ELECTROCHEMICAL DEGRADATION OF DRUG RESIDUES FROM WATER

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ABSTRACT

The aim of this work was to investigate the performance of the boron doped diamond (BDD) for the degradation and mineralization of acetylsalicylic acid (ASA), chosen as a model of the pharmaceuticals pollutants from wastewater effluents proceeded from the pharmaceutical industry.

INTRODUCTION

Acetylsalicylic acid (ASA) is better known to most people by its common name, aspirin. The possible interaction of drugs with the environment is not well-known, but international statistics shows that they can affect endocrine system of the fishes, can expect toxic effect on living algae and can favour the development of resistant strains of microorganisms [1-3]. Recently, alternative electrochemical methods are being applied to achieve the total degradation of water containing pharmaceuticals. The advantages of these electrochemical methods are environmental compatibility, versatility, security, energy efficiency, and the most important factor in applying the electrochemical method is the electrode material [4-5]. Diamond electrodes open a new opportunity for work under extreme conditions because of his hardness, the highest atomic density, chemical inertness, optical properties, thermal conductivity and electrical characterization [6].

The goal of the work was to assess the performance of boron-doped diamond (BDD) electrodes in 0.1 M Na_2SO_4 supporting electrolyte for acetylsalicylic acid (ASA) electrooxidation based on the aromatic ring degradation and mineralization degrees. The effect of the current density was study to determine the optimum working conditions for bulk electrolysis under galvanostatic regime.

MATERIALS and METHODS

The electrochemical experiments were carried out at room temperature (22-25 °C) by batch process using an undivided cell of 0.7 dm^3 volume, in 0.1 M Na_2SO_4 supporting electrolyte. The BDD/Nb electrodes (100 mm x 50 mm x 1 mm) with 280 cm^3 geometric area provided by CONDIAS, Germany were used as anodes, and stainless steel plates (100 mm x 50 mm x 1 mm) were employed as cathodes under vertical arrangement. A regulated DC power supply (HY3003, MASTECH) was used under galvanostatic regime at current densities of 5 mA cm^{-2}, 10 mA cm^{-2}, and 30 mA cm^{-2}.

After a period of time corresponding to the same charge consumption for all applied current densities, samples were drawn from the cell and ASA degradation was followed by UV-VIS spectroscopy using a Varian Cary UV-VIS spectrophotometer. ASA mineralization was check by COD parameter which was analyzed using the standard method. Aromatic ring degradation of ASA was followed based on absorbance recorded at 295 nm (A_{295}). The percentage aromatic ring degradation was determined using the expressions (1):

$$Aromatic \quad ring \quad \deg radation = \frac{(A_{295,0} - A_{295})}{A_{295,0}} x100 \quad (\%) \quad (1)$$

The electrochemical efficiency for ASA oxidation was determined based on Eq. (2):

$$E_{ASA} = \frac{(ASA_0 - ASA)}{Q * S} \times V \quad (\mathrm{g / C{\cdot}cm^2}) \qquad (2)$$

where ASA_0-ASA represent the change in the ASA concentration determined by A_{295} during experiments for a charge consumption of Q corresponding to various electrolysis time, V is the sample volume (700 cm^3) and S is the area of the electrode surface (cm^2).

The electrochemical efficiency for ASA mineralization defined as an overall efficiency for complete oxidation to CO_2 was determined based on Eq. (2) modified as (2') taking into consideration the change in COD measurements during experiments, determining (COD_0 – COD):

$$E_{COD} = \frac{(COD_0 - COD)}{Q * S} \times V \quad (\mathrm{g / C{\cdot}cm^2}) \qquad (2')$$

The mineralization current efficiency (MCE, %), defined also as current output for direct faradayc complete oxidation, for each electrolyzed solution was calculated based on Eq. (4):

$$MCE = \frac{nFV_s \Delta(COD)_{exp}}{4.32 \times 10^7 \, mIt} \times 100 \quad (\%) \qquad (3)$$

where n is the number of electrons consumed in the mineralization process of ASA, F is the Faraday constant (=96 487 C mol^{-1}), V_s is the solution volume (dm^3), $\Delta(COD)_{exp}$ is the experimental COD decay (mg dm^{-3}), 4.32 x 10^7 is a conversion factor for units homogenization (=3 600 s h^{-1} x 12 000 mg of carbon mol^{-1}), m is the number of carbon atoms in ASA, I is the applied current (A), and t is time (h). The number of electrons consumed is determined based on the overall mineralization reaction of ASA to CO_2 ($C_9H_8O_4 + 14H_2O \rightarrow 9CO_2 + 22H^+ + 22e^-$)

The specific energy consumption, W_{sp}, was calculated with the relation (4):

$$W_{sp} = \frac{(Q * V^{-1})U}{1000} \quad (\mathrm{kWh\ dm^{-3}}) \qquad (4)$$

where Q represents the specific charge consumption, U is the cell voltage (V), V is the solution volume (dm^3). Sodium sulphate solution was analytical grade from Merck, and ASA solutions were freshly prepared with double-distilled water.

RESULTS

Electrochemical degradation of ASA

The anodic oxidation of ASA on BDD electrodes in 0.1 M Na_2SO_4 supporting electrolyte has been performed under galvanostatic regime and bulk electrolysis conditions, at three different current densities. The current densities of 5, 10 and 30 mA cm^{-2} were selected based on literature [7] under water decomposition range to assure the conditions for the formation of hydroxyl radicals at the BDD surface.

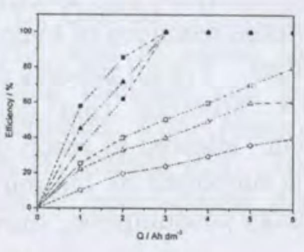

Fig.1. Evolution of ASA degradation efficiency versus charge consumption; operating conditions: ASA=0.1mM, 0.1 M Na_2SO_4 supporting electrolyte. Degradation efficiency: j=5 mA/cm^2 (■), j=10 mA/cm^2(▲) ,j=30 mA/cm^2 (●); COD removal: j=5 mA/cm^2 (□), j=10 mA/cm^2(Δ) ,j=30 mA/cm^2 (○).

In each series, the ASA degradation efficiency was monitored in terms concentration based on absorbance recorded at A_{295} [8] chosen for aromatic ring degradation and COD parameters. Under all current density conditions applied for the electrooxidation process, the degradation of ASA occurred under the action of hydroxyl radical generated, physisorbed or remained near the BDD surface.

Fig.1 shows the trend of ASA degradation efficiency as a function of charge consumption during the anodic oxidation of 20 mgL^{-1} ASA with BDD at three different applied current densities, *i.e.*, 5, 10 and 30 $mAcm^{-2}$. As can be seen in Fig.1, ASA degradation efficiency is highly dependent on the current density and becomes slower with increasing the current density. For example, at the electrolysis time corresponding to an equal charge consumption of 1 Ah dm^{-3} for all three current densities, when the current density of 5 mA cm^{-2} is applied the aromatic ring degradation efficiency reached 57.92%, while for 10 and 30 mA cm^{-2} the aromatic ring degradation efficiencies were 45.2 and 33.8% respectively for a charge consumption of 1 Ah dm^{-3}. At the electrolysis time corresponding to an equal charge consumption of 3 Ah dm^{-3}, at all applied current densities the aromatic ring degradation efficiencies reached 100%. This aspect is supported by the COD degradation degree because the best COD removal was achieved at lower current density (80%) while for higher current densities the COD removal were 62 % and 40 %, respectively.

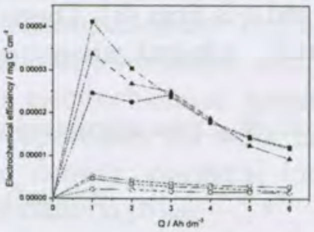

Fig.2. Evolution of ASA electrochemical efficiency versus charge consumption; operating conditions: ASA=0.1mM, 0.1 M Na_2SO_4 supporting electrolyte. Electrochemical efficiency: j=5 mA/cm^2 (■), j=10 mA/cm^2(▲), j=30 mA/cm^2 (●); COD efficiency: j=5 mA/cm^2 (□), j=10 mA/cm^2(∆), j=30 mA/cm^2 (○).

For electrochemical efficiency point of view, as a function of charge consumed during the electrooxidation process, applying the three current densities is presented in Fig.2. As it can be seen, the best electrochemical efficiency in the first part of electrolysis was achieved using the current density of 5 mA/cm2, but with the increasing the electrolysis time and implicit the charge consumption, the electrochemical efficiencies dropped for all three current densities. This could be explained by raising the current density more hydroxyl radicals are generated at the BDD but the charge consumption and specific energy consumption (Fig. 3) are higher because the acceleration of wasted reactions of hydroxyls radicals gives a relatively lower quantity of organic oxidation actions. For all process parameters that characterize the electrochemical performance for ASA, aromatic ring degradation and mineralization, applying the current density of 5 mA cm^{-2} allowed to reach the best results from technical-economical point of view. This aspect is supported by the mineralization current efficiencies in relation with the specific electrical energy consumption, shown in Fig. 3.

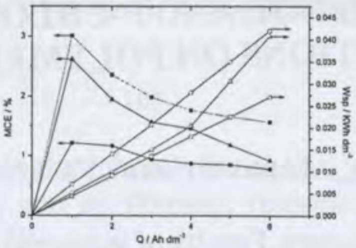

Fig.3. Evolution of ASA mineralization current efficiency, specific energy consumption and charge consumption; ASA=0.1mM, 0.1 M Na_2SO_4 supporting electrolyte. Mineralization current efficiency: (■) j=5 mA cm^{-2}, (▲) j=10 mA cm^{-2}, j=30 mA/cm^2 (●); specific energy consumption: j=5 mA/cm^2 (□), j=10 mA/cm^2(∆), j=30 mA/cm^2 (○).

CONCLUSIONS

The assessment of the performances of BDD electrodes in ASA electrooxidation process was accomplished based on the ASA degradation, electrochemical efficiencies, mineralization current efficiency and energy consumption. This study demonstrated good performance of BDD electrode to degrade and mineralize ASA from aqueous solution. Under the studied conditions the best performance of BDD electrode for ASA mineralization taking into account the technical-economical aspect was achieved at 5 mA cm^{-2}.

ACKNOWLEDGEMENTS

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