Separation and Purification Technology 157 (2016) 9–16

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Green electrochemical process for metronidazole degradation at BDD anode in aqueous solutions via direct and indirect oxidation

Hafedh Belhadj Ammar *, Mabrouk Ben Brahim, Ridha Abdelhédi, Youssef Samet

Electrochemistry and Environmental Laboratory, Department of Materials Engineering, National Engineering School of Sfax, University of Sfax, B.P. 1173, 3038 Sfax, Tunisia

ARTICLE INFO

Article history:
Received 22 May 2015
Received in revised form 16 November 2015
Accepted 18 November 2015
Available online 23 November 2015

Keywords:
Environmentally friendly
Metronidazole
BDD anode
Direct and indirect oxidation

ABSTRACT

Anodic oxidation, an environmentally friendly process has been deeply investigated to remove the antibiotic metronidazole (MTZ), dissolved in synthetic wastewaters, via direct and indirect oxidation. Experiments were conducted by boron-doped diamond (BDD) anode in the absence and presence of sodium chloride (NaCl) in the solution. However, no studies have focused on the removal of MTZ using BDD anode or under chlorination process. The chemical oxygen demand (COD) measurement during the processing allowed the evaluation of the kinetics of organic matter decay and the instantaneous current efficiency (ICE). The results have shown that the degradation of MTZ is dependent on its initial concentration, pH, applied current density and NaCl concentration. COD decay follows a pseudo first-order kinetics, and the process was under mass transport control within the range studied, regardless of the experimental conditions. The electrochemical degradation is significantly accelerated by the presence of NaCl in the solution (94% COD removal in just 120 min).

1. Introduction

Antibiotics are an important class of water pollutants due to their large variety, high consumption, and persistence in the environment. The presence of low concentrations of antibiotics compounds and their transformation products has been detected in treated sewage water. Actually, it is clearly shown that some antibiotics products cannot be eliminated during wastewater treatment [1,2]. The pollution of pharmaceutical drugs can be due to emission from production sites, direct disposal of overplus drugs in households, excretion after drug administration to humans and animals and treatments throughout water in fish farms. Since these pollutants resist the biodegradation, powerful oxidation methods have to be searched to be removed from waters, thus avoiding their potential adverse health effects on humans and animals [3–9].

MTZ (2-methyl-5-nitroimidazole-1-ethanol) is a kind of nitromidazole antibiotic that has antibacterial and anti-inflammatory properties. MTZ has been widely used clinically to treat infectious diseases caused by anaerobic bacteria and protozoans. It has also been used as an additive in poultry and fish feed to eliminate parasites. Because of the difficult-biodegradability, toxicity, potential mutagenicity, and carcinogenicity of MTZ [10,11], wastewaters originating from the production of MTZ and from industrial activities pose a major threat to the surrounding ecosystems and human health [12]. Therefore, the elimination of the MTZ from wastewater is necessary to protect the environment and health, in general.

The removal of MTZ from water can be achieved through different methods such as adsorption/bioadsorption on activated carbon [13], UV photolysis [14], heterogeneous photocatalysis [15], biodegradation [16], Fenton and photo-Fenton [17], electro-Fenton [18], the application of nanoscale zero-valent iron [19] and Electrochemical oxidation [20]. However, the metabolites formed during MTZ oxidation may be more toxic than the original pollutant, and may also need to be removed from water [21]. Therefore, complete mineralization is a better approach to dealing with MTZ in wastewater. However, because the main focus is to achieve the degradation of MTZ, reports on the mineralization and toxicity are scarce.

Electrochemical oxidation is one of the most promising electrochemical technologies for the treatment of waters with low contents of organic pollutants. Some research works have been carried out on electrochemical degradation of polluted organic compounds and some anode materials have been tested, such as SnO_2 [22,23], PbO_2 [24–26] and BDD [27–29]. High oxygen overvoltage and high current efficiencies may be obtained for this kind of electrodes, and complete mineralization of organic compounds can be achieved via oxidation by physisorbed hydroxyl radical M

---

* Corresponding author.
E-mail address: hbelhadjammar@yahoo.fr (H.B. Ammar).

http://dx.doi.org/10.1016/j.seppur.2015.11.027
1383-5866/

($HO^{\cdot}$) generated from water discharge at anode (M) surface (Eq. (1)) [30].

$$M + H_2O \rightarrow M(HO^{\cdot}) + H^+ + e^- \quad (1)$$

Many studies have shown that $HO^{\cdot}$ radicals which have strong electrophilic property and high redox potential ($E^{\circ} = 2.8$ V *vs.* SHE), reacting with most pollutants that are 106–109 times faster than those of ozone [31,32].

Moreover, it has been reported that the reaction of organic compounds (R) with electro-generated electrolytic hydroxyl radicals (Eq. (2)) is in competition with the side reaction of the anodic discharge of these radicals to oxygen (Eq. (3)) [33].

$$R + xHO^{\cdot} \rightarrow yCO_2 + zH_2O \quad (2)$$

$$M(HO^{\cdot}) \rightarrow M + \frac{1}{2}O_2 + H^+ + e^- \quad (3)$$

This competition is strongly linked to the interaction of the hydroxyl radicals with the anode surface. On the basis of this approach, and in contrast to BDD, PbO_2 anode is known to have highly adsorption properties toward hydroxyl radicals resulting in a low chemical reactivity for organics oxidation. Furthermore, common drawbacks of SnO_2 and PbO_2 are a short service-life [34], while BDD anode appears to be one of the best candidates for organic compound degradation. This is due to the wide potential window for water discharge (up to 3.5 V), remarkable corrosion stability even in strong acidic medium and its capacity to produce weakly adsorbed hydroxyl radicals that can provide fast and efficient oxidation [28,35]. It has been demonstrated that many bio-refractory compounds such as phenols [35,36], chlorophenols [37,38], pesticides [39], and industrial wastes [40] can be completely mineralized with highly current efficiency, even close to 100%, using BDD anodes.

In conventional electrochemical oxidation processes, polluted organic compounds can be removed via two ways of oxidation processes: (1) direct oxidation, in which the pollutant is oxidized (i) by electron transfer directly to the anode material or (ii) via physisorbed hydroxyl radical; (2) indirect oxidation, in which the electron transfer is mediated by an oxidant species such as (i) active chlorine (chlorine radicals ($Cl^{\cdot}$), Cl_2, HClO, and ClO^-), (ii) $S_2O_8^{2-}$, and (iii) $P_2O_8^{4-}$, when chloride, sulfate, and phosphate containing solutions are electrolyzed, respectively. Furthermore, anode material and electrolysis conditions play an important role in the efficiency of oxidant process [41]. However, there is no work related to the electrochemical degradation of MTZ under chlorination process at BDD anode in the literature.

Therefore, the present study aims to study the electrochemical oxidation process for the total removal of MTZ from its aqueous solution under chlorination process. The process was studied under galvanostatic polarization mode using a BDD anode. The degradation rate of the studied antibiotic and the efficiency and limits of such technique were investigated according to experimental parameters such as the initial concentration of MTZ, the anodic current density, pH and sodium chloride concentration.

2. Experimental

2.1. Reagents and chemicals

Metronidazole was supplied by Winthrop Pharma (Tunisia). NaCl 99.8% and supporting electrolyte Na_2SO_4 99.5% were provided by Prolabo (Paris-France). Each solution (200 mL) was prepared with water purified in Milli-Q Millipore system (Direct-Q® with pump). Sulfuric acid and sodium hydroxide of analytical grade were purchased from Aldrich and employed for pH adjustment. Dihydrate oxalic acid and acetonitrile HPLC grade were provided by Fluka and PANREAC, respectively.

2.2. Methods

2.2.1. Electrolysis set-up

All the electrolytic assays were performed in an undivided cylindrical vessel containing 200 mL solution which was stirred by a magnetic stirring bar in the electrolysis process. A BDD electrode with a geometric area of 6 cm^2 was provided by CSEM (Centre Suisse d'Electronique et de Microtechnique, Neuchâtel, Switzerland). It was synthesized by the hot filament chemical vapor deposition technique (HF-CVD) [42] on single-crystal *p*-type Si⟨1 0 0⟩wafers (1–3 mΩ cm, Siltronix). The doping level of boron in the diamond layer, expressed as B/C ratio, was about 3500 ppm. The resulting diamond film thickness was about 1 μm with a resistivity of 10–30 mΩ cm. Prior to its use in galvanostatic electrolysis assays, the electrode was polarized during 30 min with a 0.5 M H_2SO_4 solution at 50 mA cm^{-2} in order to remove any kind of impurity from its surface. A cylindrical polycrystalline platinum grid ($\phi = 5$ cm, $\ell = 2.8$ cm) was used as a cathode. The MTZ solutions were electrolyzed in a galvanostatic mode with current densities between 40 and 100 mA cm^2 and using a DC power supply (model ATTEN TPR 3003-3C-LG Precision Co. Ltd, Korea).

2.2.2. Measurements

Samples were selected depending on the time period of 0, 15, 30, 60, 90, 120, 180, 240 and 300 min.

The extent of degradation was accompanied by the determination of the chemical oxygen demand according the dichromate method [43].

The concentration of MTZ was measured by high-performance liquid chromatography (HPLC) model Perkin Elmer Series 200 which was equipped with a dual pump system and a UV–Vis detector. Injection volume was 20 μL. The mobile phase contained a mixture of acetonitrile and water at 40:60 (V/V) with a flow rate of 0.5 mL min^{-1} through a C18 reversed phase column (Waters Spherisorb 5 μm (150 mm × 4.6 mm)) at isocratic mode. The wavelength for ultraviolet (UV) detector was set at 320 nm. Dihydrate oxalic acid was used as an internal standard.

Square wave voltammetry (SWV) experiments were performed using a potentiostat–galvanostat (VoltaLab PST050), and a conventional three-electrode cell. A boron-doped diamond ($7 \cdot 10^{-2}$ cm^2) was used as working electrode. A Pt electrode (1 cm^2) and a saturated calomel electrode (SCE) were used as auxiliary and reference electrode, respectively. The MTZ concentration was also determined by SWV as electroanalytical method.

2.2.3. Current efficiency, energy consumption and limiting current

The instantaneous current efficiency (ICE) can be defined as the part of the current directly used for the oxidation of the organic compounds. It can be performed from the decrease of COD by the following relation (Eq. (4)) [44]:

$$\mathrm{ICE}\ (\%) = \frac{\mathrm{COD}_t - \mathrm{COD}_{t+\Delta t}}{8It} FV\ 100 \quad (4)$$

where *F* is the Faraday constant (96,487 C mol^{-1}), *V* the volume of the solution (L), COD_t and $\mathrm{COD}_{t+\triangle t}$ (g O_2 L^{-1}) are the chemical oxygen demands at times *t* and $t + \triangle t$, respectively. *I* is the current (A).

When recalling the electrochemical processes, two different kinetic regimes can be defined depending on the value of the current density for a given reactant concentration. (i) If the applied current density is lower than the corresponding limiting current density, the electrolysis is under charge transfer control and the current efficiency is then 100%. (ii) If the applied current density is higher than its limiting value, the electrolysis is under mass transport control.