# MINERALIZATION OF PHENOL BY A HETEROGENEOUS ULTRASOUND\Fe-SBA-15\H₂O₂ PROCESS: MULTIVARIATE STUDY BY FACTORIAL DESIGN OF EXPERIMENTS

Raúl Molina[a], Fernando Martínez[a], Juan Antonio Melero[a,*], David H. Bremner[b], Anand G. Chakinala[b]


[a.] Department of Chemical and Environmental Technology, School of Experimental Sciences and Technology, Rey Juan Carlos University, 28933 Móstoles, Madrid, Spain

[b.] School of Contemporary Sciences, University of Abertay Dundee, Dundee DD1 1HG, Scotland

[*] Corresponding author:

**Phone:** 34 91 488 81 53        **Fax:** 34 91 488 70 68

**e-mail:** juan.melero@urjc.es (J. A. Melero)

**Abstract**

A novel heterogeneous catalyst has been used for the oxidation of aqueous solutions of phenol by catalytic wet peroxide oxidation assisted by ultrasound irradiation. This composite catalyst material that contains crystalline hematite particles embedded into a mesostructured SBA-15 matrix was used successfully in the oxidation of phenol by heterogeneous Fenton and photo-Fenton processes. Ultrasound is found to enhance the activity of the catalyst in the process, without prejudice to the stability of the iron supported species. The influence of different variables, such as hydrogen peroxide concentration or catalyst loadings in the reaction was studied by factorial design of experiments. Catalyst loadings of 0.6 g/L and a concentration of hydrogen peroxide close to twice the stoichiometric amount yield a remarkable organic mineralization, accompanied by excellent catalyst stability. The coupled US/Fe-SBA-15/$H_2O_2$ process at room temperature is revealed as a promising technique for wastewater treatment.

**Keywords:** Fenton, ultrasound, CWPO, heterogeneous catalyst, SBA-15 and phenol.

# 1. INTRODUCTION

Aromatic compounds are common pollutants in the effluents of several industries. The degradation of these pollutants present in wastewater streams has emerged as an important concern during last decade. The effective removal of these pollutants is a challenging task due to environmental laws and regulations becoming more restrictive with time. Aromatic compounds are, generally, refractory to conventional chemical and biological treatments and this is the reason that other methods are being studied as alternatives [1,2]. Advanced Oxidation Technologies (AOT's) are interesting alternatives for the destruction of organic pollutants in industrial wastewater. These processes involve the generation of the non-selective and highly reactive hydroxyl radicals (HO•), which are not only one of the most powerful oxidation agents, but they have a higher oxidation potential than other chemicals commonly used in wastewater treatments [3]. Among these technologies, the oxidation of organic compounds by means of Fenton-like processes (the reaction of hydrogen peroxide with ferrous salts or other low-valency transition metals [4]) has been extensively studied over the last fifteen years [5,6]. Nowadays, efforts are mainly focused on the development of Fenton processes based on heterogeneous catalytic systems, which provide an easy separation and recovery of catalyst from the treated wastewater (one of the major drawbacks of conventional Fenton processes). Recently some interesting results in the synthesis of heterogeneous Fenton-like catalyst systems for phenol oxidation have been reported. Thus, iron species supported in different silica matrices, such as zeolitic materials [7,8], amorphous silica structures, highly ordered mesostructures [9], or even pillared clays [10] and heterogeneous systems with other low-valence transitions metals [11] have all presented high catalytic activity for phenol oxidation, accompanied with low leaching of the active transition metal.

On the other hand, the application of ultrasonic irradiation (US) in wastewater treatment has emerged as a novel advanced oxidation technology and the degradation of a wide variety of organic substrates such as chlorinated hydrocarbons [12], aromatic compounds [13], dyes [14] or phenolic compounds [15,16] have been reported in the literature using this technique. The formation and collapse of cavitation bubbles produced in the process results in extremely high temperatures and pressures inside the

bubbles, which induce the thermal decomposition of the dissolved organic compounds (pyrolytic decomposition) and the generation of free radicals (such as H•, O• or HO•) by thermal dissociation of water or some oxidant such as hydrogen peroxide, which can initiate radical oxidation reactions of the organic compounds.

In order to increase the decomposition efficiency and to reduce the time required for removing the pollutants, several authors have studied the combination of ultrasound with different oxidants such as ozone or hydrogen peroxide [17,18]. In this way, promising results have been reported for the use of the coupled US/Fe$^{+2}$/H$_2$O$_2$ technique in the mineralization of MTBE [19], p-chlorobenzoic acid [20] and 2,4-dinitrophenol [21]. However, these methods employ homogeneous iron catalysts and final precipitation treatments are necessary for the removal of soluble iron ions, with the consequent increase of operational costs. Furthermore, work on the combination of heterogeneous catalytic oxidation with ultrasound has mainly focused on the use of copper oxides [22]. Nonetheless, a recent report has discussed the benefits of the combined use of ultrasound irradiation and catalytic oxidation for decomposition of phenol, using a mixed (Al-Fe) pillared clay (FAZA) as solid catalyst [23].

The purpose of this current study is the assessment of a novel composite Fe-containing SBA-15 mesostructured material in the oxidation of phenolic aqueous solutions by means of a coupled heterogeneous Fenton-like process with ultrasonic irradiation (US/Fe-SBA-15/H$_2$O$_2$). This material has been tested successfully in other Fenton-like [9] and photo-assisted Fenton-like [24] processes. Besides the investigation of the benefits of the combined use of the ultrasound irradiation and the heterogeneous catalytic peroxide oxidation, multivariate analysis has been used to assess the conditions (oxidant and catalyst concentrations) that yield the best results in terms of organic degradation and catalyst stability.

## 2. EXPERIMENTAL SECTION

### 2.1. Catalyst preparation and characterization

Iron-containing SBA-15 mesostructured material has been prepared by co-condensation of iron (FeCl$_3$·6H$_2$O; Aldrich) and silica (tetraethoxysilicate, TEOS;

Aldrich) under acidic conditions and templated with Pluronic 123 following the synthesis route described by Martinez *et al.* [25]. The precipitation of non-soluble iron oxy-hydroxide particles was promoted by ageing of the resultant solution at 110 ºC for 24 hours under static conditions at a pH of 3.5 [26]. After the ageing step, the solid product was recovered by filtration and air dried at room temperature overnight. Transformation of hydrated iron species to oxidized microcluster and the template removal was accomplished by calcination in air at 550 ºC for 5 hours.

According to previous work [9,24,26], the material synthesised can be described as a composite that contains different iron oxides (mainly crystalline hematite) embedded into a mesostructured $SiO_2$ matrix with a wide size distribution (30 – 300 nm) and well dispersed ionic iron species within the siliceous framework. The properties of the matrix are characteristic of a hexagonally mesostructured SBA-15 material, with a calculated BET area around 470 $m^2$/g (which is slightly lower than that usually found for pure silica SBA-15 materials) and a narrow pore diameter distribution around 7 nm. The total iron content of the material was about 16 wt. %.

## 2.2. Sono-Fenton like reactions

The Sono-Fenton experiments were performed in a commercial ultrasonic processor (Cole Parmer) equipped with a titanium probe (1cm diameter) capable of operating either continuously or in a pulse mode at a fixed frequency of 20 KHz. In the present work, the experiments were carried out with the probe working in pulses, 4.0 seconds on, and 2 seconds off, which allows the system to dissipate some of the heat generated by the ultrasonic waves. The intensity of the irradiation was adjusted to 50% of ultrasonic power amplitude, which corresponds to a calorimetric measurement of 18 W (22,9 $Wcm^{-1}$). In a typical run, the probe was immersed in a 300 mL cylindrical glass reactor filled with 200 mL of aqueous phenol solution (2.5 mM is equivalent to $[TOC]_0$=179.0 ppm) and the pH was adjusted to 3.0 with appropriate amounts of $H_2SO_4$ (0.1 M). The temperature was kept constant at 22 ± 2 ºC during all reactions by an external cooling bath. The appropriate amounts of hydrogen peroxide and catalysts were added to the reactor just before switching the probe on (reaction time zero). Aliquots of 5 mL) were withdrawn every 30 minutes during 270 minutes of total irradiation time

and filtered through 0.45 μm nylon membranes before being analysed. The same experimental set-up equipped with a magnetic stirrer instead of the ultrasound probe was used for the silent experiments. In this case, the temperature was adjusted to $22 \pm 2$ ºC during the reaction with a cooling bath similar to the employed in the ultrasound experiments.

The total organic carbon (TOC) content of the initial phenol aqueous solution and the samples taken from the reaction medium was measured by wet oxidation analysis (Model 700 TOC Analyzer from OI-Analytical) using sodium persulphate and phosphoric acid as oxidising and acid reagent respectively. The hydrogen peroxide concentration was evaluated by iodiometric titration and the iron content in the filtered solution after reaction was measured by a colorimetric process in a DR/2400 Spectrophotometer (Hach Company). The iron dissolved in the medium was transformed into soluble ferrous iron by digestion with FerroVer Iron reagent (Hach Company) and then reacted with the 1,10-phenanthroline reagent to form a red-orange colour and the absorbance was measured at 510 nm.

## 3. RESULTS AND DISCUSSION

### 3.1. Preliminary Experiments

The activity and stability of heterogeneous Fenton-like catalyst (Fe-SBA-15/$H_2O_2$) in presence of heat or UV-Vis radiation have been well demonstrated in previous works [9,24]. The purpose of the current work was to determine the benefits, if any, of using ultrasound in conjunction with a heterogeneous catalyst and hydrogen peroxide (US/Fe-SBA-15/$H_2O_2$) over the silent system (Fe-SBA-15/$H_2O_2$). Figure 1 shows the TOC conversion over time of experiments performed under ultrasonic or silent conditions at 22 ºC and initial pH of 3.0. Concentrations of catalyst and oxidant were set in 0.6g$L^{-1}$ and 2.38 g$L^{-1}$, respectively. The oxidant concentration corresponds to twice the stoichiometric amount of hydrogen peroxide needed for the complete mineralization of a 2.5 mM phenol aqueous solution, according to the following reaction:

$$C_6H_5OH + 14\,H_2O_2 \rightarrow 6\,CO_2 + 17\,H_2O \qquad (1)$$
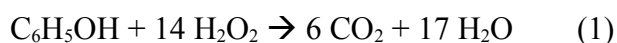
In order to ascertain the effect of other operation systems, Figure 1 also includes results of experiments performed using ultrasound in presence of hydrogen peroxide, but without catalyst (curve 4), ultrasound in presence of catalyst but without oxidant (curve 5) and only ultrasound in absence of both catalyst and oxidant (curve 1). All these preliminary experiments were carried out in duplicate.

In the selected conditions, the degradation of phenol in the sono-catalytic reaction (Figure 1, curve 3) is much higher than the silent one (Figure 1, curve 2) and it reaches values close to 40 % of TOC conversion. Comparison between the ultrasonic runs carried out in presence (Figure 1, curve 3) and in absence (Figure 1, curve 4) of the heterogeneous catalyst reveals the benefits of the catalyst in the mineralization of phenol. The initial reaction rate is increased and the final TOC conversion after 270 minutes rises from 8.5 to 38 %.
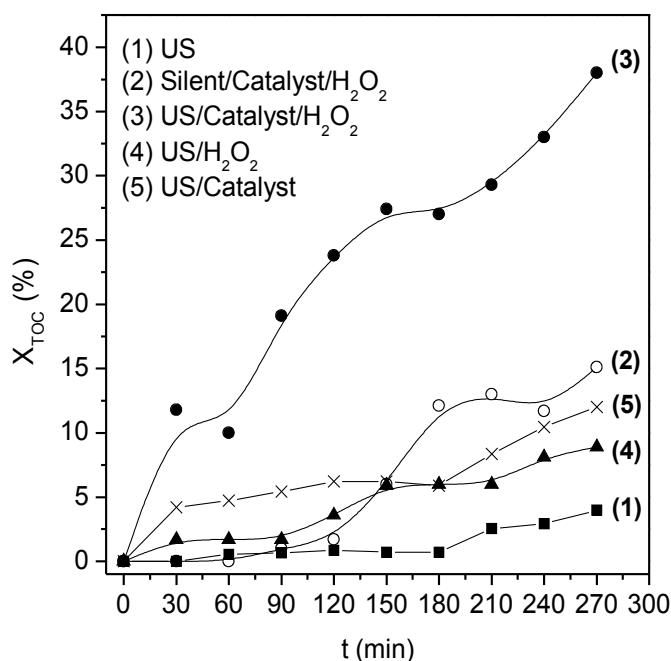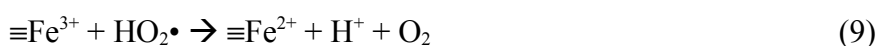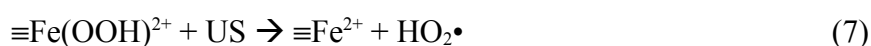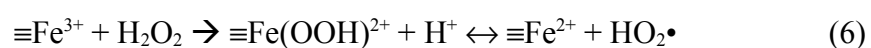


**Figure 1. Preliminary experiments carried out with ultrasound, H₂O₂ and the heterogeneous catalytic system in different combinations. Results are an average of two runs.**
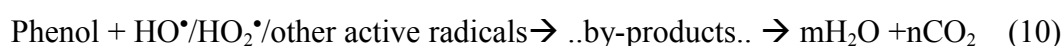
These results prove the high activity of the sono-Fenton system in the degradation of phenolic solutions, in comparison to a silent Fenton-like process or an US/hydrogen peroxide combination under similar reaction conditions. Phenol degradation due to the

potential production of active radicals by direct ultrasound irradiation of the aqueous medium in presence (Figure 1, curve 5) or absence of the catalyst (Figure 1, curve 1) but without addition of hydrogen peroxide, has been also investigated. Since the external oxidant is not added, the sonocatalytic activity of Fe-SBA-15 decreases drastically, this demonstrates a lower production of active radicals, i.e. hydroxyl radicals, through catalytic ultrasound reactions than in the presence of the oxidant. In addition, the experiment with ultrasound in absence of catalyst and oxidant shows the lowest organic degradation (Figure 1, curve 1). Thus, these preliminary results indicate the important benefit of both oxidant and catalyst for the enhancement of phenol degradation in ultrasound-assisted processes. Likewise, it must be pointed out a clear synergetic effect of US/catalyst/$H_2O_2$ system as compared to the silent Fenton-like reaction (catalyst/$H_2O_2$) and only ultrasound (US) in terms of the TOC degradation rate.

The low hydrogen peroxide to phenol ratio used in this preliminary US/catalyst/$H_2O_2$ experiment is particularly noteworthy in comparison with similar reactions reported in the literature for heterogeneous (US/CuO/$H_2O_2$, [22]) and homogeneous (US/$Fe^{2+}$/$H_2O_2$, [27]) processes, or even for other aromatic compounds, such as p-chlorobenzoic acid by US/FeOOH/$H_2O_2$ as heterogeneous system [20] or 2,4-dinitrophenol by US/$Fe^{2+}$/$H_2O_2$ as homogeneous system [21]. Based on the mechanism proposed in the literature for homogeneous systems [17,19,21], the reactions of ultrasound coupled with the Fenton-like reagent can be described by the following equations (2 to 9), where the symbol $\equiv$ represents the iron species bound to the surface of the catalyst.

$$RH + US \rightarrow \text{Degradation products} \tag{2}$$
$$H_2O + US \rightarrow H\bullet + HO\bullet \tag{3}$$
$$RH + HO\bullet \rightarrow \text{Degradation products} \tag{4}$$
$$H_2O_2 + US \rightarrow 2\ HO\bullet \tag{5}$$
$$\equiv Fe^{3+} + H_2O_2 \rightarrow \equiv Fe(OOH)^{2+} + H^+ \leftrightarrow \equiv Fe^{2+} + HO_2\bullet \tag{6}$$
$$\equiv Fe(OOH)^{2+} + US \rightarrow \equiv Fe^{2+} + HO_2\bullet \tag{7}$$
$$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+} + HO^- + HO\bullet \tag{8}$$
$$\equiv Fe^{3+} + HO_2\bullet \rightarrow \equiv Fe^{2+} + H^+ + O_2 \tag{9}$$

Typically, the degradation of the organic pollutants using sono-treatments is ascribed to direct pyrolisis (reaction 2) in and around the collapsing bubbles and/or indirect oxidation by attack of formed hydroxyl radicals (reactions 3 and 4) in the bulk solution or interface between the collapsing bubbles. In the presence of hydrogen peroxide, additionally free hydroxyl radicals can be also formed (reaction 5), which react with the organic matter enhancing the reaction 4 and hence, a boost of the organic pollutants degradation can be obtained. When hydrogen peroxide is added into an aqueous system containing $Fe^{2+}/Fe^{3+}$ species, complex redox reactions would take place (reactions 6-9). Hydrogen peroxide reacts with supported iron (III) active sites to produce the intermediate $Fe(OOH)^{2+}$, which can be dissociated into the hydroperoxyl radical and reduced $Fe^{2+}$ sites (reaction 6). The resulting $Fe^{2+}$ sites further reacts with $H_2O_2$ and generates additional hydroxyl radicals in the typical Fenton reaction labeled as 8. It is well known that a limiting step in Fenton reactions is the low kinetic rate of Fe(III) reduction to Fe(II) mediated by the formation of $Fe(OOH)^{2+}$ complex. In this sense, the dissociation of this complex to reduced Fe(II) and $HO_2^{\bullet}$ radicals can be improved by sonication (reaction 7). This is the reason because efficiency of US/Fe-SBA-15/$H_2O_2$ system for degradation of phenol is enhanced by ultrasound as compared to the silent process, in which the degradation of phenol (reaction 10) will take place by the active radicals produced as result of the ultrasonic interaction between the iron and hydrogen peroxide in acidic conditions.

$$\text{Phenol} + HO^{\bullet}/HO_2^{\bullet}/\text{other active radicals} \rightarrow ..\text{by-products}.. \rightarrow mH_2O + nCO_2 \quad (10)$$

Additionally, $Fe^{3+}$ sites can react with hydroperoxy radicals to produce more $Fe^{2+}$ sites (reaction 9), which in turn, produce more hydroxyl radicals via reaction 8. These reactions enhance the formation of hydroxyl radicals due to the Fenton process, and the consequent degradation of organic compounds in reaction 10.
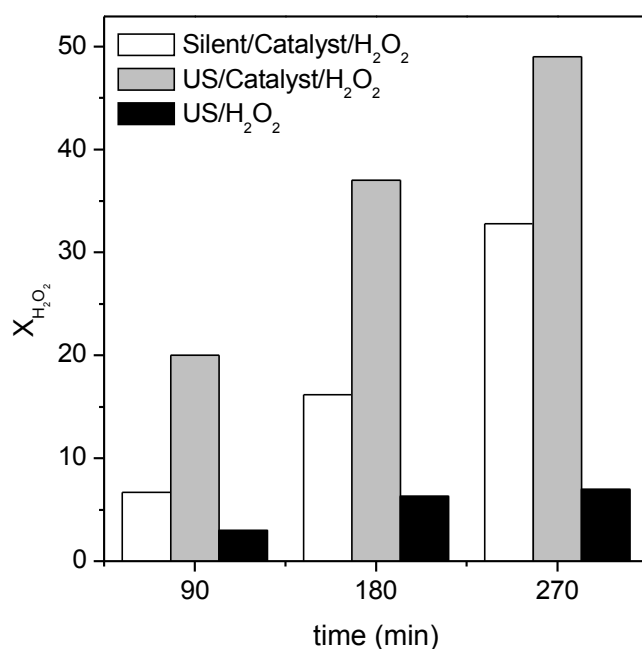
**Figure 2**. **Decomposition of hydrogen peroxide with irradiation time**

Taking into account the results of hydrogen peroxide consumption depicted in Figure 2, there is no doubt that the remarkable enhancement of the TOC mineralization for the US/Fe-SBA-15/$H_2O_2$ catalytic system as compared to the silent one, is clearly related to a higher production of hydroxyl radicals mediated by ultrasonic irradiation. Note that the presence of the catalyst in the sonicated system enhances significantly the decomposition of hydrogen peroxide, which means, that production of active radicals such as hydroxyl radical will be increased.

Another important point in a process that involves a heterogeneous catalyst is the stability of the active species during the reaction. Table 1 shows the concentration of iron species detected in the medium after three reaction times in the different processes carried out in the presence of the catalyst, as well as the equivalent loss of metal from the catalyst.

The iron loss observed for these experiments is normally attributed to the oxidizing and acid conditions in which the reactions take place, but the effect of cavitation on the catalyst surface in ultrasound systems could also play an important role. In our

particular experiments, it is remarkable that the stability of the heterogeneous catalyst under ultrasonic irradiation is even better than under silent conditions.

**Table 1. Stability of the iron species in the catalyst**

| time (min) | Silent Fe-SBA-15/$H_2O_2$ process | | US/Fe-SBA-15/$H_2O_2$ process | | US/Fe-SBA-15 process | |
|---|---|---|---|---|---|---|
| | $[Fe]_{detected}$ (ppm) | Fe lost (%) | $[Fe]_{detected}$ (ppm) | $Fe_{lost}$ (%) | $[Fe]_{detected}$ (ppm) | Fe lost (%) |
| 90 | 5.0 | 5.2 | 4.9 | 5.1 | 4,4 | 4.6 |
| 180 | 5.5 | 5.7 | 5.0 | 5.2 | 4,9 | 5.1 |
| 270 | 8.0 | 8.2 | 5.0 | 5.2 | 4,7 | 4.9 |

The amount of iron lost in the US/catalyst experiment is very similar to that lost from the US/catalyst/$H_2O_2$ conditions. In conclusion, these results show that the ultrasound irradiation of the catalyst seems to protect the iron species supported over the catalyst from leaching. A possible explanation of this effect could be the redox processes that the ultrasound induces in the iron dissolved from the catalyst to produce metallic species capable of re-adsorption over the high surface of the heterogeneous catalyst.

Therefore, the conditions and environment of the ultrasonic process result in a remarkable stability of the Fe-SBA-15 catalyst and low concentration of iron into the aqueous reaction medium.

### 3.2. Factorial design of experiments for the sono-Fenton heterogeneous system

The preliminary experiments carried out revealed the activity of the ultrasound/heterogeneous-Fenton system in the mineralization of aqueous phenolic solutions by a heterogeneous sono-Fenton process. The influence of different variables in the reaction was now studied by experimental design methodology. The variables selected are those related to Fenton-like reagents (catalyst and hydrogen peroxide concentration) in order to determinate their influence in the sono-degradation of the phenol solution using the heterogeneous catalyst in an ultrasonic process. A complete $3^2$ experimental design [28] was performed using catalyst concentration ranging from 0.2 to 1.0 $gL^{-1}$, and hydrogen peroxide concentration from 1.19 to 4.76 $gL^{-1}$. The concentrations of oxidant correspond to the stoichiometric and four times the

stoichiometric amount respectively. The initial pH was adjusted to 3.0 by addition of appropriate amounts of $H_2SO_4$ solution (0.1 M). The catalyst loadings were selected according to values previously published [24] and hydrogen peroxide concentrations were chosen taking into account the theoretical organic pollutant to oxidant ratio through reaction 1. The objective was to minimize the hydrogen peroxide concentration yet maximize degradation of phenol and the organic by-products formed in the reaction

Table 2 describes the factorial design of experiments, including the coding of the real values for the independent variables (-1, 0 and 1 for low, medium and high levels, respectively). The effect of varying the parameters was determined by measuring the decrease in TOC at 90, 180 and 270 minutes. The influence of the variables on the stability of the catalyst was ascertained by measuring the amount of iron dissolved from the catalyst during the process The values of these variables, as well as the calculated values obtained from the model, are also given in Table 2.

**Table 2. Factorial design of experiments**

| [Catalyst] (X) | [H₂O₂] (Y) | $X_{TOC}^{90'}$(%) (Z₁) | | $X_{TOC}^{180'}$(%) (Z₂) | | $X_{TOC}^{270'}$(%) (Z₃) | | $Fe^a{}_{270'}$ (%) (Z₄) | |
|---|---|---|---|---|---|---|---|---|---|
| | | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. | Exp. | Calc. |
| -1 (0.2 gL⁻¹) | -1 (1xStoich) | 14.3 | 14.1 | 15.0 | 15.1 | 19.0 | 18.7 | 3.8 | 3.4 |
| -1 (0.2 gL⁻¹) | 0 (2xStoich) | 11.5 | 12.2 | 19.2 | 19.0 | 21.2 | 23.1 | 3.1 | 3.5 |
| -1 (0.2 gL⁻¹) | 1 (4xStoich) | 12.5 | 12.8 | 16.8 | 16.9 | 20.3 | 18.7 | 4.1 | 4.0 |
| 0 (0.6 gL⁻¹) | -1 (1xStoich) | 18.0 | 19.1 | 27.9 | 27.7 | 29.2 | 31.1 | 4.2 | 4.6 |
| 0 (0.6 gL⁻¹) | 0 (2xStoich) | 19.1 | 17.7 | 27.0 | 27.5 | 36.9 | 33.2 | 4.2 | 3.4 |
| 0 (0.6 gL⁻¹) | 1 (4xStoich) | 15.3 | 16.3 | 25.3 | 25.1 | 29.3 | 31.1 | 4.2 | 4.6 |
| 1 (1.0 gL⁻¹) | -1 (1xStoich) | 20.0 | 19.7 | 28.7 | 28.8 | 29.9 | 29.9 | 8.4 | 8.3 |
| 1 (1.0 gL⁻¹) | 0 (2xStoich) | 18.2 | 18.9 | 26.8 | 26.6 | 27.8 | 29.7 | 6.1 | 6.4 |
| 1 (1.0 gL⁻¹) | 1 (4xStoich) | 15.4 | 15.6 | 25.6 | 25.7 | 31.8 | 29.9 | 9.1 | 8.8 |

ª· % wt. of iron lost from the catalyst

The experimental values acquired allow the generation of a matrix with the response variables obtained in all the reaction conditions. Assuming a second order polynomial model and a Levenberg-Marquad algorithm for nonlinear regression, predictive equations for the response variables were produced (equations 11 to 14 in Table 3), where X and Y represent the catalyst and hydrogen peroxide concentration respectively and $Z_1$ to $Z_4$ correspond to TOC conversion at 90, 180 and 270 minutes and iron leached at 270 minutes respectively. The influence of the independent variables,

and their combination, is related to the value and sign of the coefficients of the polynomial expressions. Values between brackets represent the error associated with each coefficient of the equation.

**Table 3. Predictive equations obtained by factorial design of experiment**

$Z_1= 17.7(\pm1.5)+3.4(\pm1.1)X-1.4(\pm0.9)Y-0.7(\pm0.5)XY-2.2(\pm0.5)X^2-1.2(\pm0.4)XY^2$     (11)

$Z_2= 27.5(\pm0.5)+3.8(\pm0.4)X-1.3(\pm0.3)Y-1.2(\pm0.2)XY-4.7(\pm0.2)X^2-1.1(\pm0.2)Y^2$
$\quad+1.0(\pm0.1)YX^2+1.8(\pm0.4)XY^2$     (12)

$Z_3= 33.2(\pm4.2)+3.3(\pm2.8)X-6.8(\pm1.4)X^2-2.1(\pm0.9)Y^2+2.3(\pm1.0)XY^2$     (13)

$Z_4= 3.4(\pm0.9)+1.5(\pm0.6)X+1.6(\pm0.3)X^2+1.2(\pm0.2)Y^2+0.3(\pm0.2)YX^2+1.0(\pm0.2)X·Y^2$     (14)

### 3.2.1. Influence of the variables on the activity of the heterogeneous sono-Fenton system

Values of TOC conversion at 90, 180 and 270 minutes were selected for the study of the activity of the system in the mineralization of the aqueous phenol solution. Equations 11 to 13 fit the experimental data obtained and Figure 3 shows the relationship between the experimental and the predicted values.
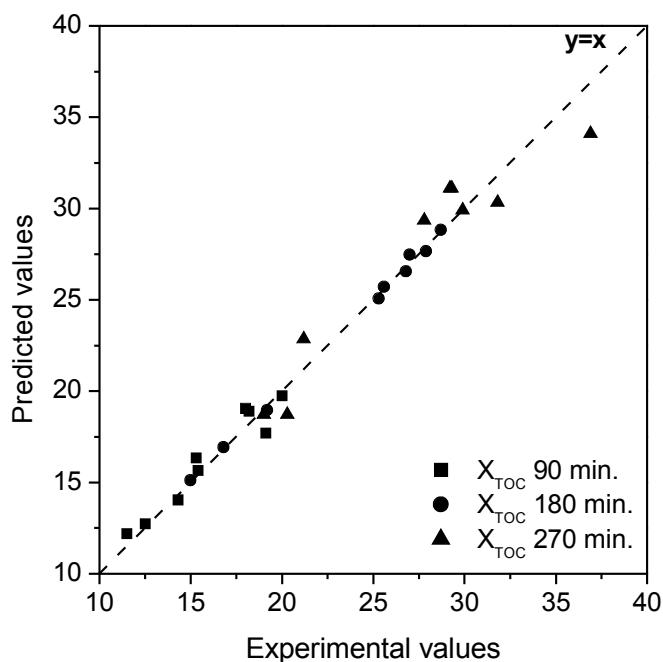


**Figure 3. Accuracy of the predicted data with respect to the experimental values**

In all cases, the values calculated with the predictive equations are very close to the experimental values obtained in all the reactions carried out.

Considering the influence of the variables with the coefficients of the equations shown above, it is remarkable that there are quadratic terms in each indicating that the responses are represented by curved surfaces. The catalyst concentration (X) is important in all the reaction times, although a negative effect is observed for both an excess of catalyst ($X^2$) and hydrogen peroxide ($Y^2$). The synergistic effect of the catalyst concentration (X) and hydrogen peroxide ($Y^2$) becomes important at the end of the reaction (270 minutes).

The graphic representation of the response curves is depicted in figure 4.



| Code | [Catalyst] | [H$_2$O$_2$] |
|------|-----------|--------------|
| -1 | 0.2 gL$^{-1}$ | Stoichiometric |
| 0 | 0.6 gL$^{-1}$ | 2xStoichiometric |
| +1 | 1.0 gL$^{-1}$ | 4xStoichiometric |

a) t=90 min.
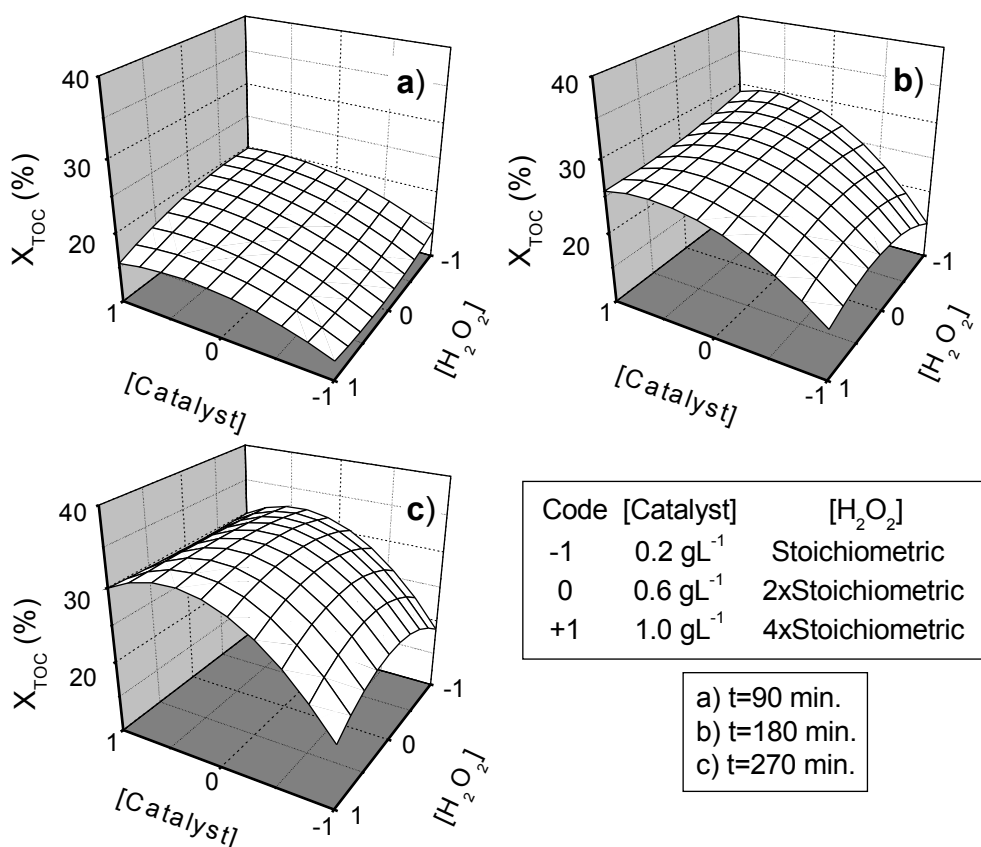b) t=180 min.
c) t=270 min.

**Figure 4. Response surfaces for the TOC conversion at (a) 90, (b) 180 and (c) 270 minutes**

The 3D-response surface at 90 minutes (figure 4-a) clearly shows an enhanced TOC conversion with increasing catalyst loadings. The beneficial effect of the catalyst is also observed at 180 minutes (figure 4-b) and this behavior is observed in all the oxidant concentration ranges studied. The maximum values of TOC conversion at 90 and 180 minutes are for high loadings of catalyst and low concentration of hydrogen peroxide. With higher amounts of catalyst, there are more active iron sites in the reaction medium and they are able to produce, the real oxidant in the phenol degradation, hydroxyl radicals by Fenton reactions enhanced with ultrasound irradiation (as shown in reactions 6 to 9) [29,30,31]. Moreover, iron $Fe^{3+}$ ions are effective oxidants for the direct degradation of organic pollutants such as the initial phenol solution or the later intermediates of reaction, coming from the partial oxidation of phenol [27]. On the other hand, there is a slight increase of TOC conversion for a given catalyst as oxidant concentration is increased. Nevertheless, the influence of hydrogen peroxide concentration can be considered negligible and the results seem to be only dependent on catalyst concentration.

A change in the behaviour is observed in the 3-D response surface at 270 minutes. Maximum values of TOC conversions are observed with catalyst concentration between 0.6 and 1.0 g/L and hydrogen peroxide concentrations around 2.38 $gL^{-1}$ (twice the stoichiometric amount of oxidant according to reaction 1). For all the catalyst loadings employed, relative maximum values are obtained around this hydrogen peroxide concentration. As has been reported in the literature, the influence of hydrogen peroxide depends of the kind of organic compound. Thus, degradation rates for trichloroethylene (TCE) and 1,3-dichloro-2-propanol (DCP), being hydrophilic and volatile compounds, are independent of the amount of hydrogen peroxide in the reaction medium [32], whereas degradation of o-chlorophenol [32], 1,4-dinitrophenol [21] or phenol [22], as hydrophobic and less volatile compounds, show a dramatic dependence on the hydrogen peroxide concentration present in the reaction medium. For the later compounds, a rise in the $H_2O_2$ concentration produces an increase in both the initial rate of mineralization and final degradation of the organic material. However, a minimum $H_2O_2$ concentration is necessary to observe any effect [21]. Some authors suggest [18] that, although the presence of hydrogen peroxide enhances the TOC conversion and the mineralization of the organic pollutant, an excess of $H_2O_2$ acts as a hydroxyl radical scavenger leading to

the generation of hydroperoxy radicals (reaction 15 and similar parallel reactions) that are less active than the hydroxyl radicals.

$$H_2O_2 + HO\bullet \rightarrow HO_2\bullet + H_2O \qquad\qquad (15)$$

This effect is also reported in the literature in the oxidation of organic compounds by means of other Fenton-like processes enhanced with UV-Visible radiation or high temperature rather than ultrasonic waves [9,33,34,35] and it could be a possible explanation for the maximum in the TOC conversion observed at intermediate concentrations of hydrogen peroxide in the range studied.

Figure 5 shows the $H_2O_2$ consumption after 270 minutes for each reaction studied and it can be seen that more hydrogen peroxide is consumed as the initial oxidant concentration is increased. Furthermore, the increase of hydrogen peroxide consumption for a given catalyst loading does not promote an enhancement of TOC conversion (see Figure 4), which seems to be in agreement with the scavenging reactions mentioned earlier. As a consequence of this, a better efficiency in the use of the oxidant for the TOC degradation is obtained at intermediate concentrations of hydrogen peroxide.
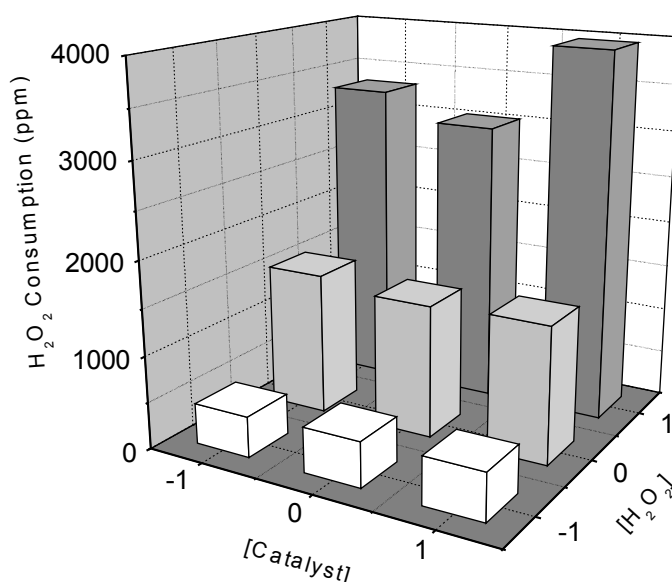


**Figure 5. $H_2O_2$ spent at 270 minutes of irradiation time**

### 3.3.2. Influence of the variables in the stability of the heterogeneous sono-Fenton system

Leaching determinations of the iron species from the Fe-SBA-15 heterogeneous catalyst were carried out in order to ascertain how strongly held the iron is by the SBA-15 silica matrix and to take into account the possibility of recovery and reuse of the catalyst. Equation 14 fits the experimental results, in terms of iron lost from the catalyst in weight percent, and Figure 6 shows the high accuracy of the data predicted by the equation with respect to the experimental data obtained in the reactions.
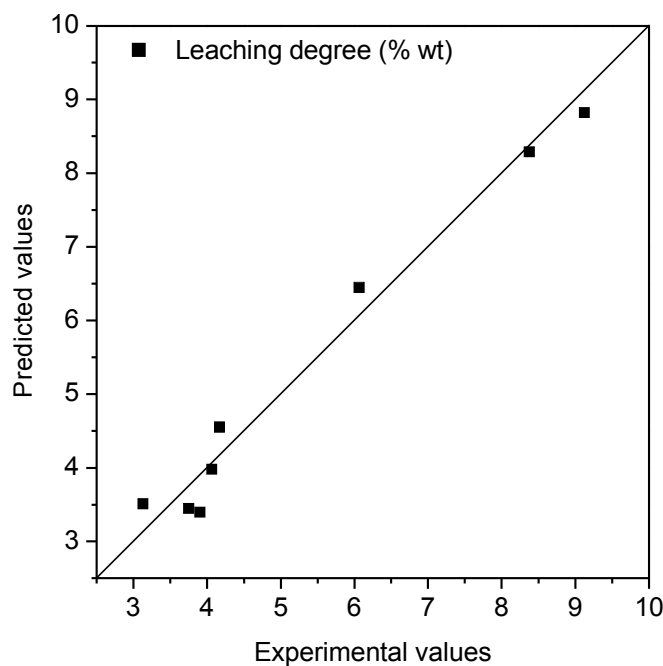


**Figure 6. Accuracy of the predicted leaching values**

Considering the coefficients of equation 14, the principal influence corresponds to changes in the concentration of the catalyst in the reaction medium ($X$, $X^2$). Only high amounts of hydrogen peroxide ($Y^2$) or the combination of hydrogen peroxide and catalyst ($XY^2$ and $YX^2$) have an appreciable influence in the degree of leaching. In all these cases, an increase in the individual variable or in the combination of both of them, as mentioned, results in an increase in the leaching as shown by plus signs before the coefficients. The 3-D response surface corresponding to equation 10 is depicted in Figure 7 and there is a strong correlation between catalyst loadings and the degree of

leaching. With medium and low concentrations of catalyst, the influence of the hydrogen peroxide is negligible, whereas at high catalyst loadings, the response surface shows relative maxima with the lowest and the highest hydrogen peroxide concentrations tested. However, the amount of iron lost from the catalyst is less than 10 % in all the cases and with 0.6 gL$^{-1}$ of catalyst (0) and 2.38 gL$^{-1}$ of hydrogen peroxide (0), conditions characterized for the highest final TOC conversion, the leaching degree is less than 3.5 %. This also shows that the Fe-SBA-15 catalyst is highly stable in the range of conditions tested.
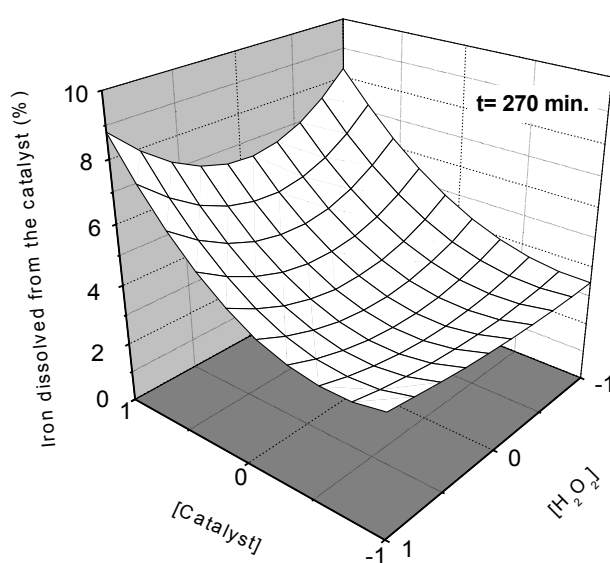


**Figure 7. 3D-response surface for the final leaching degree of Fe from the catalyst after 270 minutes of irradiation time**
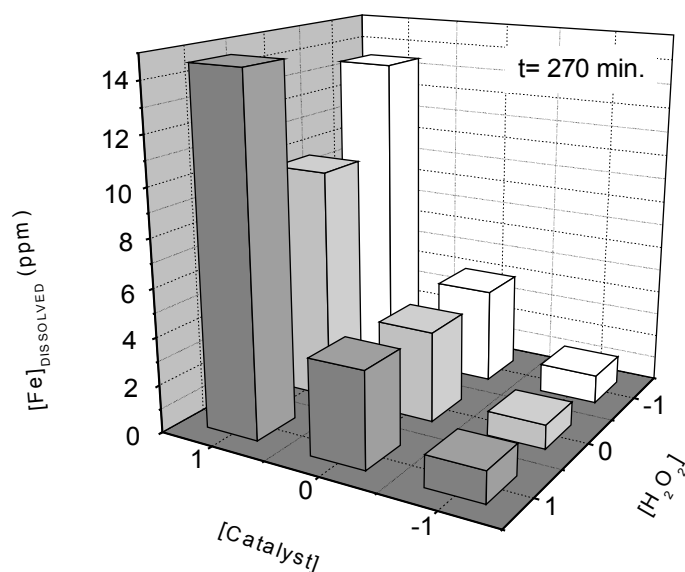
**Figure 8. Iron concentration detected in the reaction medium after 270 minutes of irradiation time**

Figure 8 depicts the iron lost from the catalyst, as concentration of iron detected in the aqueous solution after the reactions. This representation shows the amount of iron released into the reaction medium after 270 minutes of sonication. The shape is similar to that observed in Figure 7 and it is noteworthy that using 0.6 $gL^{-1}$ of catalyst (code=0) and 2.38 $gL^{-1}$ of hydrogen peroxide (code=0) the amount of iron detected in the reaction medium is less than 4 ppm. On the other hand, it must be noted that shapes of 3-D response surfaces of TOC conversion (Figure 4) and concentration of iron dissolved (Figure 8) after 270 minutes of irradiation time are fairly different, showing a maximum of TOC conversion for ca. intermediate catalyst loadings where the concentration of iron in dissolution displays a considerable decrease. Therefore, the catalytic activity of Fe-SBA-15 catalyst in ultrasound system does not seem to be dominated by the homogeneous contribution of the iron dissolved, and confirm the essential role of the supported iron species in the overall process. Nevertheless, further sonocatalytic systems should be studied using iron (III) ions as homogeneous catalyst in order to evaluate its particular contribution in these processes.

19

### 3.3. Influence of the initial pH

It is well known that the Fenton reactions proceed best in acidic media. In fact, the majority of works based on Fenton processes assisted by heating, UV radiation or acoustic cavitation have used pH values ranging from 2 to 3.5 as optimum conditions [35,36,37,38]. However, previous work performed using the Fe-SBA-15 material as the heterogeneous catalyst in the oxidation of phenol solutions by Fenton-like processes enhanced by heating or UV-visible radiation have reported interesting results in terms of activity and stability without consideration of the initial pH [9,24]. In order to determine the effect of this variable in the present process, three sets of reactions were studied at two different initial pH values. The catalyst concentration selected was 0.6 gL$^{-1}$ and the experiments were performed with one, two and four times the stoichiometric amount of hydrogen peroxide, using 3.0 and 6.5 as initial pH. A starting pH of 3.0 was obtained by the addition of sulfuric acid solution (0.1 N), and pH of 6.5 resulted without any chemical addition since this is the normal pH of phenol in solution.

The results shown in Figure 9-a, b and c reveal the beneficial effect of the acidic pH in the activity of the sonocatalytic system. The enhancement of the TOC conversion mainly for low and medium concentrations of hydrogen peroxide (Figures 9-a and 9-c respectively) is remarkable. With four times the stoichiometric amount of hydrogen peroxide (Figure 9-e), the influence of the acidic medium is negligible for the first 100 minutes. The benefit only appears at final reaction times and the increase in the final TOC conversion is less than that observed with lower oxidant concentrations. As has been mentioned earlier, the generation of hydroxyl radicals by the Fenton-like process is enhanced under acidic conditions, but paradoxically, at higher initial oxidant concentration, a rapid disappearance of hydroxyl radicals occurs due to action of hydrogen peroxide as a radical scavenger. A plausible explanation of these results could be that both parallel reactions take place in different extension depending on the initial pH, making more efficient the sono-Fenton process under non-modified initial pH conditions when a higher oxidant concentration is used.

On the other hand, Figures 9-b, d and f show pH profiles of the experiments carried out at initial pH of 3.0 and 6.5. Unlike catalytic runs starting at acidic pH, where it is almost constant along the reaction, the catalytic experiments starting at 6.5 show a pH

drop of c.a. 3.5, following different curves depending on the initial hydrogen peroxide concentration. This pH decreasing is usually attributed to the $H^+$ formation by Fenton reactions (equations 6 to 9) and the acid by-products generated from the partial oxidation of phenol. Although further studies should be done in order to clarify the distinct pH behavior depending on the oxidant concentration, a slow decrease of pH in the first 2 hours of reaction is clearly seen for the three oxidant levels, and the TOC degradation rate achieved during those periods of time must be highlighted.

Finally, it should be noted that the high TOC conversion obtained using two times the stoichiometric amount of hydrogen peroxide under a starting pH of 6.5 is accompanied with the most marked pH drop (Figure 9-c and d). Thus, the relative activity shown by the US/Fe-SBA-15/$H_2O_2$ system, without the prerequisite of reducing the pH, opens new possibilities in the study of the direct oxidation of organic compounds.
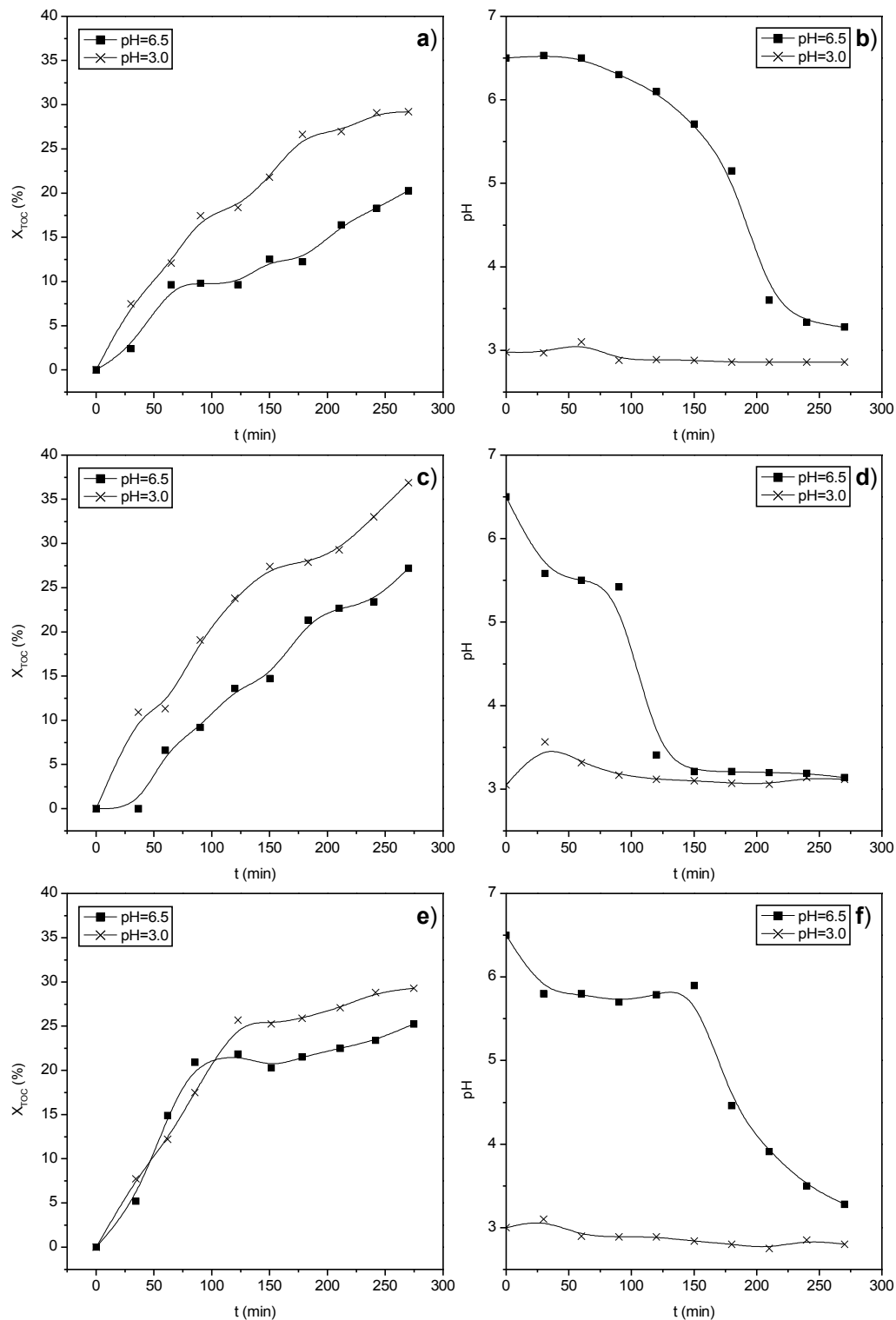
**Figure 9. Influence of the initial pH and changes in pH with selected conditions: 0.6 gL$^{-1}$ of catalyst and (a-b) 1.19, (c-d) 2.38 and (e-f) 4.76 gL$^{-1}$, corresponding to the stoichiometric, 2x and 4x the stoichiometric amount of H$_2$O$_2$ in 200 mL of a 2.5 mM phenol solution.**

## 4. CONCLUSIONS

Iron-containing SBA-15 material (Fe-SBA-15) has been shown to be a promising catalyst for the treatment of phenolic aqueous solutions by coupling of ultrasound with heterogeneous catalytic wet peroxide oxidation. In this process the outstanding effect of ultrasound irradiation in the degradation of phenol aqueous solutions is remarkable.

The factorial design of experiments carried out shows that the optimal hydrogen peroxide concentration is two times the stoichiometric amount, achieving results of TOC degradation ranging from 30 to 40 %, which represents a low oxidant dosage as compared with similar studies reported in the literature. The catalyst loading plays a more important role than the oxidant concentration in the activity of the sono-Fenton catalytic system. The remarkable stability (less than 4 ppm loss for the best reaction conditions) of the Fe-SBA-15 heterogeneous catalyst under ultrasonic irradiation is particularly noteworthy.

The results obtained with US/Fe-SBA-15/$H_2O_2$ system without previous adjustment of the pH open new possibilities for the process and elimination of the use of acid for pH reduction is a distinct possibility. In this case, different initial hydrogen peroxide concentrations involve very different TOC conversions and pH profiles with time, which may suggest that additional relationships between these variables exist. Thus, Fe-SBA-15 offers a viable alternative as a heterogeneous catalyst instead of copper oxides usually employed in the combined process (US/catalytic wet peroxide oxidation).

## 5. ACKNOWLEDGEMENTS

## 6. REFERENCES

[1] P. R. Gogate and A. B. Pandit, Adv. Environ. Res. 8 (2004) 553-597.

[2] S. Esplugas, J. Gimenez, S. Contreras, E. Pascual, M. Rodriguez, Water Res. 36 (2002) 1034-1042.

[3] L. Plant, M. Jeff, Chem. Eng. September (1994) EE16-EE20.

[4] C. Walling, Acc. Chem. Res. 8 (1975) 125-131.

5] E. Neyens, J. Baeyens, J. Hazard. Mater. 98 (2003) 33-50.

[6] G. Centi, S. Perathoner, T. Torres, M. G. Verduna, Catal. Today. 55 (2000) 61-69.

[7] N. Crowther, F. Larachi, Appl. Catal. B: Environ. 46 (2003) 293-305.

[8] G. Ovejero, J. L. Sotelo, F. Martinez, J. A. Melero, L. Gordo, Ind. Eng. Chem. Res. 40 (2001) 3921-3928.

[9] G. Calleja, J. A. Melero, F. Martínez, R. Molina, Wat. Res. 39 (2005) 1741-1750.

[10] E. Guélou, J. Barrault, J. Fournier, J. Tatibouët, Appl. Catal. B: Environ. 44 (2003) 1-8.

[11] J. L. Sotelo, G. Ovejero, F. Martinez, J. A. Melero, A. Milieni, Appl. Catal. B: Environ. 47 (2004) 281-294.

[12] A. Bhatnagar, H.M. Cheung, Environ. Sci. Technol. 28 (1994) 1481-1486.

[13] Z. Laughrey, E. Bear, R. Jones, M.A. Tarr, Ultrason. Sonochem. 8 (2001) 353-357.

[14] M. Sivakumar, A.B. Pandit, Ultrason. Sonochem. 8 (2001) 233-240.

[15] J. Berlan, F. Trabelsi, H. Delmas, A.-M.Wilhelm, J.F. Petrignani, Ultrason. Sonochem. 1 (1994) 97-102.

[16] A. Tauber, H.-P. Schuchmann, C. von Sonntag, Ultrason. Sonochem. 7 (2000) 45-52.

[17] J. G. Lin, C. N. Chang, J. R. Wu, Y. S. Ma, Water Sci. Technol. 34 (1996) 41-48.

[18] F. Chemat, P.G.M. Teunissen, S. Chemat, P.V. Baartels, Ultrason. Sonochem. 8 (2001) 247-250.

[19] B. Neppolian, H. Jung, H Choi, J. H. Lee, J-W Kang, Wat. Res. 36 (2002) 4699-4708.

[20] B. Neppolian, J-S. Park, H. Choi, Ultrason. Sonochem. 11 (2004) 273-279.

[21] Z. Guo, Z. Zheng, S. Zheng, W. Hu, R. Feng, Ultrason. Sonochem. 12 (2005) 461-465.

[22] D. Drijvers, H. Van Langenhove, M. Beckers, Wat. Res. 33 (1999) 1187-1194.

[23] A. N. Nikolopoulos, O. Igglessi-Markopoulou, N. Papayannakos, Ultrason. Sonochem. 13 (1) (2006) 92-97.

[24] F. Martínez, G. Calleja, J. A. Melero, R. Molina, Appl. Catal. B: Environ. 60 (2005) 185-194.

[25] F. Martínez, Y. Jhan, G. Stucky, J. L. Sotelo, G. Ovejero, J. A. Melero, Stud. Surf. Sci. Catal. 142 (2002) 1109-1116.

[26] K. Lazar. G. Calleja. J. A. Melero. F. Martinez. R. Molina. Influence of synthesis routes on the state of Fe-species in SBA-15 mesoporous materials. Stud. Surf. Sci. Catal. 154 (2004) 805-812.

[27] M. Papadaki, R. J. Emerya, M. A. Abu-Hassan , A. Dıaz-Bustos, I. S. Metcalfe, D. Mantzavinos, Sep. Purif. Technol. 34 (2004) 35-42.

[28] G. E. P. Box, W. G. Hunter, J. S. Hunter, Statistics for Experiments, an Introduction to Design, Data Analysis and Model Building, John Wiley and Sons, New York, 1978.

[29] S. Goskonda, W.J. Catallo, T. Junk, Waste Manage. 22 (2002) 351-356.

[30] Y. Nagata, M. Nakagawa, H. Okuno, Y. Mizukoshi, B. Yim, Y. Maeda, Ultrason. Sonochem. 7 (2000) 115-120.

[31] C. Pétrier, A. Francony, Ultrason. Sonochem. 4 (1997) 295-300.

[32] A. De Visscher, H. Van Langenhove, Ultrason. Sonochem. 5 (1998) 87-92.

[33] J. De Laat, H. Gallard, Enviro. Sci. Technol. 33 (1999) 2726-2732.

[34] C. M. Miller, R. L. Valentine, Wat. Res. 29 (1995) 2353-2359.

[35] J.J. Pignatello, Environ. Sci. Technol., 26, 944-951 (1992).

[36] A. Safarzadeh-Amiri, J.R. Bolton, S.R. Cater, Wat. Res. 31 (1997) 787-798.

[37] B. Neppolian, J-S. Park, H. Choi, Ultrason. Sonochem. 11 (2004) 273-279

[38] D. H. Bremner, A. E. Burguess, D. Houllemare, K-C. Namkung, Appl. Catal. B: Environ 63 (2005) 15-19.