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Dairy wastewater remediation using electrochemical oxidation on boron doped diamond anode (BDD)

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ABSTRACT

Treated wastewater reuse has been considered recently as one of the successful management strategies to overcome water shortage in many countries suffering from water scarcity. The non-readily biodegradable and recalcitrant pollutants in wastewater cannot be destructed by conventional treatment methods. This paper deals with the electrochemical treatment of dairy wastewater using a promising non-conventional boron doped diamond anode. During the electrochemical process, different operating parameters were investigated, such as electrolysis time, current density, supporting electrolyte, chemical oxygen demand (COD), turbidity as well as absorbance/color. The experimental work revealed that electrochemical oxidation carried out with no added electrolyte has significantly reduced the COD, turbidity and color (absorbance) by 72%, 76% and 78%, respectively. Results also showed that raising the current density from 5.1 to 7.7 mA/cm^2 has boosted COD, and color removal to 82.5% and 83%, respectively. However, the current density did not show any significant effect on the turbidity. Interestingly, it was observed that adding Na_2SO_4 and $FeCl_3$ as supporting electrolytes brought the COD removal to 91% and 97% respectively. Likewise, turbidity and color removal have been enhanced by the addition of the same supporting electrolytes.

Keywords: Boron doped-diamond anode; Dairy wastewater; Electrochemical oxidation; Supporting electrolytes

1. Introduction

Dramatic population growth, overuse of water resources, and climate change are the reasons for water shortage and crisis in many countries. In response to these problems, wastewater professionals are working hardly to identify new reliable water sources. Reuse or reclamation of treated wastewater is among the most adopted strategies to overcome the problem. However, the strict directives on water quality make the treatment process requirements increasingly stringent. Researchers have proposed different treatment technologies of wastewater including conventional chemical and biological treatment [1]. However, these conventional methods showed limited efficiency in degrading persistent and emerging organic compounds [2]. Dairy-industry is considered one of the main agro-industries generating large volumes of wastewater characterized by high chemical oxygen demand (COD) because of its high organic content [3]. The dairy wastewater streams contain proteins, carbohydrates, lipids, and suspended solids [4]. Biological treatment (aerobic and anaerobic) is one of the conventional methods applied to treat dairy-industry wastewater. However, it does not offer an optimal treatment option as it is limited by long hydraulic detention time, weak efficiency toward non-readily

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degradable organics, and high-energy requirement [5–7]. Therefore, much attention has been recently oriented toward advanced oxidation processes and more particularly to electrochemical treatment [5–9]. Electrochemical methods for wastewater treatment have attracted increasing interest due to their competitive capacity to destruct persistent and recalcitrant organics in short treatment time [10]. The design of electrochemical units is continually evolving in order to enhance the treatment efficiency. In this perspective, the principal factor in the electrolysis cell design is the electrode material. The surface of the electrode serves as the support on which pollutants are directly destroyed by the free hydroxyl radicals ($OH^{\bullet}$) released on it. The ideal electrode material should be very stable in the electrolysis medium, and characterized by high reactivity towards organics by having a high overpotential value for oxygen evolution reaction [11]. Despite the large number of electrodes that have been reported and cited in literature [12], non-active electrodes showed novel and intrinsically outstanding properties [6]. Boron doped diamond (BDD) electrode is among the promising non-active electrodes due to its large potential window in aqueous solution with low background currents [13]. From one side, BDD electrode is hard, and shows very little degradation in its electrochemical activity with time [14]. From the other side, it is stable even if electrolysis is carried out with acidic electrolytes [15]. Panizza et al. [16] did not found any loss of diamond material of diamond anodes during electrolysis 1 M H_2SO_4 (1 A/cm^2, 40°C) even after prolonged time. Furthermore, Schäfer et al. [17] reported that diamond electrodes with thin film (diamond film thickness of 1 μm) on niobium substrates (at 20 mA/cm^2, 70°C) exposed to 1.3 M H_2SO_4 has an electrode life time of 5 years. However, increasing the current density under the same conditions to 200 mA/cm^2 would give an electrode life time of 6 months [17].

This work shed light on the performance of electrochemical treatment of dairy wastewater effluents using non-conventional BDD anode. The study explores the effect of two process parameters namely, the current density and the nature of the supporting electrolyte on optimizing the COD, turbidity, and color removal during electrolysis. Wastewater effluents produced form the treatment method adopted in this work can be reused for irrigation and industrial purposes.

2. Materials and methods

2.1. Dairy wastewater samples

Dairy wastewater was collected from a local dairy product plant (Al Murooj Factory) located in Amman-Jordan. After collection, the wastewater samples were pretreated in the laboratory by centrifugation at 6,000 rpm for 15 min. Then all samples were kept in an incubator at 4°C. The characteristics of dairy wastewater after the pretreatment are listed in Table 1.

Table 1
Characteristics of dairy wastewater

Characteristics	Values
pH	6.6
Color	White and turbid
Total suspended solids TSS (mg/L)	650
COD (mg/L)	4,950
Turbidity (NTU)	17.87
Conductivity (mS)	7.4

2.2. Experimental setup

All batch assays were carried out at 25°C in a Plexiglas laboratory-scale reactor with a volume capacity of 5 L (Fig. 1). The reactor was equipped with two plate BDD electrodes one serving as anode and the other one as cathode. Each plate has an effective area of 196 cm^2 (14 cm × 14 cm), a thickness of 2.8 mm and the spacing between the two plate electrodes was 1 mm.

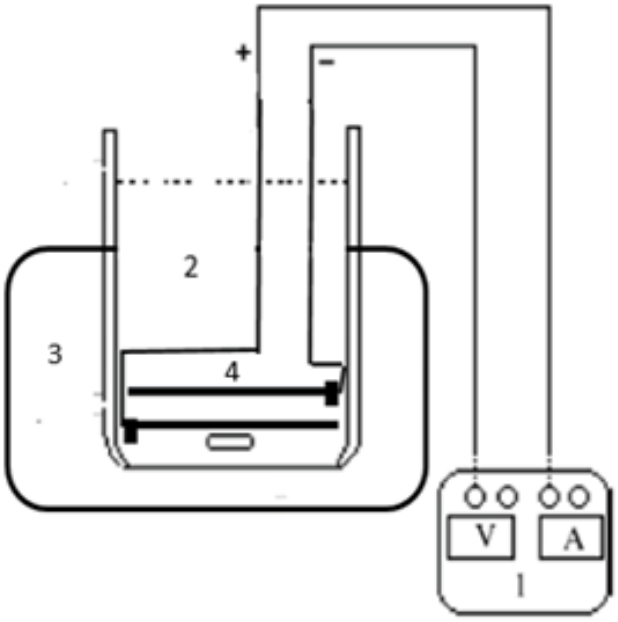

Fig. 1. Schematic diagram of experimental setup: (1) DC power supply, (2) electrochemical cell, (3) water bath and (4) BDD electrodes.

A DC power supply (Gwisntek GPC 30300) was directly connected to the electrodes. The DC provides a maximum output of 3 A and 30 V.

The electrodes were prepared in the laboratory using hot filament chemical vapor deposition coating machine (CC800/8 DIA) by two parallel filament rows, and the film thickness was measured (8 μm). The substrate used in preparing the electrodes is niobium on which the chemical deposition took place. The niobium grid was coated on both sides using two parallel filament rows for 50 h. A pretreatment of the substrate was indispensable to roughen the surface and improve the adhesion strength between the diamond and the niobium. The niobium substrates were cleaned twice in ethanol and seeded in diamond powder by using an ultrasonic device [6]. The characteristic parameters of the diamond films were performed using atomic force microscopy and the quality of BDD layers deposited on niobium substrate was examined using Raman analyses (Fig. 2).

In the present study, the effect of two operating parameters on COD, turbidity, absorbance removal during electrolysis was investigated. The parameters are current density (5.1 and 7.7 mA/cm^2), and supporting electrolyte (Na_2SO_4 and $FeCl_3$) from laboratory chemicals.

A follow up of COD variation during the 4 h of electrolysis was performed by withdrawing samples every 15 min from the reactor. The COD was measured using Hach digester (DRB 200-Germany) and Hach spectrophotometer (DR/2010-Germany). In addition, turbidity and absorbance of each withdrawn sample were measured over the electrolysis time using, Wagtech turbidity meter (UK), and Wagtech 7100 photometer (UK) respectively.

All COD, turbidity, and absorbance measurements were carried out according to the procedures cited in "Standard Methods" [18] for turbidity and absorbance were measured.

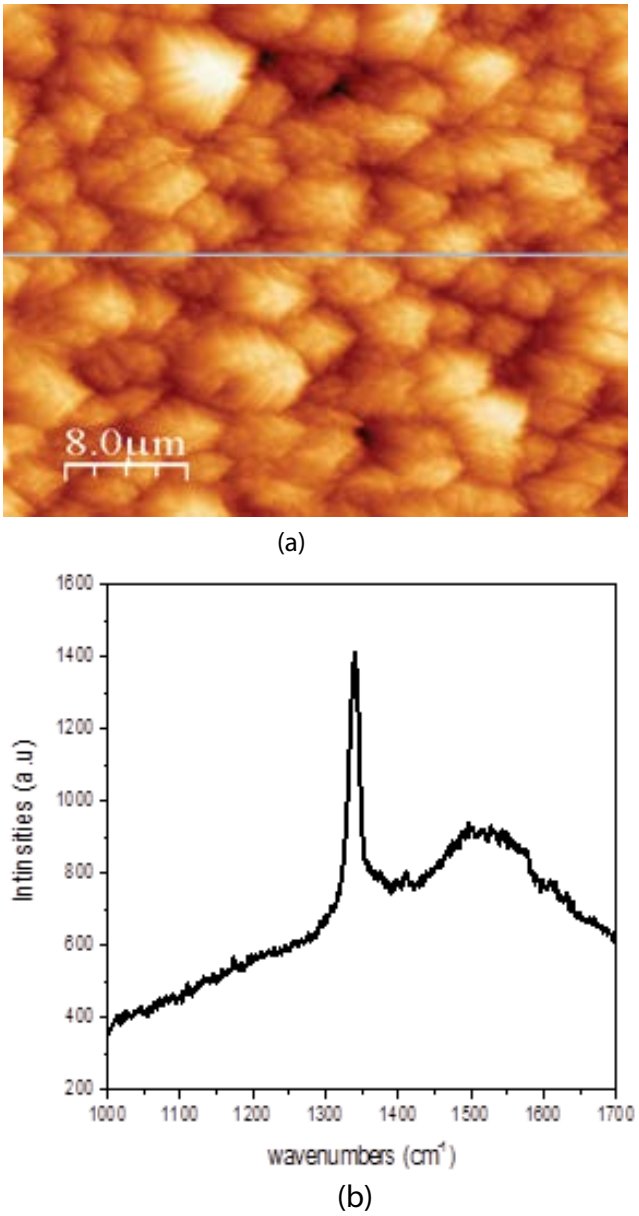

Fig. 2. (a) AFM topographies of the BDD layer on niobium substrate and (b) raman spectra of the BDD film.

3. Results and discussion

3.1. Effect of current density on COD, turbidity and color removal efficiency (no electrolyte added)

The effect of two current densities (5.1 and 7.7 mA/cm^2) on COD removal from dairy wastewater is represented in Fig. 3. The electrochemical treatment was run for 4 h. As it can be noticed, the COD removal increased from 72% to 83% as the current density increased from 5.1 to 7.7 mA/cm^2. This finding is in accordance with the results reported by [19,20]. The increase in current density accelerates generation of hydroxyl radicals on the surface of the electrode, which can maximize the mineralization of organic pollutants [20].

The curves of turbidity removal were plotted vs. the electrolysis time at two different current densities (Fig. 4). It was observed that there is a slight increase in turbidity removal percentage as the current density increases.

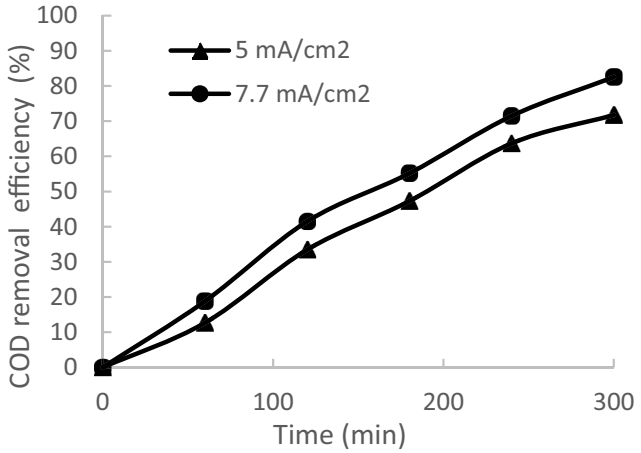

Fig. 3. Effect of current density on COD removal with no electrolyte added to wastewater.

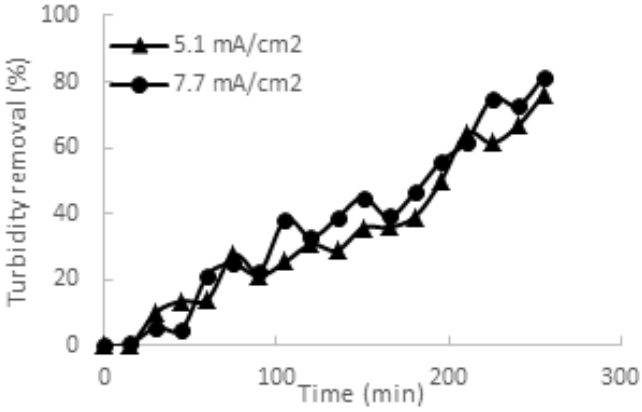

Fig. 4. Effect of current density on Turbidity removal with no electrolyte added to wastewater.

The turbidity removal percentage was 76% and 81% at current densities between 5.1 and 7.7 mA/cm^2 respectively. This result agrees with previous one reported by [21]. The slight enhancement of turbidity removal as the current density increases could be attributed to the hydrolysis of the organics originally present in dairy wastewater [22].

The efficiency of dairy wastewater treatment using electrochemical oxidation on BDD was also tested by following up the discoloration in the samples during electrolysis time. Fig. 5 illustrates the color removal percentage (absorbance reduction) at two current densities.

The results of Fig. 5 suggest that the color removal percentage increases notably throughout the electrolysis time. Consequently, it can be concluded that color-causing organics were degraded by hydroxyl free radicals during electrolysis. This conclusion is consistent with the COD abatement presented in Fig. 3. In addition, it can be seen that the color removal was enhanced to a small extent by increasing the current density. The color removal percentage increased from 78% to 84% when the current density was increased from 5.1 to 7.7 mA/cm^2 [23].

3.2. Effect of adding Na_2SO_4 or $FeCl_3$ as supporting electrolytes on COD, turbidity and color removal

3.2.1. Selection of electrolyte

Supporting electrolytes are frequently used in electrochemical oxidation in order to increase the conductivity of the treated sample, which can consequently stimulate the electro-oxidation process [20]. In this regard, two types of electrolytes were used to test their effectivity on improving the conductivity.

As it can be seen in Fig. 6, both electrolytes have noticeably increased the conductivity of the sample, which is a key factor in electrochemical oxidation. The conductivity of the wastewater sample with no electrolyte added was fluctuated around 8 mS. However, the conductivity reached values of 11.9 and 12.7 mS when Na_2SO_4 or $FeCl_3$ were added as supporting electrolytes, respectively. From another point, supporting electrolytes produce secondary oxidants most probably electro-generated on the anode surface that withstand hydroxyl free radicals in degrading the organic pollutants. Therefore, $FeCl_3$ was used as a representative electrolyte generating chloro-oxidants or ClO^- ions on the anode surface. On the other hand, Na_2SO_4 was selected as a representative of electrolytes that might produce sulfate oxidizing agents such as peroxydisulfate, which is considered as a powerful oxidant.

Based on the aforementioned results, electrolysis experiments were carried out using the two supporting electrolytes Na_2SO_4 and $FeCl_3$, which had been added to get a concentration of 1 g/L in the raw wastewater sample. As it is obvious from Fig. 7, the electrolysis results showed that the highest COD removal, at the optimal current density (7.7 mA/cm^2) selected in the previous section was obtained with $FeCl_3$.

It was reported in literature that Na_2SO_4 could produce peroxydisulfate during electrolysis, which is a powerful oxidizing agent that can stimulate the electrochemical oxidation [24]. As depicted in Fig. 7, Na_2SO_4 has enhanced by 10% the COD removal percentage as compared to the raw sample with no added electrolyte. The COD removal percentage has increased to 91% when Na_2SO_4 was added. However, COD removal was higher (97%) when $FeCl_3$

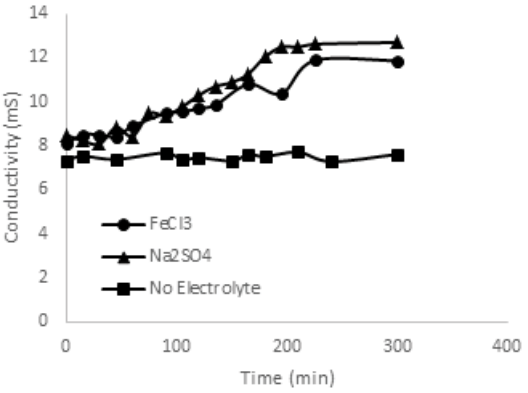

Fig. 6. Effect of supporting electrolyte on the conductivity of the treated sample at 7.7 mA/cm^2.

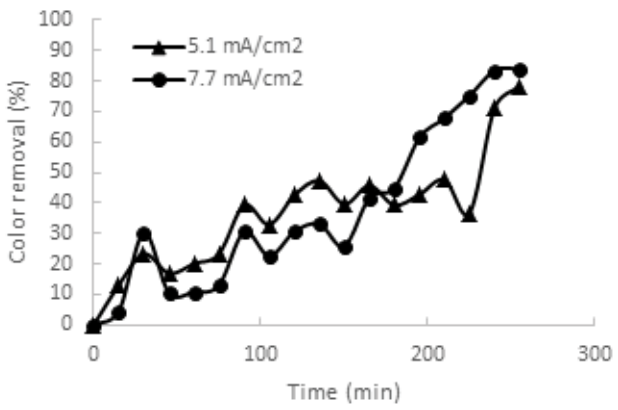

Fig. 5. Effect of the current density on color removal with no electrolyte added to wastewater.

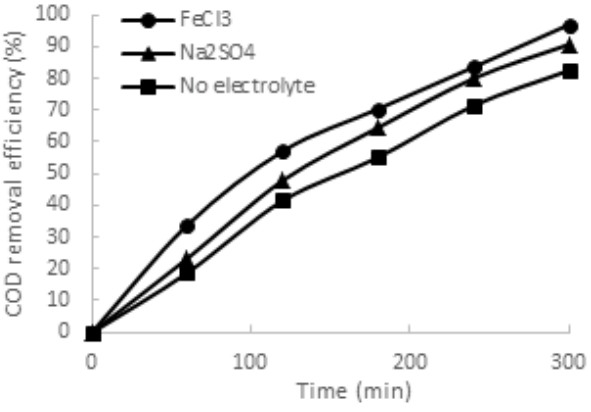

Fig. 7. Effect of supporting electrolyte on COD removal at 7.7 mA/cm^2.

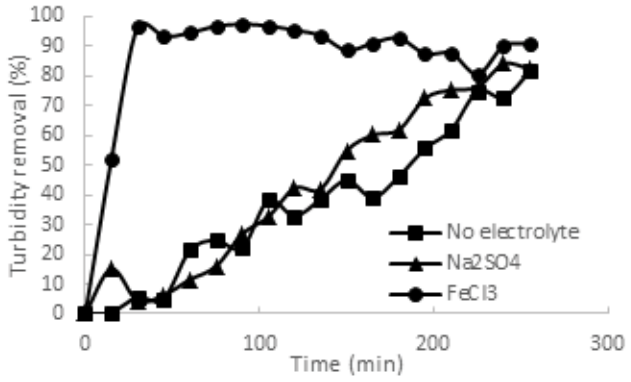

Fig. 8. Effect of supporting electrolyte on turbidity removal at 7.7 mA/cm^2.

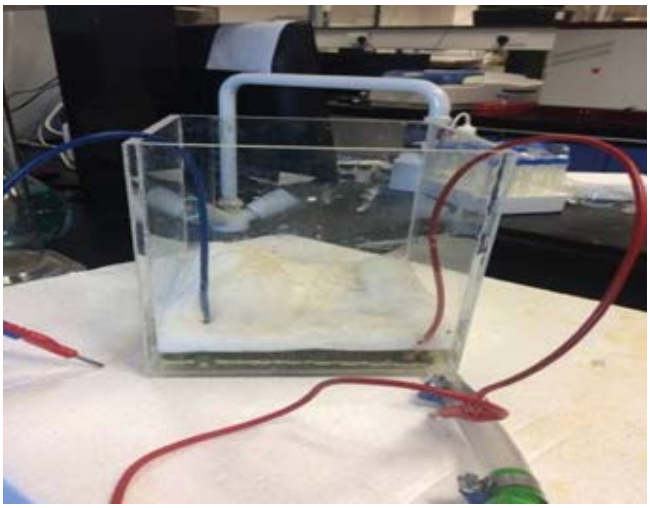

Fig. 9. Foam formation during electrolysis at a current density of 7.7 mA/cm^2.

was added to the sample. The chloride added can also be oxidized during electrolysis to form different chloro-oxidant species that can participate in the electro-oxidation of organics. As the pH of the dairy wastewater is almost neutral, the main chloro-oxidant formed is hypochlorite (OCl^-) [11]. In addition, coagulation-flotation could be also a reason behind the better performance of $FeCl_3$ in removing COD from wastewater. $FeCl_3$ coagulation–floatation results from the formation of metal hydroxides (pH = 6.4) which in turn are produced from the reaction of Fe^{3+} with hydroxyl ions upon application of current [25]. In order to confirm the previous results, turbidity reduction was tested during electrolysis in the presence of the three supporting electrolytes (Fig. 8). Turbidity results support the occurrence of coagulation–flotation during electrolysis.

Fig. 8 illustrates on one hand that that Na_2SO_4 did not contribute to the enhancement of turbidity removal of the raw wastewater sample. On the other hand, there was a dramatic increase in turbidity removal, which has reached 97% in the first 30 min of electrolysis when $FeCl_3$ was added.

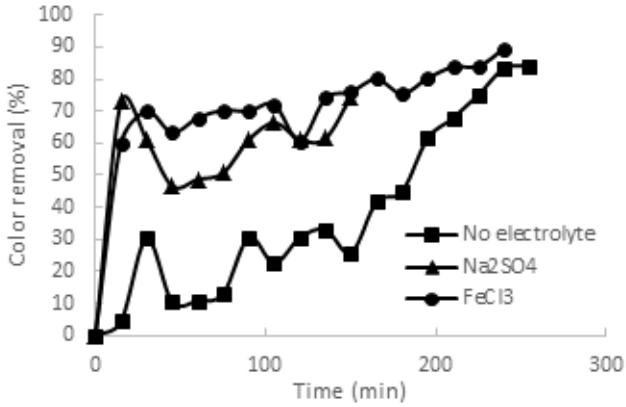

Fig. 10. Effect of supporting electrolyte on color removal at 7.7 mA/cm^2.

The hydrogen gas produced on the cathode during electro-flotation carry out dissolved organics and suspended solids to the surface of water [26]. Fig. 9 shows the foam formed by H_2 on the surface of water during electrolysis.

Fig. 10 explores the effect of adding supporting electrolytes on the color removal from dairy wastewater. The results suggest that the color removal in the samples with no added electrolyte, with Na_2SO_4, and with $FeCl_3$ was 84%, 90% and 90%, respectively. However, the kinetics of color removal in samples to which $FeCl_3$ was added was much faster than with Na_2SO_4 or with no added electrolyte.

4. Conclusion

The current study proved that electrochemical treatment on BDD anode was efficient in degrading the persistent organic content of dairy wastewater. The electrochemical process was stimulated when high current densities were applied. The maximum COD removal percentage in the raw sample was 82% at a current density of 7.7 mA/cm^2. The type of the supporting electrolyte added to the sample has an appearing effect on COD, turbidity and color removal. Adding Na_2SO_4 and $FeCl_3$ as supporting electrolytes has induced the anodic oxidation and increased the COD removal to 91% and 97% respectively. Finally, $FeCl_3$ was more efficient than Na_2SO_4 in reducing the turbidity and removing the color of wastewater in short electrolysis time.

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