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ORIGINAL ARTICLE

Electrochemical degradation of tramadol hydrochloride: Novel use of potentiometric carbon paste electrodes as a tracer

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Abstract The electrochemical removal of tramadol hydrochloride from aqueous solutions has been investigated under several operating conditions using a Pb/PbO_2 electrode. The optimum conditions of the treatment process are: current density of 1000 $mAcm^{-2}$, pH ≈6, temperature of 10 °C and initial tramadol hydrochloride concentration of 100 mg/L. The time of electrolysis is 25 min for degradation rate of tramadol hydrochloride and chemical oxygen demeaned (COD) removal is 22 h. The results were obtained by UV–Vis spectrophotometer and the presently designed electrode was coincident.

1. Introduction

Over the past few years, pharmaceuticals are considered as an emerging environmental problem due to their continuous input and persistence to the aquatic ecosystem even at low concentrations (Klavarioti et al., 2009).

The presence of residual pharmaceuticals in the environment and in the aquatic systems in particular constitutes a serious environmental problem as these compounds (a) are extremely resistant to biological degradation processes and usually escape intact from conventional treatment plants, (b) may impose serious toxic and other effects to humans and other living organisms, and (c) are present at minute concentrations, thus requiring more sophisticated and laborious analytical tools for their accurate determination. Therefore, it is not surprising that research has recently been directed towards the application of non-biological processes for the destruction of pharmaceuticals in waters with emphasis on advanced oxidation processes (AOPs) or oxidation by other means (Abu Ghalwa and Zaggout, 2006; Zourab et al., 2009).

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Tramadol hydrochloride (($\pm$) *trans*-2-[(dimethylamino) methyl]-1-(3-methoxyphenyl)-cyclohexanol) is a synthetic, centrally acting, analgesic agent used for relief of moderate to chronic pain and has no clinically relevant cardiovascular or respiratory depressant activity. Furthermore, it does not have a prostaglandin inhibitory effect. The dosage of tramadol should be adjusted to the intensity of pain and to the response of an individual patient (Its therapeutic plasma concentration is in the range of 100–300 ng L^{-1}). Tramadol is rapidly and almost completely absorbed after oral administration but its absolute bioavailability is only 65–70% due to first-pass metabolism. Approximately 10–30% of the parent drug is excreted unmetabolized in the urine (Patel et al., 2009).

After a very careful review of the literature, no mention of the degradation of tramadol hydrochloride was spotted, therefore, intended to explore the effects of electrochemical degradation of tramadol hydrochloride.

An attractive methodology is the use of electrochemical techniques, which are considered a powerful means of pollution control. These offer the possibility of in situ destruction or modification of various pollutants to less deleterious structures by anodic oxidation on high area electrodes (Gojkovic et al., 2003; Canizares et al., 2004; Jovanovic et al., 2004; Sonthalia et al., 2004; Yang et al., 2004). In electrochemical methods the main reagent is the electron (Rajeshwar et al., 1994), which is a "clean reagent", the reason that makes these methods widely used in many applications such as electrodialysis (Cherif et al., 1997), metal ion removal recovery (Winder et al., 1998), electrodeionisation (Ganzi et al., 1997) and destruction of toxic and non-degradable organics by direct or indirect oxidation (Bellagamba et al., 2002; Brillas et al., 2004; Einaga et al., 2004; Hu et al., 2004; Park and Kim, 2004). Electrochemical treatment of wastewater offers high removal efficiencies and has lower temperature requirements compared to non-electrochemical treatment. In addition, it could prevent production of unwanted side-products as there is no need for the addition of chemicals to the treated wastewaters.

On traditional electrode materials, such as Au, Pt, and C, the oxidation reaction by oxygen transfer is spontaneous and it is characterized by low reaction rate constant (Vitt and Johnson, 1992; Gattrell and Kirk, 1993). Oxygen transfer is usually favored on an anode material with high oxygen evolution overpotential. Lead dioxide, is characterized by high oxygen overpotential, therefore, it is one of the most commonly used anodes for the electrochemical degradation of many pollutants (Polcaro et al., 1999; Iniesta et al., 2001; Panizza and Cerisola, 2003; Martınez-Huitle et al., 2004) particularly when it is doped with metallic cations whose oxides have low oxygen evolution overvoltage. The metallic cations- doped PbO_2 improves the transfer rate of oxygen atom. It was reported that (Johnson and Chang, 1990; Kawagoe and Johnson, 1994; Borras et al., 2003) doping PbO_2 with bismuth improved the oxidation kinetics of several organic compounds, due to the formation of a low surface density of the bismuth oxide (Bi_2O_5) sites.

Traditional methods for dealing with textile wastewater effluents involve various combinations of biological, physical and chemical methods. These are becoming troublesome because of the large variability of the composition of the textile wastewaters. The treatment of textile wastewater from a large dyeing and finishing mill by a continuous process of combined chemical coagulation, electrochemical oxidation, and activated sludge treatment has been investigated (Abu Ghalwa and Abdel-Latif, 2005).

In this study, the electrochemical degradation of tramadol hydrochloride was investigated and the concentration of the undecomposed drug was traced by a newly developed potentiometric carbon paste electrode (Abu Shawish et al., 2010). The results were compared with those obtained using the usual UV–Vis spectroscopy-based detector and were found coincident.

2. Experimental

2.1. Reagents and materials

All reagents used were chemically pure grade. Distilled water was used throughout all experiments. Tramadol hydrochloride (TDCl, M.wt = 300.0), was obtained from Pharmacare LTD company (Ramallah-Palestine). Graphite powder, 2-nitrophenyl octyl ether (2-NPOE), Chloride, nitrate, carbonate, sulfate or phosphate of each of the following cations Na^+, NH_4^+, K^+, Zn^{2+}, Co^{2+}, Ni^{2+}, Ba^{2+}, Mg^{2+}, Mn^{2+}, Sr^{2+}, Cr^{3+}, Al^{3+} were purchased from Aldrich. Silicomolybolic acid (SMA) $H_4[SiMo_{12}O_{40}]$, phosphotungstic acid (PTA) $H_3[PW_{12}O_{40}]$ were obtained from Sigma.

2.2. Apparatus and preparation of carbon paste electrodes

All EMF measurements were carried out with the following assembly: Hg, $Hg_2Cl_2(s)$, KCl(sat.) ||sample solution| carbon paste electrode. The potential measurements were carried out at 25 ± 0.1 with a digital with a Pocket pH/mV Meters, pH315i (Wissenschaftlich-Technische Werkstatten GmbH (WTW)-Germany) under stirring conditions at room temperature (25.0 ± 1.0 °C). Modified carbon paste was prepared as described by our group (Abu Shawish et al., 2010).

2.3. Preparation of the lead/lead dioxide (Pb/PbO_2 electrode)

2.3.1. Lead surface treatment

Pretreatments of the lead substrate were carried out before anodization to ensure good adhesion of lead dioxide film. Lead was first roughened to increase the adhesion of PbO_2 deposit via subjecting its surface to mechanical abrasion by sand papers of different grades, down to 4/0.

It was then cleaned to remove sand particles or any other particles lodged in the metal surface. This was carried out by degreasing with acetone because of its ease of application and its great penetration power, and then with an alkali solution (a mixture of sodium hydroxide (50 g/L), sodium carbonate (20 g/L), trisodium orthophosphate (20 g/L) and sulfuric acid (2 g/L)). Uniform and well adhesive deposit necessitates a smooth surface with no oxides or scales. To ensure this, the lead substrate was soaked for 2 min in a good pickling solution consisting of nitric acid (400 g/L) and hydrofluoric acid (5 g/L) and then chemically polished in boiled oxalic acid solution (100 g/L) for 5 min Awad and Abo Galwa, 2005.

2.3.2. Electrochemical deposition of PbO_2

PbO_2 was deposited galvanostatically on the pretreated lead substrate by electrochemical anodization of lead in oxalic acid