Veratric acid removal from water by electrochemical oxidation on BDD anode

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Abstract: The efficiency of boron doped diamond (BDD) in the electrochemical treatment of synthetically contaminated water with veratric acid (VA), one kind of polyphenolic type compounds, is investigated in this work. A BDD electrode was practically fabricated using hot filament chemical vapor deposition (HFCVD). Later on, the BDD electrode was implemented as an anode in a batch electrolytic reactor. The effect of operating factors such as the initial concentration of VA, NaCl addition, and supporting electrolyte type (H2SO4, H3PO4 and Na2SO4) was studied. The chemical oxygen demand (COD) measurements were conducted to study the VA electrolysis kinetics. The experimental data suggested that sodium sulfate was the best supporting electrolyte as the COD removal reached a percentage of 100% using 1 mmol/dm3 as VA concentration. The kinetics of the COD decay of the VA electrolysis were found to obey the pseudo-first order model. Remarkably, the electrolysis process is significantly speeded up once chloride is added to the reaction. The complete COD removal was achieved in 60 minutes of treatment.

Keywords: Boron-doped diamond electrode, Electrochemical oxidation, Veratric acid, wastewater, Advanced oxidation processes

1. Introduction

Industrial effluents containing organic and refractory pollutants raise the call for efficient wastewater treatment methods. The increasing interest in such methods is due to the environmental damage and water quality deterioration caused by these pollutants [1]. Therefore, wastewater has to be treated before it is discharged into the drainage system [2]. A variety of conventional wastewater treatment methods have been reported in literature such as physical, chemical, and biological methods [3]. However, these methods have limitations in their operation. Biological processes need long hydraulic detention time and large reactor volumes [4]. Physical and chemical methods necessitate the handling of the large volume of sludge produced [5]. In this framework, electrochemical processes offer good opportunity for the remediation of recalcitrant and persistent organic pollutants [6-8]. Electrochemical technologies have emerged as novel treatment technologies for the elimination of broad-range organic contaminants from water. The most
important advantages of electrochemical methods for the treatment of wastewater are their high efficiency, mild operating conditions, ease of automation, versatility, and low cost [9]. Anodic oxidation of organic pollutants is guaranteed by different types of electrodes on which pollutants are directly destroyed by the free hydroxyl radicals produced on their surface [10]. This anodic oxidation might lead to complete mineralization of the organic contaminants [11]. Among the different electrodes used, boron-doped diamond (BDD) electrodes possess novel and intrinsically outstanding properties with comparing to conventional electrodes such as glassy carbon, graphite or platinum. The BDD electrodes have a large potential window in aqueous solution with low background currents [12-14]. In addition, the BDD electrodes possess distinct physical properties including: high hardness, low environmental impact, high hole mobility, high thermal conductivity and excellent resistance to radiation damage [11]. Souza et al. tested the electrooxidation of phenol on the surface of BDD anode and reported significant COD removal from water samples [15]. Similarly, Carvalho de Almeida et al. treated Brazilian petrochemical effluents by anodic oxidation on BDD [16]. Results clearly showed that BDD promotes complete COD removal (98%) due to the high amounts of effective hydroxyl radicals and peroxodisulfates generated from water oxidation. Errami et al. treated wastewater Industrial Cartons electrochemically using a BDD electrode [17]. Medeiros de Araújo et al. studied the influence of the mediated oxidation on the removal of rhodamine B (xanthene dye) solutions with conductive-diamond electrochemical oxidation and reported total removal of organic pollutants [18]. It is true that the performance of the electrolysis process depends strongly on the type of electrode used as previously mentioned. However, further enhancement can be achieved by adding a supporting electrolyte or salt to the electrochemical cell not only to increase the solution conductivity, but also to reduce the cell potential in order to make the electrochemical process feasible in terms of energy consumption [15].

This work focuses on the electrochemical treatment of synthetically contaminated water with veratric acid VA as a model organic compound found in many wastewater effluents namely: olive mill, pulp and paper, detergent, pesticides, agro- industries and pharmaceutical industries [19]. The VA oxidation was carried out in a laboratory batch reactor provided with a BDD electrode. The experimental assays were conducted to study the kinetics of VA oxidation as well as to figure out the effect of different chemical reaction operating factors such as the electrolyte type, NaCl addition and the initial concentration of VA. Up to our best knowledge, one similar study [20] has targeted and approached this topic. However, it does not explore the effect of VA initial concentration as well as the effect of supporting electrolytes other than sulfate-containing supporting electrolytes.

2. Materials, methods and devices
2.1.Materials

Synthetically polluted water with VA samples were prepared by dissolving VA C₉H₁₀O₄ (Fig. 1) in distilled water in three different concentrations (1 mmol/dm³, 2 mmol/dm³, and 3 mmol/dm³). Three supporting electrolytes were used: sodium sulfate Na₂SO₄ (50 mmol/dm³ - Sigma Aldrich), sulfuric acid H₂SO₄ (50 mmol/dm³ - Sigma Aldrich) and phosphoric acid H₃PO₄ (50 mmol/dm³ - Sigma Aldrich). Sodium chloride NaCl (Sigma Aldrich) was added to water (10 mmol/dm³).
2.2. Laboratory-scale experimental set up

Electrode preparation

The electrode substrate used in this work is made of an expanded grid of Niobium having a circular shape. The grid has a thickness of 2.8 mm and diameter of 90 mm. The expanded grid niobium, as opposed to sheets, is well flown through because of its open geometry of both gas bubbles and from the medium to be cleaned. Moreover, due to the high ratio of surface area to mass, the price per electrode substrate surface is relatively low.

The diamond coated electrodes on niobium substrate were produced by a hot filament chemical vapor deposition (HFCVD) process. Niobium substrates were pretreated by sand blasting in order to roughen the surface and therefore to enhance the adhesion strength between diamond and substrate, and meanwhile, the specific surface area was increased to expectably improve the electrochemical performance. The sand blasting was followed by twice ultrasonic cleaning in ethanol. Afterwards the substrates were seeded by ultrasonic seeding in a diamond powder suspension. The CVD-diamond coating took place in a CVD hot filament coating machine CC800/8 DIA with 1% methane CH₄ and a small amount of trimethyl borate B(OCH₃)₃ to enhance the electrical conductivity of diamond by boron-doping. The niobium grid was coated on both sides using two parallel filament rows for 50 hours. The film thickness measured in cross sections is 8 μm according to an identical test process. The surface topography, roughness, the grain size perpendicular to the growth direction and the morphologies of the diamond films were characterized using Scanning Electron Microscopy.

Electrochemical reactor

The experiments were performed in a batch electrochemical plexiglas reactor of 1000 cm³ supplemented with two BDD electrodes separated by a distance of 2 mm and they have each a total area of 65 cm². The reactor was connected to an external DC digital power supply with maximum output current and voltage of 6 A and 30 V. The working current density was 50 mA/cm² applied for a maximum process time of 350 min.

Analytical procedures
The electrooxidation assays were run to test three operating factors: supporting electrolyte type, NaCl addition, and initial VA concentration. Samples were withdrawn at regular time intervals and collected in 20 cm$^3$ glass vials. All withdrawn samples were characterized by the following procedures:

The chemical oxygen demand (COD) experimental values of treated samples were determined using dichromate standard method [21]. Each sample was introduced into commercially available digestion solution containing potassium dichromate (Hach-Germany), afterward; the solution was incubated at 148 °C for 120 minutes in a COD reactor (Hach Lange GMBH-Germany). COD measurements were performed by a spectrophotometer (DR Lange Lasa 100 Germany). Complete mineralization of VA was detected by UV spectrophotometry (UV-3600/UV-VIR spectrophotometer Shimadzu). The pH was measured using Jenway 3540 pH/conductivity meter. All samples prepared in this work have an initial pH in the range of 5.5 to 6.8.

**Determination of the rate constant**

In order to compare the kinetics of COD removal using the three supporting electrolytes, the pseudo-first order rate constant ($k$) was determined with exponential regression and least square method. The rate constant was determined based on the following equation [22]:

$$COD = COD_0 \ e^{-kt}$$

Where $COD_0$ is the initial chemical oxygen demand at the beginning of the electrolysis process. COD is the chemical oxygen demand at time $t$. $k$ is the electrolysis rate constant. $t$ is the time of electrolysis.

**Determination of the energy consumption during electrolysis**

During the experiments carried out using the three different supporting electrolytes namely, H$_2$SO$_4$, H$_3$PO$_4$, and Na$_2$SO$_4$, the current was kept constant at 50 mA/cm$^2$. The specific energy consumption using each supporting electrolyte was calculated in kWh consumed per kg COD removed according to the following equation:

$$\text{Energy consumption (kWh/kg COD removed)} = \frac{A \times V \times t}{v \times \Delta COD}$$

Where $t$ is the time of electrolysis (h); $V$ and $A$ are the average cell voltage and the electrolysis current; $v$ is the reactor volume (dm$^3$), and $\Delta COD$ is the difference between the initial COD value at process time zero and the COD value at the end of the process time (mg O$_2$/dm$^3$).

### 3. Results and discussion

#### 3.1. Testing BDD prepared electrode

Scanning electron microscopy (SEM) images and Raman spectrum of the BDD layers deposited on niobium substrate are shown in Fig. 2. The visible roughness (Fig. 1 (a, b)) of several micrometers is a result of surface roughening pretreatment of the metallic substrate surfaces. The diamond layer surface shows well (111)-faceted crystals with an average grain size of 0.6 ± 0.3 μm and the diamond thickness is around 6-8 μm. Importantly, no cracks or holes were observed and the peeling occurrence did not take place which indicates the high quality of coating process, accordingly, the electrodes area completely contributes in the electrochemical oxidation (high efficiency factor).
The quality of BDD layers deposited on niobium substrate was tested employing Raman analyses. The Raman spectrum of the diamond films (Fig. 1(c)) reveals a sharp peak at 1340 cm\(^{-1}\) that is usually associated with diamond sp\(^3\) bonding. The boron could not be detected and has not appeared in the Raman spectrum due to its low content. What is worth to be mentioned in the Raman spectrum is the broad peak with maximum at 1500 cm\(^{-1}\). This peak is assigned to C–H chains and is a typical feature of the Raman spectrum of nanocrystalline diamond (Fabisiak et al. 2006). The absence of other amorphous carbon or sp\(^2\) graphite peaks that usually appear in the range between 1450 cm\(^{-1}\) and 1600 cm\(^{-1}\) is an evidence that BDD layers can be considered as phase-pure (high quality) diamond material.

3.2. Veratric acid removal using anodic oxidation with BDD

Effect of supporting electrolyte on COD abatement during electrolysis

The efficiency of electrolysis depends on the generation of oxidants during the process time. Therefore, adding supporting electrolytes along with raw wastewater is a common approach to increase electrolyte conductivity, reduce energy consumption, and organize mass transport by electrical migration [23]. Supporting electrolytes, such as Na\(_2\)SO\(_4\), KCl, Na\(_2\)NO\(_3\), H\(_3\)PO\(_4\) and NaCl are frequently reported in literature [7, 10].

The aim of this part is to study the effect of three supporting electrolytes namely, Na\(_2\)SO\(_4\), H\(_2\)SO\(_4\), and H\(_3\)PO\(_4\) on the rate of COD abatement. Fig. 3 shows that complete COD removal was attained using Na\(_2\)SO\(_4\) at an applied current density of 50 mA/cm\(^2\) which is in accordance with the findings of Medeiros de Araújoa et al. [18] and Ealaoud et al. 2011 [20]. Therefore, Na\(_2\)SO\(_4\) is a more active supporting electrolyte than either H\(_2\)SO\(_4\) or H\(_3\)PO\(_4\). H\(_2\)SO\(_4\) was less effective than Na\(_2\)SO\(_4\) although both can produce peroxodisulfate under anodic oxidation conditions. Serrano et al. [24] reported that peroxodisulfate can be importantly electrogenerated in concentrated H\(_2\)SO\(_4\) (>2 M) upon reaction of HSO\(_4\) with hydroxyl radicals on BDD [23]. The later condition is not valid for the present study since H\(_2\)SO\(_4\) was used with a concentration of 50 mmol/dm\(^3\). In addition, it can be observed that H\(_3\)PO\(_4\) is the weakest among the three tested electrolytes. Cañizares et al. [25] indicated that peroxodiphosphate is optimally electrogenerated at pH in the range of 12-13. Fig. 2
also illustrates that COD decreases exponentially with the electrochemical oxidation time following a pseudo first order model as was also reported by [15].

![Graph showing COD vs Electrolysis time for different electrolytes](image)

**Fig. 3. Chemical oxygen demand (COD) variation with electrolysis time of three supporting electrolytes (H₂SO₄, H₃PO₄ and Na₂SO₄) for veratric acid (VA) electrolysis on boron doped diamond anode. The electrolyte concentration was 50 mmol/dm³ and veratric acid concentration was 2 mmol/dm³, the applied current density was 50 mA/cm².**

The pseudo-first order rate constant (k) values of the electrolysis process of veratric acid with the three different supporting electrolytes are illustrated in Fig. 4. The rate constants for Na₂SO₄, H₂SO₄, and H₃PO₄ were 0.016, 0.007, and 0.005 min⁻¹ respectively. The correlation coefficient was greater than 0.95 in all cases. The sulfate-containing supporting electrolytes showed higher rate constants comparing to phosphate-containing electrolyte. Consequently, sulfuric acid and sodium sulfate are more efficient than phosphoric acid in stimulating COD removal. The highest k value (0.016 minutes⁻¹) was obtained using Na₂SO₄ with a COD removal of almost 100%. This finding could be attributed to the strong oxidizing power of electrogenerated persulfate which are most probably formed due to the important overpotential for oxygen evolution on BDD anode [26].
Fig. 4. The pseudo first order rate constants \( (k) \) of the 2 mmol/dm\(^3\) veratric acid samples with three supporting electrolytes: \( \text{Na}_2\text{SO}_4 \), \( \text{H}_2\text{SO}_4 \), \( \text{H}_3\text{PO}_4 \).

**Fig. 5.** Shows the effect of supporting electrolyte nature on energy consumption during electrolysis time. The changes in specific energy consumption indicated that conducting electrochemical oxidation of VA using \( \text{Na}_2\text{SO}_4 \) as conductive electrolyte has the lowest energy requirements. In other words, the \( \text{Na}_2\text{SO}_4 \) showed the lower energy consumption with the highest % COD removal. Consequently, a reduction in the treatment cost using \( \text{Na}_2\text{SO}_4 \) was expected, as shown in Table 1.

Taking into consideration the electrical energy cost of about US$ 0.15 (U.S. currency) per kWh, the monetary value reported in Table 1 and required to degrade a unit volume (1 dm\(^3\)) of effluent.
Fig. 5. The effect of supporting electrolyte nature on specific energy consumption

Table 1 Cost required for electrochemical treatment of water contaminated with VA (2 mmol/dm$^3$) using different supporting electrolytes.

| Type of electrolyte | Cost (US$/m$^3$ treated) |
|---------------------|--------------------------|
| H$_2$SO$_4$         | 16.2                     |
| H$_3$PO$_4$         | 16.2                     |
| Na$_2$SO$_4$        | 8.1                      |

Effect of veratric acid initial concentration on COD removal during electrolysis on B
As organic aromatic compounds exist in wastewater at different concentrations, a second stage of the experiment was conducted to explore the impact of veratric acid initial concentration on the rate of oxidation on BDD anode. As depicted in Fig. 6, it is obvious that higher veratric acid initial concentration necessitates longer treatment times. However, the pseudo-first order rate constant $k$, which is determined as previously mentioned by exponential regression and least square method, has almost the same average value (0.016 minutes$^{-1}$) for the three veratric acid concentrations. Hence, The COD kinetics are independent on VA initial concentration.
Fig. 6. COD variation with electrolysis time at three different initial concentrations (1 mmol/dm³, 2 mmol/dm³, 3 mmol/dm³) of VA. Conditions: Na₂SO₄ concentration was 50 mmol/dm³ and the applied current density was 50 mA/cm². Solid line represents the fitting to the pseudo-first order equation (COD=COD₀ e⁻kt).

**Effect of the presence of chloride ions on VA oxidation**

The impact of chloride ions on COD abatement rate was investigated by adding the NaCl (10 mmol/dm³) to three solutions containing different VA concentrations (1 mmol/dm³, 2 mmol/dm³, 3 mmol/dm³) with Na₂SO₄ as supporting electrolyte. Fig. 6 (a, b and c) shows the effect of NaCl on COD variation with electrolysis time with the three VA concentrations. By comparing the curves of the COD with and without Cl⁻, it is obvious that the chloride ions increased the rate of COD abatement, which means that Cl⁻ enhanced the kinetics of VA oxidation. The most reasonable explanation is that the Cl⁻ generates supporting oxidants as hypochlorite ions and enhance the oxidation of organic compounds via electrolysis [6, 15, 26]. Moreover, the allowable concentration of Cl⁻ (7 mmol/dm³) set by EPA regulations for treated wastewater is not even exceed in this work (less than 6 mmol/dm³). Under the current experimental conditions namely acidic medium and low working current density (50 mA/cm²), the occurrence of perchlorate can be fully neglected and should not be a concern. It has been reported in the literature [27] that the generation of perchlorates is non promoted at pH less than 10 and current densities as low as 30 mA/cm² for 5844 mg/dm³ NaCl solution. In our case, the NaCl concentration is 10 mmol/dm³ which is ten times less than the aforementioned concentration and the medium is acidic which does not favor the perchlorate formation as stated. Finally, the current density used was in the range of 50 mA/cm², which is considered as previously mentioned a low density that does not support perchlorate ions production [27].
Fig. 7. COD variation with increasing electrolysis time of veratric acid solutions in three concentrations (1 mmol/dm$^3$, 2 mmol/dm$^3$ and 3 mmol/dm$^3$) with and without presence of chloride anions (Cl$^-$). Each solution contains 600 mg/dm$^3$ of Cl$^-$. 

In order to verify that VA was completely mineralized by electrolysis on BDD with no accumulation of aromatic intermediates in water, the UV spectra time evolution of VA during electrolysis was studied with UV-VIS spectrophotometry. The results are shown in Fig. 8. First, it has been shown that VA has three different $\lambda_{\text{max}}$ when it was analyzed using UV-VIS spectrophotometer which are: 218, 262, 295 nm [28]. In the range of analysis illustrated in Fig. 8, only one peak (295 nm) of VA appears in the figure. This absorption peak disappears completely and the curve is flattened after almost 3 hours of electrolysis. Hence, this is also an additional indicator of the removal of VA from water under the operating conditions mentioned in Fig. 7. In other words, during electrolysis the absorbance peak has decreased with time until it was disappeared completely after 4 hours which suggests that there was no remaining intermediates in water. This observation is consistent with the results reported by Elaoud et al. 2011 [20].
**Fig. 8.** Time evolution of the UV-VIS spectrum during electrolysis of 3 mmol/dm$^3$ of veratric acid at a current density of 50 mA/cm$^2$ measured with UV-VIS spectrophotometer.

### 4. Conclusion

Applications of boron doped diamond (BDD) as efficient anode in electrochemical treatment of organics-contaminated water are studied. It can be reported that electrochemical oxidation using BDD anode is an excellent method for wastewater treatment namely for effluents contaminated with veratric acid. Moreover, the experimental results indicated that the use of supporting electrolytes could considerably enhance the oxidation process and shorten the treatment time needed for complete oxidation of veratric acid, which in turn has direct effect on the total energy consumption. The sulfate-containing supporting electrolytes showed the fast kinetics. The maximum kinetic constant (0.016 minute$^{-1}$) was observed when Na$_2$SO$_4$ was added to water samples. Finally, it was found that further acceleration in the oxidation rate of VA can be achieved by adding chloride to the supporting electrolyte. The addition of chloride had greatly increased the process kinetics as complete oxidation of VA was achieved after about 60 min where 100 min were needed in the absence of chlorine.

### References

[1] Panizza M., Bocca C., Cerisola G. 2000 Electrochemical treatment of wastewater containing polyaromatic organic pollutants. wat. res. 9, 2601.
[2] US EPA, Title 40: Protection of Environment: Part 432- Meat and poultry products point source Category, e-CFR Data, 2009.
[3] Bevilaqua J.V., Cammarota M.C., Freire D.M., Santa'Anna G.L. 2002 Phenol removal through combined biological and enzymatic treatments. Braz. J. Chem. Eng. 19, 151.
[4] Siringi D., Home Dr., Chacha J., Mulimi L. 2013 Wastewater Remediation Using Electrochemically Produced Layered Double Hydroxides. International Journal of Engineering and Innovative Technology. 2, 61.
[5] Asselin M., Drogui P., Benmoussa H., Blais JF. 2008 Effectiveness of electro coagulation process in removing organic compounds from slaughterhouse wastewater using monopolar and bipolar electrolytic cells. Chemosphere. 72, 1727.
[6] Martínez-Huitle C. A., Ferro S. 2006 Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes. Chem. Soc. Rev. 35, 1324.
[7] Martínez-Huitle C.A., Brillas E. 2009 Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. A general review. Appl. Catal. B: Environ. 87, 105.
[8] Carlas A., Martínez H., Brillas E. 2008 Electrochemical Alternatives for drinking water Disinfection. Angandeta chemi. 47, 2.
[9] Martínez-Huitle C. A., Rodrigo M.A, Sirés I., Scialdone O. 2015 Single and Coupled Electrochemical Processes and Reactors for the Abatement of Organic Water Pollutants: A Critical Review. Chem. Rev. DOI: 10.1021/acs.chemrev.5b00361.
[10] Brillas E., Martínez-Huitle C. A. 2015 Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review. Appl Catal B: Environ. 166-167, 603.
[11] Alfaro M.A., Ferro S., Martínez-Huitle C.A., Vong Y. M. 2006 Boron Doped Diamond Electrode for the Wastewater Treatment. J. Braz. Chem. Soc. 17, 227.
[12] Martínez-Huitle C.A., Brillas E. 2008 Electrochemical Alternatives for Drinking Water Disinfection. Angew. Chem. Int. Ed. 47, 1998.
[13] I. Jum'h , M. AL-Addous , H. AL-Taani , M.S. ABD El-Sadek , N. Ayoub, 2017 Effect of boron concentration on nano-crystalline diamond deposited on niobium substrate. Digest Journal of Nanomaterials and Biostructures Vol. 12, No. 2, 589.
[14] Inshad Jum’h, Arwa Abdelhay, Hussein Al-Taani, Ahmad Telfah, Mohammad Alnaief, Stefan Rosiwal, 2017. Fabrication and application of boron doped diamond BDD electrode in olive mill wastewater treatment in Jordan, Journal of Water Reuse and Desalination, Vol. 7,No. 4, 502.
[15] Souza A., Beraldo R., Ruotolo M., Augusto L. 2013 Phenol Electrooxidation in Different Supporting Electrolytes Using Boron-Doped Diamond Anodes. Int. J. Electrochem. 8, 643.
[16] Carvalho de Almeida C., Fernandes da Costa P. R., Juliene de Macedo Melo M., Vieira dos Santos E., Martinez-Huitle C. A. 2014 Application of Electrochemical Technology for Water Treatment of Brazilian Industry Effluents. J. Mex. Chem. Soc. 58(3), 276.
[17] Errami M., Salghi R., Zarrouk A., Zougagh M., Zarrok H., Hammouti B., Al-Deyab S. 2013 Electrochemical Treatment of Wastewater Industrial Cartons. Int. J. Electrochem. 8, 12672.
[18] Medeiros de Araújoa D., Sáezb C., Martínez-Huitlea C.A., Cárizaresb P., Rodrigob M.A 2015 Influence of mediated processes on the removal of Rhodamine with conductive-diamond electrochemical oxidation. Appl Catal B: Environ. 166-167, 454.
[19] De Heredia J.B., Torregrosa J., Dominguez J.R., Peres J.A. 2001 Kinetic model for phenolic compound oxidation by Fenton’s reagent. Chemosphere. 45, 85.
[20] Elaoud S. C., Panizza M., Cerisola G., and Mhiri T. 2011 Veratric acid treatment by anodic oxidation with BDD anode . J Chem Techno Biotechnol. 87, 381–386.
[21] Dedkov Y. M., Elizarova O. V., Ke’ina S. Y. 2000 Dichromate Method for the Determination of Chemical Oxygen Demand. Journal of Analytical Chemisto. 55, 777.
[22] Mouden O., Errami M., Salghi R., Zarrouk A., Assouag M., Zarrok H., Al-Deyab S., Hammouti B. 2012 Electrochemical degradation of difenoconazole on BDD electrodes. J. chem. pharm. res. 4, 3437.
[23] Ajeel M. A., Aroua M. K., Ashri Wan Daud W.M. 2015 Anodic Degradation of 2-Chlorophenol by Carbon Black Diamond and Activated Carbon Composite Electrodes. Electrochimica Acta. 180, 22–28
[24] Serrano K., Michaud P.A., Comninellis C., Savall A. 2002 Electrochemical preparation of peroxodisulfuric acid using boron doped diamond thin film electrodes. Electrochimica Acta 48, 431.
[25] Cañizares P., Larrondo F., Lobato J., Rodrigo M. A., Sáez C. 2005 Electrochemical Synthesis of Peroxodiphosphate Using Boron-Doped Diamond Anodes J. Electrochem. Soc. 152, 191.
[26] Bouhssine I., Tazi A., Azzi M. 2013 Treatment of olive mill wastewater by electrolysis on boron doped diamond (BDD) electrode. J. Mater. Environ. Sci. 4, 354.
[27] Sánchez-Carretero A., Sáez C., Cañizares P., Rodrigo M.A. 2011 Electrochemical production of perchlorates using conductive diamond electrolysis. Chem. Eng. J. 166, 710.
[28] Robbins R. J. 2003 Phenolic Acids in Foods: An Overview of Analytical Methodology. J. Agric. Food Chem. 51, 2866.