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Integrating coagulation and Fenton's oxidation for pharmaceutical effluents treatment

Introduction

The search for new drugs able to fulfil the health requirements of modern society is pushing pharmaceutical industries to design and produce even more complex molecules. Unavoidably, during these processes a large amount of wastewater with a complex composition is produced [*Martínez et al., 2003*]. Effluents from pharmaceutical industry are originated from different operating steps such as fermentation, chemical synthesis, extraction and formulation. This leads to a highly organically charged stream whose characteristics dramatically change depending on the type of pharmaceutical which is being produced. One of the consequences is that the traditional biological systems usually applied for wastewater treatment are inefficient for this kind of effluent [*Tekin et al., 2006*]. In this context, chemical systems such as the advanced oxidation processes (AOP) are called as alternatives to handle with these biorefractory wastewaters. Among the AOPs, *Fenton's* peroxidation is industrially preferable since it operates at room conditions of pressure and temperature, does not need sophisticated equipment and requires safe and easy to handle reactants.

Although several works are reported in literature regarding the degradation of synthetic solutions of pharmaceuticals through AOPs [*Andreozzi et al., 2003; Dantas et al., 2008; Gonçalves et al., 2013*], data are still scarce regarding the abatement of actual wastewaters [*Monteagudo et al., 2013*]. *Fenton's* process was able to remove up to 56.4% of COD from a pharmaceutical wastewater [*Martínez et al., 2003*]. Moreover, *Tekin et al.* [*2006*] verified that *Fenton's* is able to improve biodegradability leading to an effluent capable to be further refined in an aerobic systems.

The application of microwave to assist *Fenton's* peroxidation proved to improve iron sludge settling and the effluents' biodegradability [*Yang et al., 2009*].

Monteagudo et al. [*2013*] reached up to 84% of TOC removal when applying a ferrioxalate-assisted solar/photo-*Fenton* system. One of the main disadvantages of this technology is related with the amount of dissolved iron required to catalyse the oxidation reaction that will lead to a large amount of sludge whose management is an environmental issue.

In this context, the aim of the present research is to analyse the activity of several solid catalysts in *Fenton* peroxidation of a real pharmaceutical wastewater and compare them with the traditional iron sulphate salt. Moreover, the integration of this oxidation system with a pre-coagulation step was evaluated. Besides, the impact of light on the treatment efficiency was still assessed. The final goal was to provide reliable data so that the industrial stakeholders could decide for a solution for their environmental problem.

Materials and Methods

Catalysts preparation and characterization

Four solid catalysts were selected: a commercial (N-150 composed by Fe_2O_3 – MnO_x, provided by *Clariant Produkte GmbH*); a laboratory prepared (Fe-Ce-O 70/30) and two low cost materials (red volcanic rock and iron shavings constituted by zero valent iron). Fe-Ce-O 70/30 was obtained by the co-precipitation of a mixed solution of cerium and iron nitrates precursors (with a molar proportion between Fe/Ce of 70/30). The precipitate was washed, dried and calcinated during 2h at 300ºC. The detailed procedure is described elsewhere [*Martins et al., 2010*].

Atomic absorption (*Perkin-Elmer 3300*) was used to determine the chemical composition of the low cost materials (after acid digestion). Elemental analysis was carried out to determine the catalysts content in C, H, N and O (*Fisons Instruments EA 1108 CHNS-O*). Surface area was obtained through the BET method (*ASAP 2000, Micromeritics*). X-ray difraction (*Philips PW 3040/00 X'Pert*) was used to infer about the materials structural characteristics.

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Treatment procedures

Coagulation was tested as a pre-treatment. The commercial acid coagulant P19 (provided by our spin-off company *Adventech* [*2015*] was selected due to the interesting results achieved when applied to other industrial effluents. The trials were carried out in a jar-test using 600 mL glass reactor. In a first step, *pH* is corrected to the desired value and coagulant is added under a constant stirring of 300 rpm, during 5 min; then the agitation speed is reduced to 30 rpm for 30 min and finally stopped to let the solids settle down. The effect of *pH* and coagulant doses was assessed.

Dark *Fenton's* experiments were performed under batch operation in an orbital agitator (*Heidoph Reax 20*) at 16 rpm in 50 mL reactors. The real effluent pH was corrected firstly using H_2SO_4 or NaOH solutions. Later, a previously defined quantity of catalyst was added and the reaction started introducing a specific amount of hydrogen peroxide (industrial grade, 50%). Samples were periodically withdrawn, filtrated using a 0.45 μm filter and alkalinized with NaOH to end the reaction and promote residual H_2O_2 elimination.

Photo-*Fenton's* installation consisted in a magnetically stirred reactor (3 L glass reactor), with a 9 W black light (*Philips*), axially placed. A glass tube with double wall was used to cool the lamp and the temperature was kept at 25°C. The lamp produces radiation with a wavelength within the range 350÷400 nm. A photon flux of 1.55 ± 0.24 μeinstein/min was determined using potassium ferrioxalate actinometry.

Analytical Techniques

Chemical oxygen demand (COD), biochemical oxygen demand (BOD) and solids (suspended and dissolved) were determined according to the Standard Methods [*Greenberg et al., 1985*]. Total organic carbon (TOC) was measured using the automatic equipment *Shimadzu 5000*. *pH* was obtained using a *Crison micropH2000* measurer. The residual H_2O_2 was attained through a colorimetric method using test strips (*Precision laboratories*). Experiments were carried out at least in duplicate and the maximum deviation for COD and TOC between runs was 5% and 2%, respectively.

Results and discussion

Catalysts and Effluent Characterization

The low cost materials chemical composition was determined by atomic absorption after the solid acid digestion. The red volcanic rock contained (w/w): 6.31% Fe; 0.03% Cu; 0.02% Zn; 0.44% K; 1.54% Na; 0.06% Cr; 0.07% Mn; 8.32% Ca and 2.31% Mg. XRD detected the presence of hematite (Fe_2O_3), quartz (SiO_2) and feldspars ($KAlSi_3O_8$-$NaAlSi_3O_8$-$AlSi_3O_8$) Iron shavings comprised almost 100% of zero valent iron (Fe^0).

Tab. 1 compares the different catalysts specific surface area.

Tab.1. Catalysts specific surface area

Catalyst	S_{BET}, [m^2/g]
Fe-Ce-O (70/30)	188.00 ± 0.02
N-150	133.00 ± 0.02
Red Volcanic Rock	3.49 ± 0.02
Iron Shavings	1.14 ± 0.04

The effluent was collected from a pharmaceutical industry that synthesizes and produces active substances and develops formulas of several therapeutic classes. Among the products it can be referred corticosteroids, antibiotics, anticholinergic and contrast agents. Tab. 2 shows the main characteristics of the stream.

The effluent shows a strong organic load as reported by the high COD, BOD_5 and TOC. Even if the BOD_5/COD (that can be used to infer about biodegradability) is not so low (0.40), the variability of the effluents composition would not allow a proper biologic oxidation. Moreover, the company specifically referred that is not interested in such treatment due to the long retention times that would be required and operation problems related with the effluents seasonality.

Tab. 2. Raw and coagulated effluent characteristics

Parameter	Raw effluent	Coagulated effluent
COD [mgO_2/L]	9520 ± 95	4270 ± 43
BOD_5 [mgO_2/L]	4710 ± 94	2441 ± 48
BOD_5/COD	0.40	0.58
TOC [mgC/L]	5134 ± 51	2855 ± 29
pH	5.4	3.0

Coagulation

The raw effluent presents a brownish colour, intense odour and suspended solids. This way, a coagulation step is advisable before the chemical oxidation treatment. *pH* is a key parameter in coagulation. Therefore, it was analysed the COD removal after using 1 g/L of P19 coagulant at different pH. According to the results attained, the best COD abatement is obtained for *pH* 3 (40%) while coagulation efficiency decreases with *pH* increase reaching only 20% for *pH* 9. The use of *pH* 3 in this pre-treatment is interesting since this is also the optimal *pH* for *Fenton's* process and further *pH* change is not required.

In a second step, the amount of P19 applied was tested within the range 0.30 – 2 g/L using *pH* 3. It was verified that 0.5 g/L of coagulant lead to the best COD removal results. The resulting effluent characteristics are reported in Tab. 2. As it can be observed the referred coagulation conditions were able to abate up to 55%, 44% and 48% of COD, TOC and BOD_5, respectively.

Dark Fenton's peroxidation

The coagulated effluent was subjected to *Fenton's* peroxidation using the four solid catalysts referred before. Moreover, for comparative purposes, homogeneous *Fenton* using iron sulphate salts (homogeneous *Fenton*) was also carried out. In all experiments 1 g/L of catalyst and *pH* 3 was applied. Additionally, 5 g/L of hydrogen peroxide was used. This concentration corresponds to 1:5 of the stoichiometric value that is theoretically required for total oxidation of the initial COD [*Eckenfelder, 2000*].

Fig. 1 shows COD and TOC removal after 120 min of *Fenton's* reaction over the different catalysts tested in this work. COD decrease is similar for all the treatment systems (values within the range 50÷60%). However, the highest efficiency is attained for the homogeneous process with up to 61% of degradation. In what regards the solid catalysts the following order of activity was found: Iron shavings (50%) ≈ Red volcanic rock (50%) < N-150 (55%) ≈ Fe-Ce-O (55%).

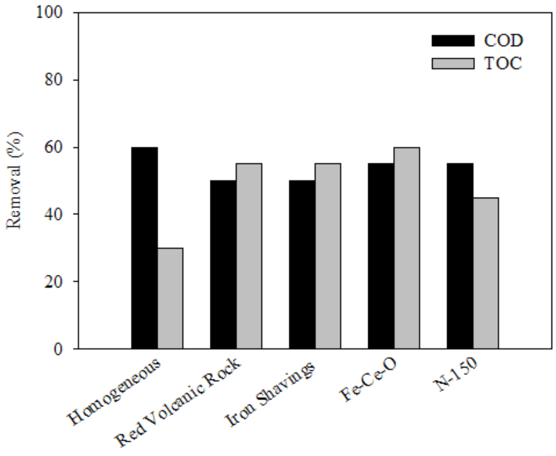

Fig. 1. Pharmaceutical wastewater COD and TOC removal after 120 min of *Fenton's* peroxidation using several catalytic materials (*pH* 3, [H_2O_2] = 5 g/L and 1gcat/L)

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Stronger differences are found when TOC removal is to bear in mind. Homogeneous *Fenton* leads to the lowest mineralization degree (30%). Higher efficiencies were found for the solid catalysts: N-150 (45%) < Red volcanic rock (55%) ≈ Iron shavings (55%) < Fe-Ce-O (60%). The higher Fe-Ce-O activity can be related with the presence of ceria. In fact, this material allows a better electronic equilibrium favouring oxidation.

The differences found between COD and TOC degradation for each treatment system is related with the selectivity of the oxidation. Reaction can be pushed preferably to partial oxidation or to total mineralization (which implies the production of CO_2 and H_2O). To evaluate this, the COD removed by partial oxidation ($COD_{partial}$) can be determined by Eq. 1.

$$COD_{Partial} = COD_0 \times \left(\frac{TOC}{TOC_0}\right) - COD \tag{1}$$

where:

$COD_{Partial}$ – COD removed by partial oxidation, [mgO$_2$/L]
COD_0 – Initial COD, [mgO$_2$/L]
COD – Final COD, [mgO$_2$/L]
TOC_0 – Initial TOC, [mgC/L]
TOC – Final TOC, [mgC/L]

The fraction of COD removed by partial oxidation (X) is given by Eq. 1.

$$X = \frac{COD_{Partial}}{COD_0 - COD} \tag{2}$$

If X is near 0, it means that the treatment is pushed towards mineralization while if X is around 1 the oxidation tends to be partial. According to the results attained for all the methodologies a $X = 0.51$ was achieved for the homogeneous process while 0.10 was attained when the solid catalysts were applied. This means that the presence of the heterogeneous materials guides the oxidation selectivity towards mineralization.

Since iron is the traditional Fenton's catalyst and the materials applied present very different composition regarding this metal, it is interesting to analyse the efficiency of the catalyst (measured as the amount of COD and TOC removed) per mg of Fe loaded to the reactor (Fig. 2). As it can be observed, from the point of view of the amount of iron applied, the red volcanic rock seems the most interesting material leading to the highest values of mgCOD and TOC removed per mg of Fe. However it should be reminded that this low cost catalyst is also composed by other metals that can be responsible for *Fenton*-like reactions which may also explain its activity. For the other solid materials much lower ratios are found.

Even though the high COD and TOC removal observed for the *Fenton's* process with the different catalysts, the effluent still does not comply with the environmental legislation for discharge into the water courses. In this context it is interesting to infer about the effect of the chemical process over the wastewater biodegradability in order to conclude about the potential of using a posterior biological system to further refine the final stream.

Tab. 3 shows the BOD_5/COD ratio for the coagulated effluent and after each oxidation process.

Tab. 3. BOD_5/COD ratio for the coagulated effluent and after each treatment. Iron leached after each heterogeneous catalytic process. (120 min of reaction *pH* 3, [H_2O_2] = 5 g/L and 1gcat/L)

	BOD_5/COD	[Fe] mg/L	% Initial Fe leached
Coagulated effluent	0.58	-	-
Homogeneous	0.67	-	-
Red volcanic rock	0.64	18.6	29.5
Iron shavings	0.58	224.0	22.4
Fe-Ce-O	0.62	6.0	1.1
N-150	0.54	2.9	0.7

Homogeneous and heterogeneous *Fenton's* process over red volcanic rock and Fe-Ce-O were able to improve biodegradability leading to BOD_5/COD ratios above 0.6.

A key point when solid materials are applied is related with the amount of active metal that is lost by leaching to the liquid. In fact, this will contribute to the catalyst deactivation besides constituting a second source of water pollution. Table 3 shows the concentration of iron found in effluent after 120 min of treatment as well as the percentage of the initially loaded Fe that leached. N-150 and Fe-Ce-O reveals the lowest Fe leaching behaviours corresponding to 0.7 and 1.1% of their initial Fe. The low cost catalysts seem less stable with more than 20% of their initial Fe being lost.

Among the tested materials, N-150 showed a lower efficiency in what regards COD and TOC removal and biodegradability enhancement. Therefore, it was decided to select the other three catalysts (red volcanic rock, iron shavings and Fe-Ce-O) to pursue the studies.

Photo Fenton

Photo *Fenton* experiments were carried out using 1 g/L of each catalyst (red volcanic rock, iron shavings and Fe-Ce-O), 5 g/L of hydrogen peroxide and *pH* 3. For comparative purposes, UV/H_2O_2 without any catalyst was also analysed. Fig. 3 shows COD and TOC removal after 120 min of each treatment.

The most efficient catalyst regarding COD removal was red volcanic rock leading to 70% and 40% of COD and TOC degradation. The lowest activity was found for Fe-Ce-O with about 60% and 35% of COD and TOC abatement.

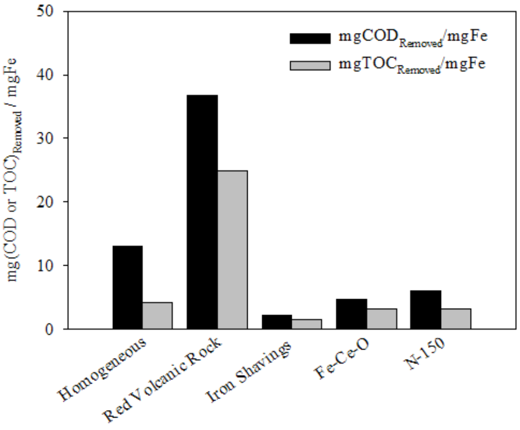

Fig. 2. Ratio between the COD and TOC removed after 120 min and the amount of iron introduced in the reactor for each process (*pH* 3, [H_2O_2] = 5 g/L and 1gcat/L)

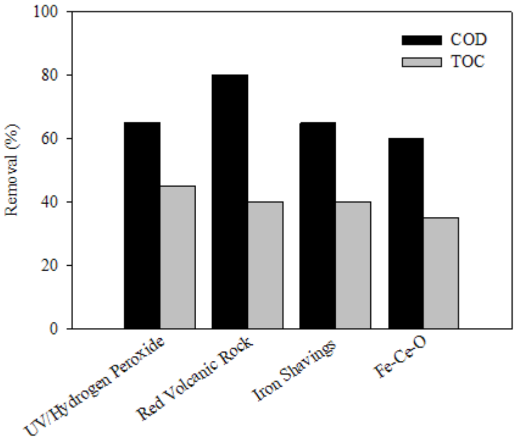

Fig. 3. Pharmaceutical wastewater COD and TOC removal after 120 min of Photo-*Fenton's* using several catalytic materials. (*pH* 3, [H_2O_2] = 5 g/L and 1gcat/L)

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It should be highlighted the UV/H_2O_2 process that, even without the presence of a catalyst, was able to remove up to 65% and 45% of COD and TOC, respectively. This is interesting since this treatment does not require the addition of a catalyst which will reduce the costs associated.

Another important aspect, is related with the catalysts leaching behaviour. The amount of iron leached after each catalytic photo-assisted treatment was 2.4, 16.0 and 11.9 mgFe/L for Fe-Ce-O, iron shavings and red volcanic rock, respectively. It is interesting to highlight that the presence of light strongly reduced the amount of iron leached by the low cost materials when compared with the dark Fenton (please recall Table 3).

Final remarks

Fig. 4 compares the results attained for COD removal by dark *Fenton* using Fe-Ce-O and red volcanic rock since these materials revealed to be the most promising catalysts for the abatement of the pollutant character of the pharmaceutical wastewater. Moreover, the photo-experiment without catalyst is also shown for comparative purposes.

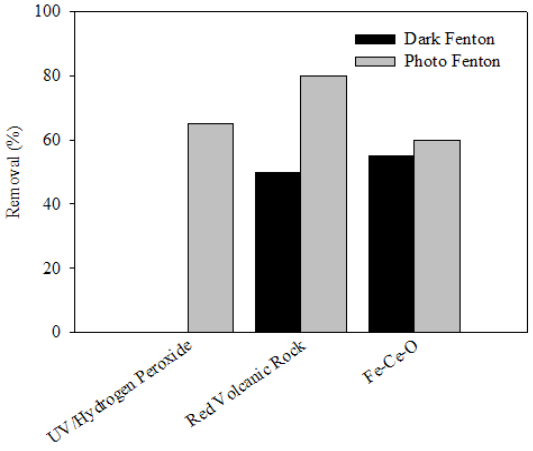

Fig. 4. Pharmaceutical wastewater COD removal after 120 min of Dark and Photo- Fenton's (*pH* 3, [H_2O_2] = 5 g/L and 1gcat/L).

The application of light improves both catalysts activity over pollutants. However, in what regards Fe-Ce-O, the COD removal is somehow lower than the one achieved when only hydrogen peroxide and light are applied. This is probably due to a less efficient light penetration caused by Fe-Ce-O particles. Nevertheless, the red volcanic rock activity is strongly enhanced by light, leading to a final COD abatement of 80% when compared with the about 50% reached by the dark system. Besides these interesting results, it should be reminded that the use of light decreased the amount of iron leached during the treatment which will reduce catalyst deactivation.

It must still be referred the COD abatement achieved by the case where only hydrogen peroxide and light were used (up to 65%). Due to these results the pharmaceutical company is now testing a pilot scale unit of UV/H_2O_2 for the depuration of their effluents.

Conclusions

The objective of the present work was to infer about the potential of Fenton's process (dark and photo) on the degradation of an actual pharmaceutical wastewater.

Firstly the wastewater was subjected to coagulation which led to up to 55% of the initial COD removal.

Different catalysts were tested, namely, the commercial N-150, the laboratory prepared Fe-Ce-O, and two low cost materials (redo volcanic rock and iron shavings).

The obtained results revealed that the Fe-Ce-O system was the most efficient in dark Fenton (55% and 60% of COD and TOC removal, respectively) while red volcanic rock showed to be the best catalytic material for the photo aided process (80% and 40% of COD and TOC removal, respectively). It was still verified that the presence of light reduced the amount of iron leached during the process which safeguards the catalysts stability.

Generally speaking, Fenton's process was able to improve the effluent biodegradability which indicates that the application of a latter biological system (probably in a municipal wastewater treatment plant) would be possible to refine the effluent.

It is still worthy to emphasise the efficiency of the light/hydrogen peroxide process that achieved up to 65% of COD removal in 120 min. This system, without the need of a catalyst, is now being explored by the pharmaceutical industry at a pilot level.

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R.C. Martins gratefully acknowledged FCT (Fundação para a Ciência e Tecnologia, Ministério da Educação e Ciência, Portugal) by the financial support under the IFCT contract (IF/00215/2014)