

Experimental Design to Optimize Degradation of Organic Compounds in Wastewater from Semiconductor Industry Using Fenton Reagent

Rodrigues, C.S.D.*, Caetano, N.S.** and Durão, H.J.A.⁺

* LSRE – Laboratory of Separation and Reaction Engineering, Chem. Eng. Dep., Fac. Eng. Univ. Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.

** Dep. Eng. Quím., Inst. Sup. de Eng. Porto, Inst. Polit. Porto, Rua Dr. António Bernardino de Almeida, 4200-072 Porto, Portugal and LEPAE – Laboratory for Process, Environmental and Energy Engineering, Chem. Eng. Dep., Fac. Eng. Univ. Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal.

⁺ UTA/IDIT – Environmental Technologies Unit, Institut of Development and Technological Innovation, Rua do IDIT – Espargo, 4520-102 Santa Maria da Feira, Portugal.

Abstract The aim of this work was to study the possibility of treating an industrial semiconductor wastewater by combining physical and chemical methods. The combined treatment consisted of pH adjustment to 2 followed by filtration and then chemical oxidation with Fenton reagent over the resulting filtered wastewater. In chemical oxidation treatment, the isolated effect of the variables on the degradation of the organic compounds - measured by chemical oxygen demand (COD) removal - was first studied: pH (3 to 5), reaction time (0.25 to 5 hours), hydrogen peroxide concentration (2.1 to 5.9 M) and FeSO₄: H₂O₂ mass ratio (1:5 to 3:2). Higher COD removal (75%) was obtained when a pH value of 3, reaction time of 4 hours, hydrogen peroxide concentration of 4.2 M and FeSO₄: H₂O₂ mass ratio of 1:5 were used. The global efficiency of COD removal by combination of the two treatments was 80%. The influence of three variables and their interactions was evaluated, using an experimental design of the type 2³. The design also allowed the conclusion that reaction time has a statistical meaning.

Keywords: Chemical oxidation; Experimental design; Fenton reagent; Semiconductor; Wastewater treatment.

INTRODUCTION

Semiconductors are important electronic products. They are widely used in computers, consumer electronic products, communication equipment, electronic control devices and scientific and medical test equipment. Due to increasing demand in recent years, average annual growth of semiconductor industry has been increasing rapidly at a double-digital rate (Lin and Kiang, 2003). Semiconductor manufacturing is a highly complex and delicate process that consists of over a hundred steps of silicon growth, oxidation, doping, photolithography, etching, stripping, dicing, metallization, planarization, cleaning, etc. (Lin and Kiang, 2003). Over a hundred of different organic and inorganic compounds are involved in the manufacturing process. A significant amount of wastewater is generated (with strong dark colour, high chemical oxygen demand (COD) concentration, presence of refractory volatile organic compounds and low biodegradability that generate negative environmental impacts), as a result of ultra pure water utilization in the washing and cleaning steps. Treatment of this wastewater by traditional activated sludge method is essentially impossible because these pollutants are chemically stable and are not completely mineralisable (Barreiro and Pratt, 1992; Fedorak and Hrudey, 1984; Reemstmsma and Jekel, 1997; Andreozzi *et al.*, 1999).

One of the most promising alternatives for wastewater treatment is based on the application of destructive chemistry (advanced oxidation processes - AOP), as a form to reduce the levels of contamination through the destruction of organic pollutants and its conversion to carbon dioxide (CO₂) and water (H₂O₂) (Martínez and López, 2001).

AOP's are based on the generation of hydroxyl free radicals, which have a high electrochemical oxidant potential. Generation of hydroxyl radicals involves the combination of classical oxidants, such as H₂O₂ or O₃ with UV radiation or a catalyst and can be achieved by a variety of reactions, such as O₃/UV, H₂O₂/UV, Fenton oxidation, photo-Fenton or titanium dioxide/hydrogen peroxide/solar radiation (Martínez *et al.*, 2003).

The advanced chemical oxidation process used in this work is Fenton type. The oxidation is based on ferrous ion and hydrogen peroxide, and exploits the very high reactivity of the hydroxyl radical produced in acidic solution by the catalytic decomposition of H₂O₂ (Eq.1) (Ramirez *et al.*, 2005):



The radicals formed in this process, react with organic materials breaking them down gradually in a stepwise process (Eq. 2 to 4) (Kuo, 1992):



Fenton oxidation depends on various factors: pH, reaction time, H₂O₂ concentration, temperature and amount of catalyst (usually expressed as the Fe²⁺: H₂O₂ ratio). Although many researchers have usually only focused on the single-factor-at-a-time approach studying the effect of each experimental parameter on the process performance while keeping all other conditions constant, this type of approach does not take into account cross-effects from the factors considered and leads to a poor optimization result (Ramirez *et al.*, 2005).

The experimental design methodology is a technique that uses mathematical and statistical tools to analyse the influence of independent variables on a specific dependent variable (response). By using experimental design methodology it is possible to estimate linear interaction effects of the factors and to make a prediction model for the response.

In this work we used an experimental design of the type 2³, with two levels (-1 and +1) and three variables, corresponding to 16 assays plus 3 in the central point (level 0).

MATERIALS AND METHODS

Wastewater

Wastewater used in the experiments was obtained from a semiconductor manufacturing plant in the north of Portugal and had a light green colour (see Figure1-a). Characteristics of the wastewater are summarized in Table 1.

Table 1 Main characteristics of the semiconductor industry wastewater used in the Fenton oxidation study

Parameter	Value
Soluble COD	21-32 g O ₂ /L
BOD	10 mg O ₂ /L
Ammonia	42 mg NH ₃ /L
NTK	3472 mg NH ₃ /L
Nickel	< 0.08 mg/L
Copper,	0.78 mg/L
Zinc	0.06 mg/L
pH	10.5 – 11.0

Fenton's reaction

The industrial wastewater was pre-treated by adjusting pH value to 2 with sulphuric acid (98%, Panreac), producing a blue sludge – as seen in Figure 1-b) – that could be removed by filtration using a glass funnel and filtering paper (18.5 cm, Whatman N°4). The wastewater obtained after filtration had a yellow colour – as seen in Figure 1 -c).

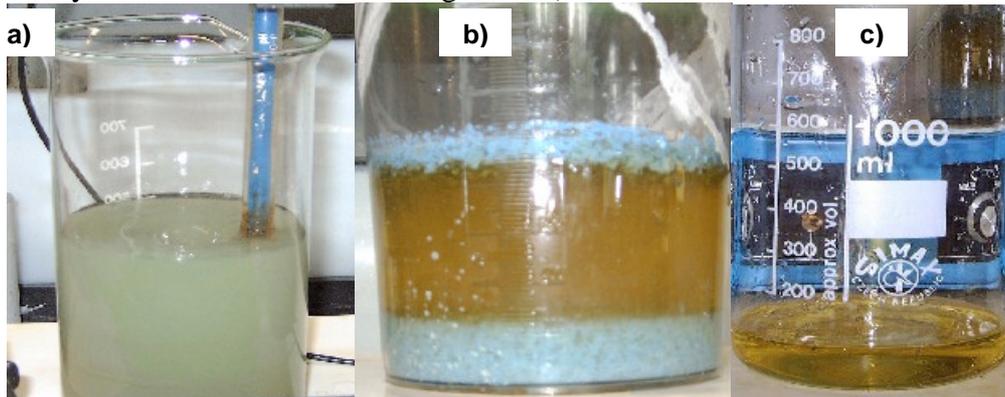


Figure 1 a) Semiconductor raw wastewater The pre-treatment application effect on semiconductor wastewater: b) wastewater after pH adjustment to 2, c) wastewater after filtration of the resulting sludge.

pH of the pre-treated wastewater was adjusted to the desired value by addition of NaOH solution (6 M, prepared with commercial NaOH from Panreac) or sulphuric acid 98% (pH measurements were done using a Hanna Instruments HI1333 meter and Hanna Instruments HI8417 electrode).

The Fenton oxidation was conducted in glass flasks under constant stirring, using a magnetic plate (Labinco, L216) and magnetic bar, by adding over the pre-treated wastewater the desired amount of hydrogen peroxide 30% (commercial, José M. Vaz Pereira) and iron sulphate solution (100 mg/L, prepared with $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ p.a., Panreac).

Soluble COD determination was done after stopping the reaction by rising the treated wastewater pH to 12 with NaOH solution (6M) and heating in thermostatic bath to 80 °C for 10 minutes (Heredia *et al.*, 2004; Martínez *et al.*, 2003). After this, the sample was left to settle for sedimentation of the resulting sludge.

A design of experiments approach was used to model and optimize the process performance. The model considered to describe our data was a first-order polynomial and the coefficients were calculated using MS-Excel.

Analytical procedures

Analytical procedures were conducted according to Standard Methods (APHA, 1999): ammonia, Nitrogen Total Kjeldahl, nickel, copper and zinc, Chemical Oxygen Demand and Biochemical Oxygen Demand.

RESULTS AND DISCUSSION

Influence of operating parameters

pH effect. pH effect was studied by conducting a series of experiments in the pH range 3 to 5. Figure 2 shows that by increasing pH value the mineralization of organic compounds decreases.

The higher COD removal (69.5%) was obtained for a pH of 3. This observation is in general agreement with those reported by previous investigations (Rivas *et al.*, 2004, Waite, 2002).

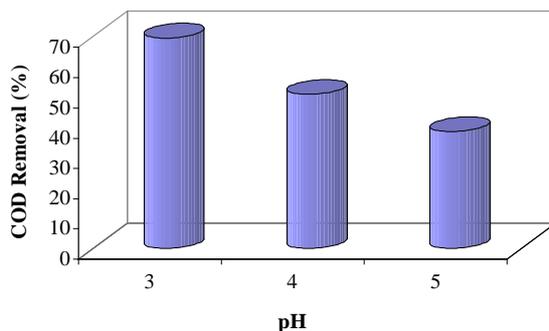


Figure 2 Effect of wastewater pH on mineralization of organic compounds. Experimental conditions: $[H_2O_2] = 4.2 \text{ M}$, reaction time, $t = 3 \text{ h}$ and $FeSO_4 : H_2O_2 = 1:5$.

For $pH < 3$, the process becomes less effective. For very low pH values, the regeneration of Fe^{2+} (through reaction between Fe^{3+} and H_2O_2) is inhibited, because Fe^{3+} peroxocomplexes formation (as intermediates) decreases when pH decreases (Lin and Lo, 1997). At pH above 3, the performance significantly decreases, mainly because the dissolved fraction of iron species decreases (Pera-Titus *et al.*, 2004). Consequently, the concentration of Fe^{2+} species also decreases because Fe^{3+} hydroxides are much less reactive than dissolved Fe^{3+} species toward H_2O_2 . The process performance is then affected, because a smaller steady state concentration of hydroxyl radicals is attained (Oliveira *et al.*, 2006). Therefore, in subsequent experiments, pH was adjusted to 3 because such an optimum value is usually independent of the other conditions used.

Effect of $FeSO_4 : H_2O_2$ mass ratio. The experiments conducted to determine the optimum $FeSO_4 : H_2O_2$ mass ratio are summarized in Table 2 and the corresponding COD removal obtained for each experiment can be found in Figure 3. The experimental conditions that lead to best COD removal (61.0%) were: $FeSO_4 : H_2O_2$ mass ratio of 1:5 and H_2O_2 concentration of 2.1 M.

Table 2 Experimental conditions in Fenton oxidation

Run	$FeSO_4 : H_2O_2$ (w/w)	$[H_2O_2](M)$	pH	Reaction time t (h)
1	3:4	0.1	3	4
2	3:2			
3	1:7	0.6		
4	1:3			
5	1:9	2.1		
6	1:5			
7	1:10	3.5		
8	1:5			

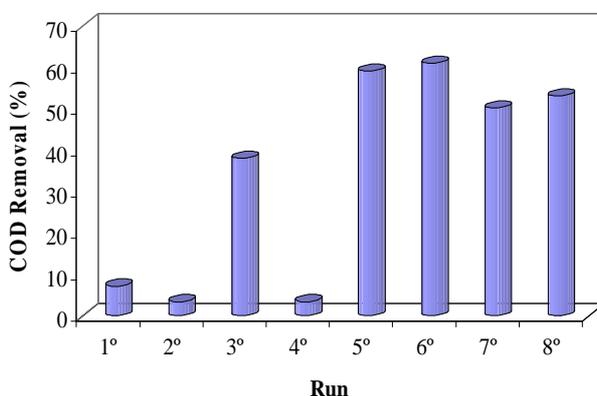


Figure 3 COD removal for the experimental conditions referred in Table 2

Effect of H₂O₂ dosage. The relationship between the degradation of organic compounds and the initial concentration of hydrogen peroxide in the Fenton process can be seen in Figure 4. The objective of this evaluation is to select the best operational H₂O₂ concentration.

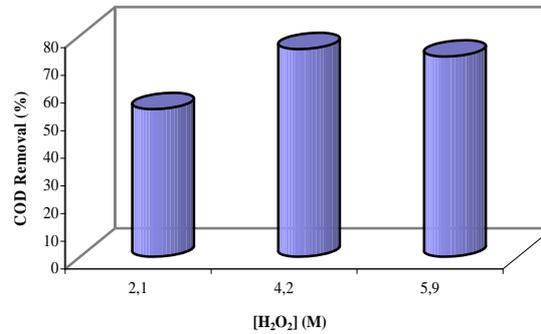
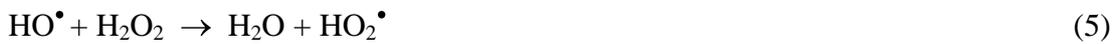


Figure 4 Effect of H₂O₂ concent. on the degradation of organic compounds (pH = 3, t = 4h and FeSO₄ : H₂O₂ = 1:5).

H₂O₂ addition from 2.1M to 4.2M increased COD removal from 53.4% to 75.1%. For H₂O₂ concentration higher than 4.2M, mineralization of organic compounds decreased. This small decrease is due to the fact that at higher H₂O₂ concentration scavenging of HO[•] radicals will occur; which can be expressed by eqs. (5) and (6) (Lucas and Peres, 2006):



Effect of Reaction time. To determine the optimum reaction time an experimental was run for 5 hours, along which several samples were taken. Figure 5 shows COD removal obtained for several reacting times, showing that the best COD removal was obtained for 3 hours reaction time (69.9% COD removal) after which remained approximately constant.

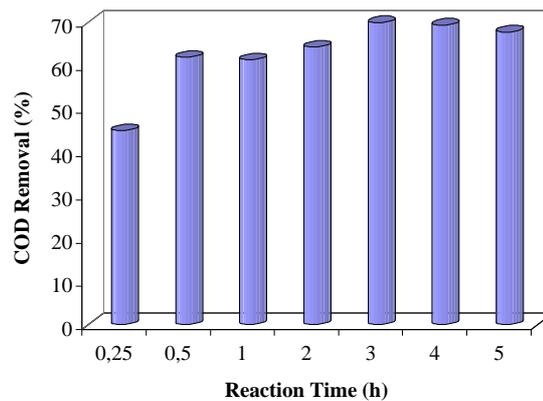


Figure 5 COD removal for different reaction times (pH = 3, [H₂O₂] = 3.1M and FeSO₄ : H₂O₂ = 1:5).

Mineralization of organic compounds is faster in short reaction time (0.5 hours), and the main reason for this well known behaviour is that ferrous ions react very quickly with H₂O₂ (rate constant is 53 mol⁻¹ dm³ s⁻¹) to produce large amounts of hydroxyls radicals: as in eq. (1), which can then react rapidly with organic compounds. Ferric ions produced can react with H₂O₂ to produce hydroperoxyl radicals (HO₂[•]) and restore ferrous ions through the following reaction scheme (Ramirez *et al.*, 2005):



However, the reaction rate for iron regeneration is much slower than that in eq.(1) (rate constant is now $0.02 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) (Ramirez *et al.*, 2005). Consequently, the rate of oxidation in this stage is slower than in the first one due to the slow production of Fe^{2+} from Fe^{3+} . We can thus say that reaction rate decrease on the second stage of the Fenton oxidation is essentially due to the fact that ferrous ions are consumed quickly, but reproduce slowly. Consequently, the oxidation rate of organic compounds is fast when large amounts of ferrous ions are present because large amounts of hydroxyl radicals are produced.

Experimental Design

An experimental study frequently constitutes a problem of difficult and slow resolution, due to the large amount of data, number of parameters and respective interactions that can influence the results. The traditional form of optimization can involve the execution of experiences where each of the parameters varies separately inside of a previously defined range of values. This procedure can lead to a quantitative relation between each variable, the answer and the mathematical model for each of the variables as isolated. However, this process, besides being inefficient (because it requires separate comments for each variable), is incapable to detect interactions between the variables and their effect in the final reply. These interactions can lead to effects higher or lower than those that are observed if the variable acts separately. To solve this problem, one applies the experimental planning technique with the objective to determine, with a minimum of effort, the effect of each factor and its interactions, inside the range of assayed values. Moreover, the assays must be run in such a way to give enough information to decide how many and which of the factors and interactions are significant and if it is or not necessary to consider a more complex model (involving a bigger number of factors and interactions) in order to conveniently describe the phenomenon under study. For this purpose, it will be necessary to appeal to statistical techniques (analysis of variance, Barker, 1994). In order to quantify the variance of the answer, we need to make experimentation in specific points in the domain of the problem, in such a way that it returns respective variance with the maximum of possible information (Morgado, 1979).

The objective of this part of the work is to collect information that allows for the determination of a mathematical model of the form below, that represents what happens in the procedure:

$$r = a_0 + \sum a_i \cdot x_i + \sum \sum a_{ij} \cdot x_i \cdot x_j + \dots + \xi$$

where ξ includes the experimental error and the effect of eventual random factors that have not been considered in the model, r is the system's answer (% COD removal) that depends on three factors: x_1 (H_2O_2 concentration); x_2 ($\text{FeSO}_4 : \text{H}_2\text{O}_2$ mass ratio) and x_3 (reaction time).

The pH value was fixed in 3, because in the preliminary assays this condition lead to higher COD removals.

In the experimental planning, to determine which of the parameters and/or interactions that they possess significantly effect the process, we started by constructing a table based on an algorithm of Yates (Barker, 1994), with a standard disposal of the assays for the factorial planning.

Table 3 shows the levels of the parameters studied for the optimization of the wastewater treatment with Fenton reagent according to a factorial drawing 2^3 , fixed in accordance with the results obtained in the preliminary assays.

Table 4 summarizes the planning of the assays of the factorial planning (algorithm of Yates), as well as the answers obtained (% COD removal) when the experimental plan was applied.

Table 3 Levels of the parameters studied for the optimization of the treatment for the Reagent of Fenton of the residual water according to an factorial drawing 2^3 .

Variable	Level		
	-1	0	+1
x_2 , Ratio $\text{FeSO}_4 : \text{H}_2\text{O}_2$ (w/w)	1:10	1:6.5	1:5
x_1 , $[\text{H}_2\text{O}_2]$ (M)	4.2	5.2	6.3
x_3 , Reaction time (h)	1	2	3

Table 4 Planning of the assays corresponding to the factorial drawing

Run	r	x_1	x_2	x_3
1	36.30	-1	-1	-1
2	31.98	1	-1	-1
3	30.28	-1	1	-1
4	14.87	1	1	-1
5	11.07	-1	-1	1
6	10.10	1	-1	1
7	11.14	-1	1	1
8	15.80	1	1	1
9	19.04	-1	-1	-1
10	14.40	1	-1	-1
11	10.97	-1	1	-1
12	9.21	1	1	-1
13	9.11	-1	-1	1
14	0.90	1	-1	1
15	0.90	-1	1	1
16	5.08	1	1	1
17	7.59	0	0	0
18	10.57	0	0	0
19	4.28	0	0	0

Note: Calculation of % COD removal had in account the dilution promoted for the hydrogen peroxide and iron solution addition

Table 5 shows the values of the interactions and effect, coefficients, variance of the results and the statistical F for the three parameters under study and all the possible interactions between them.

Table 5. Statistical analysis of the results corresponding to the experimental planning.

	Causes of the Variation	Interaction and effect	Coefficient	Variance of the Results (V_i)	Statistical F (F_i)
Variable	x_1	- 27.34	-1.71	46.71	0.76
	x_2	-33.76	-2.11	71.25	1.07
	x_3	-103.83	-6.49	673.75	10.08
Interaction 1 ^a Order	x_1x_2	10.70	0.67	7.15	0.11
	x_1x_3	24.91	1.56	38.79	0.58
	x_2x_3	39.02	2.44	95.16	1.42
Interaction 2 ^a Order	$x_1x_2x_3$	27.12	1.69	45.96	0.69
Coefficient of the Reply			14.04		
Variance of the experimental error (V_e)			66.85		

After this, a Fisher test was applied in order to eliminate the effects and interactions with no meaning. Comparing the V_i/V_e quotients = F_i to the values of $F_{\alpha_1\alpha_2}$ that can be found in F distribution tables for the degrees of freedom α_1 (n° of degrees of freedom for the numerator = n° of levels -1 = 1) and α_2 (n° of degrees of freedom for the denominator = α_c = 10) we obtain table 6

Table 6 Values of Fisher F.

Probability Level (%)	Fisher F
1	10.04
5	4.96

Comparing the values of Fisher F, in Table 6, with the statistical F (Fi) for each variable and interaction in Table 5, we observe that the statistical F of the variable reaction time is the only one that exceeds Fisher F values. Thus, we conclude that, for the range of tested conditions, reaction time is the only variable that presents statistical meaning for the treatment of this wastewater, generated in the production of printed circuits, by chemical oxidation using Fenton reagent.

Thus the model that best represents COD removal, r , from this industrial wastewater is:

$$r = 14,04 - 6,49 (t - 2)$$

CONCLUSION

In this study Fenton oxidation was used to remove organic compounds from semiconductor wastewater. The experimental design was used to evaluate which variables and/or interactions had statistical meaning. The conclusion was that only reaction time has statistical meaning.

The experiments lead to the conclusion that the best COD removal (75%) could be obtained for pH = 3, H₂O₂ dosage of 4.2 M, FeSO₄: H₂O₂ = 1:5 and 4 hours reaction time.

References

- Andreozzi, R.; Caprio, V.; Insola, A.; Marotta, R. (1999) Advanced Oxidation Processes (AOP) for water purification and recovery, *Catalysis Today*, **53**, 51-59.
- American Public Health Association (APHA) (1999). Standard Methods for the Examination of Water and Wastewater, 20th ed. APHA, Washington DC.
- Barker, T.B. (1994) *Quality by Experimental Design*. 2nd Edition, Marcel Dekker.
- Barreiro, R. and Pratt, J.R. (1992) Toxic effects of chemicals on microorganisms. *Wat. Env. Res.*, **64**(4), 632-641.
- Fedorak, P.M. and Hruday, S.E. (1984) The effects of phenol and some alkyl phenolics on batch anaerobic methanogenesis. *Wat. Res.* **18**(3), 361-367.
- Heredia, J.B., Domínguez, J.R. and López, R. (2004) Advanced Oxidation of Cork – Processing Wastewater Using Fenton’s Reagent: Kinetics and Stoichiometry. *J. Chem. Technol. Biotechnol.*, **79**(4), 407-412.
- Kuo, W.G. (1992) Decolorizing dye wastewater with Fenton’s reagent. *Wat. Res.*, **26**(7), 881-886.
- Lin, S.H. and Kiang, C.D. (2003) Combined Physical, Chemical and Biological Treatments of Wastewater Containing Organics from a Semiconductor Plant. *J. Haz. Mat.*, **B97**(1-3), 159-171.
- Lin, S.H. and Lo, C.C. (1997) Fenton Process for Treatment of Desizing Wastewater. *Wat. Res.* **31**(8) 2050-2056.
- Lucas, M.S.; Peres, J.A. (2006) Decolorization of the Azo Dye Reactive Black 5 by Fenton and Photo-Fenton Oxidation. *Dyes and Pigments*, **71**, 236-244.
- Martinez, E.C. and Lopez, G.D. (2001) Tratamiento químico de contaminantes orgánicos-El proceso Fenton, *Ingeniería Química (España)*, **375**, 149-151.
- Martinez, N.S.S.; Fernández, J.F.; Segura, X.F.; Ferrer, A.S. (2003). Pre-oxidation of an Extremely Polluted Industrial Wastewater by the Fenton’s Reagent. *J.Haz. Mat.* **B101**(3), 315 – 322.
- Morgado, R., 1979. *Experimentação Factorial*. Internal Report, FEUP.
- Oliveira, R., Almeida, M.F., Santos, L. and Madeira, L.M. (2006). Experimental Design of 2,4-Diclorophenol Oxidation by Fenton’s Reaction. *Ind. Eng. Chem. Res.*, **45**, 1266-1276.
- Pera-Titus, M., Garcia-Molina, V., Baños, M.A., Giménez, J. and Esplugas, S. (2004) Degradation of chlorophenols by means of advanced oxidation processes: a general review, *Appl. Catal. B: Environ.* **47**, 219–256
- Ramirez, J.H.; Costa, C.A.; Madeira, L.M. (2005) Experimental Design to Optimize the Degradation of the Synthetic Dye Orange II Using Fenton’s Reagent. *Catalysis Today*, **107–108**, 68-76.
- Reemtsma, T. and Jekel, M. (1997) Dissolved organics in tannery wastewaters and their alteration by a combined anaerobic and aerobic treatment. *Wat. Res.*, **31**(5), 1035-1046.
- Rivas, F.J., Navarrete, V., Beltrán, F.J. and Garcia-Araya, J.F. (2004) Simazine Fenton’s Oxidation in a Continuous Reactor. *Applied Catalysis B: Environmental*, **48**(4), 249-258.
- Waite, T.D. (2002) Challenges and Opportunities in the Use of Iron in Water and Wastewater Treatment. *Reviews in Environ. Sci. & Biotech.*, **1**(1), 9-15.