

II-086 - COMPARISON AMONG HYDROGEN PEROXIDE ADVANCED OXIDATION PROCESSES FOR THE TREATMENT OF INDUSTRIAL WASTEWATERS

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ABSTRACT

The use of AOPs (Advanced Oxidation Processes) for the treatment of industrial wastewaters has increased during the last years. The process efficiency depends on the treatment conditions (temperature, pH, reagent dosage etc.) and it is very difficult to predict it because the reaction mechanisms are strongly affected by the mutual relationship among these parameters and the wastewater composition. During this work three AOPs (Fenton, photo-Fenton, H₂O₂/UV) were studied. They were used for the treatment of a real wastewater (deriving from a chemical-pharmaceutical factory) under different conditions in a lab scale plant. Data analysis was aimed to understand the main reaction characteristics, so as to assess the suitable process and the proper treatment conditions.

KEYWORDS: advanced processes, chemical oxidation, hydrogen peroxide, industrial wastewater.

INTRODUCTION

The use of AOPs (Advanced Oxidation Processes) for the treatment of industrial wastewaters has increased during the last years. AOPs comprise various processes such as O₃/H₂O₂, Fe²⁺/Fe³⁺/H₂O₂/UV, UV/H₂O₂, and UV/TiO₂, depending on the way how to produce hydroxyl radical (•OH).

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Reaction mechanisms were investigated by several Authors (1-5), although under reaction conditions far from those typical of wastewater treatment applications (low reagent concentrations, absence of organics or presence of model substances). Also under these “simplified” conditions, complex radical chain reactions occur. Yoon et al. (6) reported that in the Fenton process the reaction pathways strongly depend on the ferrous ion and hydrogen peroxide initial concentrations, on their ratio and on the concentration and type of the organic pollutant. Organic substances can, in fact, nearly stop (it is the case, for instance, of t-Buthanol) or propagate (e.g. Methanol) the ferric ion induced radical chain reactions. Besides, some organic materials may have these two properties simultaneously (e.g. high molecular humic substances, dye etc.). It is clear, therefore, that the most suitable reagent conditions as well as the design parameters can not be predicted for real wastewaters: experimental tests must be carried out trying to understand the reaction characteristics.

The aim of this work was the study of three AOPs (Fenton, photo-Fenton, H₂O₂/UV) which were used for the treatment of a real wastewater (deriving from a chemical-pharmaceutical factory) under different conditions in a lab scale plant. Data analysis was also aimed to understand the main reaction characteristics, so as to assess the suitable process and the proper treatment conditions.

MATERIALS AND METHODS

Wastewater characteristics

The wastewater used for the experiment was characterized by a very high COD concentration (217,000 mg/L). Organic matter was mainly constituted by Methanol (70,700 mg/L) and Acetone (49,900 mg/L) together with trace compounds (chlorinated solvents). Since BOD₅ concentration was quite high (113.000 mg/L), the biological treatment could represent a suitable solution; nevertheless the wastewater was submitted to the chemical oxidation tests because it is a real wastewater, and, at the same time, its organic content is well defined (two main substances are present), thus simplifying the analytical approach and the interpretation of the reaction mechanisms. Wastewater was always diluted with distilled water at the beginning of every test, in order to reach a COD concentration around 600 mg/L.

Pilot plant and treatment procedures

Experiments were conducted in a thermostated batch reactor (2 L volume) equipped with two 125 W high pressure mercury lamps (emitted light wavelength range: 280-400 nm); wastewater mixing was achieved by means of a mechanical stirrer. The flocculation-sedimentation step was conducted in a 2 L graduated cylinder. Experiments were initiated by adding H₂O₂ to the wastewater (after ferrous sulfate dosage in the Fenton and photo-Fenton tests); some experiments were conducted with a progressive dosage of hydrogen peroxide during the test.

Reagents and analyses

Ferrous sulfate was purchased from Carlo Erba, hydrogen peroxide (35%) from Ausimont. pH was adjusted by 1 N H₂SO₄ or lime. Analyses of Fe(II) and hydrogen peroxide were carried out by using Merckoquant test strips (Merck). pH was measured by means of a pH-meter (Inolab, WTW). COD was determined accordingly with the IRSA-CNR methods (7). In order to define a rough classification of the organic matter, COD concentration was also determined by means of a modified procedure as far as the digestion step is concerned: samples were submitted to a low temperature digestion (75°C) for different lengths of time (from 10 to 120 min). In this way, measured COD accounted for the easily degradable (by means of chemical oxidation) matter.

Experimental conditions

Tested conditions were the following:

- COD initial concentration: 600 mg/L;
- H₂O₂ dosage: 150-400 mg/L;
- Fe²⁺ dosage (only Fenton and photo-Fenton processes): 10-100 mg/L;
- temperature: 15 and 25 °C;
- reaction time: 2 - 4 hours, and
- specific UV radiation power input (only for UV/H₂O₂ and photo-Fenton processes): 200 and 100 kW/kgCOD₀.

RESULTS AND DISCUSSION

Fenton process

Fenton treatment was carried out at different Fe(II) dosages (15-100 mg/L) and temperature (15°C and 25°C) with the same H₂O₂ dosage (300 mg/L), which was chosen as about one half of the initial COD (~600 mg/L). H₂O₂ was dosed progressively during the test (60 mg/L at time 0, 120 mg/L after 40 and 80 minutes, respectively).

In Fig. 1, the COD removal efficiency achieved after 120 minutes oxidation (under different conditions as far as the Fe(II) dosage and the temperature are concerned), flocculation and 120 minutes sedimentation is reported. It can be observed that the effect of both temperature and iron dosage is not appreciable. Since the molar ratio $[\text{Fe}^{2+}]_{\text{dosed}}/[\text{H}_2\text{O}_2]_{\text{dosed}}$ is lower than 1, the amount of dosed iron is not sufficient to consume all the hydrogen peroxide, as shown in Fig. 2.

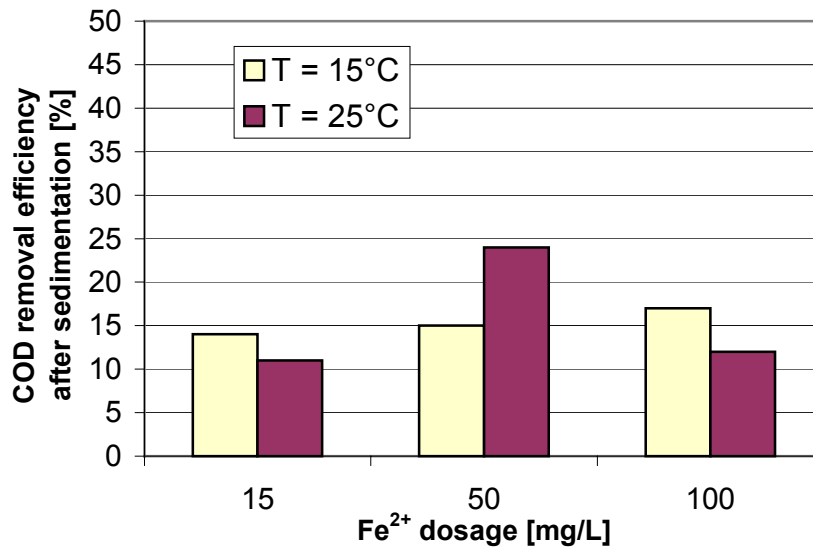


Figure 1: Fenton process – COD removal efficiency under different treatment conditions (H_2O_2 dosage = 300 mg/L)

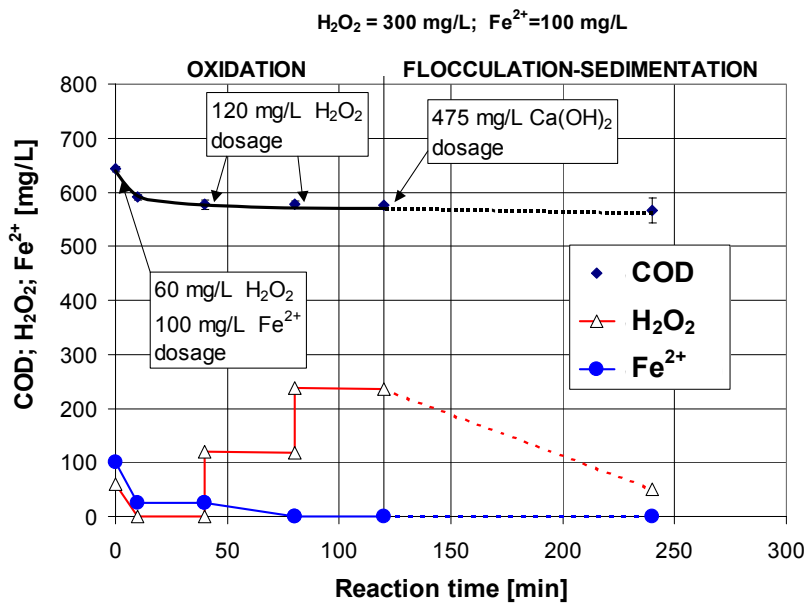
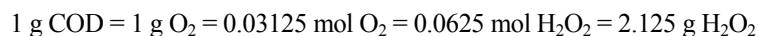


Figure 2: Fenton process – Typical concentration-time profiles for COD, Fe^{2+} and H_2O_2

The hydrogen peroxide accumulation shows that ferrous ion regeneration was stopped; in fact, as already stated, the organic matter can be an $\cdot\text{OH}$ scavenger, resulting in the interruption of the radical chain reactions which lead to the Fe^{2+} regeneration through reactions like (8): $\text{Fe(III)} + \text{HO}_2\cdot \rightarrow \text{Fe}^{2+} + \text{O}_2 + \text{H}^+$, where the $\text{HO}_2\cdot$ radical can be produced for instance by the reaction between $\cdot\text{OH}$ and H_2O_2 (1) or between the formed organic radical and dissolved oxygen (3).

The specific removal efficiency ($\text{H}_2\text{O}_{2\text{consumed}}/\text{COD}_{\text{removed}}$) were always lower than 2 (in the range 0.12-0.90); this means that the COD consumption was always higher than expected based on the stoichiometric ratio defined by the following reaction:



It was supposed that dissolved oxygen took part in the oxidation reaction, as demonstrated by several Authors (3, 6, 9, 10); in fact, atmospheric oxygen could be dissolved into the wastewater during the treatment, due to the strong stirring.

H₂O₂/UV system

This process was tested under different conditions, so as to evaluate the influence of the following parameters: H₂O₂ dosage (150-400 mg/L, single or progressive addition), reaction time (2 or 4 hours), specific power of the emitted UV light (100 and 200 kW/kgCOD₀).

As expected, instantaneous dosage of H₂O₂ led to a faster COD reduction (hydrogen peroxide is soon available), but the final result was roughly the same (Fig. 3).

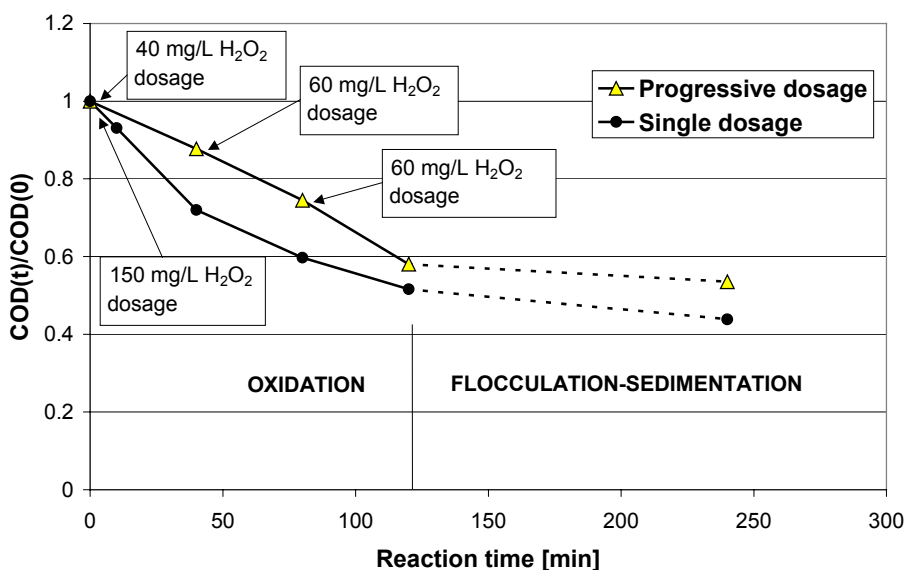


Figure 3: H₂O₂/UV system – Effect of the H₂O₂ dosage procedure (single or progressive dosage) on the COD removal efficiency

The COD removal efficiency was proportional to the H₂O₂ dosage up to 300-350 mg/L. Higher dosages did not yield higher removal (Fig. 4). It is worth to be noted that the increase in the COD reduction corresponded stoichiometrically to the increase in the H₂O₂ dosage: the global COD removal is due to a constant fraction plus a variable fraction which is predictable based on the H₂O₂ dosage (Fig. 4). This can be explained supposing that dissolved oxygen was involved in the reactions. In fact, the longer the reaction time, the higher is the constant fraction of COD removed (Fig. 4 A and B).

By reducing the power input of the UV radiation (100 instead of 200 kW/kgCOD₀) the COD removal efficiency was the same (around 70%) after 4 hours reaction (hydrogen peroxide dosage: 300 mg/L).

Photo-Fenton process

Photo-Fenton treatment was carried out at different Fe(II) dosages (10-100 mg/L) while the power input and the H₂O₂ dosage (300 mg/L, progressively dosed) were maintained constant.

The influence of the Fe²⁺ dosage was irrelevant (Fig. 5 and 6). Indeed, the UV radiation proved to be very efficient in the H₂O₂ utilization so that the addition of ferrous ion did not lead to a further improvement.

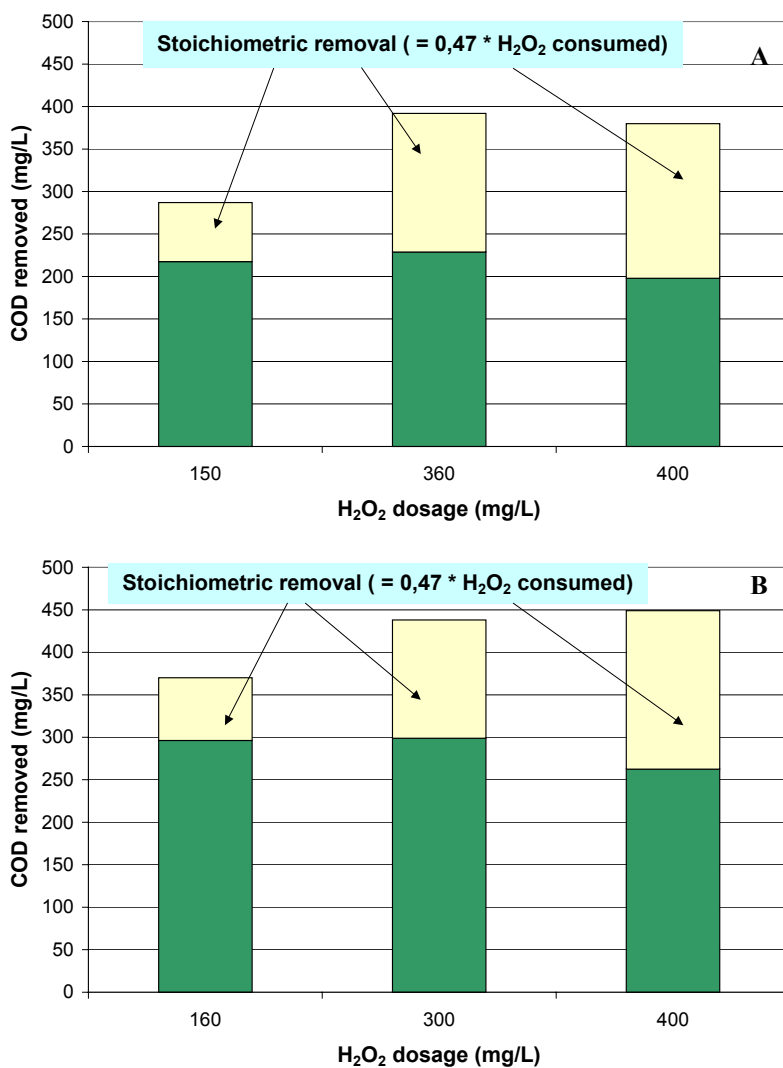


Figure 4: H₂O₂/UV system – Effect of the H₂O₂ dosage on the COD removal efficiency after 2 hours reaction (A) or 4 hours reaction (B).

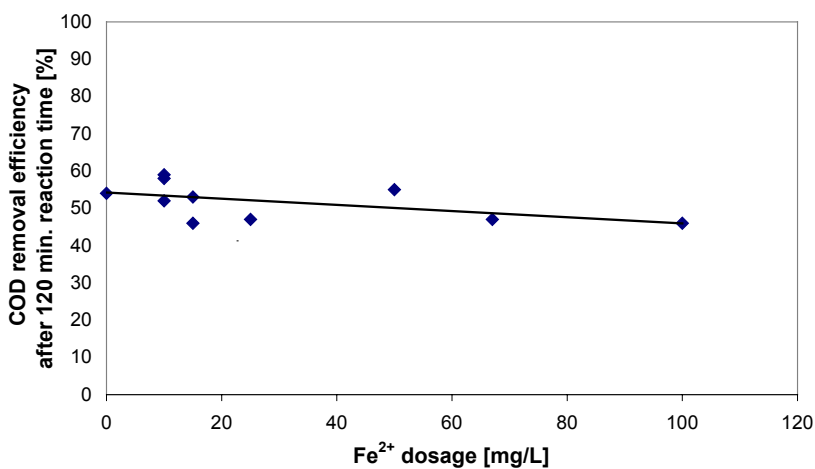


Figure 5: Photo-Fenton process – Effect of the Fe²⁺ dosage on the COD removal efficiency after 2 hours reaction

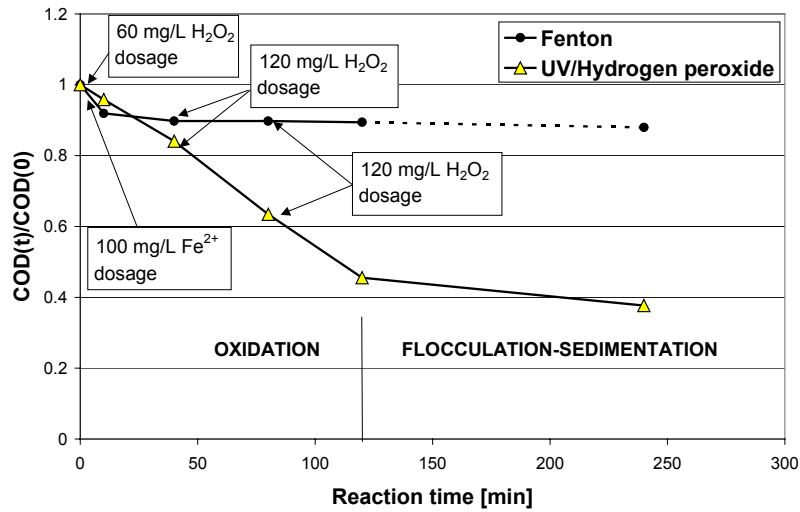


Figure 6: Comparison between Fenton process and H₂O₂/UV system

COD fractionation

In order to better understand the transformation mechanisms of the organic matter during the oxidation process, in some tests the collected samples were submitted to the COD determination under the strong conventional conditions (2 h digestion at 150 °C) and also under weaker conditions (10 minutes to 120 minutes digestion at 75°C). In this way it was possible to divide the organic matter into an easily degradable fraction (with a 10-20 min digestion at 75°C) a refractory fraction (determined only after digestion at 150°C for 120 minutes) and an intermediate fraction. In the example of Fig. 7 it can be seen how, while increasing the time reaction (i.e. while the reaction proceeded), the easily degradable fraction decreased; intermediate products were also formed which were refractory to further oxidation (see the increase passing from 20 to 120 min reaction without an appreciable reduction of the total COD). In fact, during oxidation, stable molecules are formed; in order to break their bonds, a higher amount of energy is required. These results can help in finding the suitable conditions for chemical oxidation, in particular in combined chemical-biological processes (11).

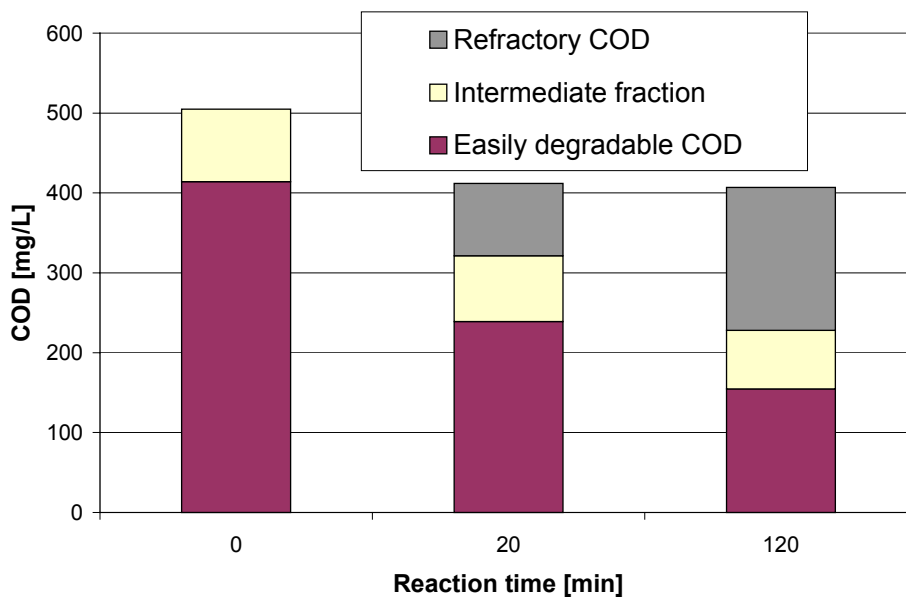


Figure 7: Transformation of the organic fraction during the oxidation process (Fenton process)



CONCLUSIONS

The main conclusions of this research are the following.

With the Fenton process (H_2O_2 dosage = 300 mg/L = $\text{COD}_0/2$, Fe^{2+} dosage = 50-100 mg/L) the COD removal efficiency was 15-20% (after the flocculation step). The organic matter showed a scavenging effect for the $\cdot\text{OH}$ radicals, thus interrupting the radical chain reaction leading to the Fe^{2+} regeneration. The specific COD removal efficiency ($\text{COD}_{\text{removed}}/\text{H}_2\text{O}_{2\text{consumed}}$) resulted higher than expected on the basis of the stoichiometric ratio, showing the probable influence of the dissolved oxygen.

The $\text{H}_2\text{O}_2/\text{UV}$ system led to a COD removal efficiency higher than 70% (after 4 hours reaction), with a H_2O_2 dosage of 300 mg/L (also with the lowest energy input: 550 kWh/kg $\text{COD}_{\text{removed}}$). The highest dosages (400 mg/L) did not yield a process improvement, probably because of the formation of intermediate refractory compounds. Also in this case, dissolved oxygen played an important role in the overall COD removal.

The addition of ferrous ion to the $\text{H}_2\text{O}_2/\text{UV}$ system did not lead to a further improvement.

The determination of the organic matter with $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation after sample digestion at low temperature (75°C) and for variable time lengths (10-120 minutes) could represent a useful integration of conventional COD data, in order to better understand the reaction mechanisms and so define the most suitable conditions for chemical treatment.

In conclusions, the results of this research show that the understanding of the reaction mechanisms is very important to define the correct treatment conditions. Nevertheless, when considering real wastewaters, these mechanisms are not predictable and a preliminary experimental phase is fundamental. Besides, since generally wastewater composition is very complex and variable, suitable analytical procedures can be a very helpful tool for the result interpretation in practical applications.

ACKNOWLEDGEMENTS

The authors thank SIR Industriale SpA for giving financial and technical support to the research

AUTHOR'S CONTRIBUTION

Giordano Urbini and Giorgio Bertanza carried out the scientific supervision and coordinated the research; Giorgio Bertanza, Roberta Pedrazzani and Maria Cristina Collivignarelli carried out the experimental work and data elaboration.

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