Anodic oxidation of slaughterhouse wastewater on boron-doped diamond: process variables effect
Arwa Abdelhay, Inshad Jum’h, Enas Abdulhay, Akeel Al-Kazwini and Mashael Alzubi

ABSTRACT
A non-sacrificial boron-doped diamond electrode was prepared in the laboratory and used as a novel anode for electrochemical oxidation of poultry slaughterhouse wastewater. This wastewater poses environmental threats as it is characterized by a high content of recalcitrant organics. The influence of several process variables, applied current density, initial pH, supporting electrolyte nature, and concentration of electrocoagulant, on chemical oxygen demand (COD) removal, color removal, and turbidity removal was investigated. Results showed that raising the applied current density to 3.83 mA/cm² has a positive effect on COD removal, color removal, and turbidity removal. These parameters increased to 100%, 90%, and 80% respectively. A low pH of 5 favored oxidants generation and consequently increased the COD removal percentage to reach 100%. Complete removal of COD had occurred in the presence of NaCl (1%) as supporting electrolyte. Na2SO4 demonstrated lower efficiency than NaCl in terms of COD removal. The COD decay kinetics follows the pseudo-first-order reaction. The simultaneous use of Na2SO4 and FeCl₃ decreased the turbidity in wastewater by 98% due to electrocoagulation.

Key words | anodic oxidation, boron-doped diamond, electrochemical reactor, electrocoagulation, poultry wastewater

INTRODUCTION
Slaughtering processes produce substantial volumes of highly polluted wastewater issued principally from the cleaning line (Awang et al. 2011; Eryuruk et al. 2011). Slaughterhouse wastewater is characterized by high organic content since it contains large amounts of fat, blood, and proteins (Awang et al. 2011). Therefore, it has been classified by the US Environmental Protection Agency as one of the most harmful effluents to the environment (Seif & Moursy 2001). Poultry slaughterhouse is one of the major slaughterhouse industries that has high usage of water, most of it for non-consumptive purposes. Similar to other slaughterhouse wastewaters, poultry processing wastewater exhibits high biochemical oxygen demand and chemical oxygen demand (COD), and it contains high suspended solids and floating material such as scum and grease (Rajakumar et al. 2011). Thus, this wastewater requires proper treatment prior to its disposal into the drainage system in order to protect public health and the environment (Bazrafshan et al. 2012). Conventional physico-chemical and biological treatment methods do not offer an optimal option to this high organic loading due to many limitations. Aerobic treatment processes are limited by the high energy consumption required for aeration (Kobya et al. 2006), whereas anaerobic treatment of poultry slaughterhouse wastewater is adversely affected by the accumulation of suspended solids and floating fats in the reactor, which causes a reduction in the methanogenic activity and biomass wash-out (Kobya et al. 2006). In addition, it is reported that anaerobic treatment is sensitive to high organic loading rates, which is a serious disadvantage (Cuetos et al. 2008). Regarding physico-chemical processes such as chemical coagulation, a moderate COD removal efficiency of 45–75% has been reported (Al-Mutairi et al. 2004; Amuda & Alade 2006). Additionally, they produce large volumes of putrefactive and bulky sludge that requires special handling.
and further treatment (Asselin et al. 2008). Nowadays, much attention has been paid to electrochemical technologies due to their competitive efficiency, cost (Palahouane et al. 2015), and treatment time compared to other traditionally used methods (Chen 2004). Electrochemical oxidation provides an efficient technique to destroy even organic compounds that are not easily biodegradable. Anodic oxidation of organic pollutants is guaranteed by different types of electrodes on which pollutants are directly destroyed by the free hydroxyl radicals produced on their surface. This direct anodic oxidation might lead to complete mineralization of the organic contaminants (Fryda et al. 2003; Alfaro et al. 2006). Many researchers had investigated electrochemical oxidation for different types of wastewater effluents using various electrodes (Cheballah et al. 2015). Aluminum and iron electrodes were successfully used to treat textile wastewater (Kobya et al. 2005), yeast industrial wastewater (Khristoskova 1984), poultry slaughterhouse wastewater (Davarnejad & Nasiri 2017) and egg-processing wastewater (Xu et al. 2002). Landfill leachate was also treated using a batch electrochemical reactor with two different electrode pairs, Fe/Cu or Al/Cu. A COD removal range from 30% to 50% was obtained (Tsai et al. 1997). Anodic oxidation has also been proposed to treat poultry slaughterhouse (Kobya et al. 2006) and cattle slaughterhouse (Eryuruk et al. 2011) using aluminum and iron electrodes. Despite the large number of papers published on the treatment of industrial wastewater by anodic oxidation (Chen et al. 2003), to our knowledge no research has been conducted on the treatment of slaughterhouse wastewater by anodic oxidation using non-sacrificial electrodes such as boron-doped diamond (BDD). BDD electrodes possess novel and intrinsically outstanding properties, comparing to conventional electrodes. The BDD electrodes have a large potential window in aqueous solution with low background currents. In addition, the BDD electrodes possess distinct physical properties including high hardness, low environmental impact, high hole mobility, high thermal conductivity and excellent resistance to radiation damage (Alfaro et al. 2006).

This study focuses on the performance of electrochemical treatment of poultry slaughterhouse wastewater using a non-conventional BDD electrode. The surface of BDD electrodes possesses over-potential to oxygen emission (Bouhssine et al. 2013) and is stable with little evidence of degradation of electrochemical activity with time (Kraft 2007). The study explores the effect of various process parameters: the current density, the dosage of Na₂SO₄ and NaCl as conductive electrolytes, the initial pH, and the addition of FeCl₃ as coagulant.

### MATERIALS AND METHODS

#### Poultry slaughterhouse wastewater samples

Poultry slaughterhouse wastewater used in this work was generated from a local plant (Al Tahooneh Chicken Company) located at Alzarqa, Jordan. The wastewaters emerging from various operations such as chicken cutting, scalding, chilling, packing, and plant cleanup are collected after being filtered using a screen filter to remove hair and solids. After collection, these effluents were pretreated in the laboratory by centrifugation at 6,000 rpm and then by sieving using 250 µm and 180 µm sieves successively. All sieved samples were maintained in a refrigerator at 4 °C.

The characteristics of the poultry slaughterhouse wastewater used in this study after laboratory pretreatment are summarized in Table 1.

#### Electrode preparation

The electrodes were prepared by hot filament chemical vapor deposition on niobium substrates which had been pretreated by sand blasting to roughen the surface in order to enhance the adhesion strength between the diamond and the substrate as well as to increase the electrochemical performance due to the increase of surface area. The niobium substrates were cleaned twice in ethanol and seeded in diamond powder by using an ultrasonic device. The coating process took place in a chemical vapor deposition hot filament coating machine by two parallel filament rows and the film thickness was measured to be 8 µm. In order to enhance the doped diamond conductivity a mixture of CH₄ (1%) and small amount of B(OCH₃)₃ was used in the coating process. All the chemical reactions were carried out at galvanostatic conditions and the characteristic parameters of the diamond films were performed using atomic force microscopy (AFM) (Figure 1(a)).

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.4</td>
</tr>
<tr>
<td>Color</td>
<td>reddish</td>
</tr>
<tr>
<td>Total suspended solids (mg/L)</td>
<td>600</td>
</tr>
<tr>
<td>Total COD (mg/L)</td>
<td>1,568</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>320</td>
</tr>
<tr>
<td>Conductivity (mS)</td>
<td>2.8</td>
</tr>
</tbody>
</table>
The quality of BDD layers deposited on niobium substrate was examined using Raman analyses. The Raman spectra of the diamond films (Figure 1(b)) exhibit a sharp peak at 1,340 cm$^{-1}$ that is usually associated with diamond sp$^3$ bonding. In the Raman spectra no boron is visible due to the low boron content with high etching resistance of the diamond layer.

**Experimental setup and procedure**

The experimental runs were performed in a batch laboratory-scale electrochemical reactor made of Plexiglas with 5 L capacity as shown in Figure 2. The reactor was equipped with two plate electrodes – one anode and one cathode – made of BDD. The total effective electrode area was 392 cm$^2$ (196 cm$^2$ each) and the spacing between electrodes was 1 mm.

The electrodes were properly rinsed prior to each experiment using an ultrasonication bath and tap water to make their surface clean and free of impurities. All batch assays were carried out at 25°C and with 1 L of poultry wastewater. The temperature of the electrolysis reactor was kept constant by using an agitated water bath. All experiments were performed at unbuffered pH.

A standard DC power supply (Gwintek GPC 30300) was used as the source of electric current for the experiments with a maximum output of 3 A and 30 V. The voltage fluctuations during the reaction were automatically monitored using a digital multimeter.

Samples were drawn regularly every 20 min in sealed and clean 20 mL glass vials and analyzed immediately afterwards. In the current study, the effect of several operating parameters on COD removal, color removal, and turbidity removal along the electrolysis time was investigated. The parameters are current density (1.28, 2.55 and 3.83 mA/cm$^2$), initial pH (6.4 and 5), Na$_2$SO$_4$ (1% and 2% w/v) (laboratory chemicals), NaCl (0.5% and 1% w/v), and FeCl$_3$ (1% and 2% w/v) (laboratory chemicals).

The percentage of COD removal was calculated as follows:

\[
\text{COD removal (\%)} = \frac{\text{COD}(\text{initial}) - \text{COD}(t)}{\text{COD}(\text{initial})} \times 100 \quad (1)
\]

where COD(initial) is the initial COD of the raw sample, and COD(t) is the COD of the treated sample at regular time intervals, $t$. 
The color removal (%) was calculated as follows:

\[
\text{Color removal} \, (\%) = \frac{\text{ABS}(\text{initial}) - \text{ABS}(t)}{\text{ABS}(\text{initial})} \times 100
\]  

(2)

where \(\text{ABS}(\text{initial})\) is the initial absorbance of the raw sample, and \(\text{ABS}(t)\): is the absorbance of the treated sample at regular time intervals, \(t\).

Current efficiency (CE) for electro-oxidation has been estimated by COD values, using the following relationship:

\[
\text{CE} \, (\%) = \frac{F \times V}{8.321 \times \Delta t} \times \frac{\text{COD}(\text{initial}) - \text{COD}(t)}{\text{COD}(\text{initial})} \times 100
\]  

(3)

where \(F\) is the Faraday constant (96,485 C/mol), \(I\) is the current (A), \(V\) is the volume (L), and \(\Delta t\) is the time (s).

Specific energy consumption \(EC\) (kwh/kg COD removed)

\[
EC = \frac{A \times V \times t}{V} \times \Delta \text{COD}
\]  

(4)

where \(t\) is the time of electrolysis (h); \(V\) and \(A\) are the average cell voltage and the electrolysis current; \(v\) is the sample volume (l), and \(\Delta \text{COD}\) is the difference in COD (mg/L).

**Analytical procedures**

COD and total suspended solids were analyzed as per procedures detailed in *Standard Methods* (APHA 1999). COD was measured by a Hach digester (DRB 200-Germany) and a direct reading Hach spectrophotometer (DR/2010-Germany). The pH and conductivity of the samples were measured using a digital calibrated Jenway 3540 pH/conductivity meter. The pH was adjusted when needed using NaOH or H\(_2\)SO\(_4\). The turbidity of the samples was measured with a Wagtech turbidity meter.

Percent of color removal in terms of absorbance was measured with a Wagtech 7100 photometer at 450 nm.

**RESULTS AND DISCUSSION**

**Effect of current density on COD removal**

Applied current is an important factor affecting the electrolysis kinetics and process economics. The effect of three current densities (1.28, 2.55, and 3.83 mA/cm\(^2\)) on COD removal efficiency is represented in Figure 3. It is obvious from Figure 3 that the COD removal efficiency increases with increasing electrolysis time. The trend of COD removal remains the same for the three current densities adopted in this investigation. An increase in the applied current density from 1.28 mA/cm\(^2\) to 2.55 mA/cm\(^2\) enhances COD removal (Errami et al. 2013) as can be seen from Figure 3. This could be justified by the fact that the increase in current density accelerates generation of hydroxyl radicals, which can maximize the mineralization of organic pollutants (Ajeel et al. 2015). However, a further increase from 2.55 mA/cm\(^2\) to 3.83 mA/cm\(^2\) did not lead to a significant increase in COD removal. For all current densities, a COD removal percentage of 100% was obtained after an electrolysis time of 200 min. Interestingly, this finding is much better and more economical than optimal results reported in literature. Kobya et al. (2006) obtained a maximum COD removal percentage of 92% and 85% with aluminum and iron electrodes respectively using a current density of 15 mA/cm\(^2\), which is much higher than the current densities used in this paper. In addition, the best result shown by Awang et al. (2011) was 85% of COD removal using aluminum electrode and 30 mA/cm\(^2\) as current density. Orssatto et al. (2016) could not achieve more than 81% of COD removal from slaughterhouse wastewater using aluminum electrode and 21.6 mA/cm\(^2\).

The results of anodic oxidation of poultry slaughterhouse wastewater were subjected to kinetic equation analysis of different reaction orders. Suitable fittings were found for the pseudo-first-order reaction and the straight lines obtained for the three current densities are presented in the inset of Figure 3. The pseudo-first-order rate constants calculated for 1.28, 2.55, and 3.83 mA/cm\(^2\) were 0.0162,
0.0196, and 0.0202, respectively, which confirms that COD removal occurs more extensively as the current density increases from 1.28 mA/cm² to 2.55 mA/cm². This is the expected behavior of a process with a significant contribution of direct electro-oxidation: the higher the current density, the higher the production of electoreagents and, hence, the higher the kinetic constant (Medeiros de Araújo et al. 2015).

It is worth noting that during electrolytic oxidation at all current densities a layer of foam appeared at the water surface. This can be explained by the production of H₂ on the cathode and CO₂ and O₂ on the anode, which in turn results in electrofloataion.

The increase in current density accelerates generation of hydroxyl radicals, which can maximize the mineralization of organic pollutants. For high current densities, the COD decreased exponentially and the CE (%) began to fall due to the mass-transport limitation and the side reactions of oxygen evolution on the anode surface as already reported by Ajeel et al. (2015). Results in Figure 4 show the trend of the current efficiency at different current densities. As can be seen, the current efficiency at 1.28 mA/cm² is 86% for the first hour of electrolysis but decreases to 53% and 36% when the applied current density is increased to 2.55 and 3.83 mA/cm², respectively. This agrees with the previous investigation of Ajeel et al. (2015).

Figure 5 presents the effect of varying current density on specific energy consumption, which was calculated according to Equation (4), during the electrolysis process. The results suggest that the specific energy consumption has increased with the treatment time as well as with current density.

The changes in specific energy consumption indicated that conducting electrochemical oxidation of poultry slaughterhouse wastewater with a current density of 1.28 mA/cm² has the lowest energy requirements. In other words, this current density showed a lower energy consumption than the other two current densities for the same percentage of COD removal. Consequently, a reduction in the treatment cost was expected.

Taking into consideration the electrical energy cost of about US$0.15 per kWh, the monetary value required to degrade a unit volume (1 L) of effluent is given by the following equation (Cabral da Silva et al. 2015):

\[
\text{Cost (US$/L)} = \frac{\text{EC kWh}}{\text{kg COD removed}} \times \frac{\Delta \text{COD removed}}{15}
\]

As is shown in Table 2 and Figure 3, a complete COD removal can be achieved with a minimum cost when using a current density of 1.28 mA/cm².

Effect of current density on color removal

The color removal is of great interest especially in the case of slaughterhouse wastewater due to the presence of blood. Figure 6 illustrates the color removal percentage using three different current densities. The results suggested that the color removal percentage increases with increasing current density (Murthy et al. 2011). The maximum color removal percent attainable is 91% with current density of 3.83 mA/cm².

Effect of current density on turbidity

Turbidity removal percentage was plotted versus electrolysis time at different current densities (Figure 7). The turbidity removal shows the same trend as the color
removal since it increases notably with increasing current density. The best turbidity removal percentage (80%) was obtained at 3.83 mA/cm². This result agrees with previous investigations in which an increase in the current density produces higher removal efficiencies (Rubí-Juárez et al. 2018). This may also have been due to the oxidative polymerization of organic pollutants originally present in slaughterhouse wastewater.

**Effect of initial pH on COD removal**

Solution initial pH is an important factor for wastewater treatment. For anodic oxidation, there are many reports on the impact of this process parameter. However, the results are diverse and even contradictory due to different organic structures and electrode materials.

In this study the effect of initial pH on the performance of the electrochemical oxidation of poultry slaughterhouse wastewater was investigated at constant current density 3.83 mA/cm². Figure 8 illustrates that there is an increase in the COD removal percentage as the initial pH value decreases. When the initial pH dropped from 6.4 to 5, the COD removal increased from 92% to 100% (Rabaaoui et al. 2016). This behavior could be attributed to several reasons. First, the electrode current efficiency in acid medium is higher than that in basic medium (Belhadj Tahar et al. 2013), and the charge transfer process is faster at low pH than at high pH (Ahmed et al. 2015). The oxidative potential of hydroxyl radicals also increases as pH decreases (Polcaro et al. 2005), thereby justifying the high reaction rate observed when lowering the pH.

**Effect of initial pH on turbidity**

The curves of percent turbidity removal as a function of electrolysis time at two different pH values are shown in Figure 9. At pH 6.4 and 5, the maximum turbidity removal percentages were 72% and 98% respectively. In other words, the turbidity removal is enhanced when the pH is decreased. As the pH drops from 6.4 to 5 an enhancement in COD removal takes place as mentioned earlier, which means implicitly that the complex organic compounds (especially oil and grease) in slaughterhouse wastewater are degraded to a large extent and become more soluble in water. Hence, the turbidity of slaughterhouse water decreases. This behavior could be a justification of the

![Figure 6](https://iwaponline.com/wst/article-pdf/76/12/3227/241707/wst076123227.pdf)

**Figure 6** | Effect of current density on color removal at 25 °C.

![Figure 7](https://iwaponline.com/wst/article-pdf/76/12/3227/241707/wst076123227.pdf)

**Figure 7** | Effect of current density on turbidity removal at 25 °C.

![Figure 8](https://iwaponline.com/wst/article-pdf/76/12/3227/241707/wst076123227.pdf)

**Figure 8** | Effect of initial pH on COD removal at 3.83 mA/cm² at 25 °C.

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**Table 2** | Cost of electrochemical treatment of poultry slaughterhouse wastewater using different current densities

<table>
<thead>
<tr>
<th>Current density (mA/cm²)</th>
<th>Cost (US$/L treated)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.28</td>
<td>0.008</td>
</tr>
<tr>
<td>2.55</td>
<td>0.02</td>
</tr>
<tr>
<td>3.83</td>
<td>0.06</td>
</tr>
</tbody>
</table>

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relationship found between the turbidity removal and the initial pH of poultry wastewater.

**Effect of the supporting electrolyte**

**Effect of Na$_2$SO$_4$ and NaCl**

Supporting electrolytes are used during electro-oxidation of wastewater or water to increase electrolyte conductivity and decrease energy consumption (Ajeel et al. 2015). Using NaCl as a supporting electrolyte generates chlorine free radicals or ClO$^-$ ions on the anode surface; these ions are considered strong oxidants that can destroy organic pollutants when used at appropriate concentrations (Martinez-Huitl & Ferro 2006). In addition, Na$_2$SO$_4$ was reported in literature as a supporting electrolyte as it can produce peroxodisulfate, which is considered a powerful oxidant that may enhance the anodic oxidation process (Canizares et al. 2004). In this part, the performance of anodic oxidation of slaughterhouse wastewater on BDD was investigated using NaCl and Na$_2$SO$_4$ as supporting electrolytes added with different concentrations at an applied current density of 3.83 mA/cm$^2$. Results in Figure 10 show that the anodic oxidation process is favored by NaCl rather than Na$_2$SO$_4$ (Brillas & Martínez-Huitl 2015). A total COD removal was achieved after 100 minutes using NaCl as supporting electrolyte with a concentration of 1%. The Na$_2$SO$_4$ had a negative impact on the COD removal as also shown in Figure 10. As the concentration of Na$_2$SO$_4$ increased, the COD removal decreased. This result is in accordance with the observations reported by Eryuruk et al. (2011). It was very likely that the anodic oxidation using Na$_2$SO$_4$ was limited by the formation of oxidizing agents, like S$_2$O$_8^{2-}$. Saracco et al. (2000) reported the complex nature of the reaction schemes which likely govern the degradation process using Na$_2$SO$_4$ as electrolyte solution. From these reactions, it can be hypothesized that S$_2$O$_8^{2-}$ was not formed on the BDD surface under the operating conditions of this study particularly the low current density. Therefore, there was no significant mediated electro-oxidation of poultry slaughterhouse.

**Effect of Na$_2$SO$_4$ and FeCl$_3$ as coagulant**

Experiments were done with Na$_2$SO$_4$ as supporting electrolyte along with FeCl$_3$ as electrocoagulant. The effect of FeCl$_3$ was not tested with NaCl as best electrolyte (as mentioned in the previous section) since they have chloride ions in common. Figure 11 depicts the effect of 1% and 2% FeCl$_3$ added with 1% Na$_2$SO$_4$ on the electrolysis of poultry slaughterhouse wastewater. It can be seen that the COD removal increased with electrolysis time for both FeCl$_3$ concentrations investigated. However, COD removal was higher with 2% FeCl$_3$ than 1% FeCl$_3$. The COD removal for 1% FeCl$_3$ and 2% FeCl$_3$ was 75% and 62% respectively. The improvement in COD removal by adding FeCl$_3$ could be due to several reasons. First, Fe$^{3+}$ and Fe$^{2+}$ ions were formed upon direct application of current and combined with hydroxyl ions in the water to form metal hydroxides (pH = 6.4) which resulted in electrocoagulation. In addition, Na$_2$SO$_4$ may generate H$_2$O$_2$ which in combination with Fe$^{3+}$/Fe$^{2+}$ resulted in the electro-Fenton reaction. Finally, the solution contained Cl$^-$ ions, which formed hypochlorite ions as oxidants (Giannis et al. 2007).

In order to prove the formation of iron hydroxides and the occurrence of electrocoagulation, turbidity was also
monitored with no FeCl₃ and when FeCl₃ was added at 1% and 2% (Figure 12). It is obvious that a maximum turbidity removal of 98% was obtained when FeCl₃ was added to water regardless of the concentration. This result confirms the electrocoagulation by iron hydroxide.

CONCLUSION

BDD anodic oxidation is found to be an effective method for the treatment of poultry slaughterhouse wastewater. The BDD electrode behaves as a hydroxyl radical generator, which resulted from the decomposition of water on the electrode surface. The electrochemical process with BDD electrode is promoted at high current densities (3.83 mA/cm²) and low pH (5). The COD decay kinetics follows a pseudo-first-order reaction. The nature of the supporting electrolyte has a great impact on COD removal. Accordingly, the direct anodic oxidation plays an important role in the efficiency of the electrochemical process. Finally, adding FeCl₃ to wastewater induced electrocoagulation.

REFERENCES


