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Treatment Of Wastewaters Containing 2-Nitroaniline And 2-Chloroaniline By BDD-Anodic Oxidation And Ozonation

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ABSTRACT

In this work, synthetic wastes polluted with 2-nitroaniline (2-NA) and 2-chloroaniline (2-ClA) have been treated with BDD-anodic oxidation and ozonation. The two technologies are able to successfully mineralize over 90 % the wastes polluted with aniline derivatives. BDD-anodic oxidation using divided electrochemical cell leads to the formation of carbon dioxide as final product. Using single-compartment electrochemical cell, only 70 % of organic carbon is transformed to CO_2 and in addition a solid effluent is formed. The COD evolution with specific electrical charge passed is linear at beginning of electrolyses and becomes exponential for very low concentrations. During ozonation treatment, the exponential decrease of COD with time can be explained by first-order chemical kinetics. © 2006 Trade Science Inc. - INDIA

KEYWORDS

BDD-anodic oxidation;
Ozonation;
Electrochemical cell;
Aniline derivatives.

INTRODUCTION

Aniline derivatives are one of the main pollutants to water environment, mainly coming from chemical processes of the dye, pharmaceutical and petroleum sectors[1-4]. Chlorinated and nitrogenated derivatives of aniline, very toxic and biorecalcitrant pollutants have been found in various environmental compartments[5-9]. Many of these aromatic amines are known or suspected to be human or animal carcinogens[1-9]. 2-Nitroaniline and 2-chloroaniline can be considered as appropriate simple models of such compounds.

The treatment with advanced oxidation processes such as Fenton process, ozonation and electrochemical oxidation, appears as one of the most promising techniques for the treatment of wastewater containing hazardous organic pollutants produced in many industrial processes[10]. The facts have been related with the generation of hydroxyl radicals (OH•). This radical is a strong oxidant agent's able to react with organics and causing its conversion to CO_2 and H_2O or at least to other organic that can be treated by biological degradation.

Recently, BDD-anodic oxidation has been widely studied with synthetic industrial wastes in lab and bench-scale plants[11-25]. It has been demonstrated that hydroxyl radicals are formed during the electrolysis on conductive-diamond anodes of aqueous electrolytes and this has allowed classifying this technology as an Advanced Oxidation Process (AOP). Besides this mechanism, the global oxidation process in conductive-diamond anodes is known to be complemented by direct electro-oxidation on the surface and also mediated oxidation by other oxidants electrogenerated on the surface from the electrolyte salts. The combination of these oxidation mechanisms has shown to increase the current efficiency of this technique, as compared with other electrochemical technologies.

During the recent years, ozone has been used for the non-persistent disinfection of water and treated wastewaters, and also for industrial wastewater treatment[26-31]. Presently, it is one of the most widely used advanced oxidation technologies. Ozone is itself a very powerful oxidant (E^0: 2.07 vs. NHE) and in certain conditions it can decompose and lead to the formation of hydroxyl radicals. In this later case, the process efficiencies are strongly increased. Three main stages can be discerned in an industrial wastewater ozonation process: the generation of ozone, the dissolution of ozone in the wastewater and the oxidation of organic matter. During the last years, many works have been published concerning the ozonation of dyes-polluted wastes.

The goal of the work described here was to compare the oxidation of aniline pollutants with two AOP technologies (ozonation and BDD-anodic oxidation) and to study the role of the electrochemical cell (single compartment or divided) in the electrochemical oxidation of organics with BDD. To do this, 2-nitroaniline and 2-chloroaniline were selected as model anilines. They are soluble in water and persistent, once discharged into a natural environment. Thus, their study is interesting not only for being possible pollutants of industrial effluents but also because they are good models of bio-resistant molecules.

EXPERIMENTAL

Analytical procedure

Total organic carbon (TOC) of the solution was determined by a TOC-5050 Shimadzu apparatus. Chemical oxygen demand (COD) was determined using a HACH DR2000 analyser. UV-visible spectra were obtained using a Shimadzu 1603 spectrophotometer and quartz cells.

Conductive diamond electrochemical oxidation

In this work, the BDD-anodic oxidation assays were carried out in single-compartment and divided electrochemical flow-cells working under a batch operation mode. Diamond-based material was used as anode and stainless steel (AISI 304) as cathode. Both electrodes were circular (100 mm diameter) with a geometric area of 78 cm^2 and an electrode gap of 9 mm. The wastewater was stored in a glass tank (0.6 dm^3) and circulated through the electrolytic cell by means of a centrifugal pump (flow rate 2.5 $dm^3\,min^{-1}$). A heat exchanger coupled with a controlled thermostatic bath (Digiterm 100, JP Selecta, Barcelona, Spain) was used to maintain the temperature at the desired set point. The experimental setup also contained a cyclone for gas-liquid separation, and a gas absorber to collect the carbon dioxide contained in the gases evolved from the reactor into sodium hydroxide. Boron-doped diamond films were provided by CSEM (Switzerland) and synthesized by the hot filament chemical vapor deposition technique (HF CVD) on single-crystal p-type Si (100) wafers (0.1**Ω**.cm, Siltronix). Electrolyses were carried out in galvanostatic mode. The pH was kept constant (pH=2) by the continuous introduction of sulfuric acid (or sodium hydroxide) to the electrolyte reservoir.

Ozonation

Ozonation experiments were carried out by continuously feeding an ozone-oxygen gas stream in a mixed semi-bach bubble reactor (continuous for gas and batch for liquid). This reactor consist of a 2.5 dm^3 jacketed cylindrical pyrex glass tank equipped with a porous gas distribution plate and baffles to increase the capacity of absorption of ozone. A mechanical stirrer (IKA WERKER model EUROSTAR DIGITAL, Germany) and a recycle pump (Emapompe, model P 022 Plastomec) are also used to promote the absorption of ozone and to obtain good mixing conditions. Pure oxygen taken from a commercial cylinder was fed into an ozone generator (Ambizon, Model GMF-10, Sistemas y Equipos de Ozonización S.L., Madrid, Spain) which is able to produce a maximum mass flow rate of 10 g h^{-1}. In the generator outlet, the stream was dried with a sample conditioner (Sample conditioning system, model SC-010-R AFX, Sistemas y Equipos de Ozonizacion S.L., Madrid, Spain). The concentration of ozone in the gas at the reactor outlet and inlet was measured with an ozone meter (Ozone analyser, Model H1 AFX, Sistemas y Equipos de Ozonizacion S.L., Madrid, Spain) and its calibration was carried out iodometrically[31]. Dissolved ozone concentration in the liquid phase was determinated spectrophotometrically (600 nm) from discoloration of the resulting solution, by the Karman indigo method[31]. In the experiments described in this work, the ozone-oxygen mixture gas stream was sparged with a constant flow rate of 0.5 $dm^3.min^{-1}$ (flow controller Cole Parmer, model #: 32907-39) and the average production of ozone was around 1 g h^{-1}. The volume of wastewater treated in each assay was 2 dm^3 and it was placed inside the reactor prior to the experiments. To increase the mixing conditions, the stirring rate of the mechanical stirrer was adjusted to 550 rpm and the flow recycled to 67.5 $dm^3.h^{-1}$. The ozone generator was switched on prior to the experiments, and only when the desired ozone percentage in the ozone-oxygen gas was reached (steady state conditions) the ozone-oxygen mixture gas stream started to be sparged into the reactor. During the experiments sodium hydroxide was added to the reactor to maintain the pH in a set point close to 12. According to literature[26-31], this is an optimum pH to promote the generation of hydroxyl radicals due to the radicalarly decomposition of the ozone molecules. The temperature was also maintained during operation at 25°C using a thermostatic bath (Tectron, model 3473200 Selecta, Madrid, Spain) by circulating the water through the jacket reactor to ensure a constant temperature inside the reactor.

RESULTS AND DISCUSSION

CDEO of organics in single-compartment electrochemical flow-cell

Figures 1 and 2 show the evolution of COD with the specific electrical charge (Q) passed during the electrochemical treatment on BDD anodes at 15 and 50 $mA.cm^{-2}$ current densities of synthetic wastewaters containing 5000 mg Na_2SO_4 dm^{-3} and 2-nitroaniline (5 mM) and 2-chloroaniline (5 mM), respectively. It can be observed, that over 90 % of COD is satisfactorily reduced for the tow compounds independently of the nature and the structure of these organics and the current density and the complete mineralization was obtained for 2-ClA especially at the current density 15 $mA.cm^{-2}$. Hence, we can suggest that the solutions of 2-NA after the electrolyses come containing other compounds (aliphatic compounds) that present more difficulty to the electro-oxidation process. At the beginning of the electrolysis, the decrease of the COD is linearly with the specific charge. This indicates that under these conditions the oxidation of the compounds are under current controlled. In contrast, at low initial

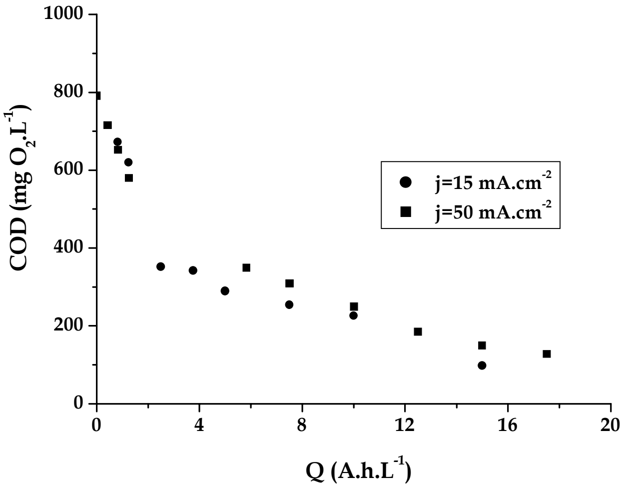

Figure 1: Influence of the applied current density on the COD evolution with specific electrical charge passed in the electrochemical oxidation on BDD anodes of 2-nitroaniline on sodium sulfate media (5000 $mg.dm^{-3}$) at pH=2 and T=25°C

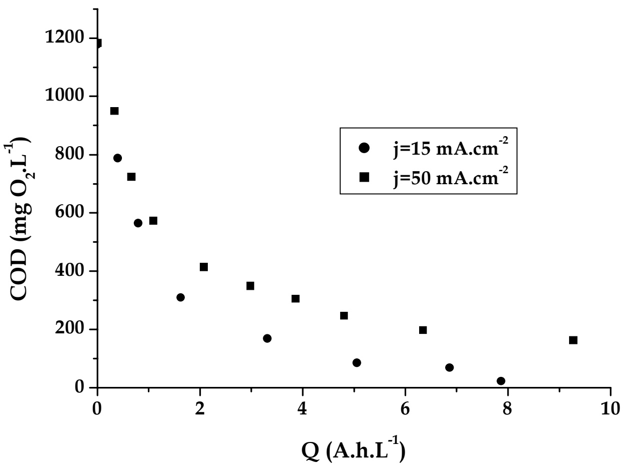

Figure 2: Influence of the applied current density on the COD evolution with specific electrical charge passed in the electrochemical oxidation on BDD anodes of 2-chloroaniline on sodium sulfate media (5000 mg.dm^{-3}) at pH=2 and T=25°C

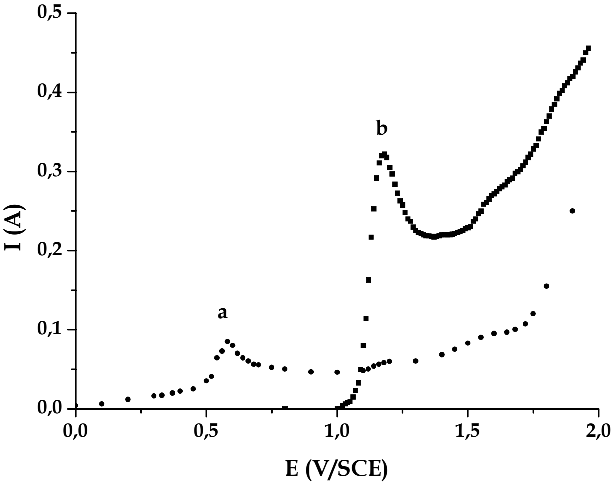

Figure 3: Cyclic voltammogramms on BDD anodes of 2-chloroaniline and 2-nitroaniline solutions on sodium sulfate media (5000 mg.dm^{-3}) at pH=2: a) 2-ClA 1 mM and b) 2-NA 5 mM. Scan rate 100 mV. s^{-1}. Auxiliary electrode : Platinum. Reference electrode: SCE

concentration, an exponentially behavior of the COD abatement is appeared and the oxidation mechanism becomes mass-transport controlled. Moreover, it can be seen that an increase in the current density resulted in a decrease in the mineralization of the matter. This behavior can be due to the side reactions of evolution of O_2, O_3 and hydrogen peroxide and persulfate ions formation. The quantity of oxidants formed is very high relatively to organics arrived at the surface of the anode and the short lifetime of the hydroxyl radicals favours the formation of O_2, O_3 and H_2O_2. In addition, the aliphatic compounds forming during the galvanostatic electroplyses are more difficult to be oxidized than the initial compounds, and need more energy to be mineralized (CO_2 and H_2O). On the other hand, it can be observed that specific electrical charge required for the mineralization of 2-ClA was very low than that required for the anodic oxidation of 2-NA. This can be explained by the difficulty of anodic oxidation on BDD of 2-NA in comparison with 2-ClA. figure 3 shows the cyclic voltammogramms on BDD of solutions containing 5000 mg Na_2SO_4 dm^{-3} and 2-Cl and 2-NA. It can be observed the presence of aniline derivatives leads to the appearance of anodic peaks in the region of stability of electrolyte and that the oxidation of 2-NA is more difficult than that of 2-ClA. This result indicate that the voltammetric behaviours of aniline derivatives are similar to those of other aromatics[11-25]. The presence of nitro group in the aromatic ring leads to more difficult oxidation but the presence of chlorine group facilitates the oxidation.

CDEO of 2-NA in divided electrochemical flow-cell

Figure 4 shows the evolution of COD with the specific electrical charge (Q) passed during the galvanostatic electrolyses on BDD anodes at 30 mA.cm^{-2} current density of synthetic wastewaters contained 5000 mg Na_2SO_4 dm^{-3} and 2-nitroaniline (5 mM) in the anodic compartment and only 5000 mg Na_2SO_4 dm^{-3} in the cathodic compartment, in single and divided electrochemical cells. In the divided cell, the two compartments are separated by standard naphion membrane. It can be observed that the COD variation is independent of the number of compartments in the experimental set-up and the mineralization is obtained in the tow electrochemical cells (single and divided). In order to see the difference between the tow electrochemical cells, total organic carbon and carbon dioxide concentrations are measured during the electrolyses.

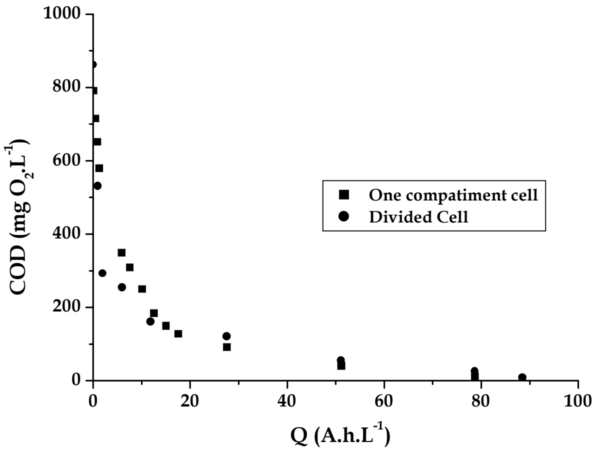

Figure 4: COD evolution with specific electrical charge passed in the electrochemical oxidation on BDD anodes at 30 mA.cm^{-2} current density of 2-Nitroaniline on sodium sulfate media (5000 mg.dm^{-3}) at pH=2 and T=25°C using single-compartment cell (*ƒ*)and divided cell (•)

Figures 5 and 6 present the evolution of TOC and CO_2 concentrations with the specific electrical charge (Q) passed during the galvanostatic electrolyses on BDD anodes at 30 mA.cm^{-2} current density of synthetic wastewaters contained 5000 mg Na_2SO_4 dm^{-3} and 2-nitroaniline (5 mM) in the anodic compartment and only 5000 mg Na_2SO_4 dm^{-3} in the cathodic compartment, in single and divided cells. It can be seen that the organic carbon is satisfactory reduced in the two electrochemical cells but it is totally transformed in CO_2 in the divided electrochemical cell and only 70 % of COT is transformed in CO_2 in the single compartment electrochemical cell. In addition, during the electrolysis in single compartment electrochemical cell, a brown colored solid compound was formed onto the cathode surface. This compound was identified as a polymer resulting from the cathodic condensation of anilines. It can be concluded that the separation of anodic and cathodic compartments leads only to the mineralization of 2-NA without formation of solid effluents witch can cause an additionally environmental problem.

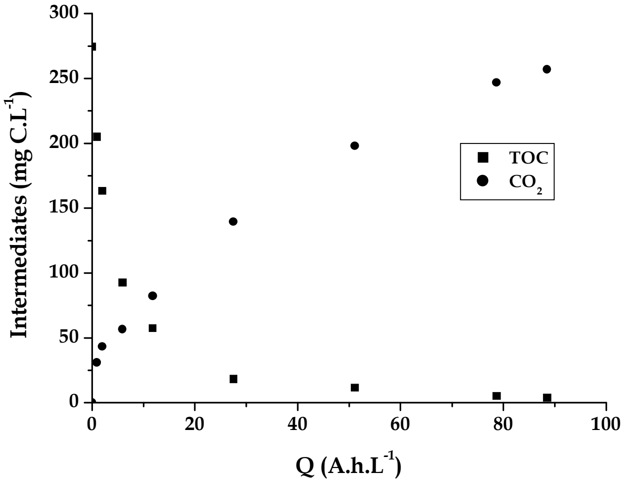

Figure 5: Variation of TOC and CO_2 concentrations with specific electrical charge passed in the electrochemical oxidation on BDD anodes at 30 mA.cm^{-2} current density of 2-nitroaniline on sodium sulfate media (5000 mg.dm^{-3}) at pH=2 and T=25°C using divided electrochemical cell

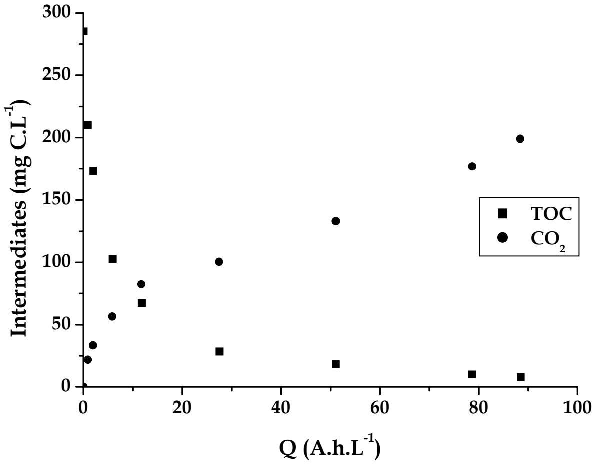

Figure 6: Variation of TOC and CO_2 concentrations with specific electrical charge passed in the electrochemical oxidation on BDD anodes at 30 mA.cm^{-2} current density of 2-nitroaniline on sodium sulfate media (5000 mg.dm^{-3}) at pH=2 and T=25°C using single-compartment electrochemical cell

Treatment of aniline derivatives by ozonation

Figures 7 and 8 show the variation of COD with time during the ozonation of wastewaters containing 2-ClA and 2-NA. It can be observed that ozonation of both compounds leads to over 90 % of COD removal. The graphs show a faster degradation of the organics in the beginning of treatment. This behavior, can be explained by the facility oxidation of the initial compounds (presence of aromatic ring).

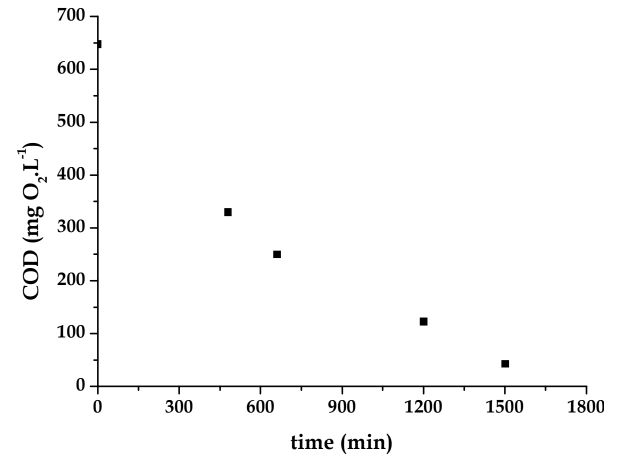

Figure 7: COD evolution with time during the ozonation treatment of 2-nitroaniline. Operation conditions. Ozone production: 1 g h^{-1}, T: 25°C, pH: 12

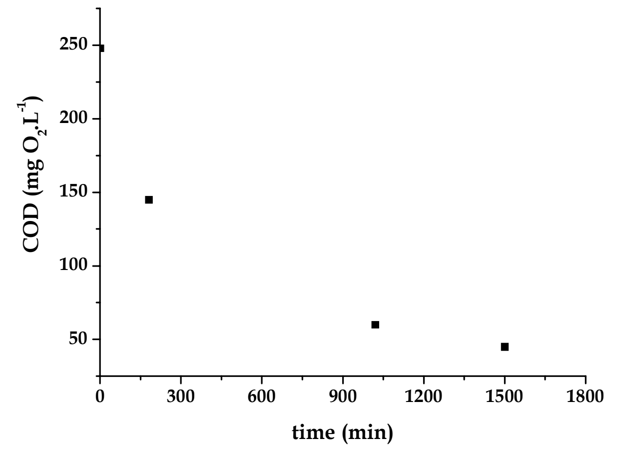

Figure 8: COD evolution with time during the ozonation treatment of 2-chloroaniline. Operation conditions. Ozone production: 1 g h^{-1}, T: 25°C, pH: 12

The COD evolution has an exponentially form with time. The COD changes with time in accordance with an exponential law (Figure 9), can be explained by first-order chemical kinetics.

It can be observed that the efficiencies of the ozonation and anodic oxidation on BDD are similar. This observation is previously reported in literature for other kind of wastes including azo dyes wastes and fine-manufacturing wastes[22,23,33]. It is reported also that the energy requirements are lower for BDD-anodic oxidation[23,33]. The choice of a technology for the treatment of a particular waste depends not only on technical but also on economical considerations.

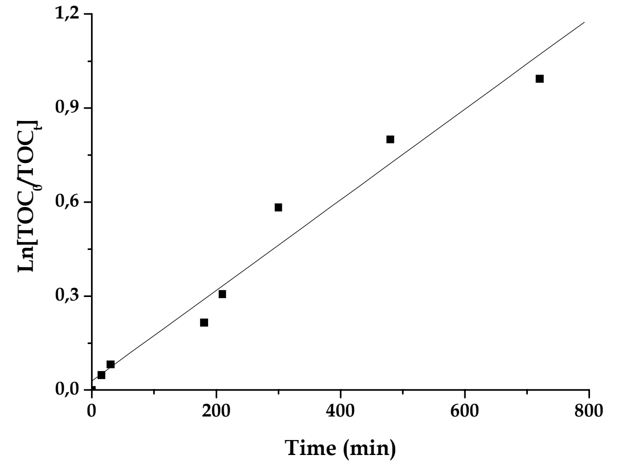

Figure 9: Variation of $Ln\frac{TOC_0}{TOC_t}$ with time during the ozonation treatment of 2-chlorooaniline. Operation conditions. Ozone production: 1 g h^{-1}, T: 25°C, pH: 12

CONCLUSION

The following conclusions can be drawn from the work described here:

(1) Both BDD-anodic oxidation and ozonation lead to 90 % of COD removal of wastewaters polluted with 2-NA and 2-ClA.

(2) Voltammetric results show that the electrochemical oxidation on BDD of 2-NA is more difficult than that of 2-ClA. This can be explained by the withdrawing effect of nitro group.

(3) Carbon dioxide is the final product in the electrochemical treatment of aniline derivatives on BDD using divided electrochemical cell but in addition to carbon dioxide polymeric compounds are formed during the galvanostatic electrolyses using single compartment electrochemical cell.

(4) The electrochemical oxidation on BDD anodes of the aniline derivatives is limited only by mass transport. The COD evolution is linear with specific electrical charge passed at beginning of electrolysis but it becomes exponential for low concentrations.

(5) During ozonation treatment, the COD evolution

with time is in accordance with an exponential law witch can be explained by first-order chemical kinetics.

(6) The choice of a technology for the treatment of a particular waste depends not only on technical but also on economical considerations. It is reported that the energy requirements are lower for BDD-anodic oxidation.

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