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Anodic treatment of acrylic fiber manufacturing wastewater with boron-doped diamond electrode: A statistical approach

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ABSTRACT

This work investigated the electrochemical treatment of acrylic fiber manufacturing wastewater (AFMW) with boron-doped diamond (BDD) electrode. A factorial design methodology was employed to evaluate the statistically important operating variables, among treatment time (1–2 h), flow rate (400–600 mL/min), current intensity (0.50–1.00 A) and initial COD load (362–723 mg/L) on the treatment efficiency, the latter was assessed in terms of COD and ammonia-nitrogen (NH_3-N) removal. The experimental results demonstrated the suitability of the BDD technology for COD removal, as well as the unique behavior in removing NH_3-N. Further investigation also revealed the superiority of BDD anode cell over DSA anode cell either in COD removal rate or in energy consumption. These results showed great potential of the BDD technology in engineering application as an effective option for treating AFMW.

1. Introduction

In the past decade, the dry-spun acrylic fiber industry has been booming in many developing countries, especially in China. This dry-spun technology is within the patents of Dubos, which offers versatile and good-quality products. However, a huge number of highly toxic wastewater will be produced during the manufacturing processes, which contains inorganic pollutants (mainly sulfates and sulfites) and organic contaminants (DMF, EDTA, amine, oil and PAN low polymer). Most of these constitutes are refractory, toxic and mutative, which resist conventional treatment techniques. Therefore, increasing concern has been expressed about the development of some powerful pretreatment options to enhance the biodegradability of the acrylic fiber manufacturing wastewater (AFMW).

Conventional treatments of AFMW include adsorption by activate charcoal, zero-valent iron and biological treatment [1]. Due to the presence of many refractory and toxic compounds, the activated sludge process is not efficient for the removal of organic pollutants though new biological reactors and processes have been developed and achieved good results, such as the anaerobic–anoxic–oxic process [1]. As a result, it still lacks effective approaches of treating AFMW to meet the strict requirements of the National Discharge Standard of China (first grade: COD < 160 mg/L; second grade: COD < 250 mg/L) (GB8978-1996) [2].

In this perspective, great interests have been aroused in the development of practical electrochemical oxidation methods to treating the industrial wastewater. This technology is environmental friendly, amendable to automation and is capable of destructing a variety of biorefractory contaminants effectively [3]. And the recent advent of boron-doped diamond (BDD) electrode has hastened its development for real applications [4]. BDD electrode is excellent hydroxyl radical generator providing wide potential window, high overpotential for oxygen evolution and unique electrocatalytic properties in the destruction of organic pollutants [5,6], making it an ideal candidate for treating real wastewaters [7–12].

In this study, we present the results of the oxidation of actual AFMW over a BDD anode regarding the effect of various operating conditions such as initial organic load, applied current, flow rate and treatment time on the conversion of COD and ammonia-nitrogen (NH_3-N). To evaluate in a coherent way the importance of the various parameters involved, a 2^4 factorial design methodology is employed. Moreover, a comparative study concerning the degradation performance and energy consumption is attempted between BDD and DSA anodes.

2. Materials and methods

2.1. AFMW

The AFMW was provided by an acrylic fiber factory, located in Jilin province, China. The effluent was subjected to coagulation by

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Table 1
Properties of AFMW samples used in this study.

Parameter	AFMW prior to coagulation	AFMW after coagulation
COD, mg/L	921	723
BOD, mg/L	420	351
NH_3-N	78	72
pH	5.7	5.6
Conductivity, mS/cm	233	225
Sulfate, mg/L	305	302

PAC (poly-aluminum chloride) to remove most of the low polymers. The effluent is transparent and colorless, but it is smelly and hot (with mean temperature around 45 °C). Its main properties prior to and after coagulation are given in Table 1.

2.2. Analytical apparatus and calculations

COD value was determined by the dichromate method. The appropriate amount of sample (3 mL) was introduced into commercially available digestion solution and the mixture was then incubated for 2 h at 148 °C in a COD reactor (TR-200A, MERCK). COD concentration was measured colorimetrically using NOVA 60 Spectroquant (MERCK, Germany). NH_3-N value was also determined colorimetrically with NOVA 60 Spectroquant. BOD (Biological Oxygen Demand) value was obtained from BOD-220A quick BOD analyzer (Tianjin Saipu Scientific Instruments Co., Ltd., China). Sweep Electron Microscopical (SEM) micrographs were obtained with S-3000N SEM analyzer (HITACHI, Japan).

The initial limiting current density ($I_{\text{lim},0}$) was defined in Eq. (1):

$$I_{\text{lim},0} = 4Fk_m \,\text{COD}_0 \tag{1}$$

F, Faraday's constants; k_m, the average mass-transport coefficient (1.267×10^{-5} m/s for 400 mL/min and 1.295×10^{-5} m/s for 600 mL/min), which was determined following the procedures described elsewhere [13]. For the cases of the present study, the initial limiting current densities are presented in Table 2.

Electrochemical treatment was undoubtedly an energy-intense process and its efficiency was usually assessed in terms of specific energy consumption (SEC, in kWh/m^3) [14]. This could be defined as the amount of energy consumed per unit mass of organic load removed as shown in Eq. (2):

$$\text{SEC} = \frac{U_{\text{cell}} \cdot I \cdot t}{3600V} \tag{2}$$

where U_{cell} is the average cell voltage (V), I is the current (A), t is the electrolysis time (s) and V is the volume of the treated solution (dm^3).

2.3. Degradation experiments

Experiments were conducted in a single-compartment electrolytic flow-cell manufactured by Kanagawa Academy of Science & Technology (Japan). Two electrodes made of commercially Diachem Nb/BDD and Nb/Pt were used as the anode and cathode, respectively (CONDIAS Corporation, Germany). Both electrodes were square, each with 77.44 cm^2 geometrical area and 10 mm inter-electrode gap. It worth outlining that, the BDD electrode, which was prepared by microwave plasma-assisted chemical vapor deposition (MP-CVD), had maintained a nice service record of over half a year before being employed in this investigation. DSA electrode (Ti/IrO_2–RuO_2) of the same size was provided by Baoji Butai Corporation (Shanxi, China). Fig. 1 presents a generalized schematic representation of the complete apparatus employed.

In a typical run, the effluent was diluted with deionized water to achieve the desirable initial COD concentration, and batch loaded in a vessel. Then, the samples were continuously recirculated in the cell through a peristaltic pump operating at a flow rate of 400 mL/h or 600 mL/min. In all cases, the working volume was 200 mL, which yielded a surface area to volume ratio (S/V) of 0.387 cm^{-1}. The current density was monitored constant by means of a potentiostat/galvanostat, and all the runs were performed at a constant temperature of 45 °C by a water bath. The treated water samples were collected at predefined times for analysis. All experiments were carried out in duplicate and good reproducibility was obtained. Regarding the abundance of AFMW, it should be noted that neither extra oxidants nor pH adjustments were preferred for experiments aiming for applications. Therefore, only limited variables were concerned in the present study.

3. Results and discussion

3.1. COD degradation

In this work, a statistical approach was chosen based on a factorial experimental design that will allow us to infer about the effect of the variables with a relatively small number of experiments [15]. Four independent variables that would affect treatment efficiency were taken into account, namely treatment time, flow rate, applied current and initial COD concentration. As shown in Table 3, each variable receives two values, a high value (indicated by the + sign) and a low value (indicated by the − sign). Initial COD and treatment time were chosen as they typically play a key role in dictating the performance (in terms of rates and costs) of industrial wastewater treatment by advanced oxidation processes (AOPs), while current was a determining factor in electrochemical reactions [16]. Treatment for 1–2 h was a reasonable timescale for most applications of AOPs, while it was decided to operate in the range 0.50–1.00 A to safeguard efficient treatment. Since a high mass-transfer coefficient would be obtained under a high flow rate, a moderate flow rate of 400–600 mL/min was adopted for running [17]. The experimental design followed in this work was a full 2^4 experimental set, which required 16 experiments.

The design matrix of the experiments was made by means of the software package SPSS 17.0. The results obtained in terms of two measured response factors (dependent variables), namely concentration of COD oxidized in mg/L (response factor Y_1) and concentration of NH_3-N removed in mg/L (response factor Y_2) are presented in Table 4.

In general, moderate to high levels of COD removal can be achieved at relatively intense conditions, i.e. long electrolysis time and/or high applied current. As can be seen in Table 4, the COD load of AFMW is effectively removed in most cases. Specifically, a highest COD removal rate of 80% is obtained in entry 14. The remaining COD concentration of this entry is only 140 mg/L, which has already met the first grade requirements of the National Discharge Standard of

Table 2
Calculations of initial limiting current density.

Entry	k_m, m/s	COD value, mol O_2/m^3	Limiting current density, mA/cm^2	Limiting current, A
1	1.267×10^{-5}	22.59	11.05	0.856
2	1.267×10^{-5}	11.30	5.23	0.428
3	1.295×10^{-5}	22.59	11.26	0.872
4	1.295×10^{-5}	11.30	5.63	0.436

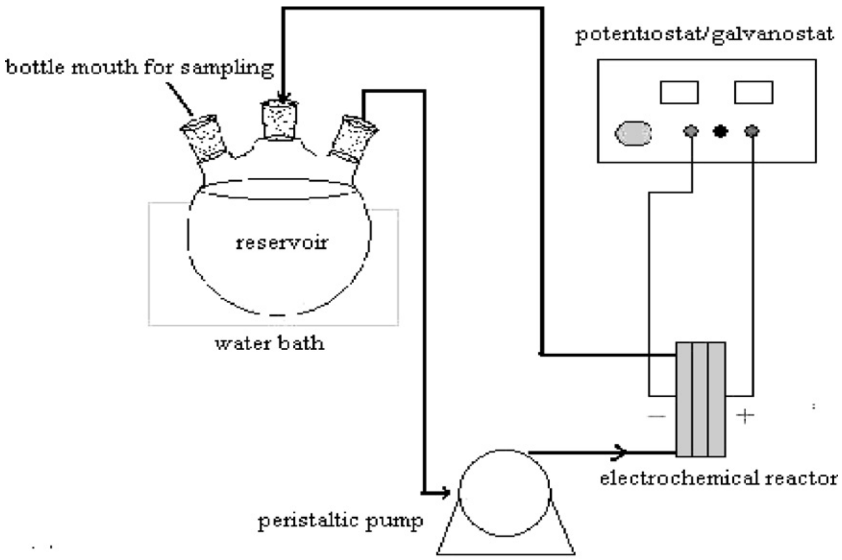

Fig. 1. The generalized schematic representation of setup of complete apparatus employed.

Table 3
- Independent variables of the 2^4 factorial design of experiments.

Level of value	X_1, time/h	X_2, flow rate/mL/min	X_3, current/A	X_4, initial COD_{Cr}/mg/L
–	1.0	400	0.50	362
+	2.0	600	1.00	723

China (COD < 160 mg/L). This tendency can be related to the strong oxidizing capability of the BDD ($^{\bullet}OH$) (hydroxyl radicals weakly adsorbed on BDD anode) continuously generated as shown in Eq. (3) [18]

$$BDD + H_2O \rightarrow BDD(^{\bullet}OH) + H^+ + e^- \tag{3}$$

On the other hand, a different tendency of NH_3-N removal is also shown. The phenomenon can be surprising if one takes into account the enhancement of BDD ($^{\bullet}OH$) as current increases. However, it can be accounted for the presence of many nitrogen-containing organics in AFMW, which may act as the precursors of newly generated NH_3-N [1]. Despite of this, the problem of NH_3-N pollution is much easier to be dealt with, i.e. by employing an active sludge system [2]. Therefore, only the case of COD removal is concerned in the following.

According to the methodology of factorial design [19], the estimation of the average effect, as well as the main and interaction effects is also made by means of the statistical package SPSS 17.0 and the results are summarized in Table 5. The average effect is the mean value of each response factor, while the main and interaction effects are the difference between two averages: main effect Z_1 and Z_2, where Z_1 and Z_2 are the average response factors at the high and low level respectively of the independent variables or their interactions.

A key element in the factorial design statistical procedure is the determination of the significance of the estimated effects. The most

Table 4
Design matrix of the 2^4 factorial experimental design and observed response factors, as well as percentage removal of COD.

Entry	X_1	X_2	X_3	X_4	Y_1	Y_2	COD removal, %
1	–	–	–	–	157	2.4	43.4
2	+	–	–	–	196	−0.2	54.1
3	–	+	–	–	176	0.8	48.6
4	+	+	–	–	237	−4.1	65.5
5	–	–	+	–	216	1.3	59.7
6	+	–	+	–	224	−1.3	61.9
7	–	+	+	–	206	4.2	56.9
8	+	+	+	–	258	0.9	71.3
9	–	–	–	+	343	−0.5	47.4
10	+	–	–	+	500	−11.1	69.2
11	–	+	–	+	278	−0.8	38.5
12	+	+	–	+	510	−8.2	70.5
13	–	–	+	+	404	−0.6	55.9
14	+	–	+	+	578	−4.9	79.9
15	–	+	+	+	475	−2.2	65.7
16	+	+	+	+	573	−6.5	79.3

Table 5
Average and main effects of the independent variables and their two and higher order interactions of the 2^4 factorial design on the response factors Y_1.

Effect	Value of effect (Y_1, COD removal)
Average effect	333.19
Main effect	
X_1	102.63
X_2	11.88
X_3	194.63
X_4	248.88
Two-factor interactions	
$X_1{\cdot}X_2$	8.12
$X_1{\cdot}X_3$	−9.81
$X_1{\cdot}X_4$	62.63
$X_2{\cdot}X_3$	10.62
$X_2{\cdot}X_4$	−9.12
$X_3{\cdot}X_4$	32.63
Three-factor interactions	
$X_1{\cdot}X_2{\cdot}X_3$	−16.12
$X_1{\cdot}X_2{\cdot}X_4$	−8.38
$X_1{\cdot}X_3{\cdot}X_4$	−9.62
$X_2{\cdot}X_3{\cdot}X_4$	19.62
Four-factor interactions	
$X_1{\cdot}X_2{\cdot}X_3{\cdot}X_4$	−21.63
Lenth's PSE	15.9
ME	34.4
SME	67.5

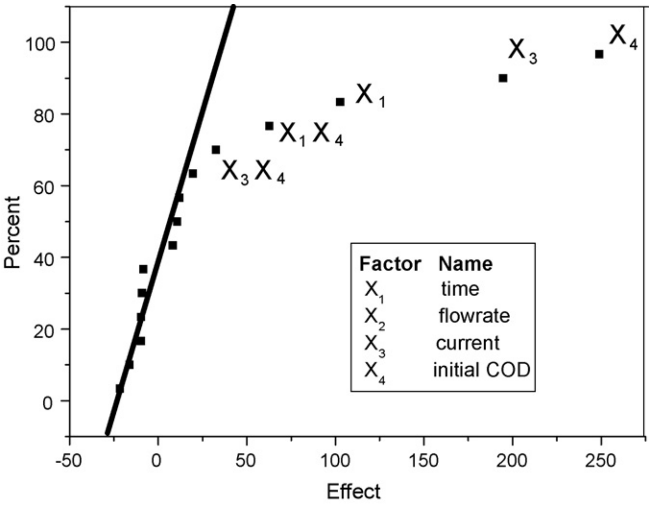

Fig. 2. Normal probability plot of the effects for the removal of COD.

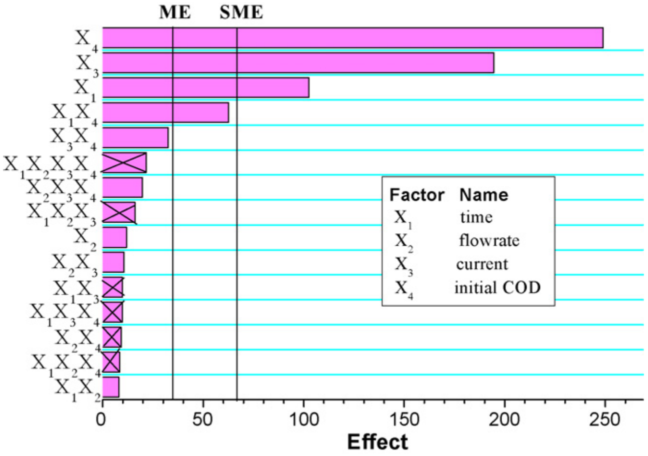

Fig. 3. Pareto chart of the effects for COD removal for the full 2^4 factorial design. Pure purple bars: positive effects; purple bars with *X* lines: negative effects. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

common way to identify the most important effects is to construct the normal probability plot [19]. In such plot, all small effects will appear on a straight line, and any effect with a significant contribution will lie away from the normal probability line. The normal probability plot for the oxidation of COD is shown in Fig. 2. There are basically four effects lie away from the straight line: in order of significance, the initial COD load, applied current, reaction time and the interaction between COD load and time. These effects are positive indicating that an increase in their level brings about an increase in the amount of COD oxidized.

To confirm these results, Pareto chart, a very useful pictorial presentation of the estimated effects and their statistical importance, is also employed. The Pareto chart displays the absolute values of the effects in a bar chart, as well as the decision lines for ME (a margin of error) and SME (a simultaneous margin of error). The pseudo-standard error (PSE), ME and SME are estimated by Lenth's method [20]. All estimated effects greater than the ME, in absolute values, are deemed significant. On the other hand, all other effects whose values are lower than the ME can be attributed to random statistical error. Moreover, an effect that exceeds the ME but not the SME should be viewed with some caution, as it may be an artifact of testing several effects. In other words, there is at most a 5% chance that one individual inactive effect will exceed the ME, while there is at most a 5% chance that any inactive effect will exceed the SME. This method offers a simple and fast approach to assess the significance of the main and interaction effects in un-replicated factorial designs.

The Pareto chart of the effects for the COD oxidation is shown in Fig. 3. There are three effects that are greater than the SME decision threshold. Among them, the two most significant ones are the influent COD (X_4) and applied current (X_3), revealing a positive effect on treatment efficiency. At this level, the effect of the starting COD concentration and applied current is much greater than that of the treatment time and flow rate. Among the interactions, only the (time) × (influent COD) is significant, which needs to be handled with some caution. These results are in good agreement with those shown in Fig. 2.

Based on the variables and interactions which are statistically significant, a model describing the experimental response is constructed as follows (Eq. (4)):

$$Y_1 = 333.19 + \left(\frac{102.63}{2}\right) X_1 + \left(\frac{194.63}{2}\right) X_3 + \left(\frac{248.88}{2}\right) X_4 + \left(\frac{62.63}{2}\right) X_1 \cdot X_4 \qquad (4)$$

where Y_1 is the mass of COD oxidized (mg/L) and X_i are the transformed forms of the independent variables.

These results are also consistent with the influent COD and applied current employed. Returning to Table 2, the four limiting currents (0.856 A, 0.428 A, 0.872 A and 0.436 A) calculated are very close to those chosen in the chemometrics study (0.50 A, 1.00 A). In this way, different reaction kinetics will be involved in some entries. For example, during the early stage of some reactions (i.e. at low current density, high COD load and/or short treatment time), the reactions are likely under current control with the instantaneous current efficiency (ICE) of 100% [17]. While for cases with low initial COD values, the processes are controlled by the rate at which organic molecules are transported from the bulk solution to the anode surface rather than by the rate at which $^{\bullet}$OH are produced. Higher limiting current densities will be obtained at higher initial COD load, which makes the influence of influent COD far more significant than other variables [12].

3.2. Comparative study with DSA electrode

It is well known that the performance of electrochemical oxidation strongly depends on many parameters, including applied current, treatment time, electrolyte type (chloride-present or chloride-free) and concentration, pH, anode material and temperature, of which the anode material has been regarded as the most important variable that governing the yield of generated oxidants (i.e. $^{\bullet}$OH) [14,21]. With this in mind, a comparative study between BDD and DSA anode was performed in this section.

Prior to the investigation of the electrode performance, a comparison on the surface morphologies of these two anodes was attempted. As shown in Fig. 4, there are marked difference between BDD and DSA electrode. The most intriguing feature of DSA electrode may be its inconsistent cracks. In accordance with some previous literatures [7,22], no significant changes have been observed for both electrodes before and after the treatment of AFMW (not shown here).

Fig. 5A shows the evolution of COD as a function of electrolysis time in BDD and DSA anodes cells under the same electrolysis conditions. The graph clearly evidences that BDD anode enable significantly faster COD removal than DSA. At the end of treatment, 65% of COD is removed in BDD anode cell, while COD is only removed by 18% in DSA anode cell. It means that the mineralization capacity of BDD anode is much stronger than that of DSA anodes. Furthermore, the representative temporal profiles of cumulative

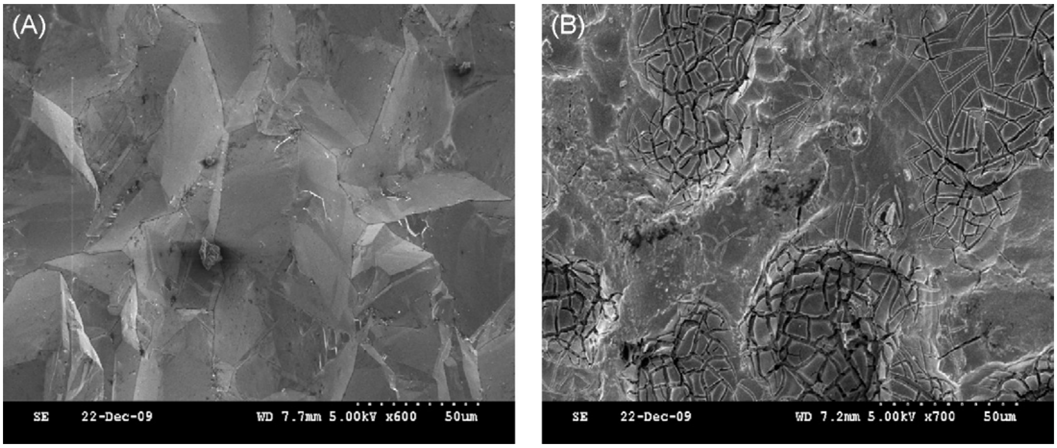

Fig. 4. SEM images of the BDD electrode (A) and DSA electrode (B).

SEC with respect to COD removal are shown in Fig. 5B. As clearly seen, SEC is much lower at BDD than that at DSA. For instance, to gain a COD disappearance of 18%, the energy required for the treatment of 1 m^3 solution were 9.51 kWh and 78.70 kWh for BDD cell and DSA cell, respectively.

The higher mineralization capacity and lower energy consumption for BDD anode may be attributed to its different degradation mechanism from DSA anodes [23]. The former involves the free hydroxyl radicals at BDD anode of higher oxygen potential, which allows hydroxyl radicals to participate in degrading COD in the bulk solution, the latter involves adsorbed hydroxyl radicals that prone to combine with each other to produce oxygen (side reaction) [23]. As a result, the production of hydroxyl radicals by BDD was about 8 times higher than that by DSA. Furthermore, the superiority of BDD over DSA anodes is also consistent with the chloride-free characteristic of AFMW. It has been well demonstrated in previous literatures that in chloride-free solutions, both the productions of $^{\bullet}OH$ and O_3 at BDD are much higher than that at DSA and Pt [6,24,25]. Since sulfate and sulfite being the main electrolytes in the effluent, the reactions of sulfate to peroxodisulfate seem quite reasonable. Peroxodisulfates can decompose to form hydrogen peroxide and other oxidants [9,23], thus some contaminants may be degraded by reaction with these electrogenerated oxidants during electrochemically advanced treatment of AFMW.

As has been mentioned above, the practice of treating AFMW using a combined process consisted in an effective pretreatment followed by an aerobic unit is preferred by most factories in China. In this view, the electrooxidation with BDD electrode obviously offers an attractive solution to this problem. Since biological processes are also likely to play an important role in a complex battery of treatments, so biodegradability tests are required to assess the biotreatability of the BDD-treated effluent. The aerobic biodegradability of AFMW samples prior to and after the BDD treatment is assessed in terms of residual BOD values. The original effluent (with initial COD of 723 mg/L) still contains a considerable content of organics that cannot be degraded aerobically. It is found that a COD removal rate of 60% (with a remaining BOD value below 170 mg/L), is enough to meet the inlet requirement of the aerobic treatment. In other words, BDD electrochemical oxidation does appear to improve the aerobic biodegradability of AFMW. In this way, a more mild operating condition may be employed to attain the desired results in a reasonable time and with an acceptable energy cost, i.e. at lower applied current and with lower S/V ratios. The results demonstrate that the BDD technology has a promising perspective in practice. Studies are underway to further optimize the process under a variety of operating conditions and to make it for actual applications.

4. Conclusions

Wastewater from the dry-spun acrylic fiber industry was electrochemically oxidized over boron-doped diamond electrodes with

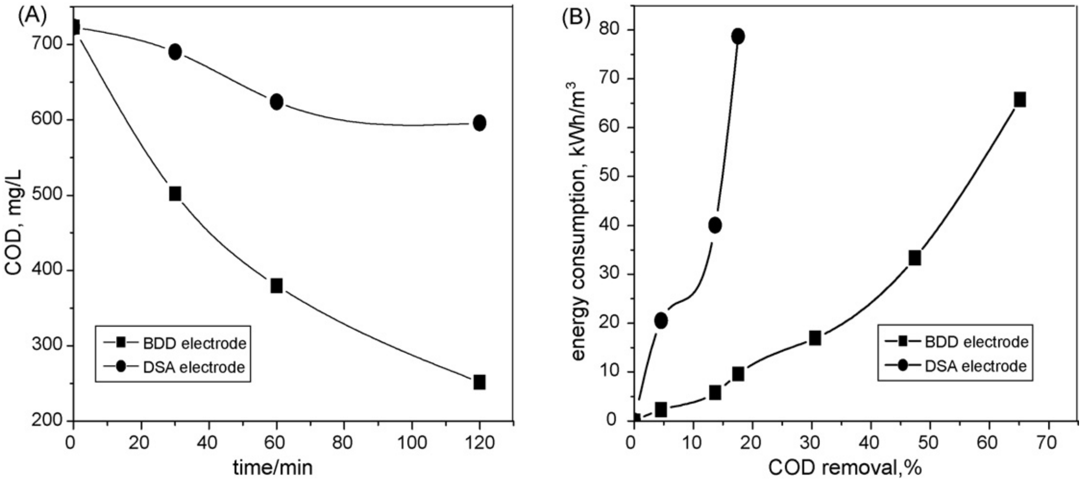

Fig. 5. (A) Comparison of the evolution of COD during electrochemical treatment; (B) evolution of the specific energy consumption against COD removal during electrochemical treatment of acrylic fiber wastewater on DSA and BDD electrode. Conditions: applied current: 0.50 A, flow rate: 400 mL/min, $T = 45 \pm 1\,^{\circ}C$.

emphasis given on the effect of various operating conditions on treatment efficiency with regard to COD removal. A factorial design methodology was followed to evaluate the importance of the various parameters involved. Applied current and the initial concentration of organic pollutants were two factors that dictate, to a great degree, the efficiency of AFMW electrochemical degradation. As a result, the electrochemical oxidation over BDD electrode was proved to be a very efficient process for AFMW treatment. The COD removal rate in BDD anode cells was much greater than that in DSA anode cells, requiring shorter reaction time and lower energy consumptions. The excellent performance of the BDD technology might be attributed to the presence of free hydroxyl radicals generated on non-active BDD electrode, as well as the chloride-free nature of AFMW.

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