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Pre-oxidation of an extremely polluted industrial wastewater by the Fenton's reagent

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Abstract

The pre-oxidation of an extremely polluted pharmaceutical wastewater (chemical oxygen demand (COD) value of 362,000 mg/l) using the Fenton's reagent has been systematically studied using an experimental design technique. The parameters influencing the COD removal of the wastewater, namely temperature, ferrous ion and hydrogen peroxide concentrations have been optimized to achieve a COD global reduction of 56.4%.

The total range of the proposed experimental design, however, could not be tested because under some conditions (hydrogen peroxide concentration over 5 M) the Fenton's reaction became violent and could not be controlled, probably due to the high exothermic effect associated with COD oxidation. For the tested conditions, the optimal values of hydrogen peroxide and ferrous ion concentration were 3 and 0.3 M, respectively, whereas temperature only showed a mild positive effect on COD removal. In addition, during the first 10 min of Fenton's reaction, more than 90% of the total COD removal can be achieved.

Fenton's reaction has proved to be a feasible technique for the pre-oxidation of the wastewater under study, and can be considered a suitable pre-treatment for this type of wastewaters.
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1. Introduction

Generation of wastewaters in industrial processes is sometimes unavoidable and in most cases a process to reduce the organic load and other contaminants must be employed

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before water discharge. To remove part of the organic load, biological processes are usually used, because they are more economic than chemical processes. In some cases, however, due to the high organic load, toxicity or presence of biorecalcitrant compounds, biological processes cannot be used, since no chemical oxygen demand (COD) removal is achieved biologically. For these wastewaters, the biochemical oxygen demand (BOD) is orders of magnitude lower than the COD. Thus, a biological treatment is not feasible. In these cases, chemical pre-treatment can adequately reduce the COD prior to biological treatment.

Among chemical processes, the advanced oxidation process (AOP) has been used to reduce the organic load or toxicity of different waters and wastewaters [1–3]. AOPs are based on the generation of hydroxyl free radicals, which have a high electrochemical oxidant potential. The generation of hydroxyl radicals involves the combination of classical oxidants, such as H_2O_2 or O_3 with UV radiation or a catalyst. The formed radicals react with organic materials breaking them down gradually in a stepwise process. The generation of hydroxyl radicals can be achieved by a variety of reactions, such as ozone/UV [4], hydrogen peroxide/UV [5], Fenton oxidation [6], photo-Fenton [5,7] or titanium dioxide/hydrogen peroxide/solar radiation [8]. The advantage of AOPs is that they effectively destroy the organic compounds, converting them mainly to carbon dioxide and water.

Among AOPs, the Fenton's reagent [9] has been efficiently used as a chemical process for wastewater treatment and pre-treatment. The Fenton's system consists of ferrous salts combined with hydrogen peroxide under acidic conditions. This reaction allows the generation of hydroxyl radicals as shown in reaction (1):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \quad (1)$$

Fe^{3+} produced can react with H_2O_2 and hydroperoxyl radical in the so-called Fenton-like reaction, which leads to regenerating Fe^{2+} (reactions (2) and (3)). Fe^{2+} regeneration is also possible by reacting with organic radical intermediates (reaction (4)) [10]:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^\bullet + H^+ \quad (2)$$

$$Fe^{3+} + HO_2^\bullet \rightarrow Fe^{2+} + O_2 + H^+ \quad (3)$$

$$Fe^{3+} + R^\bullet \rightarrow Fe^{2+} + R^+ \quad (4)$$

The Fenton's reaction has a short reaction time among AOPs; therefore, Fenton's reagent is used when a high COD removal is required [8]. A wide variety of Fenton's reagent applications have been reported, such as treatment of textile wastewaters [1,10,11], treatment of 1-amino-8-naphthol-3,6-disulfonic acid manufacturing wastewater [12], reduction of polynuclear aromatic hydrocarbons in water [13], improvement in dewatering of activated sludge [14], removal of AOX from pharmaceutical wastewater [4], treatment of brines [15,16] or treatment of paper pulp manufacturing effluents [7].

In this work, the Fenton's reagent is used to remove COD from an industrial wastewater of pharmaceutical origin characterized by its extremely high value of COD and a low value of BOD, probably due to the presence of toxic compounds, which hamper a direct biological treatment.

2. Materials and methods

2.1. Wastewater

Wastewater was obtained from a chemical plant manufacturing pharmaceutically active ingredients. Characteristics of the wastewater are presented in Table 1.

2.2. Fenton's reaction

Fenton's reaction essentially depends on three factors: temperature, hydrogen peroxide concentration and Fe^{2+} concentration. Optimization of these factors was performed by means of a Box–Hunter spherical experimental design [18]. Briefly, this technique is based in performing the experiments corresponding to the values of the factors considered which are located equidistantly to the center of a sphere. This permits to optimize the number of experiments needed to cover the whole range of values for any factor considered.

Wastewater samples were filtered to remove solids and the pH was adjusted to 4.0 before chemical oxidation process. A 100 ml sample was placed in a 500 ml Erlenmeyer flask. The flask was submerged in a temperature controlled bath and allowed to attain the preset experimental temperature. Then, $FeSO_4$ was added to the desired Fe^{2+} concentration. Finally, H_2O_2 (33% (w/v)) was carefully added to start the Fenton's reaction. The aqueous solution of Fenton's reagent and wastewater was magnetically stirred during the reaction period. Samples were withdrawn at 5, 10, 30, 60 and 90 min and immediately analyzed.

For analysis, withdrawn samples were diluted 500 times with distilled water and 1 M NaOH was added to stop the oxidation reaction (pH 12.0). To eliminate the excess H_2O_2, the diluted solution was boiled for 10 min, and then allowed to cool at room temperature. It was previously checked that the act of boiling has no effect on the COD value. Finally, samples were filtered to remove the formed ferric hydroxide and analyzed for COD.

2.3. Analytical procedures

Analytical procedures were conducted according to Standard Methods [17]: suspended solids (SS, Method 2540D), total volatile solids (TVS, Method 2540G), chemical oxygen demand (COD, Method 5220C) and biochemical oxygen demand (BOD, Method 5210B).

Table 1
Main characteristics of the pharmaceutical wastewater studied in the advanced oxidation process

Parameter	Value
Temperature (°C)	25
pH	5.32
Conductivity (mS/cm)	89.7
Soluble COD (mg O_2/l)	362000
BOD (mg O_2/l)	2900
Suspended solids (g/l)	45.95
Total volatile solids (g/l)	45.90
Toxicity (equitox/m^3)	57

Toxicity was determined by the bacterial bioluminescence test (Standard Methods, Method 8050B) using *Photobacterium phosphoreum*.

3. Results and discussion

3.1. Wastewater initial characterization

The industrial wastewater came from a fine chemicals industry which specializes in the production of pharmaceutically active ingredients. The main components of the wastewater were biguanides, but guanidines and triamines were also present.

Initial characteristics of the pharmaceutical wastewater are presented in Table 1. The value of soluble COD (362,000 mg/l) is extremely high, whereas the BOD was relatively low. This result was a COD/BOD ratio of 125 and, consequently, the wastewater must be considered as not biodegradable.

On the other hand, the wastewater contained a large amount of suspended solids (45.95 g/l, of which the 99.9% were volatile solids), which can be easily removed by filtration. Previous work showed that changes in pH and temperature did not increase the amount of solids removed by filtration.

3.2. Experimental design

A Box–Hunter spherical experimental design was proposed to study the influence of the considered factors (temperature, ferrous ion and hydrogen peroxide concentrations) on the COD removal, which was chosen as the objective function [18]. The proposed experimental design utilized the following range of variables:

- Hydrogen peroxide concentration from 0 to 6 M.
- Ferrous ion concentration from 0 to 0.6 M.
- Temperature from 25 to 55 °C.

The range of values for the three factors above were chosen according to previously values reported in literature [10,11]. In these studies, it was noted that a range of 0.11–1.82 g COD removed/g hydrogen peroxide is optimal for the Fenton's reaction, whereas ferrous ion concentration is normally one-tenth part of hydrogen peroxide concentration. Finally, temperature values are studied in the values ranging from 25 °C (corresponding to the wastewater temperature) to 60 °C.

3.3. COD removal

The experiments were carried out according to the proposed experimental design. The temperature influence on COD removal was negligible in practically all the experiments, except in some cases when a mild affect was detected. Thus, temperature does not need to be considered a factor in the pre-oxidation of the wastewater studied.

Some of the proposed experiments could not be carried out because in those cases a violent reaction with a quick boiling of the sample was observed. This phenomenon especially occurred in experiments where the concentration of hydrogen peroxide was approximately 5 M, regardless of ferrous ion concentration and temperature. This result is probably due to the high exothermic effects associated with a quick COD oxidation. Although some different strategies to add the hydrogen peroxide carefully were tested, no reliable results could be obtained from these experiments and therefore they were excluded from the experimental design.

A surface response for the values of the objective function (percentage of COD removal) obtained within the range of the values of the factors considered in the experimental design (hydrogen peroxide and ferrous ion concentration) is presented in Fig. 1 (without considering the value of temperature). In Fig. 1, an optimal area for the maximum COD removal is observed approximately at the hydrogen peroxide and ferrous ion concentrations of 3 and 0.3 M, respectively. The maximum value of COD removal for the optimal area was 56.4%. Nevertheless, it must be pointed out that the fact that the value of COD removal for some experiences could not be determined may have caused some distortions in Fig. 1.

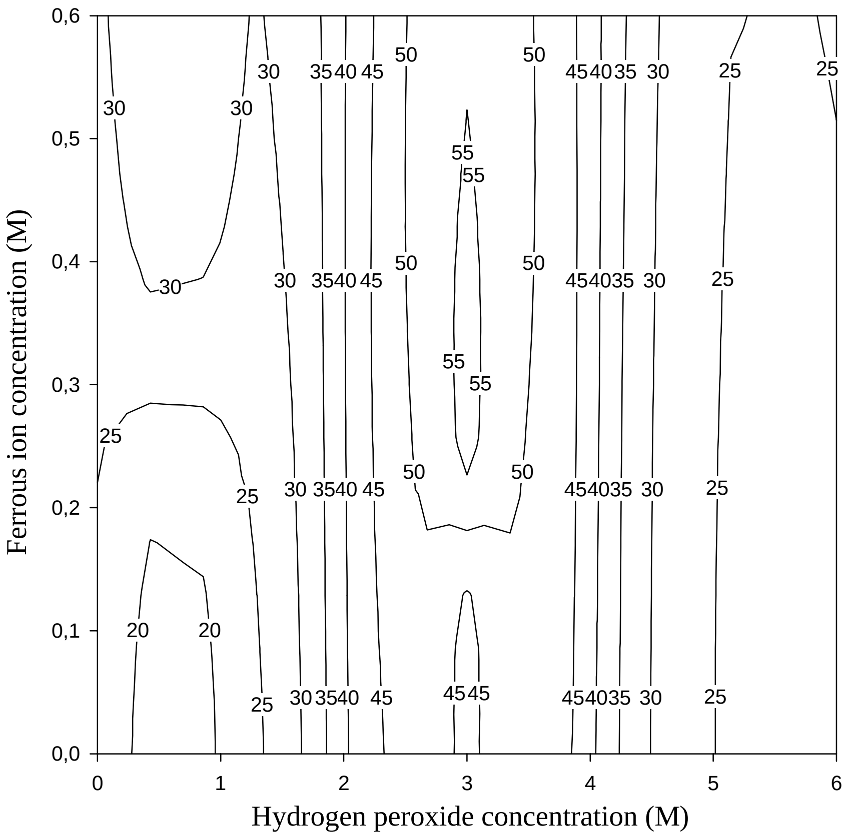

Fig. 1. Surface response for the values of the objective function (percentage of COD removal) obtained within the range of the values of the factors considered in the experimental design (hydrogen peroxide and ferrous ion concentration).

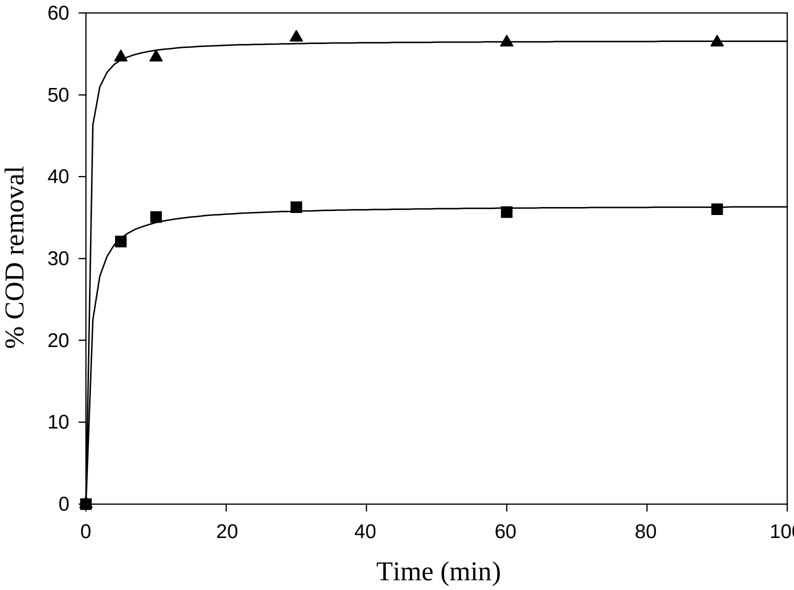

Fig. 2. Effect of Fenton's reaction time on COD removal for experiments in the advanced oxidation of pharmaceutical wastewater: (▲) $[H_2O_2] = 3\,M$, $[Fe^{2+}] = 0.3\,M$, temperature $= 40\,°C$; (■) $[H_2O_2] = 0.624\,M$, $[Fe^{2+}] = 0.53\,M$, temperature $= 52\,°C$.

Another issue that is interesting in the pre-treatment of an industrial wastewater is the total process time. In this work, it is worthwhile noting that although the Fenton's reaction sampling was carried out at different times (from 0 to 90 min), more than 90% of COD removal was achieved in the first 10 min of reaction. Fig. 2 shows the COD removal determined at different times of reaction for different experimental conditions. As can be seen in Fig. 2, in both cases, the Fenton's reaction is practically finished in the first 5–10 min. Short oxidation times are also reported by other authors [11,13].

Finally, it was hypothesized that the amount of hydrogen peroxide was not high enough to oxidize all of the COD present in the sample even under the optimal conditions for COD removal (56.4%). Since the concentration of hydrogen peroxide could not be increased due to the previously mentioned technical problems, a sequence of experiments based on repeating successive Fenton's reactions for the optimal conditions was performed in order to improve COD removal. Thus, the sample coming from a Fenton's treatment experiment was again treated under the same conditions. The results obtained, however, showed no significant increase in the COD removal (data not shown). Therefore, it could be concluded that there was no stoichiometric limitation in the Fenton's reaction.

A further investigation will be focused on the chemical/biochemical characteristics of the original compounds present in the wastewater as well as the compounds resulting from Fenton's treatment, with the objective of designing a complete treatment for the wastewater under study.

4. Conclusions

From the data here presented, we can conclude that:

(1) Operational parameters influencing the Fenton's reaction in the pre-oxidation of an extremely polluted wastewater have been studied by means of an experimental design, in which the factors considered were temperature, ferrous ion and hydrogen peroxide concentration.
(2) The optimal values of hydrogen peroxide and ferrous ion concentrations were 3 and 0.3 M, respectively; a COD reduction of 56.4% resulted.
(3) Temperature only showed a mild positive effect on COD removal. Consequently, temperature should not be considered in the optimization of the Fenton's reaction for this wastewater.
(4) In the first 10 min of the Fenton's reaction, more than 90% of COD removal can be achieved. This finding is of special interest in the industrial application of Fenton's reagent, because it permits a significant COD reduction in a very short period of time.
(5) The results here presented can be considered as an effective pre-treatment of this type of wastewaters, when direct biological treatments are not possible.

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