

Anodic oxidation of wood painting wastewater on boron-doped diamond electrodes

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Painting industry wastewaters contain some organic compounds that are refractory to biodegradation and must be eliminated by advanced wastewater treatment. Boron-doped diamond (BDD) electrodes exhibit various important characteristics, such as a wide potential window of water stability, chemical resistivity and the tendency to resist deactivation. In this work BDD electrodes were employed for the electrooxidation of organics present in wood painting wastewater. Electrolysis was carried out in an undivided cell under current limited control with a current efficiency of near to 100%. Electrooxidation using the BDD electrode enables to significantly reduce the amount of main organic components in wastewater and chemical oxygen demand (COD) up to 93%. The effectiveness of the electrooxidation slightly depends on pH and decreases with increase in pH. The specific energy consumption amounts to 20–27 kWh/kg COD when the anodic current density is 10–20 mA/cm². Electrooxidation using the BDD electrode can be a promising method for the painting wastewater decontamination.

Key words: BDD electrode, electrooxidation, wood painting wastewater

INTRODUCTION

Wood painting industry produces large amounts of wastewaters (WW), emerging mostly by rinsing of dyeing devices, contaminated by various noxious organic and inorganic compounds. Water based wood paint WW output amounts up to 500 metric tons in Lithuania annually. Since these WW, especially those which possess UV dyestuff, are characterized by a high chemical oxygen demand (COD) and toxicity and in many cases are recalcitrant to biodegradation, other decontamination methods should be employed. Many chemical and physico-chemical methods are known for the treatment of industrial WW, such as oxidation, coagulation, sorption, microfiltration, etc. Their advantages and disadvantages have been reviewed [1]. Some publications refer to the use of Fenton advanced oxidation process [2–6] coagulation [7], electroflocculation [8], nanofiltration [9] for the dyeing WW treatment, which are mostly related to the textile production wastes. One of the shortcomings of these me-

thods is the formation of by-products and sediments, which must be further processed.

Electrochemical oxidation is a promising method for WW treatment due to the possibility of complete mineralization of organics under appropriate conditions. Various types of anode surface materials (SnO₂, PbO₂, TiO₂, RuO₂, boron doped diamond) have been investigated for this purpose [10–14]. Among other electrodes boron-doped diamond (BDD) thin films deposited on p-silicon are characterized by a strong reactivity towards the oxidation of organics. The BDD electrode is distinguished by a high chemical stability and a wide potential window of water discharge. In the last decade BDD was thoroughly investigated as an electrode for organics electrooxidation. Some results of WW treatment using BDD have been summarized [15]. The mechanism and kinetic model of organics oxidation of WW [16–17] and landfill leachate [18–19] on BDD have been presented. Practically full COD reduction by electrooxidation can be achieved [16, 17, 20].

The aim of the present work was to employ the BDD electrode for the anodic oxidation of water-based wood painting WW.

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EXPERIMENTAL

The WW for the investigations was taken from the Lithuanian enterprise Universal Wood Products. The WW results from the cleaning of equipment used for painting of wood products. To separate the suspended solids the WW was pretreated with CaCl_2 , FeCl_3 , $\text{Ca}(\text{OH})_2$, and a flocculant in the plant facilities. The supernatant was employed as WW in our investigation. The main organic paint components that remained in WW are water soluble organic components: 1-butoxy-2-propanol (BP), dipropylene glycol monomethyl ether (mixture of isomers) (DGME), 2-hydroxy-2-methylpropiophenone (HMP), 2-butoxyethanol (BE) and acrylates oligomers (AO), most of them are nominated as harmful.

Electrolysis was carried out in a 300 cm³ polyethylene cell using two BDD anodes 25 × 50 mm and a stainless steel cathode, as shown in Fig. 1. The WW solution was agitated with a magnetic stirrer. BDD/Si one-side coated electrodes were purchased from the NeoCoat company. The BDD-film thickness was 3.45 μm, resistivity 100 mΩ.cm, boron concentration 700 ppm. Electrolysis was carried out at room temperature.

COD of tested solutions was established by the standard potassium dichromate oxidation method, using a Spectroquant TR 320 reactor and a Spectroquant Picco Colorimeter. The accuracy of COD analysis amounted up to ~10%. The biological oxygen demand (BOD_7) was measured using an oximeter Inolab oxi Level 2. The chloride concentration was determined by titration with an AgNO_3 solution, using potassium chromate as an indicator.

GC analysis was performed using a gas chromatograph with mass-sensitive detection (GC/MS) Shimadzu GCMS-QP 2010 (EI ionization) equipped with a 30 m length, 0.25 mm I. D. capillary column RESTEK Rtx-1701. The column temperature program was used as follows: the

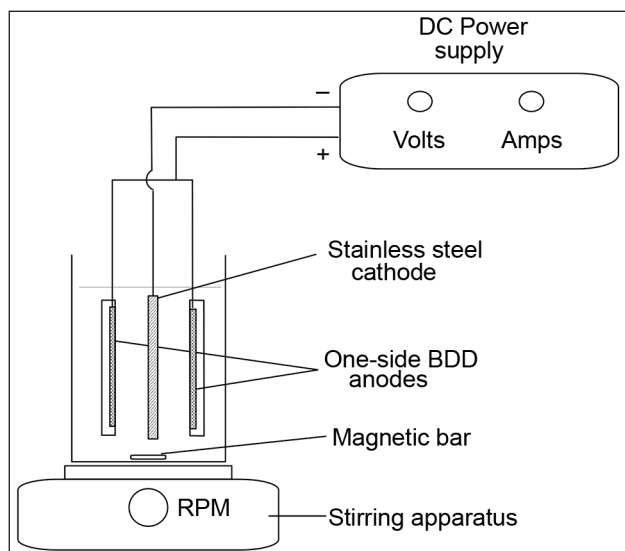


Fig. 1. The diagram of experimental setup. Distance between the cathode and anodes ~1 cm

initial temperature was 40 °C, 2 min, 20 °C/min up to 200 °C, then 50 °C/min up to 250 °C, 2 min. Data acquisition was performed using the software GCMS solution v. 2.71 and ions with m/z 30–400 (TIC) were scanned. Organics were extracted by continuous liquid-liquid extraction using analytical grade methylene chloride. Before the injection the extracted samples were filtered through a silica gel layer to remove salts and polymeric compounds. So the acrylate oligomers were not analyzed.

The elemental composition of cathode samples was investigated using a scanning electron microscope EVO 50 EP (Carl Zeiss) with an INCA INSIGHT energy dispersive spectrometer (Oxford Instruments) at 20 kV.

RESULTS AND DISCUSSION

The properties of wood painting WW treated in this study are presented in Table 1. The ratio of COD and BOD_7 values shows the resistance of WW to biodegradation. Electrooxidation

Table 1. Properties of the wastewater investigated

Chemical oxygen demand (COD), mgO ₂ /L	4 700–5 400*
Biological oxygen demand (BOD_7), mgO ₂ /L	145–180*
pH	6.2
Conductivity, mS/cm	5.5
Chloride, g/L	1.3

* Values slightly changed in the course of time.

on the BDD electrode occurs mainly through highly active, weakly adsorbed hydroxyl radicals [15]. When chloride ions are present in the solution, as is the case in this work, its anodic oxidation gives chlorine



which further produces hypochlorous acid



and next gives hypochlorite ion



Hypochlorite ions also work as an oxidizing agent.

A GC chromatogram of WW methylene chloride extract is depicted in Fig. 2. It reflects the presence of main components of WW and some negligible amounts of other impurities.

Initially electrooxidation was performed in the artificial solutions, containing individual components characteristic to WW. The dyestuff used in the plant was prepared mixing UV lacquers with trade-names WM-1654-0025, WM-2023-0060, WM-80628-112 and 3200-766001 TX099. Each of them possesses water-soluble components: BP, AO (WM-1654-0025), AO, DGME, HMP (WM-2023-0060), BP, AO, HMP (WM-80628-112), BE (3200-766001 TX099). Separate

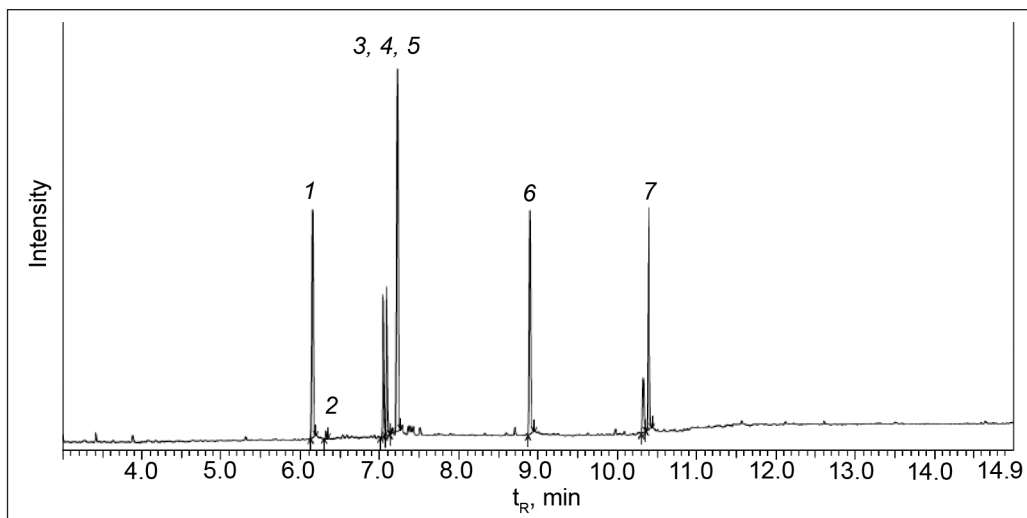


Fig. 2. Chromatogram of methylene chloride extract of the initial (WW) paint wastewater. 1 – 2-butoxyethanol, 2 – 1-butoxy-2-propanol, 3, 4, 5 – dipropylene glycol monomethyl ether (mixture of isomers), 6 – 2-hydroxy-2-methylpropiophenone, 7 – 2,2,4-trimethyl,1,3-pentanediol

lacquers were dissolved in water, the solution formed was further treated with $\text{Ca}(\text{OH})_2$, FeCl_3 to precipitate solids, filtered and then the electrooxidation was carried out as described above.

On the whole, the oxidation rate on BDD depends mainly on the operating conditions. Electrolysis was carried out at the fixed stirring rate. In order to perform the electrochemical mineralization under current limited control with maximum current efficiency the initial limiting current density (I_{lim}^0) for the given initial COD should be estimated. This was achieved measuring the limiting current (I_{lim}) for the anodic oxidation of $\text{Fe}(\text{CN})_6^{4-}$ with a concentration of 50 mol/m^3 in a supporting 1 M NaCl electrolyte and calculating the mass transfer coefficient (k_m) by the relation [17]:

$$k_m = I_{\text{lim}} / FA [\text{Fe}(\text{CN})_6^{4-}], \quad (4)$$

where k_m is the mass transfer coefficient (m/s), I_{lim} is the limiting current (A), $[\text{Fe}(\text{CN})_6^{4-}]$ is the concentration of $\text{Fe}(\text{CN})_6^{4-}$ (mol/m^3), F is the Faraday constant (C/mol) and A is the anode surface area (m^2). The measured I_{lim} was 0.16 A , so $k_m = 1.32 \cdot 10^{-5} \text{ m/s}$. The initial limiting current density at the beginning of electrolysis (i_{lim}^0) was calculated by the following equation [17]:

$$i_{\text{lim}}^0 = 4F k_m \text{COD}^0, \quad (5)$$

where COD^0 is the initial chemical oxygen demand (molO_2/m^3). The lowest COD^0 of the artificial solutions was $93.1 \text{ molO}_2/\text{m}^3$, so $i_{\text{lim}}^0 = 47.4 \text{ mA/cm}^2$. The electrolysis is controlled by the applied current (I_{appl}) when $I_{\text{appl}}/I_{\text{lim}}^0 < 1$. Electrooxidation of artificial solutions was performed at $i = 20 \text{ mA/cm}^2$. The results obtained are shown in Table 2.

Ultimate electrolysis time, adequate to the specific electric charge necessary for full organics mineralization, provided that the current efficiency is $\sim 100\%$, was calculated by the equation:

$$t_u = \text{COD} \cdot 26.8 \cdot V / 8 \cdot 1000 \cdot I, \quad (6)$$

where COD is the chemical oxygen demand, mgO_2/L , 26.8 is the Faraday constant, Ah/g-equiv , V is the electrolyte volume, L , 8 is the equivalent mass of oxygen, g/g-equiv , 1000 is the conversion number, mg/g , I is the current applied, A .

Using the ultimate electrolysis time (h), the mineralization calculated for the maximal COD ($3250 \text{ mgO}_2/\text{L}$) reaches $90\text{--}93\%$. Further electrolysis diminishes the residual COD negligibly by 7 to 9% . The results of WW electrolysis under analogous conditions are shown in Table 3. In this case the

Table 2. COD (mgO_2/L) evolution in the artificial solutions during electrooxidation with the BDD anode. Current applied 0.5 A , current density 20 mA/cm^2 . Background electrolyte $0.01 \text{ M Na}_2\text{SO}_4$, Soln. volume $V = 230 \text{ ml}$

Main components of the artificial solution	Electrolysis time, h				
	0	1	2	3	5
2-butoxyethanol (3200–766001 TX099)	2980	2450	1770	1110	210
1-butoxy-2-propanol, acrylates oligomers, 2-hydroxy-2-methylpropiophenone (WM-80628-112)	3000	2380	1720	1100	280
1-butoxy-2-propanol, acrylates oligomers (WM-1654-0025)	2900	2300	1770	1010	300
Dipropylene glycol monomethyl ether, 2-hydroxy-2-methylpropiophenone, acrylates oligomers (WM-2023-6060)	3250	2650	2060	1350	340

Table 3. COD removal from WW solution during electrooxidation with the BDD anode. Current applied 0.5 A, current density 20 mA/cm². Background electrolyte 0.01 M Na₂SO₄. Soln. volume V = 230 ml

COD, mgO ₂ /L	Electrolysis time, h					
	0	1	2	4	6	8.2
Experimental	5330	4700	4050	2740	1460	380
Theoretic eq. (7)		4680	4030	2731	1431	~0

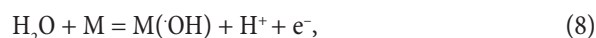
COD removal rate also reaches ~93%. i_{lim}^o calculated by the relation (Eq. 5) at the initial COD^o of 5330 mgO₂/L is 84.8 mA/cm², so $I_{appl}/I_{lim}^o = \alpha = 0.236$. When the electrolysis runs under current limited control ($\alpha < 1$), according to Kapalka et al. [17]

$$COD(t) = COD^o (1 - \alpha A k_m t/V), \quad (7)$$

where COD(t) is COD in a time t, s, $\alpha = I_{appl}/I_{lim}^o$, A is the anode area, m², V is the electrolyte volume, m³. COD evolution (Table 3) shows good accordance of experimental and theoretical data. However, at the final electrolysis stage COD removal runs slowly, evidently, out of current limited control, in addition, some compounds may be resistant to electrooxidation. The straight-line COD removal dependence on the electrolysis time was determined in the current density range of 10–40 mA/cm² (Fig. 3), when electrolysis was carried out to t_u (Eq. 6). The COD removal rate in this range reaches 90–95%, but it slightly decreases with increase in current density. During further electrolysis the COD reduction was negligible. BOD₇ after electrolysis was 21 mgO₂/L. So the ratio COD/BOD < 2.5 shows that the treated WW is favourable for biodegradation. The remaining chloride concentration amounts to 0.22 g/L. The GC chromatogram of the methylene chloride extract of electrooxidated WW showed no peaks specific to BE, DGME, HMP and BP compounds.

After the electrolysis, the stainless steel cathode was covered with a thin layer of white precipitate. The precipitate was dried and analysed by using a scanning electron

microscope and CaCO₃ was identified. Evidently, calcium ions, present in WW due to the pretreatment operation, react with the OH⁻ ions, formed at the cathode during electrolysis, giving hardly soluble Ca(OH)₂. By the desiccation Ca(OH)₂ reacts with carbon dioxide and CaCO₃ salt is formed. pH of the electrooxidated WW solution amounts to 2.3–2.4. The acidification is determined by the formation of protons during electrooxidation, according to the generally accepted mechanism [16]:



where M is anode active sites, R is organic pollutants, x and y are the stoichiometric coefficients. The cathode reaction is



As the part of OH⁻ ions is neutralized by calcium ions, the solution becomes acidic. The COD removal rate slightly depends on pH and decreases with increase in pH (Table 4).

Table 4. Dependence of the COD removal rate (RR) on pH. The initial COD of WW solution was ~4800

pH	2	4	6	9	10	12
RR, %	94	93	93	90	90	87

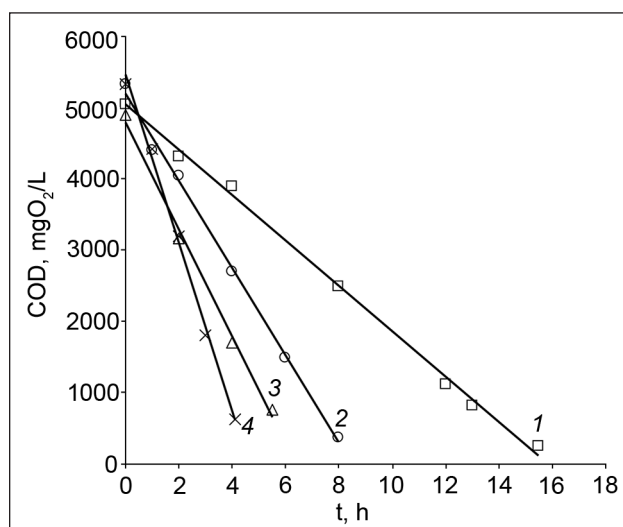


Fig. 3. COD evolution in a WW solution vs electrolysis time. Background electrolyte 0.01 M Na₂SO₄. Current density (mA/cm²): 1 – 10, 2 – 20, 3 – 30, 4 – 40

Specific energy consumption (E_s , kWh/kg COD) depends on the current applied, which controls the cell voltage. E_s was calculated by the equation:

$$E_s = ItU1000/(COD^o - COD_t) V, \quad (11)$$

where I is the applied current, A, t is the electrolysis time, h, U is the cell voltage, V, COD^o and COD_t are the initial COD and COD at the time t, respectively, mgO₂/L, V is the solution volume, l. Fig. 4 shows the dependence of E_s and U on the anodic current density. E_s and U increase by the increase of current density. Performance of electrooxidation at lower current densities is more beneficial, though it takes more time. On the whole, the cost of electricity used is comparable to the price of chemicals, required for other treatment methods. The appliance of BDD is limited by its high cost, though, by the progress of electrooxidation method, BDD production will lower in price.

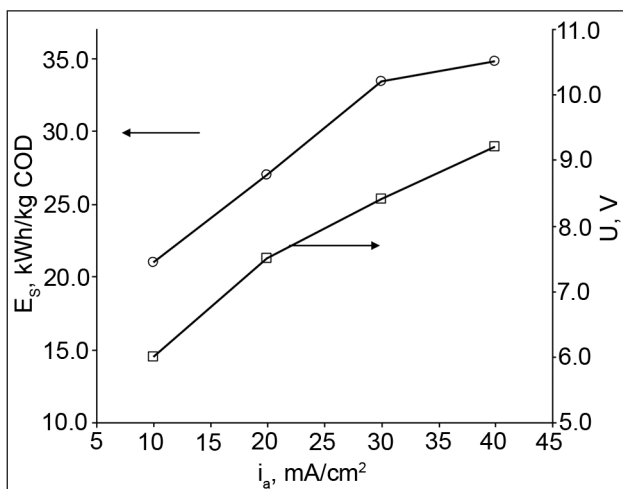


Fig. 4. Dependence of cell voltage and specific energy consumption on the anodic current density. pH of WW solution 6. Background electrolyte 0.01 M Na_2SO_4

CONCLUSIONS

Electrooxidation of water-based wood painting wastewater using the BDD electrode enables to significantly reduce the amount of main organic components and COD up to 93%. When electrolysis is carried out under current limited control ($I_{\text{appl}}/I_{\text{lim}}^0 < 1$), there is a straight line COD dependence on the electrolysis time till the COD reaches 7–8% of the initial value. During further electrolysis the COD diminishes negligibly. The effectiveness of the electrooxidation slightly depends on pH and decreases with increase in pH. The specific energy consumption amounts to 20–27 kWh/kg COD when the anodic current density is 10–20 mA/cm². Electrooxidation using the BDD electrode can be a promising method for the painting wastewater decontamination.

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DAŽŲ NUOPLOVŲ, TURINČIŲ ORGANINIŲ JUNGINIŲ, NUKENKSMINIMAS NAUDOJANT BORU LEGIRUOTĄ DEIMANTINĮ ELEKTRODĄ

Santrauka

Dažymo įrenginių nuoplovose esantys organiniai junginiai lemia šių vandenų atsparumą biologiniam nukenksminimui. Darbe apdorojant tokius vandenius buvo pasirinktas anodinis oksidavimas, naudojant boru legiruotus deimantinius elektrodus (BLD). BLD elektrodai pasižymi plačiu elektrocheminio vandens skaldymo potencialų intervalu, cheminiu inertiškumu ir atsparumu pasyvacijai. Nukenksminimo efektyvumas buvo kontroliuojamas sekant cheminio deguonies sunaudojimo (ChDS) kitimą nuotėkose bei analizuojant organinių junginių kiekio kitimą dujų chromatografijos metodu. Elektrolizė naudojant BLD elektrodus įgalino akivaizdžiai sumažinti organinių junginių kiekius nuotėkose, o ChDS dydį – apie 93 %. Nukenksminimo efektyvumas mažėja didinant terpės pH. Energijos sąnaudos siekia 20–27 kWh/kg ChDS, kai anodinis srovės tankis 10–20 mA/cm². Elektros oksidavimas naudojant BLD elektrodus gali būti sėkmingai naudojamas nukenksminant nutekamuosius vandenius.