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Techno-economical assessment of coupling Fenton/biological processes for the treatment of a pharmaceutical wastewater

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A B S T R A C T

A wastewater coming from a pharmaceutical plant of chemical organic synthesis with a TOC of ca 1.4 g/L and low biodegradability has been treated by coupling of advanced Fenton oxidation process and subsequent biological treatment. The influence of the reaction temperature, the hydrogen peroxide concentration and the iron/copper loadings as catalysts in the Fenton process were studied. A moderate oxidant concentration (7.5 mgH_2O_2/mgTOC) and a temperature of 70 °C enhanced the biodegradability of the wastewater with a TOC reduction of ca. 35%. A subsequent biological treatment operating with HRT and SRT of 2 days and 20 days, respectively, allowed increasing the TOC removal above 90%. The oxidant concentration and the reaction temperature of Fenton process as pre-treatment to increase biodegradability were significantly lower than the values of the Fenton process currently implemented in the pharmaceutical plant to achieve an almost complete mineralization of the organic matter (21.4 mgH_2O_2/mgTOC and 120 °C, respectively). The techno-economical evaluation of the coupling Fenton/biological system compared to the Fenton process as unique treatment, showed that the lower oxidant uptake of the Fenton process for the coupling system is economically more profitable than using an excess of oxidant and a higher reaction temperature for the intensive Fenton process.

1. Introduction

The pharmaceutical industry has become a serious source of water pollution mostly due to the increase of world population and the advances in medicine to fulfil national demands [1], reaching a production volume of 816 billion dollars in 2016 [2]. The pharmaceutical industry generates large quantities of wastewater varying in characteristics and concentration as a function of the manufacturing process and the year season. These effluents are mainly the result of machinery cleaning residues of the pharmaceutical products manufactured, and also, they contain other kinds of compounds used in the cleaning process, including solvents and detergents. Although it is not easy to generalize the characteristics of the effluents discharged from these industries, organic-synthesis pharmaceutical plants generally produce waste streams with high COD and salinity [3], as well as limited biodegradability. This fact hinders the application of biological treatment processes, and causes the discharge to the environment of persistent organic pollutants, recalcitrant to conventional schemes of municipal wastewater treatment plants. Advanced Oxidation Processes (AOPs) are widely considered as an efficient option to treat effluents of low biodegradability. These processes involve the generation of hydroxyl radicals (HO•) with high oxidizing and non-selective potential. AOPs have been successfully used for the removal or reduction of recalcitrant pollutants present in wastewater coming from different industries [4–9].

One of the most used AOPs is Fenton oxidation [10] which has been found to be a cost-effective treatment of refractory organic compounds from different sources [11]. Fenton processes are based on the potential activity of iron ions to produce highly hydroxyl radicals in the presence of hydrogen peroxide. The performance of Fenton processes can be enhanced by increasing the temperature up to 100–120 °C in pressurized systems or assisted UV–vis, ultrasounds or electrochemical systems at room temperature [12–15]. Nowadays, Fenton technology is commercially used to treat different kind of industrial wastewaters, including pharmaceutical wastewater effluents [16–19], although the high operation cost derived from temperature and hydrogen peroxide requirements is one of the main drawbacks of the process [20]. However, Fenton's oxidation can be used as a pre-treatment whenever the aim is to partially degrade organic compounds, increase biodegradability and/or reduce toxicity of wastewaters, usually being followed by a biological unit making the combined overall process economically attractive [21–24]. Biological sequencing batch reactors (SBR) are often

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proposed as final biological systems due to the simple, flexible and remarkable capacity to dampen compositional fluctuations of the inlet effluents [25–27]. Thus, several examples of combination of Fenton and biological-SBR have been reported for the treatment of wastewaters from bamboo, leather tanning and antibiotic pharmaceutical industries [21,28,29]. These studies proved that the coupling of both processes is an alternative for meeting discharge standards of industrial effluents.

The scope of this work has been the combination of Fenton as advanced oxidation process with a biological process for the treatment of a real pharmaceutical wastewater. In this framework, the first objective was to evaluate the influence of the reaction temperature and the concentrations of catalyst and hydrogen peroxide in order to increase biodegradability instead of increasing the mineralization of the organic matter. Secondly, the coupling of the pre-treated wastewater with a sequential biological process was assessed. Although, the treatment of pharmaceutical effluents by Fenton process has been investigated during the last years, only few papers are based on actual wastewaters. Moreover, to the best of our knowledge, there are not studies based on economic assessment of the proposed strategy. Therefore, the main challenge of this work is the techno-economical evaluation of the coupling Fenton/biological system compared to the sole Fenton treatment which is actually implemented in the pharmaceutical industry.

2. Materials and methods

2.1. Pharmaceutical wastewater generated and treatment in the pharmaceutical plant

The pharmaceutical wastewater was collected from an international drug manufacturing plant located outside Madrid (Spain) which is dedicated to producing different active pharmaceutical ingredients (APIs) for diabetes (gliclazide), depressive disorders (agomelatine, desvenlafaxine), heart-diseases such as high blood pressure (amlopidine, indapamide), angina pectoris (trimetazidine) or chronic venous insufficiency (diosmine), and cytostatics (fotemustinem, pixantrone, tipiracil). The particular composition of the wastewater streams depends on the manufacturing processes and other ongoing operations. The industrial plant is currently producing 3 m^3/h of wastewater that is treated, after solvents separation, by a commercial homogeneous Fenton process as it is shown in Fig. 1. This process is operating in a continuous stirred autoclave at 1.5 atm of air pressure, 120 °C, pH of 3 by addition of sulphuric acid and a hydraulic retention time (HRT) of 60 min. The dosage of iron and copper sulphate salts as catalysts is 0.024 mgFe/mgTOC and 0.0021 mgCu/mgTOC, respectively. The amount of hydrogen peroxide is 21.5 mgH_2O_2/mgTOC. The resultant effluent is neutralized before its discharge to the municipal sewer system with sodium hydroxide for the precipitation and subsequent decantation of the catalytic salts before its final discharge as sludge waste, which is managed by an authorized waste agent.

2.2. Fenton experiments

Fenton experiments as pre-treatments were performed in a non-pressurized 1 L batch reactor made of glass under magnetic stirring. The temperature of the reactor was controlled by the circulation of a heating fluid (silicone) flowing through an external jacket. The studied variables were the operation temperature as well as the hydrogen peroxide and the catalyst concentrations. Iron and copper sulphate were used as catalytic iron and copper sources. The pH was initially adjusted to 3 by adding of H_2SO_4, but the pH was not controlled along the experiments.

As compared to operation conditions of the current Fenton process of the pharmaceutical wastewater treatment plant: i) the temperature was decreased from 120 °C to 90, 80 and 70 °C; ii) the dosages of hydrogen peroxide were reduced to 7.5, 5.4 and 3.2 mgH_2O_2/mgTOC (35, 25 and 15% of the amount used in the pharmaceutical plant, experiments denoted as 35%_H_2O_2, 25%_H_2O_2 and 15%_H_2O_2); and iii) the catalyst concentration, in terms of iron concentrations, were set to 0.008, 0.024 and 0.072 mgFe/mgTOC (0.33, 1 and 3 times the amounts used in the pharmaceutical plant, experiments denoted as 1/3cat, 1cat and 3cat, respectively). The copper concentration was set keeping a Fe/Cu weight ratio of 11.4).

2.3. Biological sequential batch reactor (SBR)

The biological treatment was carried out in a SBR made of stainless steel using a working volume of 15 L. The SBR was sparged with air and mechanically stirred at 100 rpm in order to obtain 7.5 ± 1 mg/L of dissolved oxygen and a homogeneous suspension of the biomass. Centrifugal pumps were used for feeding and drawing streams during the cycles of the SBR. Dissolved oxygen (DO), temperature and pH were continuously monitored along the experiments.

The SBR was inoculated with 5 L of activated sludge from a full-scale urban wastewater treatment plant located in the Campus of Móstoles, Madrid (Spain). Initially, the biomass was acclimated during a 30-day period feeding an effluent coming from dissolved air flotation (DAF) unit of the pilot wastewater treatment plant located at the Rey Juan Carlos University (TOC, COD and TN of 100 ± 6 mg/L, 130 ± 18 mg/L and 36 ± 6 mg/L, respectively). In this acclimation period, the SBR was operated with cycles of 12 h. Thereafter, the pre-

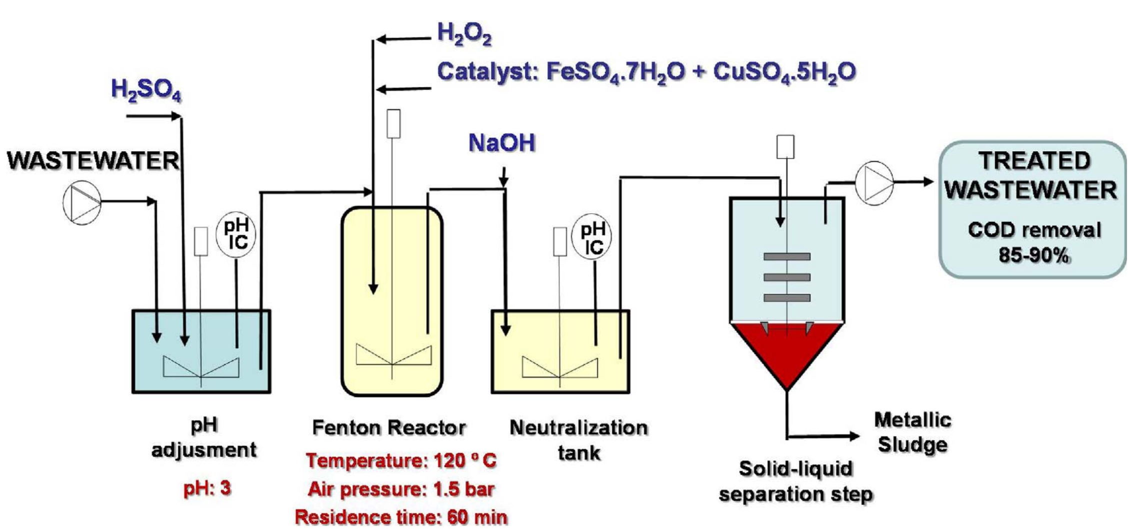

Fig. 1. Schematic view of the Fenton process at the pharmaceutical wastewater treatment plant.