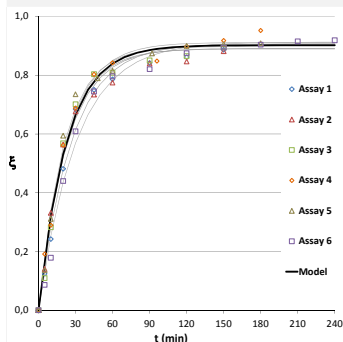


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The performance of the Fenton and photo-Fenton processes for the degradation and mineralization of Bisphenol A was investigated. A parameterized kinetic model was suitably fitted to the experimental data in order to determine two performance parameters related to the global equilibrium conversion and kinetic rate of the process. Further analysis allowed selecting those process conditions (iron and hydrogen peroxide load) that maximize the process performance. The Fenton process clearly proved to more efficiently degrade Bisphenol A under irradiation. The highest conversion rates were achieved with only the stoichiometric hydrogen peroxide load and the appropriate iron load (i.e. total Bisphenol A elimination and 90 % TOC decay).

Bisphenol A (BPA; 2,2-bis (4-hydroxyphenyl) propane) is an industrial organic chemical essentially used in plastic industry as a monomer for production of epoxy resins and polycarbonate [1,2]. It is also a well-known endocrine disruptor agent that contaminates surface waters even at low concentration [3].

Unfortunately, BPA cannot be entirely removed from water solutions by conventional treatments. Furthermore, in some cases, such treatments can lead to a series of by-products with higher endocrine disrupting action [4].

AOPs can be applied to remove BPA from water resources or industrial wastewaters [1-2, 4-8]. In particular, the irradiation of BPA in water with UV light in the presence of different amounts of hydrogen peroxide [7], or hydrogen peroxide and Fe(II) (photo-Fenton process) [1], are efficient methods for BPA photodegradation. Yet, they are energy-intensive processes and their cost is sought to be improved by reducing the reaction time as well as the consumption of reagents.

In this work, the Fenton and the photo-Fenton degradation of BPA (0,5 L, 30 mg L⁻¹) was addressed. The treatment performance was evaluated for a series of assays from a factorial design and was quantified in terms of the decay rate of total organic carbon (TOC).

Experimental data (BPA and TOC concentration profiles) were obtained in batch mode using fixed irradiation, pH and amount of BPA (30 mg L⁻¹ or 1,31·10⁻¹ mM), and varying concentrations of Fenton reagents (2,37-6,41 mM H₂O₂ and 1,42·10⁻²-3,92·10⁻² mM iron salt).

The reaction progress was monitored through the

decay of the TOC concentration from its initial value, [TOC]₀, at t=0. A semi-empirical model already tested in previous works was used for characterizing the performance of the process under study [9-10].

Given the initial conditions, the analytical expression for the TOC evolution is:

$$[TOC] = [TOC]^* + ([TOC]^0 - [TOC]^*) \cdot e^{-kt} \quad (\text{eq. 1})$$

which can be expressed in terms of conversion (ξ) by the following equation:

$$\xi = \xi^{\max} (1 - e^{-kt}) \text{ being } \xi^{\max} = \frac{[TOC]^0 - [TOC]^*}{[TOC]^0} \quad (\text{eq. 2})$$

Hence, the performance of the mineralization may be characterized by determining the two parameters of the model, ξ^{\max} (or [TOC]^{*}) and k, which can be obtained by fitting the model to the experimental data under the least squares criterion.

Materials and Methods

98% purity BPA (Aldrich) was purchased to prepare 30 mg L⁻¹ samples in distilled water. Fenton reagents, H₂O₂ 33% w/v (Panreac) and Fe₂SO₄·7H₂O (Merck) were used as received. Initial pH was set at 3.0±0.1 by adding HCl 37% (J.T. Baker). HPLC gradient grade methanol (J.T. Baker) and filtered milli Q grade water were used as HPLC mobile phases.

Experiments were conducted in a thermostatic cylindrical 500 mL Pyrex cell. The reaction mixture inside the cell, consisting of 500 mL of BPA solution and the given amount of Fenton reagent, was continuously stirred with a magnetic bar.

Temperature was 25 ± 0.5 °C and pH was 3 ±

0.2 after adding heptahydrated ferrous sulfate and hydrogen peroxide. Both, temperature and pH were monitored to ensure they kept constant along all the reaction time.

The experiments were carried out with a sunlight lamp (Ultra-Vitalux®, Osram, 300 W). The Ultra-Vitalux®, sunlight lamp consists of a quartz burner and a tungsten filament that are blended in such a way that the radiation emitted is similar to natural solar radiation. The spectral radiation presents wavelengths close to 400 nm (appropriate for photo-Fenton reaction) and up to 580 nm (useful for the Fenton-like reaction).

The reactor was irradiated from the top and there were 21 cm between the lamp and the liquid surface. The accumulated irradiance energy in the UVA region (315–400 nm) after one-hour assay was 49 kJ L⁻¹ and 11 kJ L⁻¹ in the UVB region (280–315 nm). The incident photon flux ($I = q_w A_w$) was determined by potassium ferrioxalate actinometry [11] and it was 7.09x10⁻⁵ Einstein min⁻¹.

Total organic carbon (TOC) concentration was measured at specified time intervals (5, 10, 20, 30, 45, 60, 90, and 120 minutes) by means of a Shimadzu VCHS/CSN TOC analyzer.

BPA concentration was determined via HPLC, using an Agilent 1200 series with UV-DAD array detector. The concentration of BPA was measured at every minute during the first 10 minutes.

The stationary phase was an Akady 5 μm C-18 150x4.6 mm column, maintained at 20°C and the diode array detector was set at 224 nm. The mobile phase was a mixture of methanol:water (70:30) flowing at 1 mL min⁻¹ and 20 μL samples were injected by a manual injector. Under these conditions, retention time was 3.9 minutes. A nine-level calibration curve (range 0-30 mg L⁻¹) was used for contaminant quantification. Before injection, samples were treated with methanol (in proportion 50:50) to stop reaction and prevent further degradation of BPA.

Results and Discussion

A preliminary screening was first executed. Process performance was evaluated at different experimental conditions in presence and absence of irradiation.

Regarding H₂O₂ concentration, a stoichiometric dose of 161 mg L⁻¹ was used as a reference to achieve total conversion to CO₂, H₂O and inorganic ions. Hence, 1/2, 3/4, and 5/4 the stoichiometric dose (80,5, 120,75 and 201,25 mg L⁻¹, respectively) were selected to study the influence of Fenton reagents. Table 1 summarizes the assays carried out.

Table 1. Experimental conditions for BPA degradation by Fenton and photo-Fenton process. Initial concentrations of BPA = 30 mg L⁻¹

Assay	Codified values		Variables levels			
	H2O2	Fe(II)	H2O2	Fe(II)	H2O2/BPA	Fe(II)/BPA
A	1	min	161,00	5	5,37	0,17
B	1	max	161,00	10	5,37	0,33
C	1/2	min	80,50	5	2,68	0,17
D	1/2	max	80,50	10	2,68	0,33
E	3/4	max	120,75	10	4,03	0,33
F	5/4	max	201,25	10	6,71	0,33

For each of the assays the model (eq. 2) was fit to the TOC profile and parameters k and ξ^{\max} were obtained. Figure 1 plots the treatment performance as a function of such coordinates. In all cases, BPA was not detected after 25 minutes of the Fenton treatment, and only after 10 minutes of the photo-Fenton treatment. Thus, the photo-Fenton process (orange marks) was shown to produce higher conversions at higher rates than the process in absence of light (blue marks).

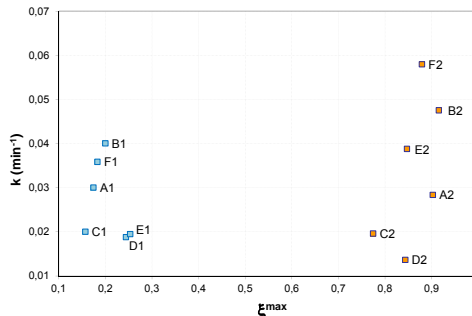


Figure 1. Results represented as a function of the two model parameters (k and ξ^{\max}). Conditions for each assay are in table 1. Blue marks (A1 to F1) are used for Fenton results and orange marks (A2 to F2) for photo-Fenton.

From this point on, only the photo-Fenton process is considered. In order to determine enhanced conditions for the photo-Fenton mineralization of BPA solutions, the dependence of the treatment output on factors such as hydrogen peroxide and iron (II) was next characterized.

Table 2. Experimental conditions for the photo-Fenton treatment of BPA solutions: star experimental design. Initial concentrations of BPA = 30 mg L⁻¹

Assay	Codified values		Variables levels			
	H2O2	Fe(II)	H2O2	Fe(II)	H2O2/BPA	Fe(II)/BPA
AA	-1	-1	120,75	5	4,03	0,17
BB	-1	1	120,75	10	4,03	0,33
CC	1	-1	201,25	5	6,71	0,17
DD	1	1	201,25	10	6,71	0,33
EE	0	0	161,00	7,5	5,37	0,25
FF	0	0	161,00	7,5	5,37	0,25
GG	0	0	161,00	7,5	5,37	0,25
HH	0	-√2	161,00	3,96	5,37	0,13
II	0	√2	161,00	11,04	5,37	0,37
JJ	-√2	0	104,08	7,5	3,47	0,25
KK	√2	0	217,92	7,5	7,26	0,25

Table 2 lists the levels of the planned assays according to a 2^2 DOE with start points and three centre points for statistical validity. Minimum and maximum factors were set at 120,75 mg L⁻¹ and 201,25 mg L⁻¹ for H₂O₂ concentration, and 5 and 10 mg L⁻¹ for iron load.

Figure 2 shows the results of the central assay of the design, which was repeated six times. A mineralization of 90.21 % is shown to be achieved with these conditions. Regarding BPA degradation, it was achieved within 4 minutes treatment.

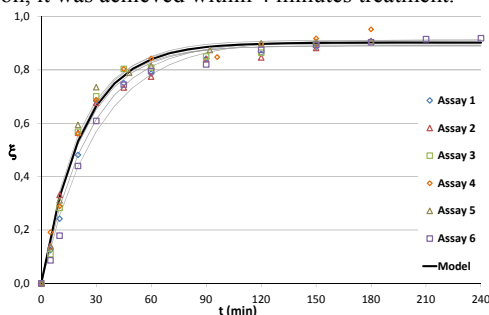


Figure 2. TOC conversion profile for the central assay of the star experimental design.

The system performance is again displayed in the k vs. ξ^{\max} chart (Fig. 3). The parametrical characterization of the influence of the Fenton reagent loads allows identifying the most promising alternatives. Mainly, assay II (11,04 mg L⁻¹ iron load) is observed to present the highest reaction rate constant, and central assays together with assay HH present the highest conversion (161 mg L⁻¹ hydrogen peroxide load).

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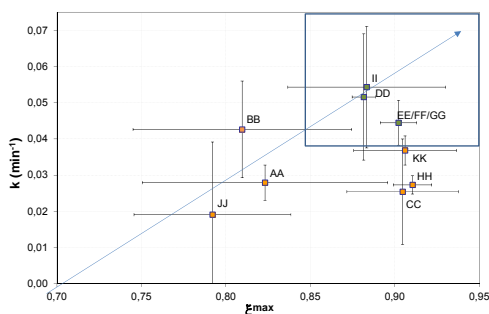


Figure 3. Detailed representation of the results as a function of the two model parameters (k and ξ^{\max}). Conditions for each set of assays are given in table 2.

Conclusions

The mineralization of Bisphenol A solutions and the degradation of the contaminant was studied. The Fenton and photo-Fenton processes were examined and for all the Fenton reagent loads evaluated, the photo-Fenton process obtained higher conversion and reaction rates than the Fenton process.

Within the experimental loads studied, increasing Fe(II) load does not provide any improvement when sub-stoichiometric H₂O₂ is used (104,08 mg L⁻¹). However, when stoichiometric H₂O₂ is supplied (161 mg L⁻¹), increasing Fe(II) shows to keep a similar level of mineralization and increase the reaction rate (50 percentage points when using 11 mg L⁻¹ Fe(II) instead of 3,96 mg L⁻¹). Regarding BPA decay it was not detected after 25 minutes of the Fenton treatment, and only after 10 minutes of the photo-Fenton treatment.

The highest conversion rates were achieved with only the stoichiometric hydrogen peroxide load and the appropriate iron load (i.e. total BPA elimination and 90 % TOC decay).