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Removal of dexamethasone from aqueous solution and hospital wastewater by electrocoagulation

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HIGHLIGHTS

► Removal of DEX and organic load from aqueous solution and hospital wastewater by EC
► Evaluation of the toxicity during the removal of DEX by EC
► Suggestion of the EC process as a pretreatment for subsequent processes

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ABSTRACT

This study is concerned with the removal of the anti-inflammatory dexamethasone from aqueous solution and hospital wastewater by electrocoagulation. The variation of the toxicity during the electrocoagulation was also studied through experiments that were designed and optimized by means of response surface methodology. The coagulation efficiency was evaluated by measuring the dexamethasone concentration by high performance liquid chromatography coupled to a diode array detector. In addition, variation was evaluated through a *Vibrio fischeri* test. The results showed an increase in the removal of dexamethasone (up to 38.1%) with a rise of the current applied and a decrease of the inter-electrode distance, in aqueous solutions. The application to hospital effluent showed similar results for the removal of dexamethasone. The main effect of the electrocoagulation was that it removed colloids and reduced the organic load of the hospital wastewater. Regarding the current applied, the calculated energy efficiency was 100%. Without pH adjustment of the aqueous solution or hospital wastewater, the residual aluminum concentration always remained lower than 10 mg L^{-1}, and, with adjustment (to pH 6.5), lower than 0.30 mg L^{-1}, at the final stage. No toxicity variation was observed during the electrocoagulation process in aqueous solution, either in the presence or absence of dexamethasone.

1. Introduction

In the last two decades, there has been evidence worldwide attributable to the discharge of wastewater containing pharmaceutical residues (Daughton, 2008; Halling-Sørensen et al., 1998; Santos et al., 2010). A number of studies have pointed to the presence of endocrine disruptors in effluents discharged in streams, e.g. as a cause of sexual disturbance in fish (Kümmerer, 2008; Woodling et al., 2006,) and mutagenicity for living organisms (Bagatini et al., 2009).

After administration and excretion, the pharmaceuticals can reach the sewage system and, then superficial waters. Investigations have shown that conventional municipal sewage treatment plants are not always effective in dealing with effluents containing pharmaceuticals (Cha et al., 2006; Jelic et al., 2011; Schuster et al., 2008; Sim et al., 2010; Sui et al., 2010). Moreover, active substances, such as ciprofloxacin, have been found in hospital effluents after local treatment (Brenner et al., 2011; Martins et al., 2008a, 2011; Vasconcelos et al., 2009).

Several processes for treating wastewater containing pharmaceuticals have been studied including the following: an improvement of conventional processes employing anaerobic reactors (Chelliapan et al., 2011) and membrane bioreactors (Wen et al., 2004), and an evaluation of advanced oxidation processes, as well as combinations of these techniques (Arslon-Alaton and Dogruel, 2004; Arslan-Alaton et al., 2004; Andreozzi et al., 2005; Borràs et al., 2011; Martins et al., 2009; Sui et al., 2010; Vasconcelos et al., 2009). Other processes, such as electrocoagulation

Abbreviations: CC, chemical coagulation; DEX, dexamethasone; EC, electrocoagulation; GC, glucocorticoid; HUSM, University Hospital of the Federal University of Santa Maria; HPLC–DAD, high performance liquid chromatography coupled to diode array detector; RSM, response surface methodology.

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(EC) have been investigated for the treatment of hospital effluent (Gürses et al., 2002; Ryan et al., 2008; Tir and Moulai-Mostefa, 2008). A study comparing EC and chemical coagulation (CC) showed that the CC needs 20 times more mass of reagent to treat the same volume of wastewater, to achieve the same degree of efficiency (Ryan et al., 2008). Chen et al. (2002) has carried out extensive study about the EC reactions.

There are a number of advantages in EC such as low-cost, easy handling, and high efficiency in the removal of organic matter. On the other hand, the sludge generation rate, the use of sacrificial electrodes, and electrical energy consumption can be cited as drawbacks (Mollah et al., 2001).

Anti-inflammatories constitute an important pharmaceutical class and include glucocorticoids (GC) that are widely used in human and veterinary medicine, but carry the risk of side effects (Reid, 2000; Schäcke et al., 2002). The most potent GC cortisone derivate used in hospitals and clinics is dexamethasone (DEX) and relatively high levels of DEX have been detected in sewage effluent (Herrero et al., 2012). Fig. 1 shows the main structure of DEX.

This study forms part of a major project which is attempting to deal with the problem of pharmaceuticals in the environment and the main objective here is to investigate the features of EC and its effectiveness in the removal of DEX from water solution and hospital wastewater. Experiment design and response surface methodology (RSM) were employed to optimize the EC operational conditions for DEX removal. In addition, the chemical oxygen demand (COD) and residual aluminum concentration were evaluated and the variation of the toxicity was monitored throughout the evaluation, with the aid of the *Vibrio fischeri* test. An analysis of the advantages of the *V. fischeri* test was undertaken by Parvez et al. (2006).

As far as we are aware, this is the first study of how electrocoagulation can be a means of removing dexamethasone from hospital wastewater.

2. Material and methods

2.1. Reagents

The DEX base (Sigma-Aldrich, Munich, Germany) standard solutions were prepared shortly before the experiments. NaCl 99.5% (Sigma-Aldrich, Munich, Germany) was used as electrolyte. Acetonitrile HPLC grade (JT Baker, Mexico City, Mexico) and analytical grade sodium formate (Sigma-Aldrich, Munich, Germany) were used to prepare the mobile phase. All the solutions were prepared with chemicals of at least analytical grade, by using ultrapure water (Millipore, Molsheim, France).

2.2. Sampling of hospital wastewater

The studied wastewater samples were collected end-of-pipe from the University Hospital (HUSM) of the Federal University of Santa Maria after leaving the sewage treatment system. A composite sample was formed by collecting samples, every 2 h, from 8:00 to 16:00 h. The wastewater samples were collected, kept in the dark, at 4–8 °C and, at end of the day, filtered (cellulose filter, 7 μm) and submitted to the EC experiments. The physico-chemical characteristics of the HUSM effluent are shown in Table 1 (different samples, different analysts).

2.3. Aliquot collection for the analytical measurements

Samples were taken in 0, 5, 15, 30 and 45 min of the EC experiments conducted. The standard solutions and the hospital wastewater samples treated, were passed through cellulose filter (7 μm), and afterwards, through PTFE Millipore filter (0.45 μm), and then, stored at 4–8 °C, in the dark, until the analytical measurement.

2.4. Analytical methods

The residual aluminum was measured by means of a 1-02 Nanocolor test (Macherey-Nagel, Düren, Germany) and UV–vis Shimadzu Multispec-1501 spectrophotometer (Schimadzu GmbH, Duisburg, Germany).

A WTW LF 196 microprocessor conductivity meter was employed for measuring conductivity and temperature; pH and dissolved oxygen (DO) were measured by using WTW pH/Oxi 340i equipment (WTW GmbH, Weilheim, Germany).

The DEX concentration was determined with the aid of a Shimadzu high performance liquid chromatography coupled to a diode array detector, and equipped with a LC-20AT pump (Shimadzu, Duisburg, Germany). The mobile phase used was acetonitrile:formate buffer [33:67] (0.0209 mol L^{-1} sodium formate, pH 3.6); the column employed was a Nucleodur CC 70/3 C18 ec equipped with a pre-column containing the same material; the flow rate was set to 0.5 mL min^{-1} and the injection volume to 50 μL; the measurement was at 254 nm. The retention time of DEX was 3.5 min under these conditions. The deconvolution method based on UV absorbance (Martins et al., 2008b) was used to estimate the organic load of the hospital wastewater.

2.5. Electrocoagulation

The electrocoagulation was carried out by using commercial aluminum electrodes (61 cm^2 effective area) immersed vertically and, in parallel, monopole configuration. NaCl was added as the electrolyte; an EC Apparatus Corporation EC570 (Milford, MA, USA) power supply and a VC-840 digital multimeter (Volcraft, Meggen, Switzerland) were used. The experimental conditions were defined by factorial design.

A glass reactor (d_e = 105 mm) was used for the treatment of 1 L of sample. The optimization step was performed using standard solution of 100 μg L^{-1} DEX, which is also used for the fortification of the hospital wastewater samples. For the measurement of the initial conductivity, (3.3 mS cm^{-1}), 2.0 g L^{-1} NaCl as electrolyte was added to the samples of wastewater, which had been previously filtered through a cellulose filter (7 μm). All the experiments were performed at room temperature (20–25 °C). The EC experiments were conducted under

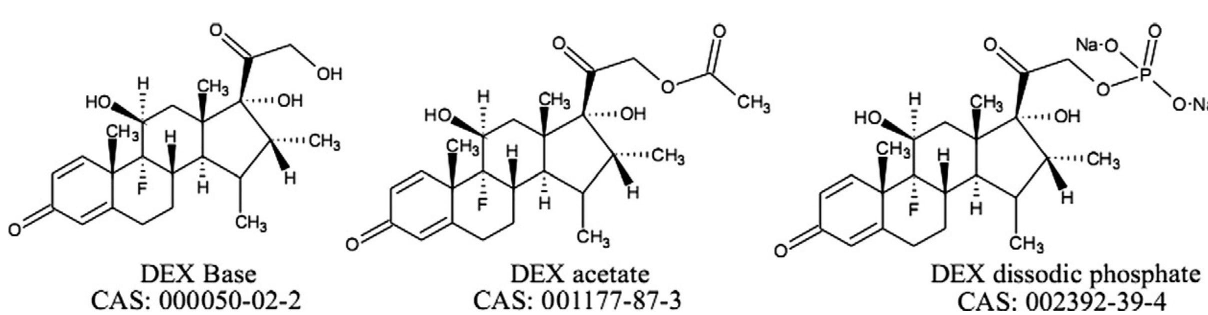

Fig. 1. Dexamethasone structures.