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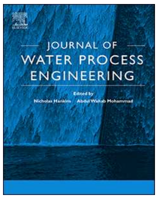

Ciprofloxacin removal: BDD anode coupled with solid polymer electrolyte and ultrasound irradiation

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ABSTRACT

Ciprofloxacin (CIP) is a broad-spectrum antibiotic of the fluoroquinolone group. The low biodegradability of this compound enhances its accumulation in the environment, with associated interference on non-target pathogens, photosynthesis of plants, alterations in the structure of algae and increasing risk of resistant bacteria development. Production plants and hospitals are the main sources of water contamination. Hence, the development of efficient technologies for the treatment of wastewaters is recommended. Here, ultrasound irradiation coupled with the electrochemical generation of hydroxyl radicals by Nb/BDD anode were investigated to remove CIP from aqueous solutions. A solid polymer electrolyte (SPE) was used to overcome the low conductivity of the solution treated. Response Surface Methodology (RSM) was applied with the aim to evaluate the effects of electric current, ultrasound irradiation and stirring rate on the removal and the energy requirements associated to the treatment. Up to 91.36 % of CIP disappearance was attained within 20 min. at 1.16 A and 520 rpm. Ultrasound irradiation at 40 kHz enhanced the removal of the compound only at low current intensity, while strongly affected the energy demand. A treatment time of 30 min. at 0.642 A and 660 rpm has been suggested to minimize the specific energy consumption, estimated to be $< 1.91\ 10^{-3}$ kWh mg^{-1}. Further research is encouraged, given the promising potential of a zero-discharge removal of several emerging pollutants as phytosanitary, pharmaceuticals and personal care products.

1. Introduction

Ciprofloxacin (CIP) is a broad-spectrum antibiotic of the fluoroquinolone group used worldwide in the treatment of urinary, respiratory, gastrointestinal, skin, bone, and joint bacterial infections [1,2]. The low biodegradability of CIP [3,4] enhances its accumulation in the environment, with associated interference on non-target pathogens, photosynthesis of plants, alterations in the structure of algae [2], and risk of resistant bacteria development [5–8].

This compound is widely detected in effluents of wastewater treatment plants (WWTPs), surface water, and groundwater [9–13]. Concentrations up to 30 mg L^{-1} and 50 mg L^{-1} have been recorded in pharmaceuticals wastewaters [2,13]. The maximum concentrations found in African water resources are higher than those reported in European based studies, as drug return programs are barely implemented in African countries [14]. Hence, inappropriate disposal of unused CIP is a primary source of water pollution [12]. After CIP administration ~50 % [2] or less [15] is absorbed in the body, while the rest is excreted. Production plants and hospitals are the most important sources of contaminated wastewaters [6]. Conventional WWTPs are not designed to deal with most of the emerging pollutants and the removal of CIP is only partially attained [1,16,17]. Only 30.5 % of the pollutant has been removed by dark chlorination in 30 min [1], it is resistant to microbial metabolism [4], activated sludge and trickling filters are not successful [6]. Moreover, sludge of WWTPs may become a relevant source of secondary pollution, as high amounts of CIP can be adsorbed (up to 2.42 mg kg^{-1}) [2]. Hence, the development of efficient technologies for the removal of pharmaceuticals in WWTPs, as well as for the treatment of wastewaters of manufacture plants, is recommended [17].

Several methods have been investigated to remove CIP from aquatic environments: adsorption [13,18–22], biodegradation [23], electrocoagulation and electroxidation [6,24–26], photodegradation over TiO_2 catalyst [27–30], UV/H_2O_2 [31] and UV/chlorine treatment [1], ozonation, Fenton and sulphate radicals-based oxidation processes [32–34]. Recently, sonochemistry has shown promising potential in the remediation of water polluted by different pharmaceuticals [35–38], as well as by CIP [17]. Sonochemical processes are based on the

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introduction of high-power ultrasound into the medium to be treated. High-pressure and low-pressure cycles, with rates depending on the frequency, are alternated. Bubbles are formed during the low pressure cycle, grow to a critical size and then collapse during a high pressure cycle, with the generation of hot spots with singular conditions of pressure (~1000 atm) and temperature (~5000 K) [39]. Sonication can be used to improve the adsorption efficiency of activated carbons [40,41], or as stand-alone technology to remove water pollutants. Hence, hydroxyl radicals are generated from water molecules and oxygen rupture and partially recombine to form hydrogen peroxide [17]:

$$H_2\,O \overset{)))}{\rightarrow} \bullet H + \bullet OH \tag{1}$$

$$O_2 \overset{)))}{\rightarrow} 2 \bullet O \tag{2}$$

$$H_2\,O + \bullet O \rightarrow 2 \bullet OH \tag{3}$$

$$O_2 + \bullet H \rightarrow \bullet O + \bullet OH \tag{4}$$

$$2 \bullet OH \rightarrow H_2O \tag{5}$$

However, only 8.09 % of degradation efficiency of CIP was observed after 2 h of ultrasonic irradiation at 35 kHz [42]. Hence, oxidative pathways induced by sonochemistry are not accompanied by significant mineralization ability [43,44], while the combination of this technique with others Advanced Oxidation Processes (AOPs) promotes the transformation of the contaminants to carbon dioxide, water and inorganic ions [44–46]. The electrogeneration of hydroxyl radicals is one of the most promising AOPs. CIP (50 mg L^{-1} in 0.10 mol L^{-1} Na_2SO_4) disappearance was recently attained in 2 h by a double-sided Ti-Pt/β-PbO_2 anode in a filter-press flow reactor, while 75 % of Total Organic Carbon (TOC) was removed after 5 h [47]. The same antibiotic (30 mg L^{-1}) has been completely removed and TOC has been reduced to 30 % by the use of a SnO_2-Sb/Ti mesh anode in 2 h at 30 mA cm^{-2} [48]. Rahmani et al. obtained a 70 % removal of CIP with similar initial concentration, time and electric current using a Ti/PbO_2 anode, whereas the Chemical Oxygen Demand (COD) was reduced by 50 % in 3 h of treatment [49]. The weaker is the interaction with the anode surface, the higher is the reactivity of the radicals; boron-doped diamond (BDD) electrodes are characterized by the weakest interaction, yielding to high mineralization rates [50]. Hydroxyl radicals are generated by water electrolysis on the anode surface, as first step in the electrochemical generation of ozone:

$$H_2O \rightarrow {}^{\cdot}OH + H+ \; + \; e- \tag{6}$$

while the hydrogen evolution occurring at the cathode does not contribute to the mineralization of the pollutant:

$$2H_2O + 2e- \rightarrow H2 + 2OH- \tag{7}$$

Here, we coupled sonication with the electrochemical generation of hydroxyl radicals by BDD anode to remove CIP from aqueous solutions. A solid polymer electrolyte (SPE) is used to overcome the low conductivity of the solution treated. Response Surface Methodology (RSM) was used to evaluate the main effects of pollutant concentration, electric current and stirring rate on the energy requirements associated to the treatment. Furthermore, optimum process conditions have been suggested in order to minimize the specific energy consumption.

2. Materials and methods

2.1. Chemicals

Ciprofloxacin (Sigma-Aldrich, Italy), analytical grade, was used as received. Tap water was used to prepare all solutions. Acetonitrile isocratic grade for liquid chromatography was purchased from Sigma Aldrich, Italy.

2.2. Electrolysis and sonoelectrolysis

Electrolysis was carried out in a single compartment electrochemical cell. The electric current was provided by an AMEL 2055 potentiostat/galvanostat. Nb/Boron doped diamond (DIACHEM®, Condias) and a Ti/RuO_2 mesh (De Nora Industries) electrodes were used as anode and cathode, respectively. The solid polymer electrolyte was a Nafion® N324 ion exchange membrane sandwiched between the electrodes. Details of the cell were provided in a previous work [51]. Experiments were carried out under galvanostatic conditions and natural pH. Aqueous solutions (0.32 dm^3) of ciprofloxacin (5 mg L^{-1}) were treated for 1 h, with current intensity ranged from 0.1 to 1.2 A. Stock solutions were prepared the same day of the tests and kept in dark, at 15 °C. Stirring rate was varied from 320 to 720 rpm. Sonication was provided at 40 kHz by the ultrasonic device SONICA 2200 (Soltec, Italy). The samples were collected at defined intervals in glass vials and analyzed immediately. Prior each galvanostatic electrolysis assays, the electrodes were cleaned to remove any kind of impurity from their surface. 2 mL aliquots were analyzed immediately after sampling at defined intervals by UV–vis spectrophotometry using a UV-1700 PharmaSpec (Shimadzu), set at the wavelength of 271.1 nm.

2.3. Experimental design

The removal efficiency was recorded at different times and a central composite design (CCD) under response surface methodology was applied to investigate the effect of the process parameters, with the aim to improve the energy efficiency of the process. The software Design Expert® 11 (Stat-Ease) was used to carry out DoE/RSM procedures. The variables here investigated were current intensity, stirring rate and presence/absence of sonication. Ranges and levels of the independent variables used for CCD design are shown in Table 1.

$$N = k[(2^n) + 2n + n_c] \tag{8}$$

The CCD consists of 2^n factorial runs, with 2n axial runs and n_c center runs (Eq. (8)), where n is the number of process variables and k is the number of levels of the categoric factor (sonication). Here, the number of experimental runs (N) is 24, as 4 factorial points, 4 axial points, 4 replicates at the center points and 2 levels of the categoric factor are considered.

The values of the axial points were selected so as to ensure the rotatability of the response surface design. The experimental sequence was randomized (Table 2), in order to reduce the effects of uncontrolled factors.

The removal efficiency was recorded and associated to the energy requirements of electrolysis and sonication. The energy consumption due to the stirrer was not taken account, as no significant change was associated to variation of the stirring rate, while this input cannot be neglected at a major scale. The responses analyzed were the removal and the specific energy consumption. A second-degree polynomial equation was used to define the target functions:

$$Y_i = k + a_1x_1 + a_2x_2 + a_3x_3 + a_{12}x_1x_2 + a_{13}x_1x_3 + a_{23}x_2x_3 + b_1{x_1}^2 + b_2{x_2}^2 + b_3{x_3}^2 \tag{9}$$

Where Y_i is the response, x_i, xj are the coded values of the process variables, k the constant coefficient, a_i the linear coefficient, a_{ij} the interaction coefficient, b_i the quadratic coefficient. The statistical

Table 1
Independent variables.

Factor	Name	Unit	Type	Minimum	Maximum
A	Current intensity	A	Numeric	0.0947	1.16
B	Stirring rate	rpm	Numeric	322.01	717.99
C	Sonication	–	Categoric	off	on