

# DEGRADATION OF 2-HYDROXYBENZOIC ACID BY ADVANCED OXIDATION PROCESSES

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**Abstract** - In this study, advanced oxidation processes (AOPs) such as the UV/H<sub>2</sub>O<sub>2</sub> and Fenton processes were investigated for the degradation of 2-hydroxybenzoic acid (2-HBA) in lab-scale experiments. Different [H<sub>2</sub>O<sub>2</sub>]/[2-HBA] molar ratios and pH values were used in order to establish the most favorable experimental conditions for the Fenton process. For comparison purposes, degradation of 2-HBA was carried out by the UV/H<sub>2</sub>O<sub>2</sub> process under Fenton experimental conditions. The study showed that the Fenton process (a mixture of hydrogen peroxide and Fe<sup>2+</sup> ion) was the most effective under acidic conditions, leading to the highest rate of 2-hydroxybenzoic acid degradation in a very short time interval. This same process led to a six-fold acceleration of the oxidation rate compared with the UV/H<sub>2</sub>O<sub>2</sub> process. The degradation of 2-hydroxybenzoic acid was found to follow first-order kinetics and to be influenced by the type of process and the experimental conditions. The experimental results showed that the most favorable conditions for 2-HBA degradation by the Fenton process are pH around 4-5, [Fe<sup>2+</sup>] = 0.6 mmol.L<sup>-1</sup>, and [H<sub>2</sub>O<sub>2</sub>]/[2-HBA] molar ratio = 7. The hydroxylation route is explained here for the two processes, and the results are discussed in the light of literature information.

**Keywords:** Advanced oxidation processes; 2-hydroxybenzoic acid; Waste treatment.

## INTRODUCTION

Because of the more rigid and restrictive current environmental laws, many studies aimed at the developments of more efficient and less aggressive methods for the treatment of industrial effluents are being carried out. There are several ways of treating industrial wastewater containing organic pollutants: incineration, adsorption, biological treatment, and chemical and electrochemical oxidation processes. The applicability of these treatments depends on different factors, such as the reliability, control, economic aspects, and efficiency of the method (Andreozzi et al., 1999). Different advanced oxidation processes for the elimination of organic pollutants from wastewater, such as the Fenton process, the photo-assisted Fenton-process, UV/Fe<sup>3+</sup>-oxalate/H<sub>2</sub>O<sub>2</sub>, photocatalysis, the ozone water system, Mn<sup>2+</sup>/oxalic acid/ozone, H<sub>2</sub>O<sub>2</sub> photolysis, O<sub>3</sub>/UV and others, have been developed and

investigated by several research groups (Andreozzi et al., 1999). These technologies, as opposed to the conventional phase-separation techniques (adsorption processes, stripping techniques), consist mainly of destroying the contaminants by chemical oxidation, so that mineralization of the contaminants to carbon dioxide and water, or at least the transformation of these compounds into harmless products, is achieved.

Oxidation using aqueous hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in the presence of native or supplementary ferrous ion (Fe<sup>2+</sup>) produces the Fenton reagent (Brillas et al., 1998), which yields free hydroxyl radicals (•OH). These strong, nonspecific oxidants can rapidly degrade a variety of organic compounds. Oxidation by the Fenton reagent is most effective under acidic pH (ranging from 2 to 4), and it becomes ineffective under moderately to strongly alkaline conditions (Andreozzi et al., 1999). The reactions are extremely rapid and follow second-

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order kinetics. In other processes such as  $\text{H}_2\text{O}_2/\text{UV}$ , the hydroxyl radicals are generated through photolysis of hydrogen peroxide under ultraviolet radiation (Legrini et al., 1993). Since the 1960s, numerous researchers have used this latter process to oxidize various organic substances into water and  $\text{CO}_2$ . Recently, commercial units employing this process have been developed for the on-site oxidation of organic pollutants in groundwater. The success of this process has been generally attributed to the stoichiometric formation of hydroxyl radicals ( $\bullet\text{OH}$ ) by the photolytic decomposition of  $\text{H}_2\text{O}_2$ . However, the generation of  $\bullet\text{OH}$  does not depend only on the chemical stoichiometry of  $\text{H}_2\text{O}_2$  decomposition, but also on the quantum yield. The so-called "cage effect" is probably responsible for the limited formation of  $\bullet\text{OH}$  in aqueous systems. Therefore, the yield of  $\bullet\text{OH}$  radicals is only half the theoretical stoichiometric value.

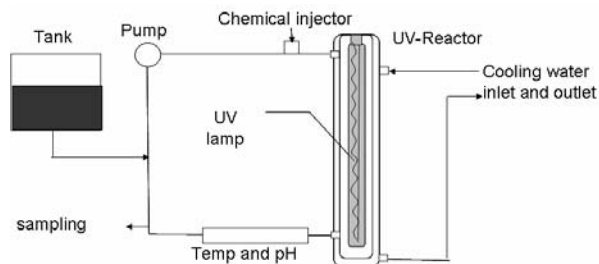
2-Hydroxybenzoic acid (2-HBA) has been widely used as an intermediate in the manufacture of pharmaceuticals and cosmetics, and it is introduced into the environment by a variety of industrial and natural sources (Guinea et al., 2008). It is a key ingredient in many skin-care products for the treatment of acne, psoriasis, calluses, corns, keratosis pilaris, and warts. This aromatic organic compound is very toxic and it is widely present in pharmaceutical industrial effluents (Guinea et al., 2008). It can stimulate skin and mucous membrane, and react with protein. In addition, it can bring about tinnitus, qualm, naupathia and electrolytical turbulence. Knowing the different problems this compound can cause, as well as the sites where they occur, 2-HBA has been chosen as the substrate for the investigation reported in this study.

## EXPERIMENTAL

### Chemical Oxidation Processes

Fenton experiments were performed in a cylindrical UV reactor (25 cm x 5 cm of diameter), with a capacity of 0.5 L, but without irradiation. An inlet and outlet were provided for electrolyte circulation through the reactor; the solution was stored in a thermoregulated glass tank and circulated through the reactor using a peristaltic pump (Fig. 1), at a constant flow rate of  $165 \text{ dm}^3 \text{ h}^{-1}$ . This process was performed at different  $[\text{H}_2\text{O}_2]/[2\text{-HBA}]$  molar ratios, using the most favorable  $\text{Fe}^{2+}$  concentration and pH established in this work. For comparison purpose, degradation of 2-HBA was carried out by the  $\text{UV}/\text{H}_2\text{O}_2$  process under the most favorable experimental conditions.

As for the  $\text{H}_2\text{O}_2/\text{UV}$  process, the reaction was carried out in a photo-reactor equipped with a mercury lamp (photochemical reactor with a high pressure mercury lamp TQ 718 of 250 W, from Heraeus Noblelight Company in Germany). The reactor was cylindrical (25 cm x 5 cm of diameter), with a capacity of 0.5 L, and it was made of quartz glass for transmittance of radiation. The schematic diagram of the experimental set-up used in the study is shown in Figure 1. Temperature and pH were measured at the beginning and end of each experiment.



**Figure 1:** Schematic diagram of photocatalytic oxidation system experimental set-up.

### Techniques and Instrumentation

Solution samples (2 mL) were taken from the reaction vessel at appropriate time intervals. One drop of the enzyme catalase was also added to each sample to decompose any residual hydrogen peroxide and to prevent it from reacting with organic substrates during the analysis. Also, a filtration step was done to eliminate the Fe-residues in solution, before High Performance Liquid Chromatographic (HPLC) analysis. Concentration changes of 2-HBA and by-products were determined by HPLC and spectrophotometric measurements. For the chromatographic analyses, a Varian Model 9050/9012 HPLC equipped with a Nucleosil C18 column (4.6 mm x 250 mm) was used; the mobile phase was a mixture of phosphoric acid (solution at pH 2): acetonitrile 35:65, at a flow rate of  $0.4 \text{ mL} \cdot \text{min}^{-1}$ ; the UV detector was set at 300 nm. Chromatographic retention times were compared with those of commercially available standards (2-DHBA; 2,3-DBHA; 2,5-DHBA; and catechol). Spectrophotometric measurements (UV-Vis) were performed using an HACH DR/2010 Portable Datalogging Spectrophotometer.

### Solutions

For each experiment, 2-HBA solutions ( $1,000 \text{ mg L}^{-1}$ , Fluka reagent) were prepared using ultrapure deionized water as solvent. The laboratory unit was first filled with the 2-HBA solution (0.25 L). Then, for each experiment, the pH value of the solution

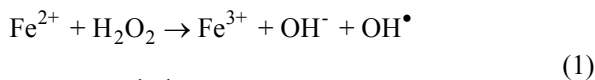
was adjusted to around 4.5 with buffer solution or sodium hydroxide ( $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$  or  $\text{NaOH}$ , respectively). Hydrogen peroxide was added as a concentrated solution (3 %).  $\text{Fe}^{2+}$  solutions were prepared with  $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ .

In the case of the Fenton process, the pH value of the solution was set at the desired value before the startup, and then a given amount of iron salt was added and mixed very well with 2-HBA before addition of a given volume of hydrogen peroxide. For runs using the  $\text{UV}/\text{H}_2\text{O}_2$  system, hydrogen peroxide was injected into the reactor before the beginning of each run. The time at which the ultraviolet lamp was turned on was considered time zero or the beginning of the experiment, and it was set simultaneously with the addition of hydrogen peroxide. The reagents used were employed without any further purification.

## RESULTS AND DISCUSSIONS

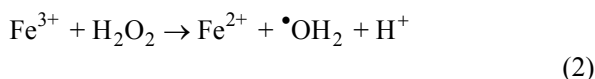
### Effect of $\text{H}_2\text{O}_2$ and $\text{Fe}^{2+}$

In the Fenton process, under acidic conditions, a  $\text{Fe}^{2+}/\text{H}_2\text{O}_2$  mixture produces hydroxyl radicals (Reaction 1):

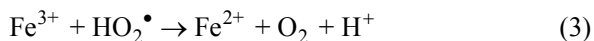


$$k = 76.5 \text{ M}^{-1}\text{s}^{-1}$$

The  $\text{Fe(III)}$  formed can react with  $\text{H}_2\text{O}_2$  in the so-called Fenton-like reactions (Reactions 2–4), regenerating  $\text{Fe}^{2+}$  and thus supporting the Fenton process:

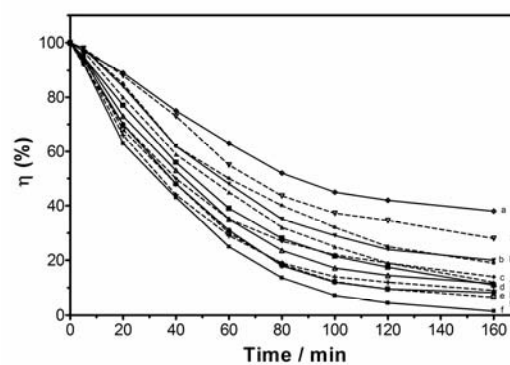


$$k = 2 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}$$

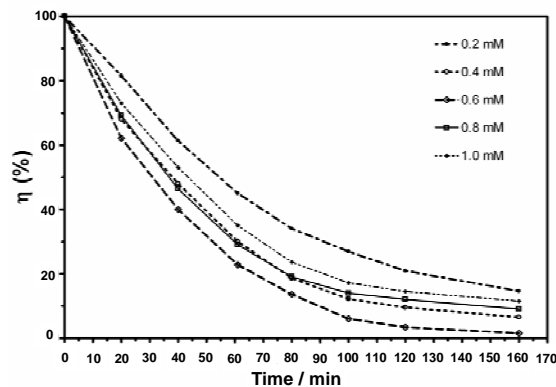


Many authors suggested the  $\text{Fe}^{2+}$  to  $\text{H}_2\text{O}_2$  mass ratio to be most favourable at 1 to 10, but it must be optimised for a particular wastewater to minimize scavenging effects. Reaction time depends on pollutant,  $\text{H}_2\text{O}_2$  and  $\text{Fe(II)}$  concentrations. Iron and  $\text{H}_2\text{O}_2$  are cheap and non-toxic, there are no mass transfer limitations due to its homogenous catalytic nature and the process is easy to run and control. It has been widely used for treatment of highly polluted textile and paper mill wastewaters, as well as

pharmaceutical wastewaters (Buxton et al., 1988). Therefore,  $\text{H}_2\text{O}_2$  should be added at the most favorable concentration, so that the best degradation is achieved. To determine the concentrations of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  in the Fenton process, experiments were carried out at 14 different  $[\text{H}_2\text{O}_2]/[2\text{-HBA}]$  molar ratios. Then, experiments were performed at the best  $[\text{H}_2\text{O}_2]/[2\text{-HBA}]$  molar ratio for 5 different  $\text{Fe}^{2+}$  molar concentrations (0.2, 0.4, 0.6, 0.8 and 1.0  $\text{mmol.L}^{-1}$ ), as depicted in Figures 2 and 3. The best 2-HBA elimination performances were obtained at  $[\text{Fe}^{2+}] = 0.6 \text{ mM}$  and  $[\text{H}_2\text{O}_2]/[2\text{-HBA}] = 7$ , so these experimental conditions were selected for the study of the pH effect and for the comparison between the Fenton and the  $\text{H}_2\text{O}_2/\text{UV}$  processes.



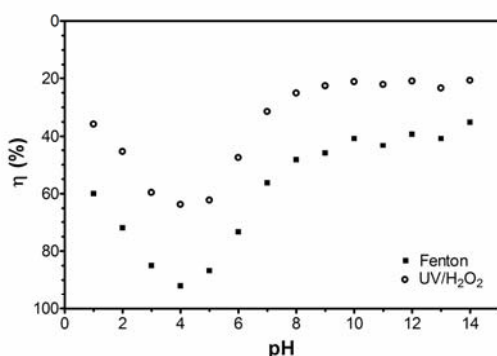
**Figure 2:** Removal efficiency of 2-HBA by the Fenton system. The effect of different  $[\text{H}_2\text{O}_2]/[2\text{-HBA}]$  molar ratios (a) 2; (b) 3; (c) 4; (d) 5; (e) 6; (f) 7; (g) 8; (h) 9; (i) 10; (j) 11; (k) 12; and (l) 13.  $\eta(\%) = [(C_0 - C_F)/C_0] \times 100$ , where  $C_0$  and  $C_F$  are the initial and final concentration, respectively.



**Figure 3:** Effect of  $\text{Fe}^{2+}$  dosage on % degradation of 2-HBA by the Fenton oxidation.  $\text{Fe}^{2+}$  molar concentrations (0.2, 0.4, 0.6, 0.8 and 1.0  $\text{mmol.L}^{-1}$ ).  $\eta(\%) = [(C_0 - C_F)/C_0] \times 100$ , where  $C_0$  and  $C_F$  are the initial and final concentration, respectively.

## pH Effect

The pH value has a decisive effect on the oxidation potential of  $\cdot\text{OH}$  (Kim et al., 1997). Furthermore, the concentrations of inorganic carbon and of the  $\text{Fe}^{2+}$  hydrolytic species are strongly affected by the pH value (Kim et al., 1997). Because the pH effect on the [2-HBA] removal efficiency is an important parameter in the Fenton and the  $\text{H}_2\text{O}_2/\text{UV}$  processes, the experiments were carried out in the pH range 2 – 14, under the above-mentioned conditions (Figure 4). The pH value around 4-5 was the best for the Fenton and the  $\text{H}_2\text{O}_2/\text{UV}$  processes. Hydrogen peroxide was most stable in the pH range 3-4, but its decomposition rate rapidly increased with increasing pH above pH 5 (Meeker et al., 1965). The [2-HBA] removal efficiency rapidly decreased with increasing pH in the pH range 6–14. Our results are in good agreement with those of previous reports (Meeker et al., 1965; Feuerstein, 1981; Bigda, 1995). When the pH of the solution was higher than 5, the [2-HBA] removal efficiency rapidly decreased with increasing pH not only because of the decomposition of hydrogen peroxide (Feuerstein, 1981), but also as a result of the deactivation of the ferrous catalyst due to the formation of ferric hydroxyl complexes (Bigda, 1995). In these cases, during the runs samples of analyte were withdrawn, filtered and analyzed for the concentration of residual 2-HBA and oxidation products in the solution.



**Figure 4:** Removal efficiency as a function of pH.  $\eta(\%) = [(C_0 - C_F)/C_0] \times 100$ , where  $C_0$  and  $C_F$  are the initial and final concentration, respectively

## Fenton Reaction

Production of hydroxyl radicals by the Fenton reagent (Haber et al, 1932; Pignatello et al., 2006) occurs by a mixture of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  salts (Equation 1). This reactant is an attractive oxidizer for wastewater

treatment; however, the Fenton process requires strict pH control because the best yields are obtained at pH values ranging between 3.0 and 5.0 (Pignatello et al., 2006). In our experiments, the pH value was adjusted to around 4.5 using either  $0.1 \text{ mol.L}^{-1}$  NaOH or  $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$  buffer solutions.

Figure 5a shows the elimination of 2-HBA as well as the formation and disappearance of the main reaction intermediates (2,3-dihydroxy benzoic acid (2,3-DHBA); 2,5-dihydroxy benzoic acid (2,5-DHBA); and catechol (CT)), by the Fenton reaction carried out at pH=4.5, adjusted with NaOH. Complete elimination of 2-HBA was achieved after 150 min. As for the intermediates, only 2,5-DHBA and CT were totally eliminated; a small amount of 2,3-DHBA remained in solution.

As can be seen in Figure 5b, the same intermediates mentioned above were detected at pH=4.5 when this was adjusted with buffer solution. In this same figure, it is possible to observe the complete elimination of 2-HBA after 150 min, but intermediates 2,3- and 2,5-DHBA were generated in larger amounts in the case of Fig. 5a. In both processes, further degradation of the main intermediates led to a mixture of malic, maleic, and fumaric acids, which were oxidized to oxalic acid. This acid can also be produced from the dehydrogenation of glycolic acid, followed by hydroxylation of the resulting glyoxylic acid. Glycolic and glyoxylic acids undergo a parallel oxidation to formic acid, which is directly converted into  $\text{CO}_2$ . Oxalic acid is slowly transformed into  $\text{CO}_2$ , but it mainly forms Fe/oxalate complexes (Pignatello et al., 2006). The identification of carboxylic acids was performed according the HPLC conditions described in the experimental section, varying the wavelength in order to identify them using standards compounds.

## $\text{H}_2\text{O}_2/\text{UV}$ Process

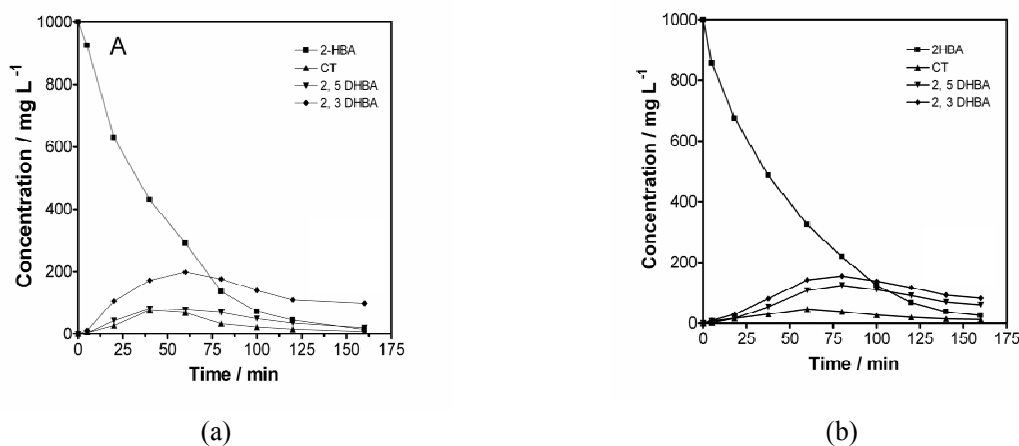
The  $\text{H}_2\text{O}_2/\text{UV}$  process occurs upon irradiation of the pollutant solution containing  $\text{H}_2\text{O}_2$  with UV light at wavelengths shorter than 280 nm. This causes the homolytic cleavage of  $\text{H}_2\text{O}_2$ , as shown in Equation 5 (Andreozzi et al., 1999; Pignatello et al., 2006).



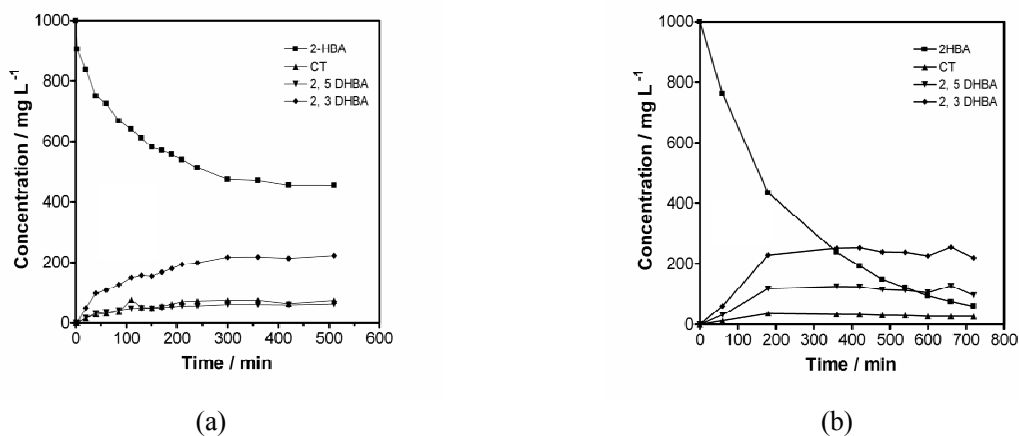
In our case, the  $\text{H}_2\text{O}_2/\text{UV}$  process was carried out at  $25^\circ\text{C}$ , with an initial concentration of 2-HBA of  $1,000 \text{ mg L}^{-1}$ . Hydrogen peroxide was added at a  $[\text{H}_2\text{O}_2]/[\text{2-HBA}]$  molar ratio of approximately 7,

similar to the one used in the case of the Fenton reaction. During the oxidation of 2-HBA at pH 4.3 adjusted with NaOH, the main product was 2,3-DHBA, whereas CT and 2,5-DHBA were produced in minor amounts. The complete elimination of 2-HBA was not achieved (Figure 6a). When the  $H_2O_2/UV$  process was carried out at pH = 4.5 adjusted with buffer solution, the production of 2,3-DHBA was only moderately increased. However, complete degradation of 2-HBA was attained (Figure 6b) after 700 min. In addition, the degradation of the main intermediates led to a mixture of malic, maleic and fumaric acids, which were oxidized to oxalic acid. Total by-product elimination was verified by analytical techniques after 1,400 min.

In the  $H_2O_2/UV$  process, hydroxyl radicals generated from the direct photolysis of hydrogen peroxide were the species mainly responsible for 2-HBA elimination. However, hydrogen peroxide may also react with these radicals and hence act as an inhibitor of 2-HBA degradation. As can be deduced from Fig. 6a, when the pH was adjusted with NaOH solution the hydroxyl radical scavenging effect became important and the 2-HBA degradation rate decreased (Haber et al, 1932; Pignatello et al., 2006). This may be due to auto-decomposition of  $H_2O_2$  to oxygen and water and the recombination of  $\cdot OH$  radicals. Since  $\cdot OH$  radicals react with  $H_2O_2$ ,  $H_2O_2$  itself contributes to the  $\cdot OH$  scavenging capacity (Pignatello et al., 2006).



**Figure 5:** Elimination of 2-HBA by the Fenton process A) pH adjusted with NaOH solution B) pH adjusted with buffer. Evolution of the main intermediates: 2,3-DHBA; 2,5-DHBA and CT.



**Figure 6:**  $H_2O_2/UV$  process for the degradation of 2-HBA A) pH adjusted with NaOH solution B) pH adjusted with buffer solution. Evolution of the main intermediates: 2,3-DHBA; 2,5-DHBA and CT.

### Comparison Between Both Processes

In the Fenton and H<sub>2</sub>O<sub>2</sub>/UV processes, the times necessary for the complete elimination of 2-HBA were substantially different, the Fenton process being much faster than H<sub>2</sub>O<sub>2</sub>/UV. Moreover, the Fenton reaction led to the complete oxidation of 2-HBA and its intermediates, while total conversion from 2-HBA to DHBA compounds was not attained with the H<sub>2</sub>O<sub>2</sub>/UV process. The decrease in 2-HBA concentration was observed as a function of time in both the H<sub>2</sub>O<sub>2</sub>/UV and Fenton processes, and data were fitted to a first-order rate model [Eq. (6)]:

$$\ln \frac{C_t}{C_0} = -k_0 t \quad (6)$$

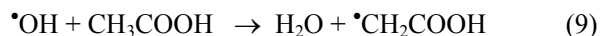
where C<sub>0</sub> and C<sub>t</sub> are the concentration of 2-HBA at times 0 and t, respectively; k<sub>0</sub> is a first-order rate constant (in min<sup>-1</sup>), and t is the time (in min). Table 1 shows reaction rate constants for 2-HBA oxidation. Fig. 7 shows that the Fenton process led to a higher rate of 2-HBA oxidation. Table 1 shows that the rate of 2-HBA oxidation obtained with the Fenton reaction system is 18 and 6 times higher compared with the H<sub>2</sub>O<sub>2</sub>/UV system and depends on the type of solution used to adjust the pH value (NaOH or buffer solution). A similar behavior was observed by other authors when these techniques were compared (Lipczynska-Kochany, 1992; Benitez et al., 2000; Trapico and Kallas, 2000), and this difference has also been commented and analyzed by Pignatello *et al.* (2006) in their critical review. The higher efficiency of the Fenton process may be associated with the higher reaction rate of reaction (1) compared to (5), thus producing more hydroxyl radicals. The reactions of HO· with organic compounds lead to the formation of carbon-centered radicals. The hydroxyl radical—always present in vanishingly small concentration—reacts in well-known ways with organic compounds, principally by abstracting H

from C H, N H, or O H bonds, adding to C C bonds, or adding to aromatic rings. In addition, the participation of other oxidant species could be taken into consideration (Pignatello et al., 2006). When air is present in the solution, the radicals produced in reaction (1) may react with O<sub>2</sub> to give HO<sub>2</sub>· (O<sub>2</sub><sup>-</sup>), peroxy radicals R-OO·, or oxyl radicals R-O·:



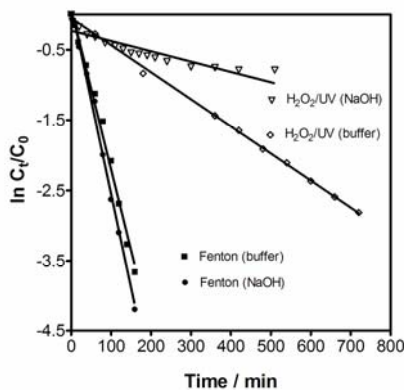
The bimolecular reaction of R· with O<sub>2</sub> is faster (rate constants are typically in the order of 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>) and usually irreversible, increasing the global reaction rate and consequently, the efficiency of the process. The organic intermediates formed in the first stage of the oxidation may react further with HO· and oxygen, with the overall process leading eventually to mineralization to CO<sub>2</sub> and H<sub>2</sub>O. Evolution of CO<sub>2</sub> is slower than disappearance of the initial compound and ordinarily decreases in rate with time as products become less and less reactive with HO·.

In the case of the processes carried out in the solution containing buffer, the efficiency was significantly lower, possibly because of the generation of radicals that contribute to the oxidation of one of the oxidizable sites in 2-HBA. In fact, the acetic acid radical was detected by Metreveli et al. (2002) when they used ESR to analyze an irradiated acetic acid solution. These radicals (·CH<sub>2</sub>COOH) may initiate many radical reactions with 2-HBA, as observed by Sionkowska in the oxidation of collagen (Sionkowska, 2006). Therefore, the degradation of 2-HBA is minor or complete only at longer times, under acetic buffer conditions with respect to solutions adjusted with NaOH (Pignatello et al., 2006).



**Table 1: Values of reaction rate constants for 2-HBA degradation by different types of oxidation processes**

Type of oxidation process	k <sub>0</sub> (min <sup>-1</sup> )
Fenton (pH adjusted with NaOH solution)	0.02662 ± 0.00077
Fenton (pH adjusted with buffer solution)	0.02287 ± 0.00081
H <sub>2</sub> O <sub>2</sub> /UV (pH adjusted with NaOH solution)	0.00147 ± 0.00018
H <sub>2</sub> O <sub>2</sub> /UV (pH adjusted with buffer solution)	0.00385 ± 0.00005



**Figure 7:** First-order plots for the degradation of 2-HBA by the  $\text{H}_2\text{O}_2/\text{UV}$  and Fenton processes.

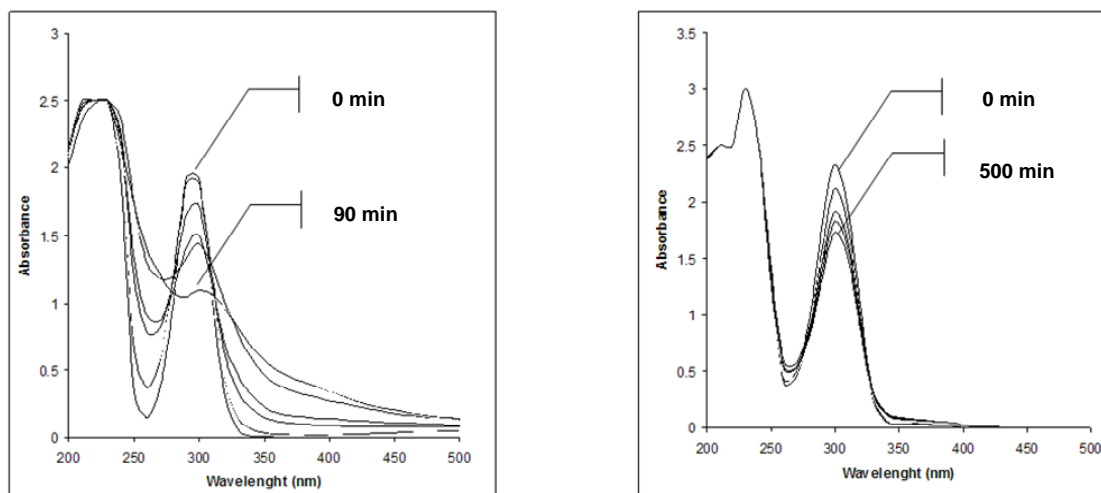
### Monitoring 2-HBA Degradation by UV Spectroscopy

2-HBA degradation by both of the processes investigated in this work was also monitored by spectrophotometric measurements, because UV-Vis spectroscopy provides a straightforward way of following the elimination of an aromatic compound from an aqueous solution. The UV spectra of 2-HBA degradation at  $25^\circ\text{C}$  obtained at pH 4.5 adjusted with NaOH solution confirmed that 2-HBA is more rapidly eliminated by the Fenton reaction compared with the  $\text{H}_2\text{O}_2/\text{UV}$  process (Figure 8). The UV spectra of the latter process showed an unimportant decrease in the concentration of the organic compound. However, the differences in the spectra are perhaps due to the production of intermediates, which also absorb in the same spectral range as 2-HBA.

### Hydroxylation Pathway

Various research groups (Smith et al., 1963; Fleszar et al., 1983; Kunai et al., 1986; Guo et al., 1992; Oturan et al., 1995) have studied the hydroxylation of aromatic compounds and the dependence of this reaction on the experimental conditions and on the interactions between the organic compounds and the chemical reagents added to the solution. Indeed, aromatic hydroxylation has been previously used as a method for measuring the production of hydroxyl radicals both *in vitro* (Halliwell, 1978; Richmond et al., 1981) and *in vivo* (Halliwell et al., 1987; Grootveld et al., 1986), and this reaction has also been employed in studies involving inflammation inhibitors (Oturan et al., 1992a). In these works, 2-HBA was the most frequently employed organic substrate, as a hydroxyl radical trap. In addition, the selectivity for the intermediates and products obtained from 2-HBA can also be diverse, and it is an interesting property

for identifying hydroxyl radicals. The main products of the hydroxylation of 2-HBA with hydroxyl radicals (Fenton reaction (Jen et al., 1998; Scheck et al., 1995; Pattwell et al., 2001; Diez et al., 2001; Coudray et al., 2000)) are 2,3- and 2,5-DHBA. According to the results obtained in this present paper,  $\cdot\text{OH}$  radicals have a strong preference for attacking position 3- rather than 5- during 2-HBA oxidation by the Fenton and  $\text{H}_2\text{O}_2/\text{UV}$  processes. The exclusive hydroxylation in the positions *ortho* and *para* to the phenol group is an evident characteristic of the ring substituents (Augood et al., 1959). Thus, hydroxylation of a phenol, like 2-HBA, leads to substitution in the positions *ortho* and *para* to the hydroxyl groups only (Loebl et al., 1951). Considering the electrophilic character of the hydroxyl radical, the attack of  $\cdot\text{OH}$  on the *o:m:p* positions of phenol occurs in the ratio 0.48:0.08:0.36 (Oturan et al., 1992b; Raghavan et al., 1992). Both of the products 2,3-DHBA and 2,5-DHBA have been obtained during 2-HBA oxidation in several works (Oturan et al., 1992a, b; Oturan et al., 1995; Raghavan et al., 1992; Grinstead et al., 1960) employing  $\text{Fe}^{2+}$ . However, 2,3-DHBA was preferentially formed because  $\text{Fe}^{2+}$  can either react with the OH groups of the molecule or form a ferryl ion, which interacts with the hydroxyl substrate, often giving a complex. Mason et al. (1957) have postulated the existence of a ferryl species ( $\text{Fe}_p\text{O}^{++}$ ) as the active intermediate, where the iron is complexed via a chelating structure that may occupy up to five of the six available coordination positions. On the other hand, Groves et al. (1974; 1976) have used this mechanism to describe the hydroxylation of cyclohexanol, which is strongly supported by the formation of stereoselective hydroxylation products. These interactions have also been observed by Lunak et al. (1994) and Lang et al. (1994) during the photochemical hydroxylation of 2-HBA, where the formation of 2,3-DHBA was favored.



**Figure 8:** UV-Vis spectra recorded to follow the 2HBA degradation at pH adjusted with NaOH in both cases and at 25°C. (A) Fenton and (B) H<sub>2</sub>O<sub>2</sub>/UV.

In the Fenton reaction, the attack of  $\cdot\text{OH}$  occurs because of its extremely high radical activity. These radicals preferably attack at the *ortho* and *para* positions to the hydroxyl group of 2-HBA. In this case, ferryl ions are also formed, as proposed by Manson (1957) and Groves et al. (1974; 1976), and they react with the OH group of 2-HBA. The  $\text{Fe}_p\text{O}^{++}$  species give a specific O atom, thus favoring hydroxylation at the *ortho* position. The parallel evolution of two mechanisms explains the higher yields of 2,3-DHBA compared to 2,5-DHBA in the Fenton reaction, as well as the preferential formation of the hydroxylation product.

Concerning the selectivity obtained with the H<sub>2</sub>O<sub>2</sub>/UV process, it suggests that a different hydroxylation mechanism takes place. Ogata and co-workers (1980) have proposed that hydroxylation may be initiated by excitation of an aromatic substrate in the presence of H<sub>2</sub>O<sub>2</sub>. Formation of specific intermediates was detected during the photo-oxidation of benzoic acid; for this reason an oxidation mechanism was hypothesized where the production of  $\alpha$ -keto-carboxylic acids takes place. These acids may be formed from 2,3-DHBA due to the preferential hydroxylation at the 3- position of 2-HBA produced from benzoic acid. After hydroxylation, ring rupture is attained, and the  $\alpha$ -keto-carboxylic acids are finally oxidized to CO<sub>2</sub> and H<sub>2</sub>O. Lunak et al. (1992) explained that the photochemical hydroxylation of an aromatic ring by hydrogen peroxide occurs through photodissociation of the latter reagent into two hydroxyl radicals, with a subsequent attack on the ring, where UV light is absorbed by H<sub>2</sub>O<sub>2</sub>. Results of a mechanistic study of

a substrate-sensitized reaction showed that hydroxylation of 2-HBA by H<sub>2</sub>O<sub>2</sub> photolysis (254 nm) and/or 2-HBA excitation (313 nm) led to [2,3-DHBA]/[2,5-DHBA] isomer ratios ranging from 1.12 to 2.46 (Lang et al., 1996). When the pH effect, the H<sub>2</sub>O<sub>2</sub> concentration, and the irradiation times were studied, once again the formation of 2,3-DHBA was favored compared with 2,5-DHBA (Lang et al., 1996). So the results obtained by Lunak et al. (1992) are in agreement with our current data.

## CONCLUSIONS

This study on the treatment of wastewater containing 2-HBA by the Fenton and H<sub>2</sub>O<sub>2</sub>/UV processes allows one to draw the following conclusions:

The Fenton oxidation rate is influenced by many factors such as the pH value, the [H<sub>2</sub>O<sub>2</sub>]/[2-HBA] molar ratio and the concentration of the ferrous salt. The degradation conditions are a pH value of 4.5, a [H<sub>2</sub>O<sub>2</sub>]/[2-HBA] molar ratio of 7, and a ferrous salt concentration of 0.6 mmol.L<sup>-1</sup>. Under the most favorable conditions found for the Fenton process, the [2-HBA] removal efficiencies were 98.5 and 97.5%, achieved after 150 min. of reaction, depending on the solution used for the adjustment of the pH value, NaOH and buffer solution, respectively.

As for the H<sub>2</sub>O<sub>2</sub>/UV oxidation process, the most favorable conditions were a pH value of 4.5, and a [H<sub>2</sub>O<sub>2</sub>]/[2-HBA] molar ratio of 7. The [2-HBA] removal efficiencies were about 54 and 92 %, respectively.



depending on the solution used to adjust the pH value, NaOH and buffer solution, respectively. These removals were obtained after 700 min. On the basis of these results, it can be stated that the H<sub>2</sub>O<sub>2</sub>/UV process presents a lower [2-HBA] removal efficiency compared with the Fenton process.

Finally, more efficient methods for destroying organic pollutants from wastewaters at lab and pilot plant scale are being developed from the advanced oxidation technology (Nogueira et al., 2008; Muhammad et al., 2008; Luna et al., 2006; Silva et al., 2002; Tôrres et al., 2007; Santos et al., 2006; Azevedo et al., 2009). The most suitable materials and optimized experimental conditions are established in most photocatalytic and catalytic techniques for different reactor configurations. However, much more research efforts are needed to clarify the removal efficiency and degradation attained for a larger variety of pollutants to apply these methods to industrial level. Research focused to the application of these methods to color removal and production of more biodegradable compounds as an alternative of pre-treatment stage for biological post-treatment should be performed to propose more economical coupled methods.

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