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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 ((±) *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 solution (100 g/L). This acid solution was electrolyzed galvanostatically for 30 min at ambient temperature using an anodic current density of 100 mA/cm^2. The cathode was stainless steel (austenitic type), the two electrodes were concentric with the lead electrode being axial. This arrangement gave the formation of a regular and uniform deposit (Awad and Abo Galwa, 2005).

2.4. Electrolysis

Electrolysis of the aqueous solutions containing tramadol hydrochloride was carried out in a one-compartment Pyrex glass cell of 50 ml volume with the prepared Pb/PbO$_2$ electrode as anode (where lead oxide is the surface material) and austenitic stainless steel as cathode. DC power supply (model GP 4303D, LG Precision Co. Ltd, Korea) was used. The samples were then analyzed by three methods: UV–Vis spectrophotometer at 271 nm (Shimadzu, Japan), potentiometric determination of tramadol hydrochloride using the presently designed electrode and COD (mg O2l-1), which was measured by a closed reflux titrimetric method (PHA, 1992). The experimental conditions were varied to test the effect of the following parameters: conductive electrolyte type, NaCl concentration, temperature, current density, pH, time of electrolysis and the initial concentration of tramadol hydrochloride.

2.5. Potentiometric determination of tramadol hydrochloride using the presently designed electrode

A newly designed chemically modified carbon paste electrode (the presently designed electrode) as well as the spectrophotometric method was used in the determination of all TDCl samples. Calibration curves were prepared and used to calculate the concentration of tramadol hydrochloride in all solutions by the UV method as well as the potentiometric method. In all cases the results obtained by both methods were coincident. This can be seen cleary from Fig. 1–6.

3. Result

3.1. Effect of conductive electrolyte type

As clearly seen in Fig. 1, the best electrocatalytic degradation of tramadol hydrochloride is found in NaCl as the salt. The electrocatalytic efficiency of tramadol hydrochloride was 89% using Pb/PbO$_2$ electrode while that of COD removal was 99.8%. NaCl appears to be the most effective electrolyte from which removal of tramadol hydrochloride and significant depletion of COD was observed. In this electrolyte, the Pb/PbO$_2$ electrode exhibited its highest electrocatalytic activity. Therefore, NaCl was selected as the conducting electrolyte in which all the following investigations were carried out.

3.2. Effect of sodium chloride concentration

This effect is shown in Fig. 2, with experiments employing 25 min and 22 h reaction periods for tramadol hydrochloride and COD, respectively. Under the above conditions both tramadol hydrochloride and COD removal efficiency increased with the increasing of NaCl concentration up to 1 g/L.

3.3. Effect of current density

Both tramadol hydrochloride degradation and COD removal increased with increasing of the applied current density as indicated from Fig. 3. The decrease in the concentration of tramadol hydrochloride and COD was sharp at low current density, 1000 mA/cm^2 (which is considered the limiting current density), followed by a gradual decrease with increasing of the current density upto 2500 mA/cm^2 at which complete degradation of tramadol hydrochloride and COD removal took place.

It has been found that the Pb/PbO$_2$ electrode exhibited its highest electrocatalytic activity towards the degradation of tramadol hydrochloride in NaCl at 1000 mA/cm^2 applied current density. Therefore, this value is considered the optimum current density for the electrocatalytic degradation of the investigated tramadol hydrochloride in NaCl.

3.4. Effect of solution pH

The results in Fig. 4 indicated that the electrocatalytic degradation rate of both tramadol hydrochloride and COD increased with the increasing pH of the solution in acidic media. However, the electrocatalytic degradation rate decreased with the increasing pH of the solution in basic media. It is found that the electrocatalytic degradation rate of tramadol hydrochloride and COD was maximum at pH $\approx$6.

3.5. Effect of time of electrolysis

Tramadol hydrochloride was effectively removed in 25 min by electrochemical oxidation using Pb/PbO$_2$ electrode. In addition, COD removal was in 22 h.

3.6. Effect of temperature

At low temperature, 10 °C, degradation of tramadol hydrochloride and COD removal was high as displayed in Fig. 5, which presents the concentration of the remaining tramadol hydrochloride and residual COD as a function of temperature. The rate of degradation of tramadol hydrochloride and COD removal decreased significantly with increasing of the solution temperature upto 40 °C. However, further decrease in temperature below 10 °C showed no effect.

3.7. Effect of initial tramadol hydrochloride dosage

The effect of different initial concentrations of tramadol hydrochloride (20–200 mg/L) on the rate of degradation and corresponding COD removal is displayed in Fig. 6. Total removal of tramadol hydrochloride and COD can be achieved from samples containing upto 100 mg/L. However, increasing of tramadol hydrochloride concentration above this level resulted in a decrease in the rate of electrocatalytic degradation.

It was repeatedly observed that the COD removal was practically complete as the value measured for the residual tramadol hydrochloride was consistently less than 0.14%. This result can be easily seen by examining the figures.

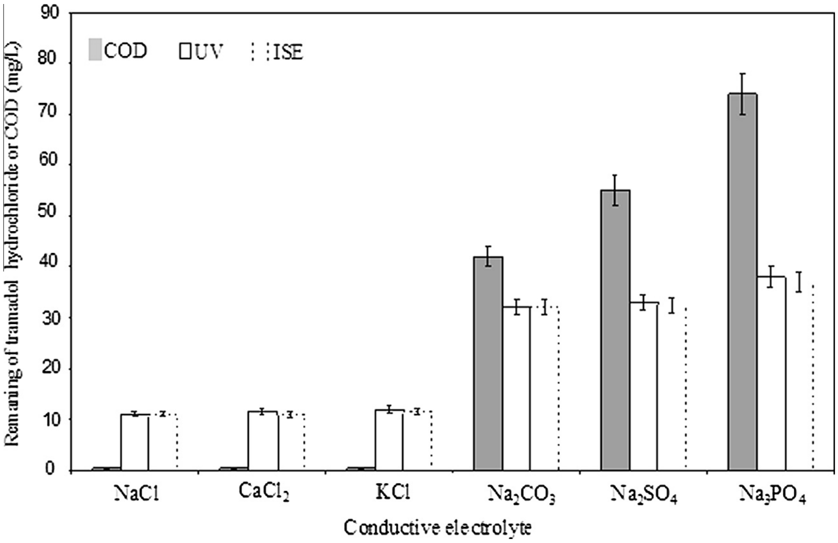

Figure 1 Effect of conductive electrolyte type on the removal of tramadol hydrochloride and COD at current density. of 1000 mA/cm^2 pH 6, initial concentration load of 100 mg/l, NaCl 1 g/l, 25 min, 22 h (COD) and temperature 10 °C.

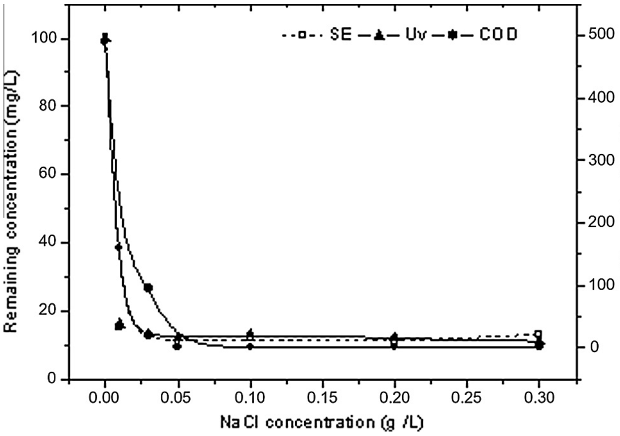

Figure 2 Effect of NaCl concentration on the removal of tramadol hydrochloride and COD at initial tramadol load concentration of 100 mg/l, current density of 1000 mA/cm^2. 25 min, 22 h (COD), temperature of 10 °C and pH 6.

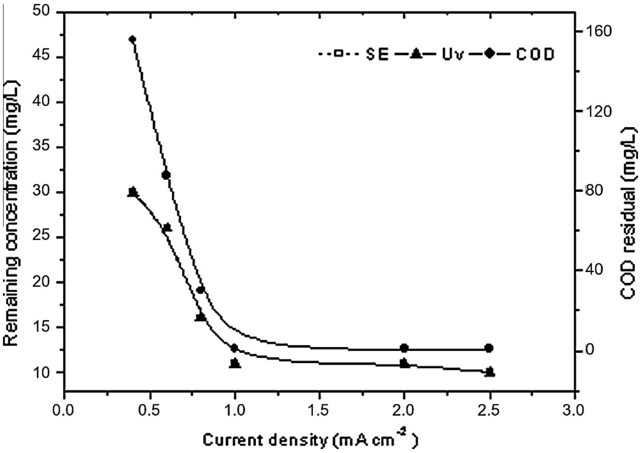

Figure 3 Effect of current density on the removal of tramadol hydrochloride and COD at initial tramadol hydrochloride load concentration of 100 mg/L, 25 min, 22 h (COD), temperature of 10 °C, pH 6 and NaCl 1 g/L.

4. Discussion

Electrochemical oxidation of many organic pollutants in aqueous solutions on the anode could take place by direct electron or oxygen atom transfer. In addition to direct oxidation, organic pollutants can also be treated by an indirect electrolysis generating chemical reactant to convert them into less deleterious products. Oxidation of these pollutants might go right to carbon dioxide and water via successive reactions. Each of these methods could proceed through several steps, such as mass transport, adsorption and direct or indirect reaction at the anode surface (Belhdi et al., 1997).

The direct electrochemical oxidation of organic compounds could generally occur via a mechanism in which the first step is the oxidation of water molecules on the electrode surface (MO_x), giving rise to the formation of hydroxyl radicals according to (Comninellis, 1994):

$$MO_X + H_2O \rightarrow MO_X[OH^{\cdot}] + H^+ + e^- \quad (1)$$

The produced hydroxyl radicals can oxidize the underlying oxide lattice to a higher state forming the so-called higher oxide:

$$MO_X[OH^{\cdot}] \rightarrow MO_X[O] + H^+ + e^- \quad (2)$$

The only role of the formed higher oxide is participation in the selective oxidation of the organic pollutants (R) without complete incineration:

$$MO_X[O] + R \rightarrow RO + MO_X \quad (3)$$

It is to be noted that the above route can take place only if the transition of the underlying oxide to a higher oxidation state is

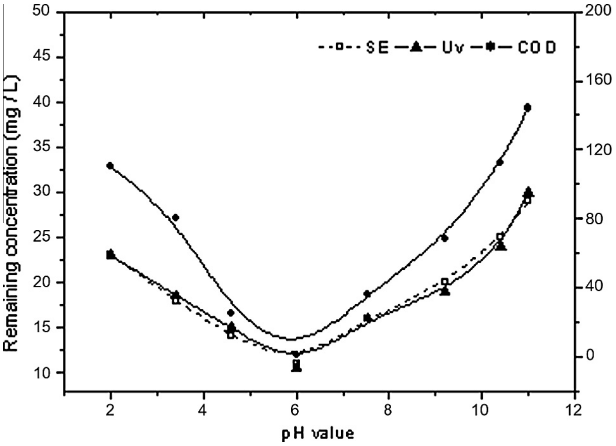

Figure 4 Effect of pH value on the removal of tramadol hydrochloride and COD at initial tramadol hydrochloride load concentration of 100 mg/L, current density of 1000 mA/cm^2, 25 min, 22 h (COD), temperature of 10 °C and NaCl 1 g/L.

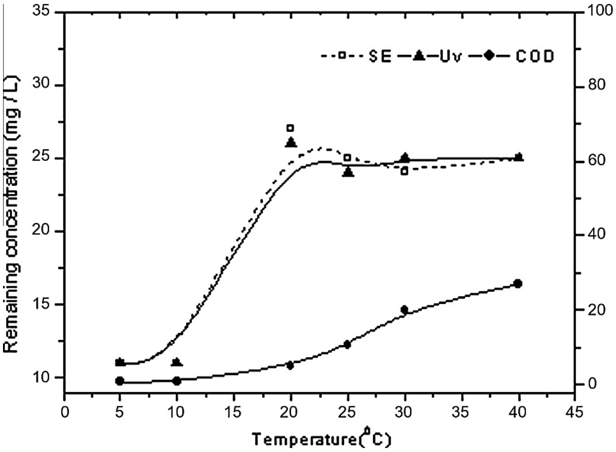

Figure 5 Effect of temperature on the removal of tramadol hydrochloride and COD at initial tramadol hydrochloride concentration of 100 mg/L, current density of 1000 mA/cm^2, 25 min, 22 h (COD), NaCl 1 g/L and pH 6.

possible. Such electrodes of this class are called "active electrodes". However, if this is not possible, the electrogenerated hydroxyl radicals could directly oxidize the organic compound to carbon dioxide and water that predominantly causes the combustion of the organic compound:

$$MO_X[OH^\bullet] + R \rightarrow M + mCO_2 + nH_2O + H^+ + e^- \quad (4)$$

This class of electrodes is called "non-active electrodes".

On the basis of the above view, the lead dioxide anode employed in this investigation is characterized by high oxygen overvoltage by which ($OH^\bullet$) is generated from the oxidation of water according to Eq. (1). However, PbO_2 does not have a higher oxidation state, consequently it is classified as a "non-active electrode". It was reported that lead dioxide electrode is hydrated (Panizza and Cerisola, 2003). The electrogenerated hydroxyl radicals are expected to be more strongly adsorbed on its surface compared with many other electrodes such as boron doped diamond. This electrode is well-known to have weak adsorption properties due to its inert surface on which hydroxyl radicals are very weakly adsorbed. These radicals make lead dioxide anode very reactive towards organics causing their oxidation. Complete degradation of the organic pollutants followed by the reaction with adsorbed hydroxyl radicals forming carbon dioxide and water.

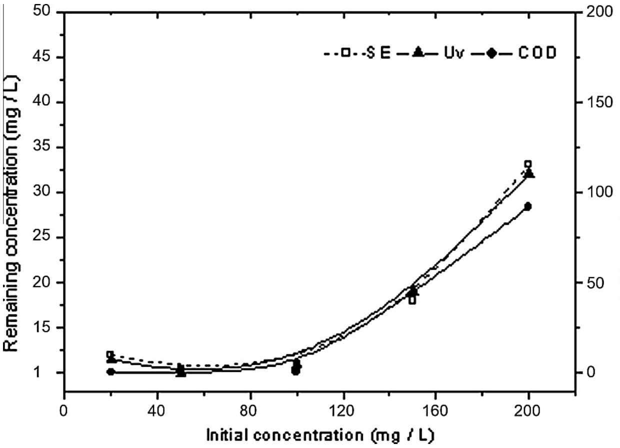

Figure 6 Effect of initial tramadol hydrochloride concentration on its removal and COD at current density of 1000 mA/cm^2, 25 min, 22 h (COD), temperature at 10 °C, pH 6 and NaCl 1 g/L.

Indirect electrochemical oxidation of organic pollutants occurs via "in situ" electrogeneration of catalytic species with powerful oxidizing property. These species are capable of eliminating the detrimental pollutants from their solutions by converting them into harmless compounds. Although a large number of electrogenerated oxidants can be used such as Fenton's reagent (Do and Chen, 1994) and ozone (Tatapudi and Fenton, 1993), hypochlorite ion is the most widely employed oxidant in wastewater treatment (Do and Chou, 1990; Krstajk et al., 1991). The mechanism of its electrogeneration from a solution containing chloride ions involves two steps, the first is oxidation of chloride ions to chlorine at the anode surface according to Cristina and Cerisola (2000).

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad (5)$$

and the second is formation of hypochlorous acid:

$$Cl_{2(aq)} + H_2O \rightarrow HClO + Cl^- + H^+ \quad (6)$$

which undergoes dissociation into hypochlorite and hydrogen ions:

$$HClO \rightarrow ClO^- + H^+ \quad (7)$$

The results of the present investigation have shown that the electrocatalytic degradation of tramadol hydrochloride on the lead dioxide anode occurred very efficiently in the presence of NaCl as a conductive electrolyte. In NaCl solution, the oxidation of the investigated tramadol hydrochloride could occur directly via the reaction of these organic compounds with the electrogenerated hydroxyl radicals adsorbed on the lead dioxide surface. In addition, indirect electrochemical oxidation may possibly take place by participation of the electrogenerated hypochlorite ions produced from the naturally occurring chloride ions in the processed water according to Eqs. (5)–(7). The hypochlorite ions in turn, contribute to higher degradation rate of the organic pollutants from their solutions. The OCl^- anion is a powerful oxidizing agent. It enhances the degradation of the pollutant. Therefore, the addition of NaCl provides the effective Cl^- ion which inturn is the main source for formation of OCl^- ion. From Figs. 1 and 2 NaCl is considered as the most preferential electrolyte. This observed behavior may be due to the small size of Na^+ which increases the ion mobility. From Fig. 1, it is clear that Na_3PO_4 and Na_3SO_4 are the less effective electrolytes in degradation. This behavior may be attributed to the formation of an adherent film on the anode surface which poisoned the electrode process. These electrolytes do not contain chloride ion which is the main source of OCl^-. In addition, they may form stable intermediate species that could not be oxidized by direct electrolysis. These observations were confirmed in other studies (Awad and Abo Galwa, 2005).

It is known that the rate of diffusion of ions increases with increasing of the temperature. In the present work, it was that found the remaining concentrations of tramadol hydrochloride have the smallest value at 10 °C as shown as in Fig. 5. Decomposition of TDCl and COD removal performed at above 20 °C has been lower with concurrent evolution of chlorine gas. This is likely due to damage of the adsorbed film on the anodic side.

It is believed that chorine is electrochemically generated first in a solution that contains the chloride ion as given in Eq. (5). Raising temperature decreases the solubility of chlorine in water and reduces the amount of the hypochlorite ion produced. This will consequently lower the rate of decomposition of tramdol hydrochloride. Furthermore, raising temperature above 30 °C will transform the hypochlorite into chlorate and perchlorate which have lesser activity in degradation.

In this study, the electrodegradation was carried out at current densities ($1000\ mA/cm^{-2}$) as shown in Fig. 3. At these values there is a great possibility of electrogeneration of Cl_2 and OCl^- in solution (Gregory and Stead, 1978). It was reported that any increase in the current densities (above $1000\ mA/cm^{-2}$) promotes the formation of oxygen as shown in Eq. (8).

$$MO_X[OH^*] \rightarrow MO_X + 1/2O_2 + H^+ + 2e^- \quad (8)$$

The produced hypochlorous acid oxidized the organic matter by regeneration of the chloride ions, according to the reaction:

$$R + HClO \rightarrow RO + Cl^- + H^+ \quad (9)$$

As reaction 9 shows, the analyte is caused to acidify over time. At $pH \approx 6$, the formation of hypochlorous acid is predominant (Pourbaix) and the remaining TDCl is a minimum, as shown in Fig. 4. Indeed, at higher pH there will be the formation of hypochlorite ion, which is less oxidizing. At more acidic pH levels chlorine will be formed, which causes loss of Cl_2 gas. It has been indicated from the above discussion that the presence of ions (such as chloride) in the conductive electrolyte is capable of generating the powerful oxidizing species. The conditions at the electrode surface play a paramount rule in the electrocatalytic degradation of organic pollutants on modified electrodes.

5. Conclusions

The electrochemical treatment of simulated wastewater containing tramadol hydrochloride has been investigated in different conductive electrolytes and under several operating conditions using Pb/PbO_2 electrode. The results of this study revealed the following:

- The electrocatalytic activity of the lead dioxide electrode depends on the conductive electrolyte.
- The highest electrocatalytic activity was achieved in the presence of NaCl (1 g/L) in which the degradation of the investigated tramadol hydrochloride occurs by both direct as well as indirect oxidation.
- The best result were found at $pH \approx 6$. Acidic and basic media may affect the electrolytic process.
- The rate of the degradation of tramadol hydrochloride and COD removal decreased significantly with increasing of the solution temperature to 40 °C.
- The optimum conditions of the treatment process are: current density of $1000\ mA/cm^{-2}$, pH ≈ 6, temperature of 10 °C and initial tramadol hydrochloride concentration 100 mg/L. The time of electrolysis 25 min for degradation rate of tramadol hydrochloride and COD removal is 22 h.
- Controlling the operating factors could lead to complete electrocatalytic degradation of tramadol hydrochloride in NaCl.
- Analyses by both methods (UV–Vis spectrophotometer and the presently designed electrode) were coincident in all cases.

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