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APPLYING THE BDD ELECTRODE IN THE PROCESS OF REMOVING PHARMACEUTICALS BY ELECTROCHEMICAL OXIDATION

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Abstract: *Pharmaceuticals and their metabolites are inevitably emitted into the waters. The adverse environmental and human health effects of pharmaceutical residues in water could take place under a very low concentration range; from several µg/l to ng/l. These are challenges to the global water industries as there are no enough efficient processes for removing these pollutants. An efficient technology is thus sought to treat these pollutants in water and wastewater. Research involving electrochemical oxidation of emerging contaminants using BDD electrode is relatively new and more relevant information is still needed to obtain the desired result. The present work reports experimental results of the electrochemical oxidation of Ibuprofen (Ibu) solutions using boron-doped synthetic diamond (BDD) electrode. Electrochemical characterization of Ibu in a solution of 0,05 M Na_2SO_4 using cyclic voltammetry (CV) and the results of Ibuelectro oxidation using BDD electrode with current density of 30 mA /cm^2 during 6 hours were shown. By using UV-VIS spectrophotometry and determination of Chemical Oxygen Demand (COD) decrease of the initial Ibu concentration has been shown, from 375 mg/l to 70 mg/l or 81,4% and decrease of COD value from 960 mg O_2/l to 210 mg O_2/l or about 78%, with a specific charge of 36 A h/l.*

Keywords: *BDD electrode, ibuprofen, electrochemical oxidation*

INTRODUCTION

The main source of water resources contamination withpharmaceutical products (PPs) are humans and animals treated with different medicaments. In the case of human consumption, it depends on the location of consumers such as private households, hospitals, schools or retirement facilities. Their main route of entry to the aquatic environment is through excretion and wastewater cycle. Nevertheless, expired PPs are also often discarded and may find their way to the environment via landfill leachate and/or wastewater effluent [1]. It has been found out in a survey conducted in South Eastern England that 63.2% of the people disposes unwanted or expired pharmaceuticals in the household waste, 21.8% returns them to pharmacists and 11.5% empties them into the sink or toilet. A small percentage takes them to municipal waste sites that have special waste facilities [2]. Consequently, there are efforts to mitigate this problem by the proper disposal of unused pharmaceuticals. In Europe, drug take-back programs for expired pharmaceuticals are established [3]. This means that it is necessary for the member states of the European Union (EU) to make sure that appropriate collection systems are available for unused or expired pharmaceuticals [4].

Pharmaceuticals taken up by humans or animals are generally absorbed and are subjected to biodegradation/metabolism inside the body. This process alters the chemical structure of the active molecules, which often results in a change in the physicochemical and pharmaceutical properties. Incomplete metabolism in the body and subsequent excretion may lower or enhance water solubility [5]. The pharmaceuticals and their bioactive metabolites thus continually enter the aquatic environment as excretion via urine or feces into raw sewage, either treated or untreated [6]. A study conducted by Castiglioni et al. [7] about the removal of pharmaceuticals in six sewage treatment plants in Italy demonstrated a low overall removal rate of mostly below 40%. As such, wastewater treatment plants do not offer a viable barrier against pharmaceuticals.

Pharmaceuticals present in the environment can also come from hospital sources. A study about the presence of selected human pharmaceutical wastes in hospital effluents was conducted by Thomas et al. [8]. It was found that analgesics and beta-blockers were detected in high concentrations with paracetamol having the highest maximum concentration from all selected pharmaceuticals with values ranging from 178 µg/l up to 1300 µg/l. Alternatively, the source of veterinary pharmaceuticals found in the environment can be due to direct and indirect releases. Direct release to the environment is usually through application in aquaculture. On the other hand, indirect release can also occur through the administration of pharmaceuticals to animals being treated, commonly via run-off and leaching of animal excretion [9].

Ibuprofen (Ibu) or 2-(4-isobutyl phenyl) propionic acid, is the first of the non-steroidal anti-inflammatory drugs (NSAID) derived from propionic acid which is sold in many countries. It is important to emphasize that in 2005 this drug took 17th place on the list of the most commonly prescribed medications in the United States [10] or 2300 t/year. Studies were also performed in countries such as Germany, Spain, Switzerland, France, Italy, Sweden, Canada and Denmark, where the quantifications for Ibu in wastewater effluents varied from 60 to 3400 ng/l [11]. In numerous studies, the analysis of concentrations of pharmaceuticals found in surface waters, detected were concentrations of ibuprofen from 0.05 to 0.28 mg/l [12]. Considering all these facts, it is vital to develop a process with significant potential to remove pharmaceuticals residue.

WWTP effluents have been considered as an important source of micro pollutants for aquatic environments; therefore advanced treatment technologies such as ozonation [13] and activated carbon filtration [14] as well as a combination of ozone and hydrogen peroxide [15] are required to reduce the emission of micro pollutants via WWTPs effluents.

The wide application of boron-doped synthetic diamond (BDD) electrodes extends to more specific areas, for instance, the electrochemical oxidation or reduction of emerging contaminants such as pharmaceuticals,which also received more attention in recent years because of their growing presence in the environment. Moreover, there is also research studies aimed at comparing the performance of BDD electrodes with Pt electrodes for the electrochemical oxidation of pharmaceuticals. The oxidation of ibuprofen yielded better results in favor of the BDD anode in comparison with Ti/Pt/PbO_2electrode [16]. Also the results showed that the substrate was destroyed faster on a Pt anode but complete mineralization was only achieved on the BDD anode in all media. This is because intermediates such as carboxylic acids are completely converted into CO_2 with the BDD while they remain stable in solution using Pt electrode [17].

Several research studies are available in the literature, mostly on the electrochemical oxidation of individual pharmaceuticals such as sulfamethoxazole and acetaminophen on BDD electrodes. Li et al. [18] investigated the oxidation of sulfamethoxazole, an antibiotic, at a BDD anode using sodium sulfate (Na_2SO_4) as background electrolyte. Mineralization with high current efficiency was achieved with not known toxic by-product formation as a result of partial oxidation.

Research involving electrochemical oxidation of emerging contaminants using BDD electrode is relatively new and more relevant information is still needed to obtain the desired result. This paper presents experimental results of the electrochemical oxidation of Ibu solutions using BDD electrode.

MATERIAL AND METHODS

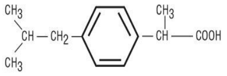
The pharmaceutical certified product Ibu was of analytical grade (99.6 %) and provided by the Pharmaceutical Laboratory Galenikaa.d., Beograd, Serbia. Stock solution of ibuprofen, concentration of 0.375 g/l was prepared in 0.05 M Na_2SO_4. The solution Na_2SO_4 was made by using Na_2SO_4 salt p.a. quality provided by Centrohem, StaraPazova, and demineralized water.

Cyclic voltammeter (CV) experiments were carried out in the custom designed three–electrode system which consisted of a standard calomel reference electrode (SCE) ($Hg|Hg_2Cl_2$ in 3.5 M KCl, $E = +0.250$ V vs. NHE at 25 ℃), coiled platinum wire as a counter electrode and a highly BDD working electrode at the cell bottom with a surface of 0.8 cm^2 bounded by a chemically resistant rubber o–ring. Cyclic voltammeter experiments were performed by potentiostat – galvanostatGamry G300 control.

Electrochemical experiments were conducted at room temperature (22–25 ◦ C) in a 250ml cell, using batch mode. BDD ($20 cm^2$) electrode was used as anode, and stainless steel foils, with an identical area to the anodes, were used as cathodes. All anodic oxidation assays were performed under galvanostatic conditions, with imposed current densities of $30 mAcm^{-2}$, which is characterized in previous works as the optimum current density for the Ibu oxidation on BDD [16], for a volume of 100 ml of solution. A potenciostat/galvanostat , model PAR EGG, was used as the power supply.

The basic solution of Ibu in 0.05 M Na_2SO_4 had characteristics according to Table 1.

Table 1

Ibuprofen	c, mg/l	pH	COD, mg O_2/l
	375	6	960 ± 35

The change in the concentration of Ibu was monitored by UV-Vis spectrophotometer (Shimadzu UV 1800) at a wavelength of 264 nm and calibration curves. Chemical Oxygen Demand (COD) determinations were made following the titrimetric method, according to standard methods [19].

RESULTS AND DISCUSSION

Electrochemical characterization

Cyclic voltamogram of Ibu solution containing 0,05 M Na_2SO_4 with BDD electrodes are shown in fig. 1. At the potential higher than 0,75 V vs. Hg/Hg_2Cl_2,the current density increase with adding Ibu. The increased current density may result from the direct electro oxidation of Ibu at BDD electrode. When the potential exceeds 1.3 V, the anodic currents increased largely with potential, which may be result of electro oxidation of Ibu plus the evolution of oxygen. With the evolution of oxygen, the active species such as hydroxyl radicals, H_2O_2, or O_3 can be produced, which lead to the indirect oxidation of Ibu.

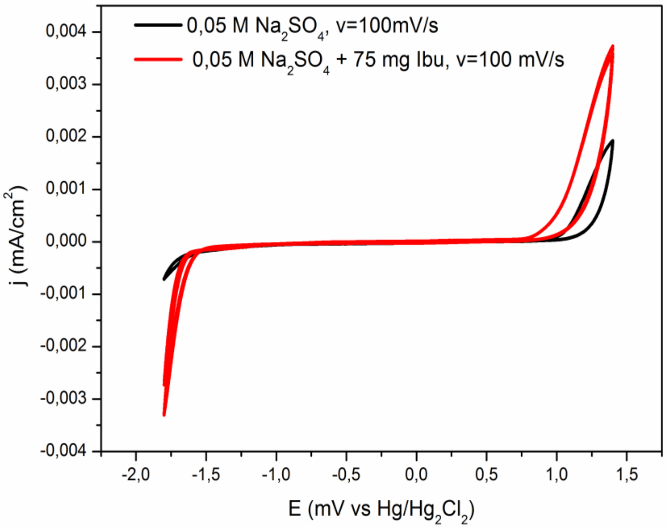


Figure 1. Cyclic voltammograms of Ibuprofen (1,83mM/l) in 0,05 M Na_2SO_4 solution at BDD electrode

Effect of electro oxidation of Ibu at BDD electrode

Electro oxidation of Ibu, initial concentration of 375 mg/l, is performed on BDD electrode. The change in the concentration of Ibu was monitored by UV-Vis spectrophotometer after 1, 3 and 6 hours of electro oxidation. According to the spectro-photometric results, Figure 2, Ibu solution has two peaks (264 and 272 nm). Based on the literature data [20] for the determination of Ibu, the peak at 264 nm was selected. The concentration of Ibu present in each sample was calculated by determining the value of absorbance for each sample at the peak of 264 nm and by using the calibration curve. Figure 2 showsdecrease in absorbance values for peak typical for Ibu (264 nm). Based on the calibration curve, Figure 3, Ibu concentrations were determined after 1, 3, and 6 hours of electro oxidation.

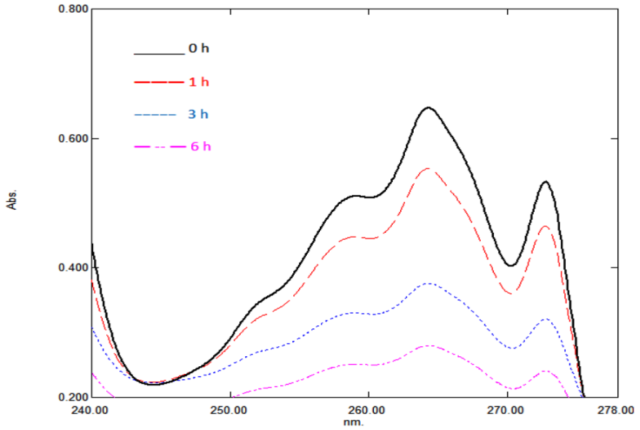


Figure 2. *Electro oxidation of Ibu at BDD electrode at various reaction times: UV–Vis spectra of reaction of Ibu solution (initial Ibu concentration 375 mg/l; 0,05 M Na_2SO_4electrolyte)*

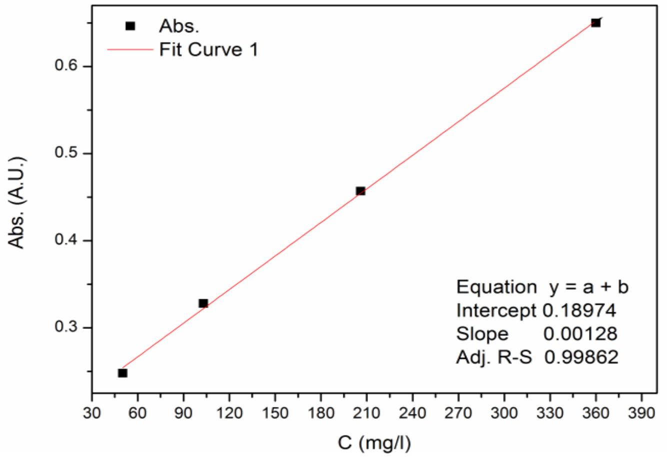


Figure 3. *Calibration curve of Ibuprofen in 0,05 M Na_2SO_4 at 264 nm*

It was observed extremely decreasing in initial Ibu concentration over the time of 1, 3 and 6 hours from 375 mg/l to 288, 147, i 70 mg/l, respectively. The highest percentage of Ibu removal was 81,4%, after 6 hours of electro oxidation, Figure 4. These results suggested that the intermediates were produced at the initial reaction time, which were degraded with the extension of reaction process.

The possibility of Ibu removal by electro oxidation was additionally confirmed by determining the value of COD in the Ibu solution after 1, 3 and 6 h, in relation to specific charge,Figure 5. The obtained results showed a COD reduction of 78% compared to the solution with the initial concentration of Ibu, after 6 h of electro oxidation on BDD electrode.

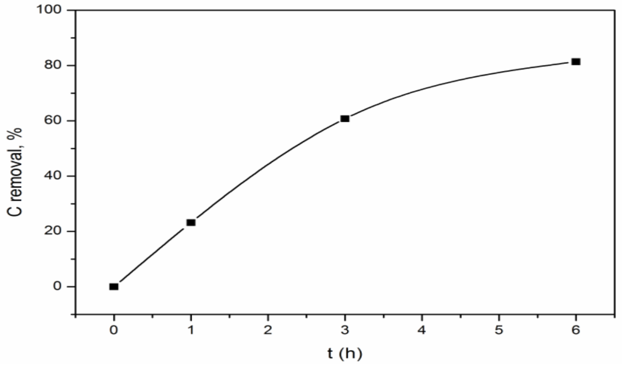


Figure 4. *Decrease in the concentration of Ibu in solution after different times of electro oxidation at BDD electrode*

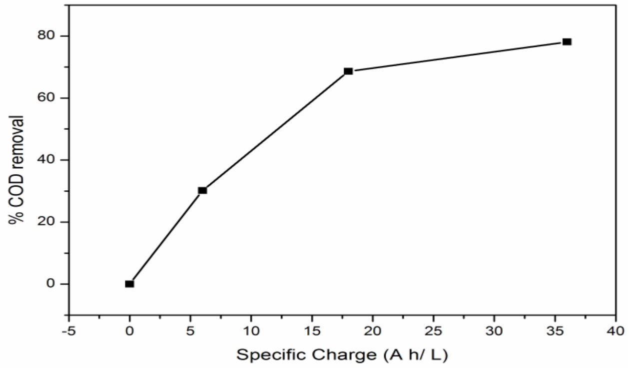


Figure 5. *Variation of COD removal as a function of the specific charge passed during electrolysis of Ibu performed with BDD electrode*

No remarkable degradation of Ibu was achieved at anodic potential below 1.2 V, for which H_20 electrolysis nearly cannot occur, which indicated that the contribution of direct oxidation is not significant. The other possible mechanism responsible for the Ibu degradation is indirect oxidation mediated by several oxidants produced from the oxidation of water. Reactive oxidants such as •OH, O_3, H_2O_2, and $•O_2^-$ can be considered as candidate oxidants [21]. The most common oxidation is the •OH radicals formed by the one-electron oxidation of water. Additionally, otherreactive oxidants can also be responsible for the Ibu degradation.

CONCLUSION

The aim of this study was to examine the possibilities of Ibu removal from aqueous solution in the reaction of electro oxidation onBDD electrode. The effective removal of Ibufrom aqueous solutions using BDD anode has been shown. Regarding the Abs (264 nm),for the current densities of 30 mV/cm^2 Iburemoval from aqua solution can be possible up to 81%. The possibility of Ibu removal by electrochemical degradation wasalso confirmed by the results of COD which have demonstrated the removal of 78%compared to the initial value.

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REFERENCES

[1] *Roig, B., Pharmaceuticals in the Environment: Current Knowledge and Need Assessment to Reduce Presence and Impact, IWA Publishing, 2010.*

[2] *Bound, J. P., Voulvoulis N., Household Disposal of Pharmaceuticals as a Pathway for Aquatic Contamination in the United Kingdom, Environmental Health Perspectives, Vol. 113, pp. 1705-1711, 2005.*

[3] *Hemminger, P., Damming the Flow of Drugs into Drinking Water, Environmental Health Perspectives Vol. 113, pp. A678-A681, 2005.*

[4] *Castensson, S., Pharmaceuticals in the Environment, Pharmaceutical Waste, ed. Kümmerer K., pp. 489-499. 2008.*

[5] *Kümmerer, K., Pharmaceuticals in the environment: sources, fate, effects and risks. Springer-Verlag Berlin Heidelberg, 2004.*

[6] *Daughton, C. G., Ternes, T. A., Pharmaceuticals and Personal Care Products in the Environment: Agents of Subtle Change? Environmental Health Perspectives Vol. 107, pp. 907, 1999.*

[7] *Castiglioni, S., Bagnati, R., Fanelli, R., Pomati, F., Calamari, D. and Zuccato, E., Removal of Pharmaceuticals in Sewage Treatment Plants in Italy. Environmental Science & Technology, Vol. 40, pp. 357-363, 2006.*

[8] *Thomas, K. V., Dye, C., Schlabach, M. and Langford, K. H., Source to sink tracking of selected human pharmaceuticals from two Oslo city hospitals and a wastewater treatment works, Journal of Environmental Monitoring Vol. 9, pp. 1410-1418, 2007.*

[9] *Boxall, A. B. A., Kolpin, D. W., Halling-Sørensen, B., Tolls, J., Peer Reviewed: Are Veterinary Medicines Causing Environmental Risks?, Environmental Science & Technology Vol. 37, pp. 286A-294A, 2003.*

[10] *Richards, S. M., Cole, S. E., A toxicity and hazard assessment of fourteen pharmaceuticals to Xenopuslaevis larvae, Ecotoxicology Vol. 15(8) pp. 647–56, 2006.*

[11] *Farré, M., Ferrer, I., Ginebreda, A., Figueras, Olivella, M. L., Tirapu, L., Vilanova, M., Barceló, D., Determination of drugs in surface water and wastewater samples by liquid chromatography-mass spectrometry: methods and preliminary results including toxicity studies with Vibrio fischeri, J. Chromatogr. A. Vol. 938(1-2), pp. 187-97, 2001.*

[12] *Heberer, T., Stan, H. J., Determination of trace levels of dichlorprop, mecoprop, clofibric acid, and naphthylacetic acid in soil by gas chromatography/mass spectrometry with selected-ion monitoring, J. AOAC Int. Vol. 79(6), pp. 1428–33, 1996.*

[13] *Zimmermann, C., Chymkowitch, P., Eldholm, V., Putnam, C.D., Lindvall, J. M., Omerzu, M., Bjoras, M., Kolodner, R. D., Enserink, J. M., A chemical-genetic screen to unravel the genetic network of CDC28/CDK1 links ubiquitin and Rad6-Bre1 to cell cycle progression, Proc. Natl. Acad. Sci., Vol. 108(46), pp. 18748-53*

[14] *Nowotny, N., Epp, B., Von Sonntag, C., Fahlenkamp, H., Quantification and modeling of the elimination behavior of ecologically problematic wastewater micropollutants by adsorption on powdered and granulated activated carbon, Environ. Sci. Technol., Vol. 41, pp. 2050-2055. 2007.*

[15] *Klavarioti, M. et al., Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes, Environment International Vol. 35, pp. 402–417, 2009.*

[16] *Ciríaco, L. et al., ElectrochimicaActa, Vol. 54, pp. 1464–1472, 2009.*

[17] *Sirés, I., Cabot, P.L, Centellas, F., Garrido, J.A., Rodríguez, R.M., Arias, C., Brillas, E., Electrochim. Acta, Vol. 52, pp. 75, 2006.*

[18] *Li, S., Bejan, D., McDowell, M. S., Bunce, N. J., Mixed first and zero order kinetics in the electrooxidation of sulfamethoxazole at a boron-doped diamond (BDD) anode, J ApplElectrochem Vol. 38, pp. 151-159, 2007.*

[19] *Eaton, A.D., Clesceri, L.S., RiceE. W., Greenberg,A. E., Franson,M. A. H., Standard Methods for the Examination of Water and Wastewater: Centennial Edition, 21st Edition, ISBN: 0875530478, American Public Health Association, Washington, D.C. pp. 1368,2005.*

[20] *Jasinska, A., Ferguson, A., Mohamed, W. S., Szreder, T., The study of interactions between ibuprofen and bovine serum albumin, Food Chemistry and Biotechnology, Vol. 73 pp. 15-24, 2009.*

[21] *Michaud, P.A., Panizza, M., Ouattara, L., Diaco, T., Foti, G., Comninellis, C., J., Appl. Electrochem., Vol. 33, pp. 151, 2003.*

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