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Application of electrochemical/BDD process for the treatment wastewater effluents containing pharmaceutical compounds

M. Fernanda García-Montoya [a], Silvia Gutiérrez-Granados [a], Alejandro Alatorre-Ordaz [a], R. Galindo [a,b], Rubén Ornelas [a], Juan M. Peralta-Hernández [a,*]

[a] Universidad de Guanajuato, DCNE, Depto. De Química, Campus Guanajuato, Cerro de la Venada S/N, Pueblito de Rocha, Guanajuato, GTO 36040 CP, Mexico
[b] Consejo Nacional de Ciencia y Tecnología, Av. Insurgentes Sur 1582, Benito Juárez, Crédito Constructor Ciudad de México, DF, C.P. 03940</PostalC>, Mexico

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ABSTRACT

The degradation of solutions with paracetamol and diclofenac has been studied by electro-oxidation (EOx), in a reactor with a boron-doped diamond (BDD) anode and a stainless steel cathode. Different current densities were applying: 1.56 to 6.25 mA/cm^2. Close to 50% of mineralization is always achieved due to the great concentration of $^{\bullet}OH$ generated at the BDD surface under EOx, with release of NH_4^+ and NO_3^- ions. Same solutions have been comparatively treated with electro-Fenton (EF/BDD) process, improved the mineralization reached 80% of efficiency. Reversed-phase chromatography was carrying out to identify some by products that evolve under de degradation process.

Introduction

In the last years, pharmaceutical residues have been great attention for their potential environmental pollutant, principally for its high bioactive chemical content. This kind of compounds are considered as emerging pollutants in waste wastewaters because they still remain unregulated or are currently undergoing a regularization process, such as is the case from Mexico. Principal emerging contaminants are present in the pharmaceuticals, personal care products, endocrine disrupters and have been found introduced into the environment in the wastewater, surface and groundwater and even drinking water at small concentrations ranging from 0.1 to 20 μg/L [1,2]. The residue of the anti-inflammatory drug in different species has been reported in some countries such as Pakistan [3].

In this context, paracetamol (*N*-acetyl, 4-aminophenol) is an analgesic and anti-inflammatory commonly used in the world for humans and animals. Their presence has been reported in effluents from hospitals [4,5], treatment plants [6,7], in bodies of water, surface and groundwater [8,9] at concentrations ranging from 29 to 246 μg/L.

Meanwhile, diclofenac (2-[2-(2,6-dichlorophenyl) amino-phenyl] ethyl) is a standard drug used in the renal monitoring, it is also present in many pharmaceutical formulations for the treatment of various diseases [10]. This compound has a high resistance to biodegradation and accumulates in the bodies of water, thus appearing as a persistent toxic waste in effluent treatment plants. It has been detected in surface waters in some countries such as Austria, Pakistan, Germany and the United States, where it has been found that drug concentrations have reached 4.4 μg/L [11].

Current alternative water treatment technologies are therefore required to improve treated effluent quality. In advanced oxidation processes (AOPs), free hydroxyl radicals ($^{\bullet}OH$), which are responsible for organic degradation are produced. Due to their strong unselective oxidative power, these free hydroxyl radicals are able to oxidize and mineralize almost any organic molecule, yielding CO_2 and inorganic ions as final products, and may therefore be used as water treatment technologies to remove these contaminants [12–14]. Among the AOPs, electrochemical advanced oxidation processes (EAOPs) have been adjusted for the elimination of toxic and biorefractory organic compounds from wastewaters under the on-site achievement of free radical $^{\bullet}OH$ [15]. In some EAOPs, this free radical can be efficiently generated from hydrogen peroxide (H_2O_2) continuously generated to the solution via the two-electron cathodic reduction of injected O_2,

* Corresponding author. Tel.: +52 47 37 32 75 55.
E-mail address: juan.peralta@ugto.mx (J.M. Peralta-Hernández).

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reaction (1), from Fenton's reaction (2) [16]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (1)$$

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^\bullet OH + OH^- \quad (2)$$

The efficient O_2 reduction from atmospheric air via reaction (1) allows an efficient H_2O_2 generation, which is viable using carbonaceous cathodes including graphite [17], carbon nanotubes [18], activated carbon fiber [4], carbon sponge [12], graphite felt [19], carbon–polytetrafluoroethylene (PTFE), gas (O_2 or air) diffusion [20,21] and BDD surface [22–24]. The advantage is that the H_2O_2 is considered a "green" chemical that yields oxygen gas and water as by-products.

The most well-known EAOPs is the electrochemical oxidation (EOx), in such method, organics compounds are more widely degraded by physisorbed $M({}^\bullet OH)$ generated from water discharge at a large O_2-overpotential anode (M) at high current [25]:

$$M + H_2O \rightarrow M({}^\bullet OH) + H^+ + e^- \quad (3)$$

In this context, the preferred anode in EOx is a boron doped diamond (BDD) thin film deposited onto Si, Ti or Nb [14,25]. BDD exhibits remarkable technological properties and generates very large amounts of reactive BDD(•OH), occasioning in a larger $O_{2_}$overpotential that improves the oxidation of organics compared to that observed at traditional anodes such as Pt [26,27].

Electro-Fenton (EF) is the best known EAOP based on the H_2O_2 generation [28–30]. In this process a catalytic amount of Fe^{2+} is added to the polluted solution to react with H_2O_2, thus producing Fe^{3+} and ${}^\bullet OH$ in the bulk from Fenton's reaction (2) at optimum pH 2.8–3.0. The main improvement of EF over more conventional Fenton's reagent (Fe^{2+}/H_2O_2) is the cathodic regeneration of Fe^{2+} by reaction (4), which accelerates Fenton's reaction and enhances the mineralization [31].

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (4)$$

In recent researches, our group has been carry out the experiences in a new process so called electro-Fenton/BDD, which consist in a some arrangement using BDD-BDD electrodes such as cathode and anode. This system has been tested to degrade different organic compounds, such as azo dyes, pesticides such as 2,4-D and tannery waste waters [24,28,32]. Table 1 presents some reviews for different conditions of drugs wastewater treatment using different oxidation processes.

The aim of this paper is presents a study on the performance of the EOx and EF/BDD treatment of aqueous paracematol and diclofenac solutions using stainless steel and BDD anodes. EOx and EF/BDD degradations have also performed under the same conditions to clarify its mineralization process. All experiments were carried out with a solution concentration 50 and 100 mg/L to better know the oxidation power of each method.

The influence of drugs concentration and current intensity on the mineralization process of EOx and electro-Fenton/BDD was also explored. The drugs decay and the evolution of intermediates were followed by chromatographic techniques to clarify the synergistic action of the hydroxyl radical produced by EOx and EF/BDD processes.

Experimental

Chemicals

Paracetamol ($C_8H_9NO_2$) and diclofenac ($C_{14}H_{10}C_{l2}NO_2$) was purchased from Sigma–Aldrich. Anhydrous sodium sulfates were of analytical grade from Karal. Solutions were prepared with ultrapure water from a Millipore–Elix system with resistivity $>18\ M\Omega$ cm and their pH was adjusted with analytical grade sulfuric acid purchased from J.T. Baker. Other chemicals and solvents were of high-performance liquid chromatography (HPLC) or analytical grade from Merck, Sigma-Aldrich and Panreac.

Electrochemical reactor and procedures

Electrochemical experiments were performed at room temperature in a 4 L undivided filter flow press reactor equipped with two electrodes. The anode and cathode electrodes have a geometrical area of 64 cm^2 of niobium plate with a diamond-coated film thickness of 2–7 μm. BDD electrodes were provided by Metakem GmbH^{TM}, Germany. For the EOx process, BDD anodes and stainless steel cathodes were used. The inter-electrode gap was 2 cm. The synthetic solutions were placed in the reservoir and recirculated through the system using a diaphragm pump, as seen in Fig. 1. The flow rate is kept constant at 2 L/min.

The degradation of paracetamol and diclofenac solutions was carried out under current-controlled electrolysis conditions at 1.56, 3.12, 4.68 and 6.25 mA/cm^2 using a BK Precision—1688B power supply. Assays were monitored by TOC using a Shimadzu TOC-L. Prior to the electrolysis, compressed air was bubbled for 30 min through the solution. The reaction intermediates were analyzed using an HPLC CC5, Solvent Deliver System PM80, fitted with UV–vis detector 116A and temperature control LC-22C. The mobile phase was a 30/70% (v/v) mixture of methanol/ phosphate buffer adjusted to pH 2.6 at 0.8×10^{-3} mL/min flow rate. The concentration of the phosphate buffer was 1×10^{-3} M and the column was an Alltima HPC18 of 5l with 4.6 mm ID and 150 mm length. NH_4^+ and NO_3^- ions were quantified. The evaluation of H_2O_2 accumulation in the system was carried out by testing H_2O_2 generation in the different electrolyte solutions. The H_2O_2 concentration was determined using the $Ti(SO_4)_2$ titration method and spectrophotometric analysis at λ = 407 nm.

Results and discussion

Electro-oxidation (EOx) process

A solutions of paracetamol, 50 mg/L and 100 mg/L (corresponding to 37.5 mg/L and 51.5 mg/L of TOC) at pH 3.0 was initially electrolyzed at 1.56, 3.12, 4.68 and 6.25 mA/cm^2 at 35 °C for 3 h to degradation using a BDD anode. In both drugs, the solution pH

Table 1
Reviews for different conditions of drugs treatment using various oxidation process.

Oxidation process	Pollutants	Studied conditions	Reference
EOx	17α-ethinylestradiol	Anode: Ti/SnO_2 20 mg/L of drug in 100 mL M Na_2SO_4, pH 6.2 79% TOC removal	[33]
EOx	Ibuprofen	Anode: BDD 1.75 mM of drug in 200 mL 75% TOC removal M Na_2SO_4, pH 3	[34]
EOx	Ketoprofen	Anode: BDD 200 mL of 5 μm drug 0.1 M Na_2SO_4, pH 6.0 100% TOC removal	[35]
EOx-EF	Chloroxylenol	Electrodes: Pt, BDD, GDE 100 mg/L of drug in 100 mL M Na_2SO_4, pH 3, 1 mM Fe^{2+} 58% TOC removal	[36]
EO_x-EF-PEF-SPEF	Propranolol	Electrodes: Pt, BDD, GDE 154 mg/L of drug in 100 mL M Na_2SO_4, pH 3, 0.5 mM Fe^{2+}	[37]