Chemical Engineering and Processing 94 (2015) 93–98

Contents lists available at ScienceDirect

Chemical Engineering and Processing: Process Intensification

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

Electrochemical degradation of amoxicillin in aqueous media

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ARTICLE INFO

Article history:
Received 10 October 2014
Received in revised form 19 December 2014
Accepted 20 December 2014
Available online 24 December 2014

Keywords:
Amoxicillin degradation
Electrochemical oxidation
Emergent contaminants
Electrocoagulation
Intensification with ultrasound

ABSTRACT

Removal of some contaminants present in effluent water, like pharmaceuticals, has become a major issue. Amoxicillin is a very widely used antibiotic, but its natural metabolism inside the human body, makes that its concentration in excretions reach important levels. This leads to lofty rates contaminated water, mainly in the health care facilities effluents and some domestic wastewaters. The presence of this antibiotic in water can cause serious alterations in aquatic ecosystems. In order to avoid these harmful effects, the amoxicillin should be degraded. The current methods employed in the voidance of this drug are mainly chemical oxidation by Fenton reagents, flocculation and photochemical treatments, but its efficiency are still limited. In the present work, electro-assisted process has been performed, forming flocs that can trap into its structure the amoxicillin molecules. In this process, iron anode acts as provider for the non-soluble iron oxides, which are flocs promoters. Fenton reactions are not discarded, so these tests were also carried out, using an ultrasound probe improving the micro mixing, and accelerating the Fenton reagents formation. The amoxicillin elimination amount was more than 80% in a non-optimized electrochemical cell thanks to the flocs formation. Ultrasound seems to diminish the electrocoagulation process.

1. Introduction

Water is essential compound for life in earth; nonetheless it has been contaminated with a great number of agents related with human activities. Some of these pollutants are the so-called emergent contaminants. Regulation on treatment and emission for these substances, have received little attention in most countries around the world. Its inclusion as dangerous materials depends upon the damage to human health, as well as its presence and spread in water resources [1]. Some of the most important emergent contaminants are the antibiotics. Its occurrence in wastewaters can lead to resilient bacterial families. Besides it can affect the natural development, growing and mobility for a wide range of microorganisms, affecting the ecosystems reached by discarded antibiotics.

Oxidation treatments can be used in antibiotics elimination from wastewaters. Advanced oxidation has been recently studied and reported by several researchers, mainly because of its high remove rates [2]. These processes are focused in the formation of highly reactive species, like hydroxyl radicals ($^{\bullet}OH$). The presence of these short-life reactants, leads to high oxidation potentials that can be used in the destabilization of some bonds present in the organic molecules, in order to obtain less harmful materials. The most common advanced oxidation processes are photocatalysis, electrolysis, ozonation, Fenton reactions, ultrasound and catalytic wet air oxidation. Its combination can be employed in order to obtain higher efficiencies in the emergent contaminants degradation [2,3].

In the electrochemical oxidation, hydroxyl radicals are formed according to Eq. (1), where MOx is a metallic oxide. Water oxidation is the other anodic reaction (Eq. (2)). Eqs. (3) and (4) are the cathodic reactions that leads to hydrogen peroxide formation and water reduction respectively.

Anode:

$$MOx + H_2O \leftrightarrow MOx(^{\bullet}OH) + H^+ + e^- \quad (1)$$

$$H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \quad (2)$$

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http://dx.doi.org/10.1016/j.cep.2014.12.007
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Cathode:

$$O_2 + 2H^+ + 2e^- \leftrightarrow H_2O_2 \quad (3)$$

$$2H_2O + e^- \leftrightarrow H_2 + 2OH^- \quad (4)$$

On the other hand, Fenton reaction occurs in the presence of some transition metals like iron. Eqs. (5) and (6) show a simplification for this process. Hydroxyl radicals are formed with hydrogen peroxide in the presence of a reducing agent, Fe(II) in this case.

Fenton:

$$Fe^{2+} + H_2O_2 \leftrightarrow Fe^{3+} + {}^{\bullet}OH + OH^- \quad (5)$$

$$Fe^{3+} + HO_2 \leftrightarrow Fe^{2+} + O_2 + H^+ \quad (6)$$

The hydroperoxyl radical ($^{\bullet}HO_2$) acts as reducing agent, forming Fe(II) facilitating Reaction (5), which also indicates that peroxide presence is needed in the $^{\bullet}OH$ radical production, and then the cathodic reaction (Eq. (3)) must be running in order to ensure the Fenton reagents formation.

Radicals participating in Fenton reactions are difficult to obtain, requiring very specific conditions, with a rigorous control of pH below 4. As this approach is made for wastewater treatment, Fenton route can result in an expensive way. On the other side, coagulation or electrocoagulation can be economically feasible and more robust process because it uses wide range of pH in order to form precipitated species. Even then, it is important to note that coagulation and radical's formation can take place simultaneously; this is possible if all conditions are conveniently arranged.

Electrocoagulation is a process carried out in an electrochemical cell, where a sacrifice anode dissolves itself, giving non-stable ions [4,5]. When a critical concentration is reached, these ions start insoluble flocs formation, which are generally hydrophobic. The flocs tend to trap into its structure some components present in solution (e.g., amoxicillin). Coagulation is particularly useful in contaminants removal, because of the solid formation breaks pollutants colloidal stability. Moreover due to its hydrophobic nature, mechanic flocs removal, charged with the unwanted impurities, can be achieved in an easy manner [6,7].

The most used sacrifice anodes in electrocoagulation processes are made from iron and aluminum. These two metals have wide range of pH where some oxide, hydroxide or oxohydroxide can be precipitated [8]. In this case, electricity is used to ensure a high oxidation rate, but it can be employed too in the Fenton reagents formation. As iron is cheaper than aluminum, it is more widely used, forming ferrous and ferric hydroxide and some kind of ferric oxohydroxide like goethite.

Amoxicillin might be removed via floc formation, but also via Fenton reactions. In this sense, ultrasound could improve antibiotic removal from wastewater, because its capability to enhance the micro mixing and due to highly reactive hydroxyl radicals are generated by the acoustic cavitation as shown in Eq. (7). In addition, the organic pollutants can be pyrolized increasing the removal efficiency [9].

$$H_2O \rightarrow OH^{\bullet} + H^{\bullet} \quad (7)$$

In the present work, systematic studies were carried out in order to establish the conditions where amoxicillin is eliminated from synthetic solutions with higher concentration than wastewater effluents. The electrochemical potential for the amoxicillin degradation was established using microelectrolysis tests. This value was used in a non-optimized electrochemical reactor, where the direct electro-oxidation and electrocoagulation were performed. In addition, the effect of 20 kHz ultrasound wave during the electrocoagulation process was also evaluated.

2. Methodology

2.1. Microelectrolysis

The electrochemical potential for the amoxicillin degradation was firstly located in a typical three electrodes microelectrolysis cell. The working electrode was a vitreous carbon disk, with 0.19 cm^2 geometrical area; a graphite rod was used as counter electrode. The reference Hg/Hg_2O_2 electrode, which has −0.140 V vs normal hydrogen electrode (NHE), was also used. The cell's electrodes were connected to a PARC 263A Potentiostat-Galvanostat, conducive to establish, control and monitor the potential sweeps carried out in the working electrode. The PARC equipment was controlled with a PC running the EChem suite; the same software was used in order to obtain and handle data.

Two solutions were studied, a blank one containing only 0.1 M KCl as supporting electrolyte, and the problem solution, simulating a real effluent with amoxicillin at 30 $mg\,L^{-1}$ (ppm) solution. The latter containing the same support electrolyte used in the blank solution. JT Baker and Alfa brands reagents were used, all with at least 99.9% of purity. Water was deionized (18 $M\Omega\,cm^{-1}$) before the dissolutions preparation.

2.2. Amoxicillin degradation tests

The amoxicillin degradation was performed in a cylindrical batch reactor, with 250 mL of capacity, fabricated on Pyrex glass. A magnetic agitator provided continuous stirring during the experimental runs. In selected experiments, tests with ultrasonic irradiation were carried out using a 40 mm probe attached to the ultrasonic generator Hielscher UP200S (200 W, 24 kHz).

Synthetic solutions were prepared with 30 ppm amoxicillin and 0.1 M KCl as a support electrolyte. As in the microelectrolysis tests, deionized water and high purity reagents were used. A commercial iron plate with a geometrical area of 9.22 cm^2 was employed as anode.

According to the microelectrolysis results, constant potential was imposed on each test using a DC power source. Potential was monitored using the same Hg/Hg_2O_2 reference electrode, connected to a milimultimeter. Current was directly acquired from power source and manually registered during each test.

Samples were taken from electrolyte and analyzed in order to verify the amoxicillin depletion during each experiment. The quantification was performed using an HPLC Thermo Scientific with a C8 column, connected to a UV–vis spectrometer Thermo Scientific UV200. Acetonitrile and monobasic potassium phosphate was pumped as mobile phase, with a flow of 1.5 $mL\,min^{-1}$.

2.3. Scanning electron microscopy

When solid was obtained in the degradation tests, it was analyzed using energy-dispersive X-ray spectroscopy (EDS) in a Seizz scanning electron microscope (SEM), connected to an INCA probe. A 14 kV voltage was applied in the chemical analysis.

3. Results

3.1. Microelectrolysis

The electrochemical behavior of amoxicillin concentration in water was analyzed using a triangular voltammetry technique. In such procedure, a potential (E) lineal sweep is applied and the