Degradation of Organic Compounds from Industrial Pharmaceutical Effluent Through Advanced Oxidation Processes

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This paper presents an experimental study focused on the degradation of an industrial pharmaceutical effluent through advanced oxidation processes. In the present study, two procedures (Fenton and photo-Fenton) were applied to the degradation of organic compounds from the pharmaceutical effluent; these are focused on the influence of the operational parameters on the efficiency of the oxidation of the organic compounds from the effluent and determining the optimal operating conditions in view to obtain a greater process performance. The degradation process was studied by monitoring the changes in the organic substrate concentration using chemical oxygen demand (COD), total organic carbon (TOC) and high-performance liquid chromatography (HPLC) analyses. The results suggest that the techniques applied could be used to remove organic compounds from industrial pharmaceutical effluent.

Keywords: advanced oxidation processes; Fenton and photo-Fenton procedures; pharmaceutical and its effluents; organic compounds

Industrial effluents contain mainly chemical and solvent residues that are used or produced during the fabrication process. Therefore, it is important to know the production processes and the chemicals used.

Pharmaceutical compounds have raised increasing concerns over the past years due to their effects on the environment. Many pharmaceutical products are used in human and veterinary medicine and are released into the environment through metabolic processes. These compounds are not completely degraded in the wastewater treatment plants and many of them are discharged into the environment [1, 2].

The characteristics of these pharmaceutical effluents differ widely. Therefore, a process selected for one type of wastewater may not be suitable for another type [3].

Moreover, the pharmaceutical companies are one of the major contributors concerning hazardous and toxic effluents. These industries generate large volumes of wastewater during the production process. Due to strict limits in the legislation for wastewater, these industries are interested in finding viable solutions to eliminate toxic compounds contained in the wastewater and industrial effluents.

Thus, efforts are being made to find specific solutions suitable for each type of effluent.

Pharmaceutical industries generate effluents and wastewater which change their characteristics and quantity function of the manufacturing processes. For example, gelatin is a significant contaminant in pharmaceutical wastewater. Gelatin is usually a constituent of the drug capsules, which makes them easy to swallow. In the composition of the capsules one can find also different dyes.

The treatment processes are also recommended to transform the wastes into a biodegradable form. When the effluent is biodegradable it is easy to treat it in the wastewater treatment plant. Other treatment possibilities consist in using the advanced oxidation processes (AOPs); the Fenton processes (Fe^{2+}/H_2O_2; $Fe^{2+}/H_2O_2/UV$) represent an efficient way to mineralize pharmaceuticals. The Fenton processes have been studied for their prospective applications in unmanageable wastewater treatment [4, 5].

AOPs are used to generate HO• radicals, because the HO• radicals have a high oxidation potential and can destroy recalcitrant organic and inorganic molecules which are extremely resistant and non-selective.

The oxidation process is determined by the very high oxidative potential of the $HO^•$ radicals generated into the reaction medium through different mechanisms [6- 10].

The Fenton process involves the use of iron salts and hydrogen peroxide in producing of hydroxyl radicals. This reaction is spontaneous and can occur without the influence of the light.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + OH^-$$

It can be considered that the rate of the pollutant degradation increases through the photochemical reaction in the UV-Fenton processes. In this case, the regeneration of Fe^{2+}, with the production of new HO• radicals, follows a photo reduction process:

$$Fe^{3+} + H_2O \rightarrow Fe(OH)^{2+} + H^+$$
$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO\bullet$$

In the photo-Fenton process, in addition to the above reactions, the formation of hydroxyl radicals occurs also through the following reactions:

$$Fe^{3+} + H_2O + h\nu \rightarrow HO\bullet + Fe^{2+} + H^+$$
$$H_2O_2 + h\nu \rightarrow 2HO\bullet$$

Some authors describe more reactions in defining the photo-Fenton process [10, 11].

Anyhow, the efficiency of the various AOPs depends both on the rate of generating free radicals and on the extent of

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contact between the radicals and the organic compounds [12-18].

The parameters which determine the efficiency of the oxidation process are: the structure of the organic compounds, the hydrogen peroxide and the catalyst concentrations, the wavelength and intensity of the UV radiations, the initial solution *p*H and the reaction contact time [14].

The major studies refers to the removal of organic compounds from wastewaters using synthetic solutions with predetermined concentrations [5-7, 14, 17].

The objectives of this paper include the study of the influence of the operational parameters on the efficiency of the oxidation of the organic compounds from an industrial pharmaceutical effluent through advanced oxidation processes, of Fenton and photo-Fenton type and determining the optimal operating conditions in obtaining a greater process performance.

Experimental part

Materials and methods

The industrial pharmaceutical effluent was collected from a pharmaceutical plant located in Bucharest. The sample was stored in a dark place at 4°C. Then, the sample was analysed in order to put in evidence the degradation of organic compounds.

The laboratory experiments were conducted at room temperature (20 ± 2^0C). The degradation of the organic compounds was performed in a laboratory installation with continuous recirculation (fig. 1).

Fig. 1. Laboratory work installation (Fenton and photo-Fenton procedures)

The main component of the laboratory installation is the reactor with the following characteristics: reaction volume 1.5 L, total solution volume 2.5 L, recirculation flow rate 1.0 L/min; it is equipped with a high pressure mercury lamp, of 120 W, coaxially positioned. The oxidation degree of the organic compounds from the pharmaceutical effluent was studied by monitoring the changes in the organic substrate concentration using chemical oxygen demand (COD), total organic carbon (TOC) and high-performance liquid chromatography (HPLC) analysis. Chemical oxygen demand analyses were performed with a Digestor DK6. The total organic carbon (TOC) analyses were performed using a Multi N/C 2100 (Analitikjena) TOC-analyzer. High-performance liquid chromatography (HPLC) analyses were done using an Ultimate 3000 "Diode Array" chromatograph, detector UVD-3000, C18 Acclaim 120 Dionex. The HPLC reactives were provided by Merck Chemicals Germany. The samples collected from the reactor at predetermined times were stabilized using MnO_2 crystalline powder so that the unreacted H_2O_2 could quickly decompose, and then they were filtered. For the COD analysis, the samples were corrected in terms of the *p*H using a 40% (w/w) NaOH solution for the Fe ions precipitation, and then they were filtered; the *p*H value was measured with Jenway 370 pH-meter. The other reagents used in this work were analytical grade, made in Romania.

Results and discussions

Advanced oxidation processes provide a better efficiency in removing organic compounds at low temperatures, and this is one of the advantages of these procedures.

In the Fenton processes a series of operational parameters are very important, such as the *p*H of the reaction medium, $Fe^{2+/3+}$ concentration,H_2O_2 concentration and the reaction time.

The experimental program was the following:

- the work solution volume (industrial pharmaceutical effluent), 2500 mL;
- the determined initial concentration of the work solution, COD_0 = 76000 mg O_2/L;
- the corrected *p*H 2 ÷ 4 (the initial water *p*H was 6);
- the concentration H_2O_2 0 ÷ 200% stoichiometric ratio;
- the catalyst ($FeSO_4{\cdot}7H_2O$) concentration 0 ÷ 200 mg Fe^{2+}/L;
- reaction time: 0 ÷ 180 min

The quantitative evaluation of the oxidation process was performed determining the amount of COD [mg O_2/L) and calculating the degree of oxidation, expressed as the efficiency of the degradation of the organic compounds:

$$\eta\ [\%] = \frac{COD_0 - COD_t}{COD_0} \cdot 100 \qquad (1)$$

where:

COD_0 is the COD value of the initial solution (industrial pharmaceutical effluent);

COD_t is the COD value.

The influence of the reaction time

The study of the degradation of the organic compounds from the pharmaceutical effluent was performed in the following conditions: COD_0 = 76000 mg O_2/L; the initial *p*H = 6; the catalyst concentration = 100 mg Fe^{2+}/L; the H_2O_2 concentration = 50% in excess of stoichiometric one; the reaction time: 0 ÷ 180 min.

The comparative tests (Fenton and photo-Fenton) presented in the figure 2 put in evidence the relative scarce degradation efficiency (21.05% in the case of the Fenton process and 24.35% in the case of photo-Fenton one indicating a high stability towards oxidation of the organic compounds present in the pharmaceutical effluent, which can be attributed to the formation of reaction intermediates having a high resistance to oxidation.

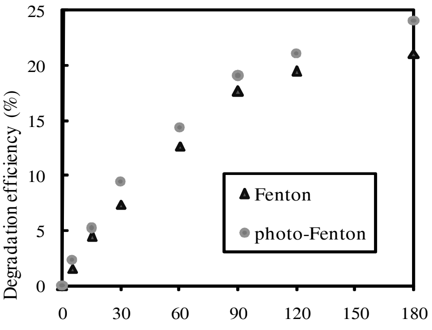

Fig. 2. Evaluation of the oxidation process in correlation with the reaction time; *p*H = 6

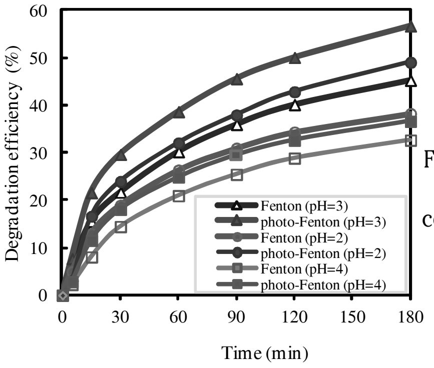

Fig.3. Evaluation of the oxidation process in correlation with the *p*H

The influence of pH

The *p*H of the reaction medium plays a decisive role in the advanced oxidation processes and this is one of the points of interest in the experimental studies. It is generally accepted that the optimum *p*H of the reaction medium in photo oxidative processes is in the range 2 ÷ 4 [1-5, 14].

The influence of *p*H has been put in evidence in the following conditions: COD_0 = 76000 mg O_2/L; initial *p*H (corrected) = 2 ÷ 4; catalyst concentration 100 mg Fe^{2+}/L; concentration H_2O_2 50% excess of stoichiometric one; reaction time 0 ÷ 180 min.

The evaluation of the oxidation in time at different initial *p*H values is presented in figure 3. As can be seen, under similar working conditions, the degree of oxidation is influenced by the initial *p*H of the solution, the maximum value being obtained at a *p*H = 3 (45.26% in the case of Fenton process and 56.68% in the case of photo-Fenton one). At lower values †of the initial *p*H of the work solution (*p*H = 2), the degree of oxidation decreases due to the process of protonation of the molecules of H_2O_2 leading to the formation of oxonium ions, which are more stable towards oxidation, no longer participating in the generation of HO• and HO_2• radicals active in the oxidation. At higher values of the initial *p*H of the solution (*p*H = 4), the degree of oxidation decreases in more pronounced way due to the precipitation of the Fe^{3+} ions to Fe $(OH)_3$ and the formation of complexes of the type $[Fe(OH)(H_2O)_5]^{2+}$. As a result, the generation of HO • and HO_2 • radicals is strongly limited by the disappearance in the solution of the active centers associated with the $Fe^{2+/3+}$ ions and the absorption of the UV radiation by the Fe $(OH)_3$ and $[Fe(OH)(H_2O)_5]^{2+}$.

The influence of Fe^{2+} concentration

The study of the influence of the catalyst concentration (expressed as mg Fe^{2+}/L) was performed in the following experimental conditions: COD_0 = 76000 mg O_2/L; pH (corrected) = 3 and reaction time of 180 min.; the catalyst concentration was successively 0, 50, 100 and 200 mg Fe^{2+}/L; the H_2O_2 concentration 50% excess (related to stoichiometric one).

The evaluation of oxidation process, expressed as a dependence of the degree of oxidation on catalyst concentration is presented in figure 4.

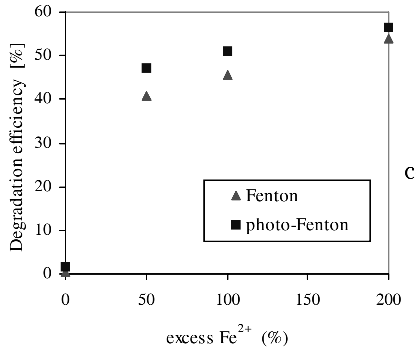

Fig.4. Evaluation of the oxidation process in correlation with the concentration of catalyst (Fe^{2+})

In the absence of the catalyst the oxidation process occurs unsatisfactorily. Increasing this concentration to higher values (50, 100 200 mg Fe^{2+}/L) the oxidation efficience increases, due to the generation of additional radicals in the reaction medium, being the highest at 200 mg Fe^{2+}/L. From economical reasons, the concentration of 100 mg Fe^{2+}/L can be considered as acceptable one.

The influence of H_2O_2 concentration

The hydrogen peroxide is the main supplier of HO_x radicals, considered as the strongest oxidation agent. The influence of the excess of H_2O_2 was performed in the following conditions: COD_0 = 76000 mg O_2/L; *p*H (corrected) = 3; the catalyst concentration 100 mg Fe^{2+}/L; the H_2O_2 excess (related to stoichiometric one) 0, 50, 100 and 200%; the reaction time 180 min.

The experimental data are presented in figure 5. One can observe that in order to achieve a high level of oxidation degree a high concentration of H_2O_2 is required. Increasing the excess of H_2O_2 above 100% it is sufficient to obtain such oxidation degree. Evidently, the H_2O_2 concentration must be correlated with the nature and concentration of the organic substrate.

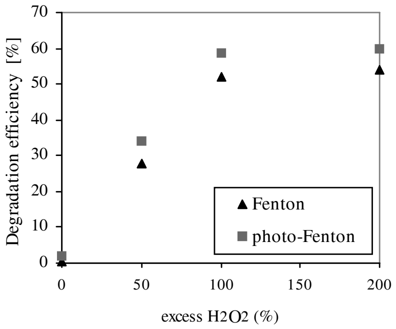

Fig. 5. Evaluation of the oxidation process in correlation with the concentration of the hydrogen peroxide

So the optimal parameters resulting from the obtaining results are the following: the solution *p*H = 3; the catalyst concentration 100 Fe^{2+}/L; the H_2O_2 excess 100%; In figures 6 and 7 are presented the experimental results obtained in these conditions, analysing the chemical oxygen demand COD (fig. 6) and total organic carbon TOC (fig. 7).

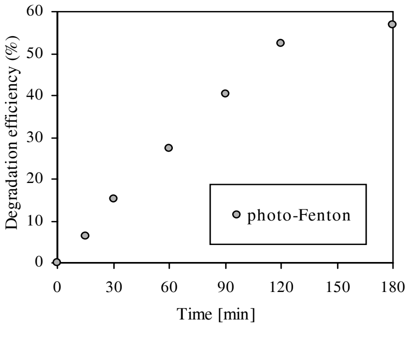

Fig.6. Kinetics data expressed as time dependence on the degradation efficiency by COD values

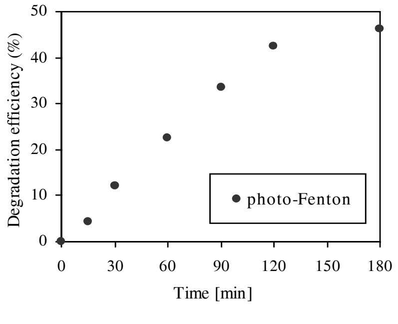

Fig. 7. Kinetics data expressed as time dependence on the degradation efficiency by TOC values

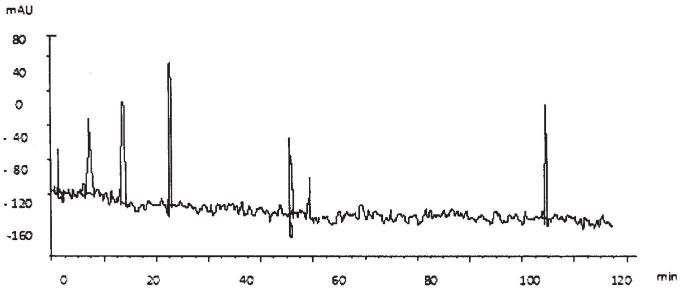

Fig. 8 Chromatogram of the pharmaceutical effluent

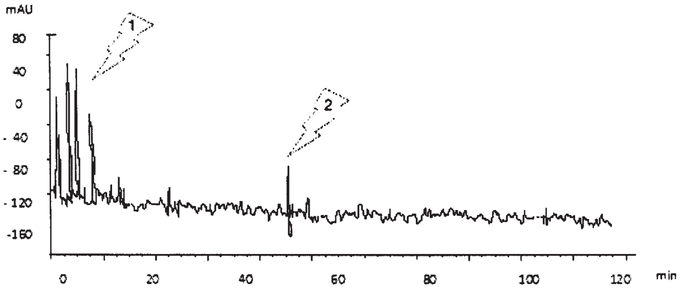

Fig. 9. Chromatogram of the sample after 180 min of reaction time (photo-Fenton)

For the pharmaceutical effluent studied (COD_0 = 76000 mg O_2/ L; TOC_0 = 34800 mg/L), after 180 min of reaction at ambient temperature, the efficiency of the degradation of the organic compounds is about 57% (expressed as COD) and 46% (expressed as TOC) indicating a moderate degree of oxidation of organic compounds. This can be attributed to the formation of lower organic acids as oxidation intermediates, causing a decrease in the efficiency of the oxidation, both through their higher stability towards oxidation and through their interaction with the catalytic component (the ionic species of iron) with the formation of inactive complexes in the oxidation process.

In order to clarify the behaviour of the pharmaceutical effluent tested in Fenton and photo-Fenton conditons, chromatographic analyzes were carried out, in following conditions: the injection volume 200 mL; operating speed: 0.5 mL/min; temperature: 40°C; analysis time 120 min.; solvent SDS 18 g/L.

The chromatographic analyzes (figs. 8 and 9) and their details (figs. 10 and 11) indicate that the sample taken after 180 min of reaction contained organic acids (tartaric, fumaric, malonic, succinic) and gelatin. All these compounds confer resistance to removal, due probably to the presence of the gelatine which limits the applicability of the advanced oxidation processes.

Conclusions

The study put in evidence the influence of the main factors involved in the oxidation process of some organic compounds contained in pharmaceutical wastewaters.

The efficiency of the oxidation of organic compounds contained in aqueous solutions using catalytic and photo-catalytic Fenton type procedure depends on a number of factors, like the nature and initial concentration of organic compounds, the ratio organic substrate/hydrogen peroxide, the initial *p*H solution, the concentration of the catalyst and the reaction time. All these parameters determine the generation of HO• and HO_2• radicals due especially to presence of H_2O_2 and Fe^{2+} catalyst which are the basic parameters in the Fenton and photo-Fenton processes.

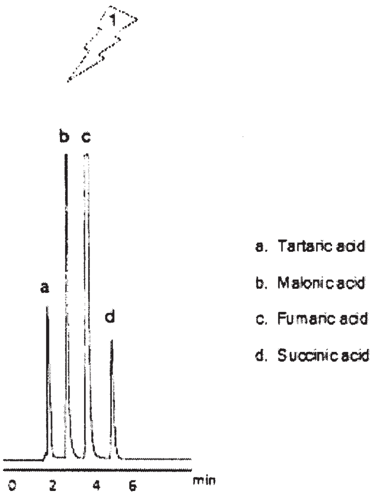

Fig. 10. Chromatogram (detail 1 in fig. 9)

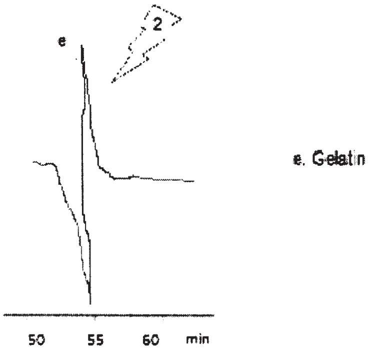

Fig. 11. Chromatograms (detail 2 in fig. 9)

The optimal values of the basic parameters determined experimentally are the following: the H_2O_2 excess (reported to the stoichiometric one) 100%; the catalyst concentration ($FeSO_4 \cdot 7H_2O$) 100 mg Fe^{2+}/L; the initial *p*H of solution 3.

A larger excess of H_2O_2 determines a limitation of HO• and HO_2• radicals formation due to a “scavenger” effect. An excess of catalyst concentration over 100 mg Fe^{2+}/L is not necessary because its insignificant effect an oxidation efficiency.

Due to the scarce oxidation rate of organic impurities it is necessary to ensure a relatively long time of oxidation process (about 180 min). This low oxidation rate is due to the stability of organic compounds explained by formation of relative stable intermediates (organic acids) and gelatine and by formation of complexes with the iron ions, thus blocking the catalytic and photo-catalytic formation of HO• and HO_2• radicals. That is why in these working conditions, the oxidation efficience is only 57% (expressed as COD) and 46% (expressed as TOC).

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