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Kinetic model for phenolic compound oxidation by Fenton's reagent

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Abstract

A kinetic model is developed for the oxidation of phenolic compounds by Fenton's reagent. In the first stage a rigorous kinetic model is applied to calculate the different kinetic rate constants for the oxidation process of *p*-hydroxybenzoic acid.

In a second phase a competitive method is applied to calculate these kinetic constants for another 10 phenolic compounds present in agroindustrial and pulp paper wastewaters. These 10 phenolic compounds were: β-resorcylic acid, 3-(4-hydroxyphenyl)-propionic acid, ferulic acid, protocatechuic acid, caffeic acid, *p*-coumaric acid, vanillic acid, syringic acid, veratric acid and 3,4,5-trimethoxybenzoic acid. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Fenton's reagent; Kinetics; Phenolic compounds; *p*-hydroxybenzoic acid; AOPs

1. Introduction

Olive oil extraction and table olive production give rise to highly contaminant wastewaters. This is a major environmental problem in Mediterranean countries in general, and particularly in certain areas of Spain and Portugal where there are many small plants.

Most of their pollutant properties have been attributed to the phenolic compounds, because of their toxicity (Hamdi, 1992) and inhibitory character (Gonzalez et al., 1990) to the anaerobic digestion. Likewise, distillation of different wine fractions and pulp paper processing produce wastewaters containing important amounts of these phenolic compounds.

As a result of this situation and the more stringent regulations concerning effluents released into rivers and streams, new technologies have been developed to reduce these refractory contaminants.

For example, Fenton's reagent is a system based on the generation of very reactive oxidising free radicals, especially hydroxyl radicals, which have a stronger oxidation potential than ozone, 2.8 V for $^{\cdot}OH$ and 2.07 V for ozone (Prengle and Mauk, 1978). The Fenton's oxidation process has also been employed successfully to treat different industrial wastewaters (Lin and Peng, 1995; Lin and Lo, 1997).

In this work a kinetic model is developed for the oxidation of phenolic compounds by Fenton's reagent. In the first phase a rigorous kinetic model is developed and applied to calculate the kinetic rate constant for the reaction between hydroxyl radicals and *p*-hydroxybenzoic acid. In a second phase a competitive method is applied to calculate this kinetic constant for another 10 phenolic compounds, which are very common in a great

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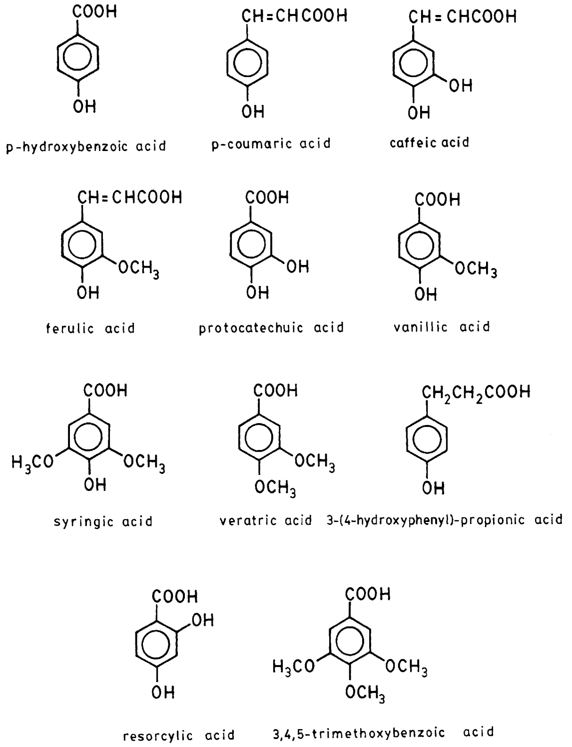

Fig. 1. Phenolic compounds.

variety of industrial wastewaters (olive oil processing industries, table olive industries, wine-distilleries, pulp paper processing, etc.). These 10 phenolic compounds were: β-resorcylic acid, 3-(4-hydroxyphenyl)-propionic acid, ferulic acid, protocatechuic acid, caffeic acid, *p*-coumaric acid, vanillic acid, syringic acid, veratric acid and 3,4,5-trimethoxybenzoic acid (see Fig. 1).

2. Materials and methods

Analytical grade phenolic acids were obtained from Sigma. Hydrogen peroxide (33% w/v) and ferrous sulfate heptahydrate were obtained from Merck.

The reactor consisted of a 1000 ml glass cylinder provided with the necessary elements (inlets for stirring, sampling and measuring the temperature) for the development of the experiments. This reactor was kept at the desired temperature within ±0.5°C. Initially, the reactor was loaded with 500 ml in all cases, and the initial concentration of each phenolic compound was 100 ppm.

At regular times of reaction, samples were withdrawn to determine the phenolic acids remaining. These samples were analysed by HPLC, using a Waters chromatograph with a 996 photodiode array detector and a Nova-Pak C18 Column. Detection was at 280 nm with a mobile phase composed of a methanol:water:acetic acid mixture (15:82.5:2.5 in volume) at a flow rate of 1 ml/min.

Retention times were: for the group 1 of compounds, *p*-hydroxybenzoic acid, β-resorcylic acid, 3-(4-hydroxyphenyl)-propionic acid and ferulic acid, 3.8, 5.0, 7.3 and 13.1 min, respectively; for the group 2, protocatechuic acid, *p*-hydroxybenzoic acid, caffeic acid and *p*-coumaric acid, 2.4, 3.8, 5.4 and 10.6 min, respectively; finally for the group 3, *p*-hydroxybenzoic acid, vanillic acid, syringic acid, veratric acid and 3,4,5-trimethoxybenzoic acid, 3.8, 5.0, 6.3, 14.3 and 23.9 min, respectively.

3. Results and discussion

The first stage was the kinetic study of the degradation of *p*-hydroxybenzoic acid by Fenton's reagent. After having carried out this kinetic study and evaluated their kinetic rate constant, a similar study was performed to test the degradation of three mixtures of phenolic compounds using a competitive method. Finally, the kinetic rate constants of the radical reaction between the hydroxyl radical and each one of the phenolic compounds was determined.

3.1. Oxidation of p-hydroxybenzoic acid by Fenton's reagent

Oxidation experiments of *p*-hydroxybenzoic acid by Fenton's reagent were carried out by varying the initial

Table 1
Degradation experiments of *p*-hydroxybenzoic acid by Fenton's reagent[a]

Experiment	*R* (mol/mol)	$[H_2O_2]_0$ (mol/l)	$[B]_0$ (mol/l)	$-(d[B]/dt)_0 \times 10^6$ (mol/l s)
F-1	2	2.90×10^{-3}	1.45×10^{-3}	6.43
F-2	2	1.45×10^{-3}	7.24×10^{-4}	5.38
F-3	2	7.24×10^{-4}	3.62×10^{-4}	3.46
F-4	4	5.80×10^{-3}	1.45×10^{-3}	12.4
F-5	4	2.90×10^{-3}	7.24×10^{-4}	11.2
F-6	4	1.45×10^{-3}	3.62×10^{-4}	6.05

[a] $[Fe^{2+}]_0 = 1.45 \times 10^{-4}$ mol/l.

concentrations of hydrogen peroxide and the phenolic compound, and keeping the ratio between both concentrations ($R = [H_2O_2]_0/[B]_0$) constant between the values 2 and 4. Table 1 details the experimental conditions of these experiments, with a constant value of $[Fe^{2+}]_0 = 1.45 \times 10^{-4}$ mol/l. As it is observed, there is an increase in the degradation rate ($-d[B]/dt$) of the phenolic compound when the $[H_2O_2]_0$ is increased.

As an example, Fig. 2 shows the evolution of the phenolic concentration versus time for the experiments carried out to a value of $R = 2$. It shows a continuous decrease of the phenolic acid concentration by effect of the generated radicals.

The oxidation mechanism of an organic compound by Fenton's reagent is very complex, and thought to occur in the following stages:

$$H_2O_2 + Fe^{2+} \xrightarrow{k_1} Fe^{3+} + OH^- + OH^\bullet \tag{1}$$

$$B + H_2O_2 \xrightarrow{k_2} B_{ox} \tag{2}$$

$$B + OH^\bullet \xrightarrow{k_3} B_{ox} \tag{3}$$

$$H_2O_2 + OH^\bullet \xrightarrow{k_4} HO_2^\bullet + H_2O \tag{4}$$

$$OH^\bullet + Fe^{2+} \xrightarrow{k_5} Fe^{3+} + OH^- \tag{5}$$

$$Fe^{3+} + H_2O_2 \xrightarrow{k_6} Fe^{2+} + H^+ + HO_2^\bullet \tag{6}$$

$$Fe^{3+} + HO_2^\bullet \xrightarrow{k_7} O_2 + Fe^{2+} + H^+ \tag{7}$$

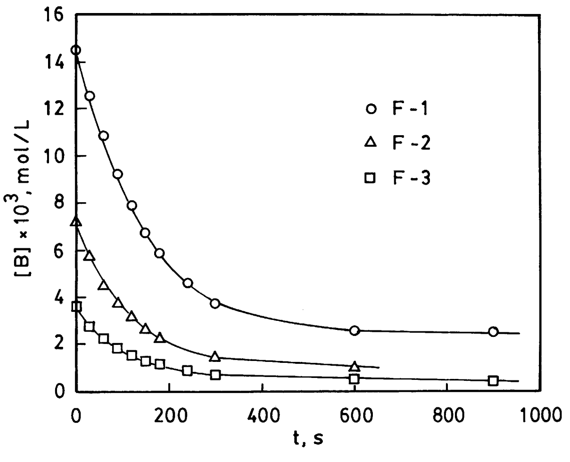

Fig. 2. Evolution of the p-hydroxybenzoic acid concentration in oxidation by Fenton's reagent using a relationship $[H_2O_2]_0/[B]_0 = 2$ mol/mol. Experiments F-1, F-2 and F-3.

Reaction (1) shows the generation of hydroxyl radicals (Walling, 1975) which react with the organic compound (reaction (3)). On the other hand, reaction (2) shows the direct action of hydrogen peroxide towards the phenolic compound, while reactions (4) and (5) show the scavenger effect of hydroxyl radicals due to the Fe^{2+} ion and the hydrogen peroxide (Walling and Kato, 1971; Buxton et al., 1988). Finally, reactions (6) and (7) indicate the possible ways of reaction of Fe^{3+} with H_2O_2 and new generation of Fe^{2+}, and with hydroperoxyl radicals.

Reactions (1), (3), (4) and (5) imply the $OH^\bullet$ radical, by generation or consumption. Therefore, their net reaction rate of generation can be expressed as follows:

$$\frac{d[OH^\bullet]}{dt} = k_1[H_2O_2][Fe^{2+}] - k_3[OH^\bullet][B] - k_4[H_2O_2] \times [OH^\bullet] - k_5[OH^\bullet][Fe^{2+}]. \tag{8}$$

Assuming the steady state condition for hydroxyl radicals ($d[OH^\bullet]/dt = 0$), the concentration of these radicals can be expressed in the form:

$$[OH^\bullet] = \frac{k_1[H_2O_2][Fe^{2+}]}{k_3[B] + k_4[H_2O_2] + k_5[Fe^{2+}]}. \tag{9}$$

On the other hand, the organic compound is destroyed by reactions (2) and (3), therefore its degradation reaction rate can be written as:

$$-\frac{d[B]}{dt} = k_2[B][H_2O_2] + k_3[B][OH^\bullet]. \tag{10}$$

Substituting expression (9) in (10), we obtain:

$$-\frac{d[B]}{dt} = k_2[B][H_2O_2] + k_3[B] \times \frac{k_1[H_2O_2][Fe^{2+}]}{k_3[B] + k_4[H_2O_2] + k_5[Fe^{2+}]}. \tag{11}$$

This equation includes five rate constants. As previous experiments carried out for the oxidation of this phenolic compound with hydrogen peroxide alone revealed that no degradation was obtained, it can be considered that $k_2 = 0$. In addition, k_4 value was provided by Walling (1975), being $k_4 = 3 \times 10^7$ l/(mol s), and k_5 for the oxidation of Fe^{2+}, was reported by Dorfman and Adams (1973), being $k_5 = 3 \times 10^8$ l/(mol s).

In order to evaluate the rate constant of the reaction between p-hydroxybenzoic acid and hydroxyl radicals k_3, as well as the rate constant k_1, Eq. (11) is rewritten in the form:

$$\frac{[B]_0[H_2O_2]_0}{\left(-\frac{d[B]}{dt} - k_2[B][H_2O_2]\right)_0} = \frac{k_5}{k_1k_3} + [B]_0\frac{k_3 + k_4R}{k_1k_3[Fe^{2+}]_0}, \tag{12}$$

where R is the initial concentration ratio $[H_2O_2]_0/[B]_0$. According to this Eq. (12), a plot of the first term versus

$[B]_0$ must provide a straight line for every series of experiments with the same R value. The initial concentration of catalyst $[Fe^{2+}]_0$ was constant in all the experiments. The slope of this plot can be expressed as follows:

$$\text{Slope} = \frac{k_3 + k_4R}{k_1k_3[Fe^{2+}]_0}. \tag{13}$$

In this expression all the parameters are known except the kinetic rate constants k_1 and k_3. Therefore, if the value of this slope is determined for the experiments carried out with $R = 2$ and $R = 4$, one will have a two equations system with two constants, k_1 and k_3.

Fig. 3 shows this plot for the experiments carried out for both R values. All the parameters required for the first member calculation, included the values of $(d[B]/dt)_0$ are shown in Table 1. As can be seen, the points lie satisfactorily around straight lines. Carrying out one least-squares regression analysis is obtained, for each slope, the values 559.3 and 544.8, for $R = 4$ and $R = 2$, respectively.

The value obtained for k_3 was 2.19×10^9 l/(mol s) at 30°C (the rate constant for the reaction between p-hydroxybenzoic acid and hydroxyl radicals) and the value for k_1, 13.01 l/(mol s). The radical reaction constant between the hydroxyl radical and p-hydroxybenzoic acid is into the usual range 10^8–10^{10} l/(mol s) of these reaction rate constants (Buxton et al., 1988; Haag and Yao, 1992).

3.2. Oxidation of the phenolic compounds mixtures by Fenton's reagent

In this second stage, the simultaneous decomposition of a mixture of phenolic compounds by Fenton's reagent was carried out at 30°C. Due to the existence of analytical interferences among them, they were divided in three compound groups. The group 1 was composed of: β-resorcylic acid, 3-(4-hydroxyphenyl)-propionic acid, ferulic acid and as reference compound p-hydroxybenzoic acid. The group 2 was composed of: protocatechuic acid, caffeic acid, p-coumaric acid and the reference compound. Lastly, the group 3 was composed of: vanillic acid, syringic acid, veratric acid, 3,4,5-trimethoxybenzoic acid and p-hydroxybenzoic acid.

In all the experiments a progressive decrease of the different compounds is appreciated with reaction time. Fig. 4 shows the disappearance curves of the phenolic compounds of the group 1. Similar plots were observed in the groups 2 and 3.

The purpose of this series of experiments was to determine the mentioned rate constant k_3 for the reaction between the hydroxyl radicals and each individual phenolic compound. This determination could be performed under certain specific conditions, by means of a competitive kinetic model. This method has been previously used by several authors for the degradation of some organic compounds by oxidants like ozone, UV radiation or hydroxyl radicals.

This process of oxidation by ·OH radicals could be carried out in a system containing a mixture of compounds B and a reference compound R, whose rate constant is known. According to the previous mechanism, the equation of the reaction between each organic B and the ·OH radical can be expressed by the reaction (3):

$$B + OH^{\cdot} \xrightarrow{k_3} B_{ox} \tag{3}$$

Assuming a first-order reaction with respect to the radical concentration and the phenolic acid concentration, the reaction rate can be expressed as:

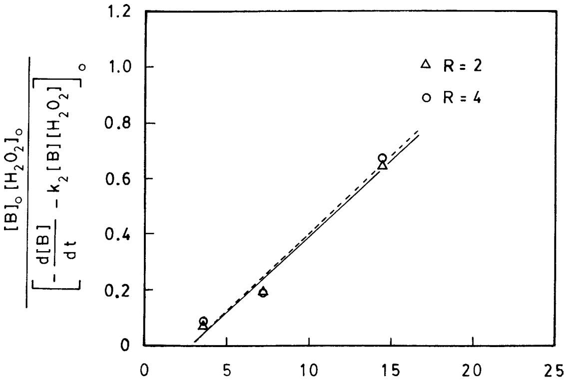

Fig. 3. Determination of k_3 constant in oxidation experiments of p-hydroxybenzoic acid by Fenton's reagent.

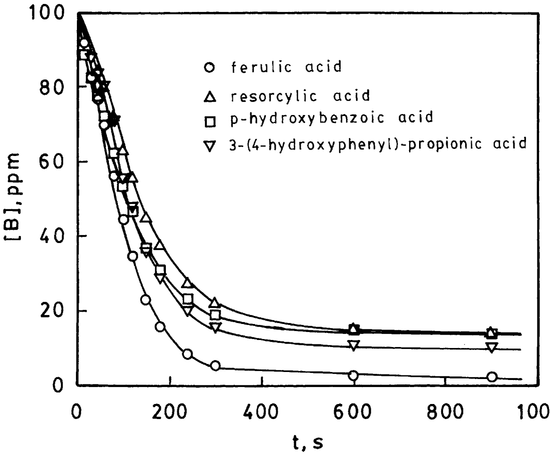

Fig. 4. Evolution of the concentration of each phenolic compound along the oxidation experiment of the group 1.

Table 2
Values of $\ln([B]_0/[B])$ and $\ln([R]_0/[R])$ in the oxidation of phenolic mixture 1 by Fenton's reagent

Time (min)	$\ln([R]_0/[R])$	$\ln([B]_0/[B])$		
	p-Hydroxybenzoic acid	β-Resorcylic acid	Ferulic acid	3-(4-hydroxyphenyl)-Propionic acid
0	0	0	0	0
0.25	0.12	0.08	0.08	0.08
0.50	0.19	0.13	0.19	0.12
0.75	0.26	0.18	0.26	0.17
1	0.32	0.23	0.36	0.21
1.33	0.47	0.34	0.58	0.33
1.66	0.63	0.47	0.81	0.58
2	0.76	0.59	1.06	0.74
2.5	1.00	0.80	1.47	1.02
3	1.18	0.99	1.83	1.23
4	1.46	1.30	2.45	1.59
5	1.66	1.52	2.89	1.84
10	1.90	1.88	3.53	2.16
15	1.97	1.98	3.71	2.22

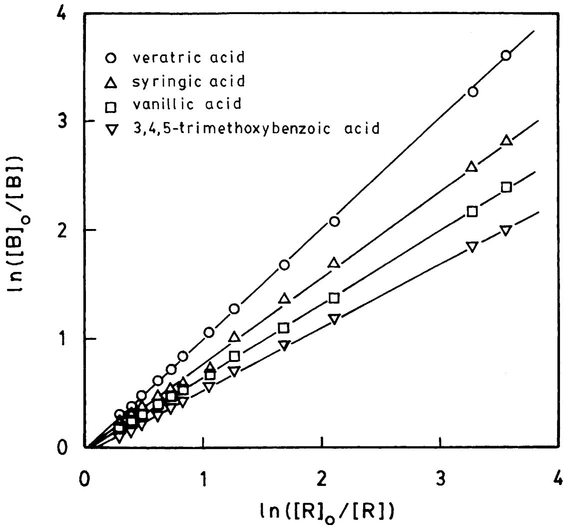

Fig. 5. Plot of $\ln([B]_0/[B])$ versus $\ln([R]_0/[R])$ for the group 3 of phenolic compounds.

$$-\frac{d[B]}{dt} = k_B[B][OH^\cdot], \tag{14}$$

where k_B is the rate constant of reaction (3) for every compound B. Similary to the Eq. (14), the reference compound presents the following rate equation:

$$-\frac{d[R]}{dt} = k_R[OH^\cdot][R]. \tag{15}$$

By dividing both Eqs. (14) and (15) it is obtained:

$$\frac{d[B]}{d[R]} = \frac{k_B}{k_R}\frac{[B]}{[R]} \tag{16}$$

and integrating between $t = 0$ and $t = t$:

Table 3
k_B/k_R and k_B values for each phenolic compound

Phenolic compound	k_B/k_R	$k_B \times 10^{-9}$ (l/(mol s))
3-(4-hydroxyphenyl)-Propionic acid	1.172	2.57
Ferulic acid	1.754	3.84
β-Resorcylic acid	0.991	2.17
Protocatechuic acid	0.307	0.67
Caffeic acid	0.821	1.80
p-Coumaric acid	1.155	2.53
3,4,5-Trimethoxybenzoic acid	0.567	1.24
Vanillic acid	0.672	1.47
Syringic acid	0.791	1.73
Veratric acid	1.011	2.21

$$\ln\frac{[B]_0}{[B]} = \frac{k_B}{k_R}\ln\frac{[R]_0}{[R]}, \tag{17}$$

where k_R is now the already deduced rate constant for the reference compound (*p*-hydroxybenzoic acid) and k_B is the rate constant for each one of the remaining phenolic compounds. A plot of $\ln([B]_0/[B])$ versus $\ln([R]_0/[R])$ yields a straight line, whose slope is the ratio of rate constants k_B/k_R. As k_R is already known ($k_R = 2.19 \times 10^9$ l/(mol s)), k_B can be determined for each phenolic compound.

As an example, Table 2 shows the calculated values of $\ln([B]_0/[B])$ and $\ln([R]_0/[R])$ for the group 1.

Fig. 5 shows this plot as an example for the group 3 of phenolic compounds. As can be seen, the excellent alignment of the points around straight lines confirms the goodness of the described method. After regression analysis, the slopes k_B/k_R for each compound are deduced, and using the previously known k_R, the rate constants k_B for the remaining acids are determined. The values are exposed in Table 3.

Table 4
Hydroxyl radical rate constants in aqueous solution

Compound	$k_{HO^\cdot} \times 10^{-9}$ (l/(mol s))[a]	$k_{HO^\cdot} \times 10^{-9}$ (l/(mol s))[b]
Pentachlorophenol	4	–
Diethyl phthalate	4	–
1,2,4-Trichlorobenzene	4	–
m-Dichlorobenzene	5.0	5.5
2,3,3',5,6-Pentachlorodiphenyl	5	–
2,3,7,8-Tetrachlorodibenzodioxin	4	–
Methoxychlor	20	–
Hexachlorocyclopentadiene	2.2	2.6
Alachlor	7	–
Atrazine	2.6	5.9
Simazine	2.8	5.9
Carbofuran	7	–
Lindane	1.1	2.6
Dinoseb	4	–

[a] Haag and Yao (1992).
[b] Buxton et al. (1988) or Lal et al. (1988).

These values are concordant with the deduced values for other similar compounds (Haag and Yao, 1992). As can be seen in Table 4, all the rate constants are in an order of 10^9 l/(mol s) except methoxychlor whose rate constant is 2×10^{10} l/(mol s).

4. Conclusions

A kinetic model is applied for the oxidation of phenolic compounds by Fenton's reagent. The application of this model for *p*-hydroxybenzoic acid leads to the determination of the radical production rate constant ($k_1 = 13.01$ l/(mol s)) and to the rate constant for the reaction between hydroxyl radicals and *p*-hydroxybenzoic acid ($k_3 = 2.19 \times 10^9$ l/(mol s)). After this determination, the application of a competitive method allows to calculate this rate constant for an other 10 phenolic compounds.

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