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Review

Effect of a modified photo-Fenton procedure on the oxidative degradation of antibiotics in aqueous solutions

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ABSTRACT

The aim of this study was to evaluate a modified photo-Fenton procedure as a suitable advanced oxidative process to degrade antibiotics in aqueous solutions. The classical photo-Fenton procedure was modified using a photo-catalytic reactor with continuous recirculation, which was equipped with a high pressure cylindrically shaped mercury lamp centrally and coaxially positioned and surrounded by iron mesh. The oxidation of the organic substrate could occur simultaneously through homogeneous and heterogeneous photocatalytic mechanisms due to Fe^{2+} ions from the solution and $Fe^0/Fe^{2+/3+}$ species formed on the surface of the iron mesh. The antibiotic degradation process was studied by monitoring the organic substrate concentration using chemical oxygen demand (COD), total organic carbon (TOC), high-performance liquid chromatography (HPLC) and Liquid chromatography coupled with mass spectrometry (LC-MS) analyses, in connection with monitoring the solution pH and the $Fe^{2+/3+}$ concentration as function of the reaction time. During the oxidative process, the formation of iron oxy–hydroxyl species on the surface of the iron mesh and iron ionic species in the solution was observed. The efficiency of the antibiotics degradation, obtained using the modified photo-Fenton procedure is similar to that obtained through the classical photo-Fenton procedure. The advantage of this method is that it is a simple and inexpensive procedure. In addition, no additional materials with photo-catalytic activity are necessary for the procedure, and the initial pH of the solution no longer needs to be corrected.

Contents

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1. Introduction

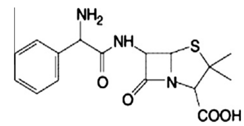
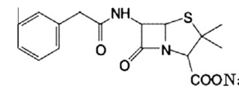
The extent to which antibiotics can be metabolised by human beings and animals is variable. Depending on the quantities of antibiotics used and their rates of excretion, antibiotics can be released into effluents and can reach sewage treatment plants [1–3]. Data available on antibiotics (from the ampicillin, erythromycin, tetracycline and penicilloyl groups) indicate their capability to exert toxic effects on living organisms, such as bacteria and algae, even at very low concentrations. These antibiotics are practically non-biodegradable and have the potential to survive sewage treatment, which leads to the persistence of these compounds in the environment and the potential for bio-accumulation [4]. The presence of antibiotics in the environment has favoured the emergence of antibiotic-resistant bacteria, increasing the possibility of infections, as well as the need to find new and more powerful antibiotics. As expected, antibiotic-contaminated water is incompatible with conventional biological water treatment technologies [5].

Antibiotics have the potential to affect the microbial community in sewage systems and can affect bacteria in the environment, there by disturbing the natural elemental cycles [3]. If the antibiotics are not eliminated during the purification process, they pass through the sewage system and may end up in the environment, primarily in the surface water. This outcome is of special importance because the surface water is a possible source of drinking water [6]. The degradation of the antibiotics by advanced oxidative processes has been demonstrate to be reasonably suited and quite feasible for application as a pretreatment method by combining it with the biological treatment [4]. The pretreatment of effluents containing penicillin by advanced oxidative processes based on O_3 and H_2O_2/O_3 did not completely remove the toxic procaine penicillin G from the effluents, which can lead to serious inhibition of the treatment of activated sludge [7]. One of the novel technologies for treating polluted sources of industrial wastewater and drinking water is the photo-Fenton process, in which hydroxyl radicals are generated in the presence of the H_2O_2, Fe^{2+} catalyst and UV radiation.

Advanced oxidative processes of the Fenton and photo-Fenton type can be used for the degradation of antibiotics in wastewater [8] or for increasing their biodegradability in biological wastewater treatment [9]. Unlike the complete amoxicillin degradation, the mineralisation of the organic compounds from solution is not complete in the Fenton oxidative process, due to formation of refractory intermediates [10]. The degradation of amoxicillin by the photo-Fenton process that use the iron species as catalysts ($FeSO_4$ and a potassium ferrioxalate complex) and solar radiation reduces the bactericide effect of the amoxicillin but the toxicity may persist, due to the intermediates formed during the oxidative process. The toxicity decreases significantly when these intermediaries are converted to short chain carboxylic acids, which subsequently allows further conventional treatment [11]. The homogeneous photo-Fenton process is limited by its narrow working pH range (2.5–4) and requires the correction of the solution pH for iron precipitation and catalyst separation and recovery. Otherwise, high amounts of metal-containing sludge can be formed and the catalytic metals can be lost in this sludge. Due to these disadvantages, several attempts have been made to develop a heterogeneous photo-Fenton procedure by immobilising active iron species on solid supports. Because iron is relatively inexpensive and nontoxic, it has been widely used in various environmental treatment processes [12,13].

In the heterogeneous photo-Fenton process, various iron-containing catalysts can be used, such as iron bulk catalysts (iron oxy-hydroxyl compounds: hematite, goethite and magnetite) or iron-supported catalysts (zeolites, clays, bentonite, glass, active carbon and polymers) [13–15].

Table 1
Characteristics of antibiotics.

Antibiotics	Ampicillin (AMP)	Penicillin G (PEN G)
Chemical formula	$C_{16}H_{19}N_3O_4S$	$C_{16}H_{17}N_2O_4SNa$
Molecular mass	349.41 g/mol	356.4 g/mol
Structure		

The heterogeneous photo-Fenton process requires that the catalyst have a high catalytic activity and a high stability in the reaction medium. At high concentrations of the iron-containing catalyst, an important decrease of the UV radiation effect may occur due to the turbidity (small particles are suspended in solution). A relevant fraction of the incident radiation can be lost via scattering; therefore, it is no longer available to induce the photo-Fenton process [12].

The pH of the reaction medium affects the photocatalytic performance (for pH values greater than 3 the oxidative efficiency decreases significantly) but it also affects the leaching of Fe from the support (for pH values less than 3 a higher amount of Fe is released into the solution) [12,14].

The advanced oxidative processes, or even the hybrid methods, may not be useful in degrading large quantities of effluent economically and it is therefore advisable to use these methods for reducing the toxicity of the pollutant stream to a certain level below which the biological oxidation can achieve the complete mineralisation of the biodegradable products [16].

The aim of this study was to evaluate a modified photo-Fenton procedure as a suitable advanced oxidative process to degrade certain antibiotics, such as ampicillin and penicillin G, in aqueous solutions.

The new proposed photo-Fenton procedure uses a photocatalytic reactor equipped with a high pressure mercury lamp and an iron mesh (cylindrically shaped, as well as centrally and coaxially positioned) as a precursor of active photocatalytic iron species.

2. Materials and methods

2.1. Materials

The antibiotics used in this work (Table 1) were ampicillin (AMP) and penicillin G (PEN G), in the form of crystalline powder

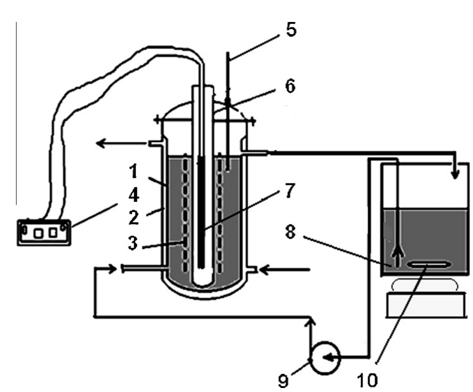


Fig. 1. Photo-Fenton procedure: diagram of work installation. (1–Photo-catalytic reactor; 2–Cooling jacket; 3–Iron mesh, cylindrical shape; 4–UV lamp source; 5–Thermometer; 6–Quartz tube; 7–UV lamp; 8–Recirculation reservoir; 9–Recirculation pump; 10–Magnetic stirrer).