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Electrochemical oxidation of mustard tuber wastewater on boron-doped diamond anode

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ABSTRACT

Boron-doped diamond (BDD) anode is a promising material for bio-refractory wastewater treatment in recent years. Due to the high conductivity of mustard tuber wastewater (MTWW), anodic oxidation of MTWW was evaluated using BDD as an anode, in order to diminish chemical oxygen demand and ammonium. The influence of several operating parameters including the applied current density, the dilution of the MTWW samples and the initial pH on the performance of electrochemical oxidation was investigated. At a current density of 50 mA cm^{-2}, a dilution ratio of 1:2, without pH adjustment and 240 min of processing, the removal efficiencies achieved were 80.4% for COD and 100% for ammonium, and the corresponding specific energy consumption was 45.8 kWh m^{-3}. The normalized concentration of COD and ammonium followed zero-order reaction kinetics with high correlation coefficients. The process was proved to be effective in degrading MTWW, despite this effluent's usual refractoriness to biological treatment.

Keywords: Mustard tuber wastewater; Electrochemical oxidation; Boron-doped diamond (BDD) anode; Hydroxyl radical

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1. Introduction

Groundwater contamination is a major challenge of the twenty-first century [1]. The pollution caused by industrial and agriculture wastewaters should be taken into consideration seriously. Fuling district, located in Chongqing, is famous for the production of pickled mustard tuber. Mustard tuber wastewater (MTWW) is a high-salinity effluent originated during pickled mustard tuber production. It often contains organic compounds, ammonium and inorganic salt, and it is estimated to be about 3.5 million m^3 discharged annually in this district [2]. As the self-purification capacity of the reservoir water body decreased, proper treatment and safe disposal of MTWW are necessary for the protection of the aqueous environment of the Three Gorges Reservoir.

In recent years, several treatment processes have been attempted to treat high-salinity industrial wastewaters such as anammox [3,4], sequencing batch reactor [5], aerobic granular SBR [6], oxygen-limited

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autotrophic nitrification–denitrification [7], constructed wetlands [8], and combined processes [9,10]. Due to the inhibition of biomass caused by high salt concentrations, conventional biological processes are ineffective for the high-salinity wastewater treatment [11]. Inoculation of halophilic bacteria is a favorable alternative for improving treatment efficiency of biological process [12,13]. Moreover, microbial fuel cells [14], bio-electrochemical process [15,16], and electrochemical oxidation [17–19] were also tested in the treatment of high-salinity wastewater.

Electrochemical oxidation has been proposed as an efficient and environment-friendly alternative for treating non-biodegradable organic contaminants [20–22]. In addition, it exhibited some excellent advantages such as robustness, versatility, and amenability to automation and for its little or no need for addition of chemicals [22,23]. Under appropriate conditions, electrochemical oxidation could significantly degrade organic compounds, ammonia nitrogen, and color. In traditional electrochemical oxidation process, organic compounds are directly oxidized by electron transfer from the anode materials surface or indirectly oxidized by hydroxyl radical and active chlorine, and ammonium is degraded by indirect oxidation process with active chlorines [24–26].

Anode materials play an important role in the electrochemical oxidation process, which affects the current efficiency strongly [20]. Boron-doped diamond (BDD) anode stands out for its wide potential window, high electrochemical stability, low background current and its high resistance to corrosion, erosion, and fouling [27]. Application of BDD anode in wastewaters treatment, including landfill leachate [23,27–29], olive oil wastewater [30], textile wastewater [31], dye wastewater [32], and coking wastewater [20], has also been studied. The process proves efficient in the treatment of saline industrial wastewaters [16,17].

The primary objective of this study is to evaluate the performance of electrochemical oxidation of MTWW on BDD anode. This process could be capable to work in emergency situations. Firstly, the effect of several operating parameters on the removal of chemical oxygen demand (COD) and ammonium was determined. Secondly, the evolution of organic compounds was confirmed using UV–vis spectra. In addition, the reaction kinetics of COD and ammonium was also established.

2. Experimental

2.1. Mustard tuber wastewater

The MTWW samples were collected from the equalization basin of a wastewater treatment plant in a pickled mustard tuber factory, located in Fuling district. In order to keep the wastewater characteristics unchanged, the collected MTWW sample was stored in a refrigerator at 4℃. The physicochemical characteristics of MTWW are summarized in Table 1.

Table 1
The main physicochemical characteristics of MTWW

Parameters	Average value
pH	6.50
Conductivity (mS cm^{-1})	26.4
COD (mg L^{-1})	3,250
TOC (mg L^{-1})	980
NH_4^+-N (mg L^{-1})	215
Cl^- (g L^{-1})	24.5

2.2. Apparatus

The experimental apparatus consisted of an electrochemical reactor, a magnetic stirring, and a DC power supplier. The electrochemical cell was a cylindrical vessel with 1 L working volume. The cell was with an inner diameter of 12 cm and a height of 10.2 cm. A tantalum sheet coated with BDD, supplied by Tianjin University of Technology, was used as the anode and stainless steel (AISI 201) as the cathode. Both of the electrodes were with a geometric area of 29.25 cm^2 each and inter-electrode gap of 1 cm. Batch electrochemical oxidation assays were conducted under galvanostatic conditions, provided by a M8872 DC power supplier (Maynuo Electronics, China). In order to keep the wastewater homogeneous, MTWW was stirred constantly by a magnetic stirring.

2.3. Analytical procedures

During the experiments, bulk samples were withdrawn from the reactor at regular intervals and conveniently analyzed. The COD was measured spectrophotometrically using a DR5000 spectrophotometer (Hach, USA) according to manufacturer's procedure. In order to avoid the interference of high concentration of chlorine, the samples were adequately diluted to obtain the concentration of chlorides <2 g L^{-1}. The ammonium (NH_4^+-N) was measured by Nessler's reagent spectrophotometry. The chlorides (Cl^-) were analyzed by silver nitrate titration. The conductivity was measured using a sensION5 conductivity meter (Hach, USA). The pH was determined using a HI9124 portable pH meter (HANNA, Italy). The UV–vis spectra of the solutions were measured on a DR5000 spectrophotometer at different UV/Visible wavelengths using a 1-cm pathlength quartz cell.

The general current efficiency (GCE, in %) for the anodic oxidation was calculated according to Eq. (1) [33]:

$$\mathrm{GCE} = \frac{\Delta \mathrm{COD}}{8It}\mathrm{FV} \tag{1}$$

where ΔCOD is the removed COD (kg m^{-3}), I is the current (A), F is the Faraday constant (96,487 C mol^{-1}), V is the volume of the treated wastewater (m^3), t is the electrolysis time (s), and 8 is the oxygen equivalent mass (g eq^{-1}).

Specific energy consumption (E_c, in kWh m^{-3}) was calculated as per Eq. (2) [34]:

$$E_c = \frac{UIt}{3,600\mathrm{V}} \tag{2}$$

where U is the average cell voltage (V), and other parameters are stated the same as above.

3. Results and discussion

3.1. Effect of dilution ratio

It was proved that dilution ratio was a significant operating parameter in electrochemical oxidation [17,28]. The dilution ratio was defined as the volume of MTWW vs. the total volume of water and MTWW. The influence of dilution ratio on electrochemical oxidation performance was investigated by performing the electro-oxidation experiments using MTWW without any dilution (1:1) and diluting it 1:2, 1:4, and 1:5. The variations of COD (a) and NH_4^+-N (b) as a function of electrolysis time for these electrochemical oxidation assays were drawn in Fig. 1. As demonstrated in Fig. 1(a), for dilution ratios of 1:1 and 1:2, a regular linear decay for COD removal that is typically controlled by applied current was found. However, a different behavior was observed for higher dilution ratios. The reasonable explanation is that the amount of organic matter to oxidize is lesser with high dilution ratio which leads to quick oxidation. The same phenomenon was obtained by Fernandes et al. [28] when BDD anode was applied to treat biologically pretreated landfill leachate. As shown in Fig. 1(b), higher dilution ratios promoted higher removal efficiency of ammonium, and the variation of ammonium followed a regular linear decay at any dilution ratio. This is due to the existed high concentration of chlorides and all the experimental assays were under current control instead of mass transfer control [24]. Higher dilution ratio may cause the decrease of absolute amount of contaminants to be removed and also increases the operating cost. Therefore, the dilution ratio of 1:2 would be favorable for the MTWW treatment, yielding removal efficiencies of COD and NH_4^+-N for 80 and 100%, respectively.

3.2. Effect of current density

The effect of current density on electrochemical oxidation efficiency was investigated at different values (30, 40, 50, and 60 mA cm^{-2}). The variations of COD (a) and NH_4^+-N (b) with electrolysis time were illustrated in Fig. 2. As shown in Fig. 2(a), COD removal followed a linear decay with electrolysis time at any current density considered. It was promoted by the increase in current density. For instance, the COD removal rate reached up to 74% after electrolysis of 240 min at a current density of 50 mA cm^{-2}. Fig. 2(b) shows that NH_4^+-N could be completely removed at any applied current density. During the electrolysis of MTWW, 19.6–45.9% of NH_4^+-N was converted to nitrate at the applied current densities and the concentration of nitrate increased with the increase in the applied current density. The time required for NH_4^+-N abatement was shortened at higher current density. This indicated that degradation of COD and NH_4^+-N on BDD performed well at high current densities, which was in agreement with other researchers' findings in electrochemical oxidation of wastewaters using BDD anode [17,19]. However, the increase in current density also brought about the higher energy consumption but little improvement of removal efficiency. Considering the specific energy consumption at different current densities, current density of 50 mA cm^{-2} would be appropriate for the electrochemical oxidation of MTWW.

3.3. Effect of pH

Due to the difference of anode materials and the nature of wastewaters, it did not come to an agreement about the effect of pH value [18–20,23]. In order to explore the effect of pH on the electrochemical oxidation of MTWW, electrochemical oxidation assays were conducted at pH value of 4, 6.8 (original), 8, and 10. Fig. 3 shows the variation of COD (a) and NH_4^+-N (b) with electrolysis time. To compare with acidic conditions, the COD removal was promoted slightly in alkaline conditions. As demonstrated in Fig. 3(a), the evolution of COD removal followed a similar trend at different pH. This effect may be due to the nature of

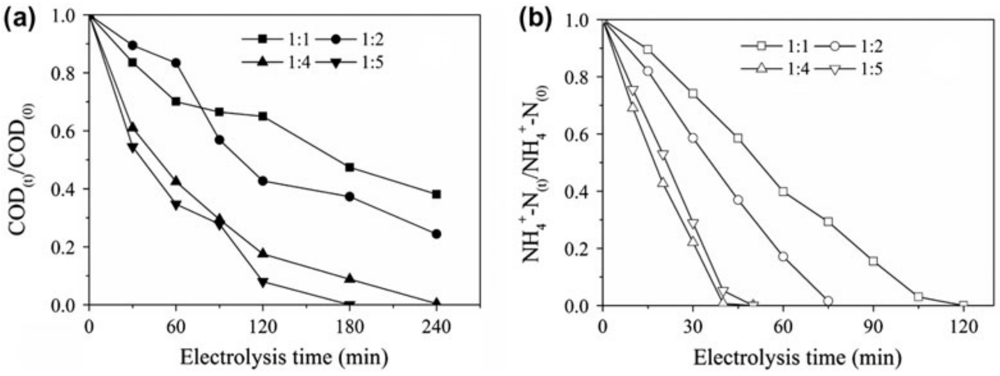

Fig. 1. Effect of dilution ratio on COD (a) and NH_4^+-N (b) degradation during the electrochemical oxidation of MTWW. Current density = 50 mA cm^{-2}; no adjustment of pH.

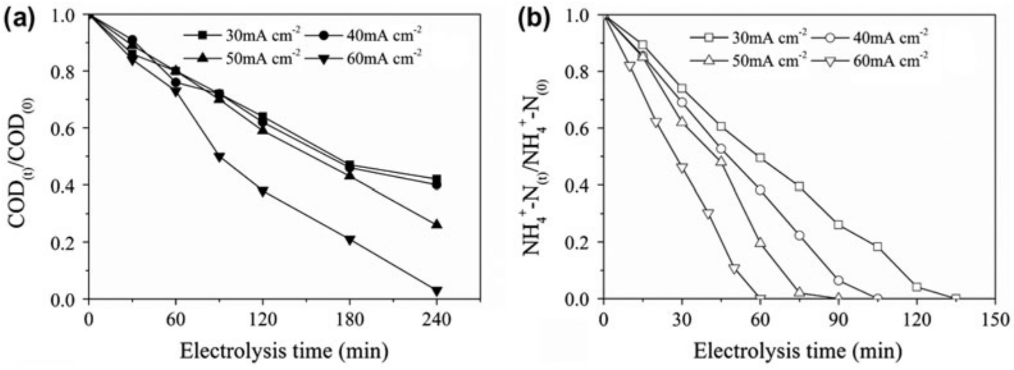

Fig. 2. Effect of current density on COD (a) and NH_4^+-N (b) degradation during the electrochemical oxidation of MTWW. Dilution ratio = 1:2; no adjustment of pH.

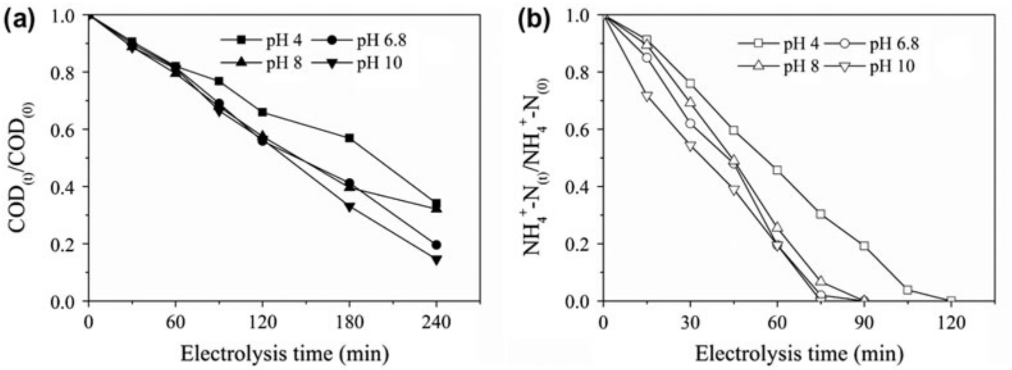

Fig. 3. Effect of initial pH value on COD (a) and NH_4^+-N (b) degradation during the electrochemical oxidation of MTWW. Dilution ratio = 1:2; current density = 50 mA cm^{-2}.

organic compounds existed in MTWW and the oxidation activity of BDD anode. As shown in Fig. 3(b), basic conditions also favored the removal of NH_4^+-N, but the improvement was not noteworthy when pH increased from 6.8 (the original pH) to 10. The evolution of solution pH and active chlorine concentration at different initial pH was shown in supplementary materials (Figs. S1 and S2). It was also noted that NH_4^+-N could be completely removed at any pH. This confirmed that the indirect oxidation of ammonium with active chlorines was predominant under the operating conditions applied in this work; ammonia stripping would be another pathway of NH_4^+-N removal. In order to reduce treatment cost, the adjustment of pH is not recommended during the electrochemical oxidation of MTWW.

3.4. UV–vis spectra

In order to explore the evolution of organic contaminants during the electrochemical oxidation of MTWW, the UV–vis spectra of effluent at different electrolysis time were profiled in Fig. 4. For the original wastewater, there was an absorbance peak appeared at 270 nm, which was corresponding to the π–π^* electron transition of aromatic compounds. Moreover, a shoulder in the UV–vis spectra occurred at the wavelength range of 260–294 nm during the time

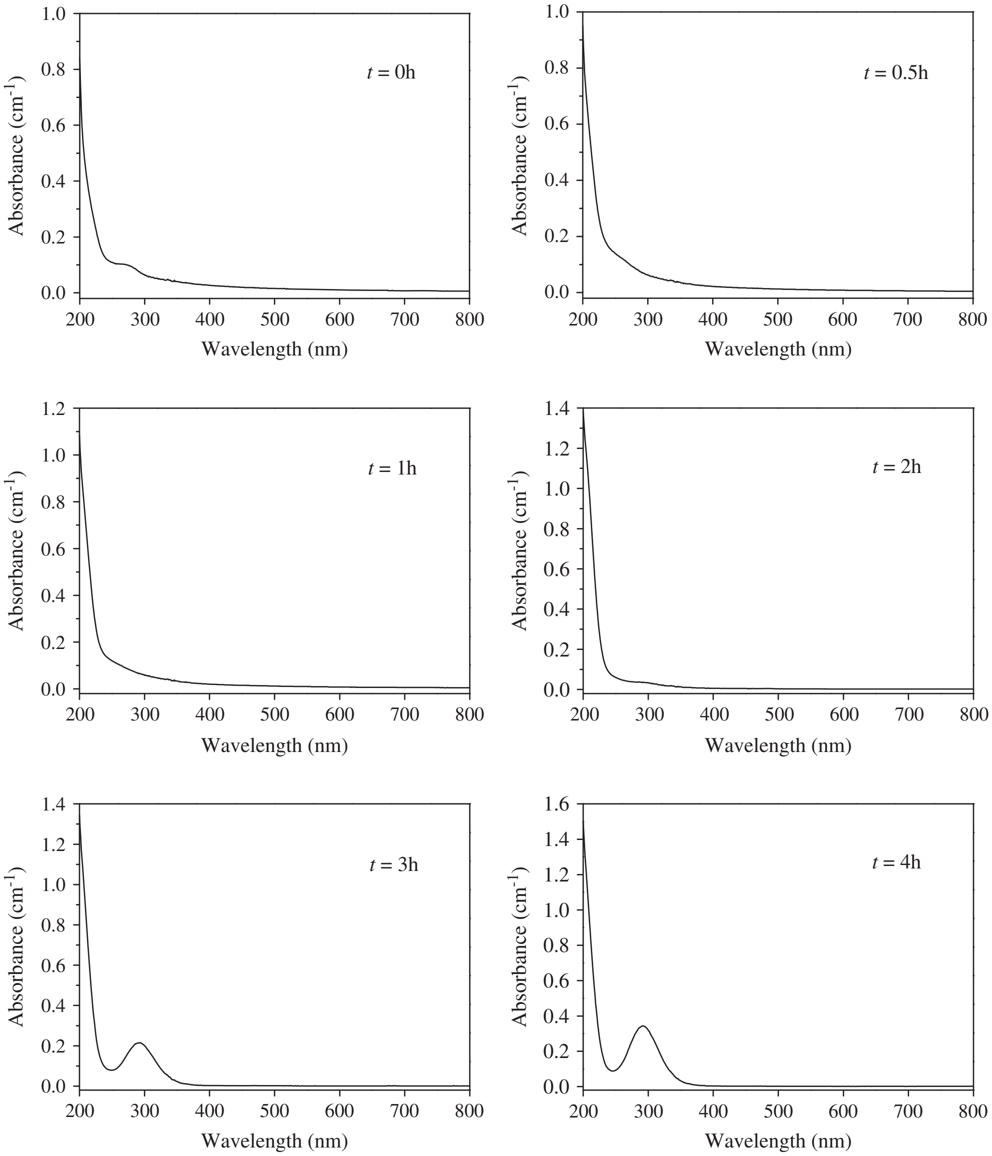

Fig. 4. UV–vis spectra of the treated MTWW. Current density = 50 mA cm^{-2}; no adjustment of pH; dilution ratio = 1:2.

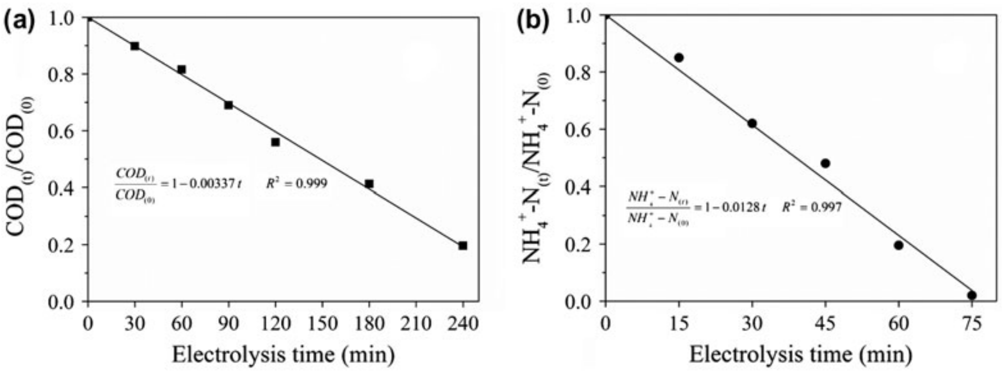

Fig. 5. Kinetics of normalized COD (a) and NH_4^+-N (b) concentration profiles in electrolysis time under the optimal conditions. Current density = 50 mA cm^{-2}; no adjustment of pH; dilution ratio = 1:2.

interval from 3 to 4 h. It may be associated with π–π* electron transitions for phenolic substances, aniline derivatives, and polycyclic aromatic hydrocarbons [35]. The variation of UV–vis spectra was perhaps caused by the formation of intermediates during the electrolysis of MTWW.

3.5. Kinetics of normalized COD and NH_4^+-N

Under the optimal conditions, the evolution of normalized COD and NH_4^+-N concentration were shown in Fig. 5. Both of them followed the zero-order reaction kinetics with high correlation coefficients ($R^2 > 0.99$). The apparent zero-order kinetic constants for normalized COD and NH_4^+-N concentration were 0.0034 and 0.0128 min^{-1}, respectively. The NH_4^+-N removal was faster than COD, which implied that indirect oxidation was predominated in the electrochemical oxidation process. Díaz et al. [36] reported similar behavior of COD removal with electrolysis time during the treatment of aquaculture saline water on BDD anode under galvanostatic conditions. On the contrary, a pseudo-first order kinetic was well fitted to the variation of ammonium during the electrochemical oxidation of landfill leachate with an initial ammonium concentration of 1,060 mg L^{-1} at 116 mA cm^{-2} [37]. The diversity was probably caused by the composition of wastewaters and the hydraulic conditions in the electrochemical reactors.

3.6. General energy efficiency and energy consumption

For industrial application of electrochemical oxidation, the estimation of treatment costs is very significant. Fig. 6 reported the variation of specific energy consumption and general energy efficiency as a function of electrolysis time, under the optimal operating conditions obtained previously. Linear increase in the specific energy consumption was found. The energy consumption was about 45.8 kWh m^{-3} consumed at the electrolysis time of 240 min. During the electrochemical process, GCE varied from 51.5 to 61.9% indicating that electrochemical oxidation was high efficient for MTWW treatment. Nevertheless, the energy consumption is relatively high for practical application as a single treatment process; integrated processes should be taken into consideration in the decontamination of MTWW.

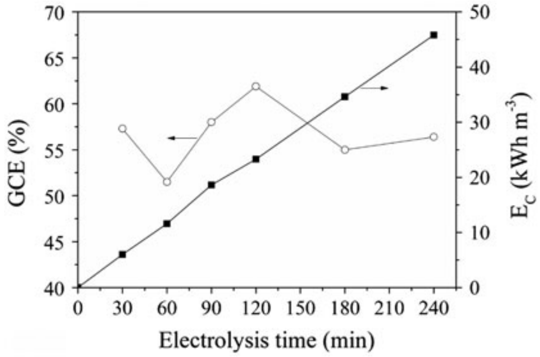

Fig. 6. Variation of GCE and *Ec* as a function of electrolysis time under the optimal conditions. Current density = 50 mA cm^{-2}; no adjustment of pH; dilution ratio = 1:2.

4. Conclusions

The electrochemical oxidation could be a feasible and high-efficient alternative for the abatement of MTWW. During the electrolysis, ammonium was completely removed, and 80.4% of COD was electrodegraded, with specific energy consumption of 45.8 kWh m^{-3}. The applied current density and dilution ratio have a determinable effect on the performance of electrochemical oxidation process, and the effect of pH was not noteworthy. The optimal operating conditions for electrochemical oxidation of MTWW were that a current density of 50 mA cm^{-2}, without pH adjustment and dilution ratio of 1:2. The normalized COD and NH_4^+-N concentration followed zero-order reaction kinetics with high correlation coefficients ($R^2 > 0.99$).

Supplementary material

The supplementary material for this paper is available online at http://dx.doi.10.1080/19443994.2014.975285.

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