing concentration of NaCl and the higher reaction rate constant (103 x $10^{-4}$ $min^{-1}$) was obtained at 2% of NaCl supporting electrolyte (Table 1). This indicates that the 2-NBA molecules were easily attacked by hydroxyl radicals at lower concentration of NaCl. These results are in agreement with previously reported results [21]. The effect of supporting electrolyte on rate constant increased with decreasing concentration of NaCl and the higher reaction rate constant (103 x $10^{-4}$ $min^{-1}$) was obtained at 2% of NaCl supporting electrolyte. This indicates that the 2-NBA molecules were easily attacked by hydroxyl radicals at lower concentration of NaCl. These results are in agreement with previously reported results [21].

**Table1. Effect of NaCl concentration on the values of the rate constant and the % COD**

| Electrode | NaCl (%) | Rates constant, K ($min^{-1}$) | COD removal (%) |
|---|---|---|---|
| BDD | 1 | $42\times10^{-4}$ | 47 |
| | 2 | $103\times10^{-4}$ | 86 |
| | 3 | $72\times10^{-4}$ | 74 |
| $SnO_2$ | 1 | $21\times10^{-4}$ | 40 |
| | 2 | $33\times10^{-4}$ | 55 |
| | 3 | $29\times10^{-4}$ | 50 |

**Effect of the applied current density**

The effect of current density on the electrochemical process was reported in several studies [20-22]. It is an important factor affecting the electrolysis kinetics. Two reaction zones of an anode can be distinguished: electrochemical reaction zone (i.e., anodic surface and diffusion layer) where direct oxidation by electron transfer and or OH occurs, and chemical reaction zone (i.e., bulk liquid) where compounds are oxidized by electro generated oxidant species. Degradation as says of 10 mg/L of 2-NBA solutions was performed using the BDD and $SnO_2$ electrodes at different current densities (Fig. 4 & 5).

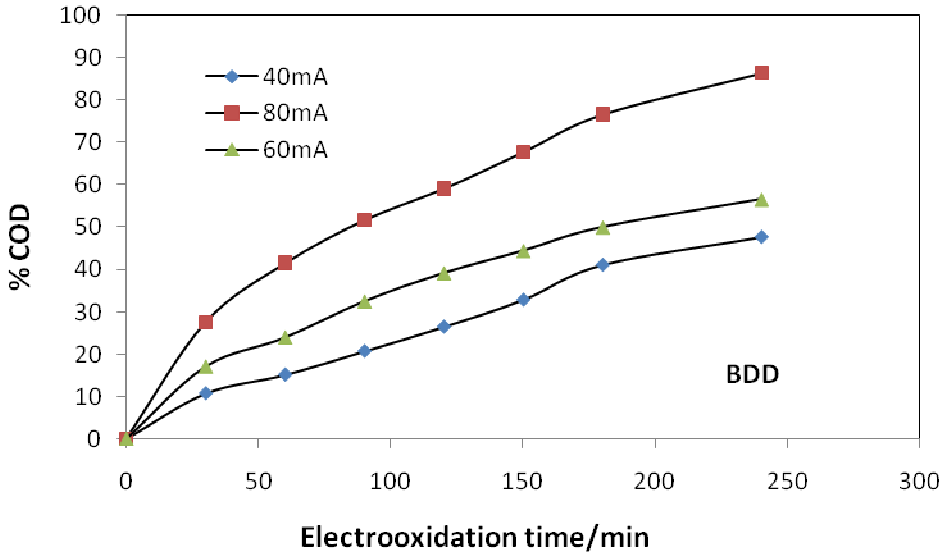


**Figure 4. Electrooxidation at BDD anode: effect of applied current on the %COD (10 mg.L$^{-1}$ 2-NBA solution, pH=6.2, and T = 25°C)**

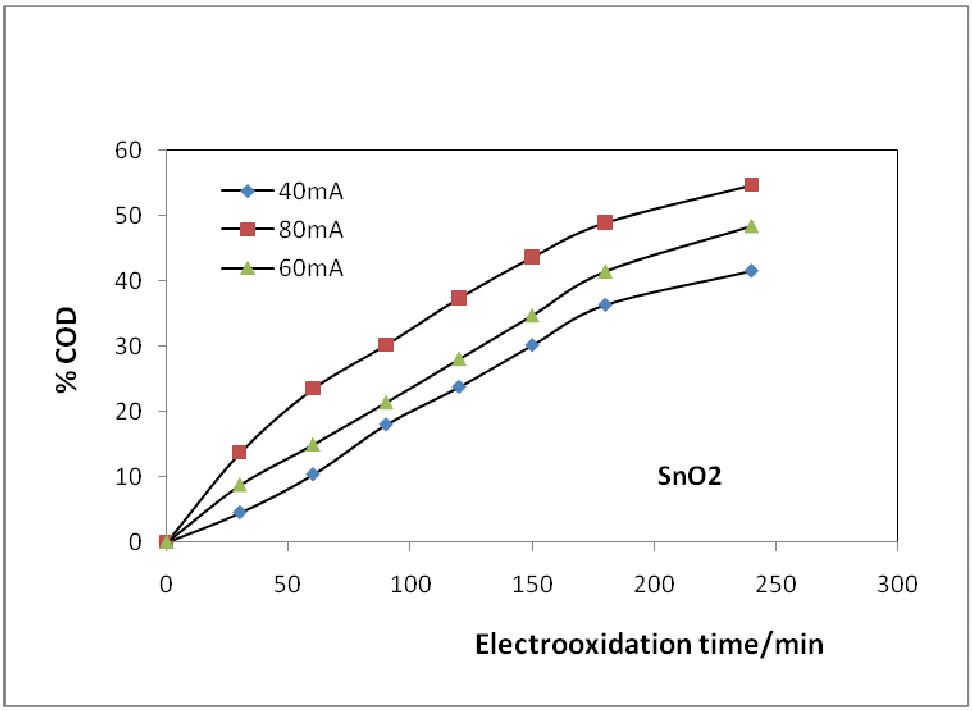


**Figure 5. Electrooxidation at $SnO_2$ anode: effect of applied current on the %COD (10 mg. L$^{-1}$ 2-NBA solution and T = 25°C).**

Overall, COD removal efficiency increased with increasing applied current density. As illustration, when the current is increased from 40 mA $cm^{-2}$ to 80 mA $cm^{-2}$, % COD removal increased from 47% to 86% for BDD and from 41% to 58% for $SnO_2$.

Table 2 shows the effect of applied current concentration on the values of the rate constant.

**Table 2. Effect of applied current concentration on the values of the rate constant and the % COD**

| Electrode | Current density ($mA.cm^{-2}$) | Rates constant, K($min^{-1}$) | COD removal (%) |
|---|---|---|---|
| BDD | 40 | $27\times10^{-4}$ | 47 |
| | 60 | $34\times10^{-4}$ | 56 |
| | 80 | $83\times10^{-4}$ | 86 |
| $SnO_2$ | 40 | $22\times10^{-4}$ | 41 |
| | 60 | $27\times10^{-4}$ | 55 |
| | 80 | $33\times10^{-4}$ | 58 |

The pseudo first-order constant of 2-NBA (k) varies from 83 x 10-4 min-1 for 80 mA/$cm^2$ of BDD, 33 × 10-4 min-1 for 80 mA/$cm^2$ of $SnO_2$. This is exemplified in Table 2. From these results it was calculated that the best applied current is 80 mA $cm^{-2}$.

## CONCLUSION

The electrochemical degradation of high concentration 2-NBA in sodium chloride-mediated wastewater at a BDD electrode was investigated in comparison with $SnO_2$ anode. This work is a first attempt to investigate the degradation of 2-NBA in the electrochemical treatment with direct electrooxidation. In 2% of NaCl, the electrochemical degradation efficiency of 2-NBA on BDD electrode was much greater than that on $SnO_2$ with a COD removal of 86% on BDD anode and 58% on $SnO_2$ anode. When comparing the performances of both anode materials, at 80 mA. $cm^{-2}$, the degradation efficiency is much higher for the BDD anode than that of $SnO_2$ anode. This means that the rate of mineralization is higher for the BDD anode. These results lead to the conclusion that the BDD electrode is the most efficient compared to $SnO_2$.

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