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Kinetic modelling of colour changes in aqueous solutions of phenol oxidized by sono-Fenton technology

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ABSTRACT

Colour formation in oxidized phenolic waters treated with (ultrasonic, US) sono-Fenton is favoured by operating at pH = 3.0. In these conditions, $FeOH^{2+}$ species is predominant and its presence would generate an additional supply of hydroxyl radicals, which would increase the degradation yield of phenol. The maximum intensity of colour originated in the water (0.74 AU) is obtained when conducting the treatment with 4.0 mol H_2O_2/mol phenol and ratios about 20.0 mg Fe^{2+}/kW. At these conditions, a notable presence of catechol is detected. The formation of $Fe(OOH)^{2+}$ with US waves could establish interactions with the organic matter, as catechol or certain carboxylic acids, like 2,5-dioxo-3-hexenedioic, generating (hydro)peroxo iron (II) complexes that would induce colour. A kinetic modelling is proposed of the catalytic effect exerted by the dosage of iron and the irradiation of US waves in colour kinetics. The induction of colour is adjusted to zero-order kinetics, while the discolouration evolves in a kinetics of third order. Iron exerts a catalytic effect greater than that of US waves in the colour induction stage. Thus, the colour formation increases with iron concentration according to 0.0131 (AU L/mg/min), while the decolouration rate increases according to 0.0262 (AU^2 L/mg/min). Working at US = 0.50 kW, the rate of water colouring shows an important increase. This effect may be due to the fact that the ratio between iron and ultrasound waves 20.0 mg Fe^{2+}/kW may lead to the formation of (hydro)peroxo-iron(II) complexes.

Keywords: Colour; (Hydro)peroxo complexes; Kinetic modelling; Phenol; Sono-Fenton

1. Introduction

Phenol is a compound utilized in numerous studies as a reference of contaminant due to its high toxicity and wide use in the industrial sector [1]. Phenol is quite toxic; causing death or serious side effects even at very low concentration. Therefore, it is considered a priority pollutant [2,3]. The environmental risks due to the raising spill of phenolic compounds in the environment have aroused the current concern to develop viable treatments for effective elimination. Phenol products are dumped into wastewater by various industries, such as paper mills, refineries or agrochemicals. Due to their variety and high persistence, they can affect the conditions of ecosystems and pose a threat to humans, being a source of contamination of surface and groundwater [4].

Suitable water for consumption must be subjected to quality controls, ensuring the elimination or reduction of those components, which are harmful to both humans and environment. Therefore, a series of organoleptic parameters (colour, turbidity), physical (temperature, conductivity), chemical (pH, dissolved oxygen) and microbiological (coliforms, streptococci) are commonly evaluated. Within this classification, colour is included as one of the control parameters regulating the proper functioning of the wastewater treatments [5].

When phenolic wastewaters contaminated are treated with advanced oxidation processes (AOPs), they acquire a

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strong dark colour that must be eliminated. This fact is due to the mechanism of oxidation of phenol to carbon dioxide and water [6,7], which occurs through the formation of intermediates of coloured nature [8,9]. Simultaneously, the treated water undergoes an increase of toxicity [10–12]. This result indicates the creation of intermediate compounds with high chemical stability and difficult to mineralize [13].

Fenton technology is one of the most widely used AOPs to decompose persistent organic pollutants of low biodegradability. It is based on the formation of hydroxyl radicals through the reaction of hydrogen peroxide and ferrous ion in acid medium. The main advantage is the simple and economical application [14]. However, ferrous ions rapidly oxidize to ferric ones, which react moderately with the oxidant, declining the treatment. In order to accelerate the degradation of the pollutant load, the conversion of Fe^{3+} into Fe^{2+} is intensified applying ultrasonic (US) irradiation to the reaction system [15]. In addition, US waves enhance the reactions producing hydrogen peroxide, so that diminishing the amount of oxidant necessary to carry out the process. Moreover, sludge is minimized as a consequence of the treatment [16–18].

This work presents a kinetic modelling of the effect exerted by some of the main control parameters of sono-Fenton technology in the colour, when oxidizing phenol-polluted water. It is worthy to remark that the processes of water discolouring by Fenton processes [9] and ultraviolet irradiation [19] have been studied extensively. However, research on discolouring of wastewater by sono-Fenton process is scarce [20–22].

Processes based on US waves are usually complex and described by complicated mathematical models, which consider the effect of the parameters depending on the treatment application. If the US process is studied from the physical point of view, chemical reactions are not considered within the cavitation bubbles [23–25]. Nevertheless, when admitting the reactions inducted by the formation of bubbles and their collapse, mathematical modelling is based on the kinetic study of the reaction rate [26–28]. These models allow predicting the decomposition rate of organic compounds [29–31], determining the degradation degree as a function of the pollutant load of the water [32]. The estimations let evaluating the production of radicals generated through cavitation bubbles, as well as the consumption of radicals involved in the degradation of the contaminants [33].

2. Materials and equipment

Oxidation of contaminated water with Ph_o = 100.0 mg/ L phenol (C_6H_6O, Scharlau 90%) is conducted using sono-Fenton technology. The tests are run in a sonolytic reactor consisting of a 1 L stirred tank reactor, immersed in a 6 L capacity US large area oscillating tank (Bandelin electronic DK 156 BP) made of stainless steel. The experimental set up has been drawn and explained in previous studies by Villota et al. [20]. The equipment has an US output of 720 W, heat power of 600 W and frequency of 35 kHz, electric power consumption of 3.4 A and a nominal voltage of 230 V. The reactor is provided with a digital built-in heating, thermostatically adjustable between 20°C and 80°C and an integrated thermometer, accuracy ±1.5°C. Power setting from 10% to 100% is controlled by a microprocessor that produces a power emission of waves between US = 0–0.72 kW.

The high-frequency generator converts the 35 kHz frequency into mechanical vibrations by transducers underneath the tank. As a result of these vibrations, millions of microvacuum bubbles are formed in the water. They implode during the high pressure phase and create pressure waves (cavitation process). US waves are transmitted to the water in the bath with the batch reactor submerged. The US bath uses special frequency modulation around an optimally fixed operating point. A quite homogeneous US field is achieved.

This US bath is provided with a program data memory for precise and reproducible work. It allows selecting time, temperature, power and degasification, and storing up to 10 variations. Exact setting of all parameters guarantees recreate results, being RFI-proof. The reproducibility of the oxidation tests conducted was considered based on the mean of the colour of the values analysed, obtaining a mean value of the standard deviation around 5%. The estimated error bars for each reaction are shown in the analysed colour kinetics (Figs. 1(a), 3(a), 5(a)).

2.1. Experimental methods

To conduct the process, 500 mL of contaminated water is poured into the batch reactor, agitated with a rod stirrer (Heidolph RZR 2101 electronic). pH is maintained steady at around 3.0 by rationing 0.05 M NaOH with an automatic pump (Watson Marlow 400), connected to a pH meter (Kent EIL 9142). Next, the US reactor is turned on and the operation parameters are adjusted, keeping temperature at 25.0°C. The catalyst ($FeSO_4 \cdot 2H_2O$, Panreac 80%) is poured in the wastewater, as ferrous ions Fe^{2+} = 2.0–50.0 mg/L. Once the mixture is homogenized, the oxidant is added (H_2O_2, Foret 30%), beginning the reaction. The oxidant dosage is expressed as an oxidizing molar ratio to phenol, R = 0–14.0 mol H_2O_2/mol C_6H_6O. Next, samples are analysed during the first 120 min. Finally, the samples are stored for 7 d to measure in the steady state.

2.2. Analytical methods

Concentration of phenol and its degradation intermediates is analysed using a high performance liquid chromatography equipment (Agilent Technologies 1200 Series), coupled to a UV/Vis spectrophotometer that detects aromatic compounds at λ = 210, 242 and 280 nm. A Phenil C18 column 5.0 mm in diameter (Waters) is utilized with an diluent, consisting of a mixture of $MeOH/H_2O$ (20/80) at a flow rate of 1.0 mL/min. Samples of 25.0 mL are injected at a pressure of 3,000–3,300 psia and 25°C. Besides, colour of the samples is measured with a UV/Vis spectrophotometer (Uvikon Kontron) at λ = 455 nm [9].

3. Results and discussion

3.1. pH effect

Fig. 1(a) shows the colour that the oxidized waters acquire as a function of the operating pH. The tests were conducted at the stoichiometric ratio R = 14.0, which allows degradation of the phenol to carbon dioxide and a concentration

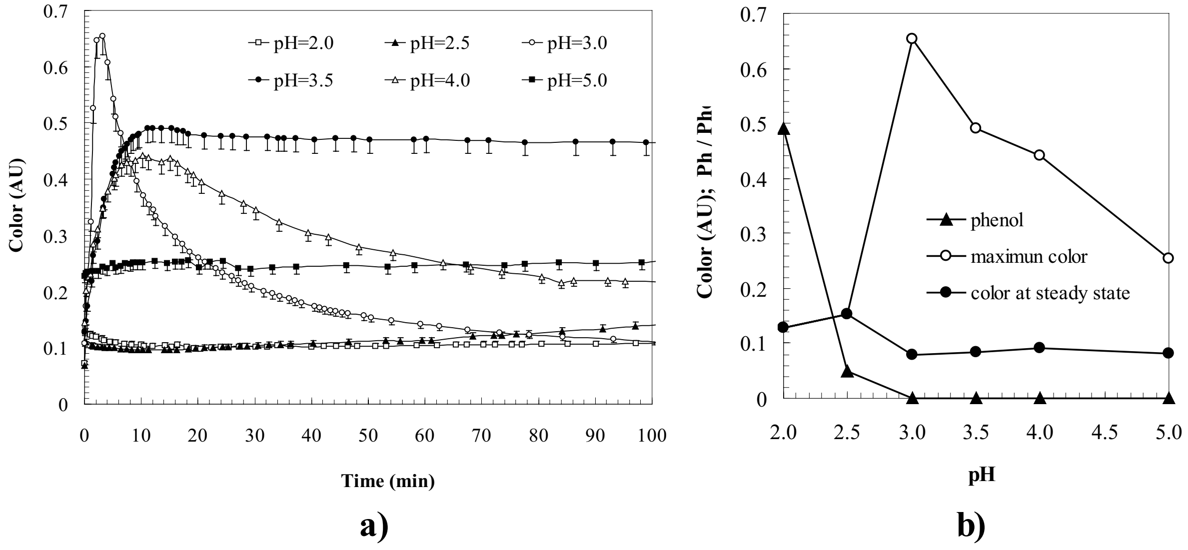


Fig. 1. (a) pH effect on the kinetics of colour during the oxidation of phenol solutions by sono-Fenton. (b) pH effect on the colour levels of wastewaters oxidized. Experimental conditions: Ph$_o$ = 100.0 mg/L; R = 14.0 mol oxidant/mol phenol; Fe^{2+} = 20.0 mg/L; T = 25.0°C; US = 0.72 kW; 35 kHz.

of catalyst Fe^{2+} = 20.0 mg/L, favouring the oxidation performance [20,34]. When oxidation starts, the catalyst added as ferrous ions evolves to higher oxidation states depending on pH. Operating at pH = 2.0–2.5 the water does not present significant colour variations, because the catalyst are colourless ferrous ions.

Increasing the pH to 3.0, enlarges the oxidation efficiency and the colour induction presents the kinetic evolution of reaction intermediates. During the first 3 min of reaction, the water increases colour, until reaching a maximum value (Colour$_{max}$ = 0.65 AU). Afterwards, the colour slowly fades to steady state (Colour$_\infty$ = 0.08 AU). This evolution could be associated to the regeneration cycle of iron where, in a first stage, the colourless ferrous ions would be oxidized to ferric ones. In turn, these ions would give rise to FeOH^{2+} and Fe(OOH)$^{2+}$ species, which can react with the organic matter, resulting in the formation of very coloured metal complexes. Next, in the second stage, these species would gradually evolve to colourless ferrous ions.

Operating at pH between 3.5 and 4.0, the water enlarge colour more gently, until reaching a maximum at 12 min, decreasing moderately for several days to steady state. In this case, the ferrous catalyst is oxidized to ferric species reducing the activation of the Fenton reactions. On the other hand, at these levels of acidity, the regeneration of the catalyst is lessened. Conducting at pH = 5.0, iron is in oxidized form and can induce formation and precipitation reactions of hydroxides [35].

Fig. 1(b) shows the effect of pH on the maximum colour levels and on the enduring colour that persists in the steady state in the oxidized samples. When evaluating the highest colour induced in the water, it reaches a maximum at pH = 3.0, similarly to the cases of utilizing UV or dark Fenton [36]. This could be due to an additional contribution of hydroxyl radicals from the decomposition of the FeOH^{2+} complex, which are the majority iron species formed at that acidity [37]. This additional charge of radicals would lead to the degradation of phenol under optimal conditions.

Conducting over pH = 3.0, the maximum colour generated decreases linearly when enlarging the pH, according to a ratio of 0.2 AU/pH unit. When analyzing the steady state, it is confirmed that the colour is diminished in all cases up to values around 0.09 AU. This would mean that the reaction intermediates causing the colour are decomposed into carboxylic acids of a colourless nature, and the residual colour enduring in the water would be produced by the iron species in solution. This recalcitrant colour would be related to the concentration of catalyst used in the treatment. Moreover, below pH = 3.0, the output of phenol degradation decreases when acidifying the medium, leaving a residual colour around 0.15 AU. This colour would come from the contribution of the iron species in solution plus the coloured aromatic intermediates resistant to oxidation.

3.2. *Effect of oxidant dosage*

Fig. 2 shows the kinetics of colour changes analysed during the oxidation of phenol, using different dosages of oxidant. From these results, Fig. 3(a) is estimated, displaying the maximum and residual colour induced in the waters as a function of the oxidant dosage, expressed as a molar ratio of hydrogen peroxide to phenol (R = mol H_2O_2/mol C_6H_6O). In all the tests conducted, it is confirmed that the phenol is completely degraded in the steady state.

As the oxidant ratio increases from R = 0 to R = 4.0, the maximum colour in the water intensifies, reaching a peak at 0.76 AU at R = 4.0. This molar ratio could lead to the degradation of phenol into muconic acid [7]. In this stage of oxidation, the formation of the coloured species takes place, contributing with greater intensity to the colour (quinones). Analyzing the residual colour of the waters at the steady state, it is verified that they present lower levels of colour,

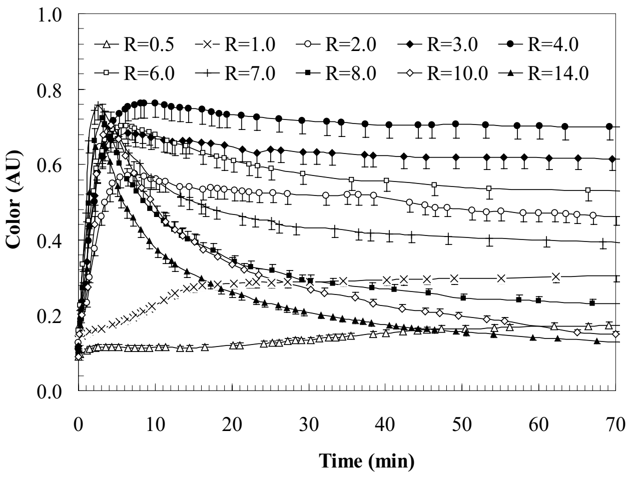


Fig. 2. Effect of oxidant dosage on the kinetics of colour during the oxidation of phenol solutions by sono-Fenton. Experimental conditions: Ph_0 = 100.0 mg/L; pH = 3.0; Fe^{2+} = 20.0 mg/L; *T* = 25.0°C; US = 0.72 kW; 35 kHz.

because some of those species are gradually degraded, resulting a ratio between oxidant dose and colour intensity of the water around 0.14 AU mol C_6H_6O/mol H_2O_2.

Utilizing greater ratios (*R* = 4.0–14.0), the maximum colour generated in the water diminishes linearly at 0.0115 AU/mol oxidant. It is noteworthy that studies in photo-Fenton and dark-Fenton systems obtained similar results [8,9]. The residual colour decreases progressively as the oxidant load enlarges. In this stage it is observed that using *R* = 10.0 the colour fades completely, down to levels similar to those of the initial solutions of phenol. This molar ratio would lead the mechanism of phenol degradation through the ortho-substituted pathway [19], until the formation of muconic acid ($C_6H_6O_4$) that would be degraded to maleic acid ($C_4H_4O_4$) (Eq. (1)) and, finally, to malonic acid ($C_3H_4O_4$) (Eq. (2)):

$$C_6H_6O_4 + 10OH^{\bullet} \rightarrow C_4H_4O_4 + 6H_2O + 2CO_2 \tag{1}$$

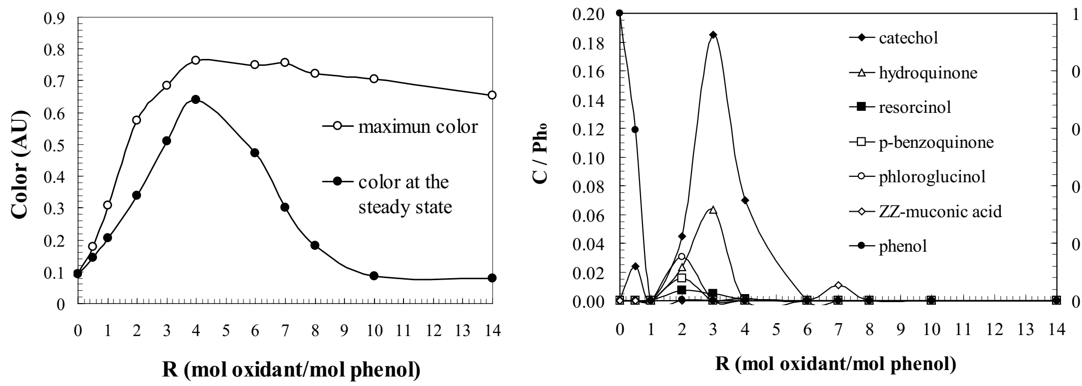
$$C_4H_4O_4 + 4OH^{\bullet} \rightarrow C_3H_4O_4 + 2H_2O + CO_2 \tag{2}$$

Moreover, phenol degradation by-products are analysed, in order to identify the nature of the species contributing to colour the water (Fig. 3(b)). It is found that operating at *R* = 4.0 a notable presence of catechol is detected, although none of the identified species have a maximum concentration. This result could indicate that the formation of metallic complexes with the organic matter would determine the kinetics of the colour evolution. Given the nature of the iron species generated by the US waves, it is acceptable considering the formation of (hydro)peroxo iron (II) complexes by reacting $Fe(OOH)^{2+}$ species with catechol, which would lead to muconic acid [38]. On the other hand, the origination of (hydro)peroxo iron (III) could occur with carboxylic acids having an ortho-substituted keto group (type 2,5-dioxo-3-hexenedioic acid). Conducting at ratios over *R* = 10, which would lead to the formation of malonic acid, a colourless water is obtained.

3.3. Kinetic study of the iron catalytic effect

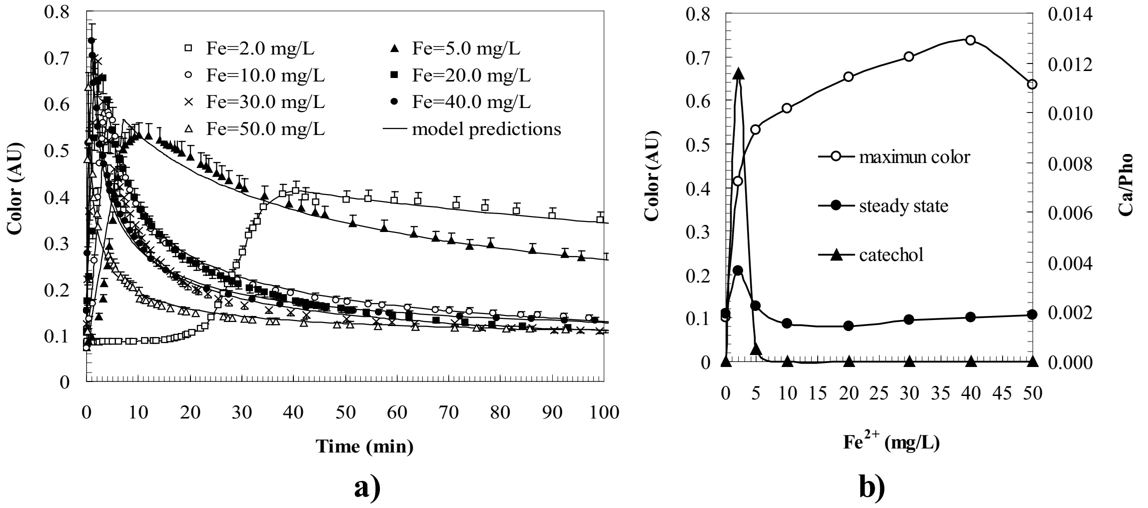
Fig. 4(a) presents the kinetics of colour when carrying out the oxidation tests with dosages Fe^{2+} = 2.0–50.0 mg/L. The concentration of ferrous ions determines the rate of formation and colour degradation. Furthermore, it intervenes in the reaction mechanism, establishing the colour intensity of the water. On the other hand, the results show that, when using concentrations below Fe^{2+} = 5.0 mg/L, the colour formation undergoes a delay period of around 20 min. This fact is due to operate with lack of catalyst.

Fig. 4(b) presents the maximum colour of the water in the steady state, based on the dosage of iron catalyst. The results indicate that the iron concentration interval suitable to conduct the process under the tested conditions is Fe^{2+} = 5.0–40.0 mg/L. Within this range, a linear increase in the intensity of the colour acquired by the water can be estimated, as a function of the iron dose around 0.006 AU L/mg Fe^{2+}. Increasing doses of iron over Fe^{2+} = 40.0 mg/L, the



a) b)

Fig. 3. (a) Effect of oxidant dosage on the kinetics of colour during the oxidation of phenol solutions by sono-Fenton. (b) Effect of oxidant dosage on the formation of reaction intermediates. Experimental conditions: Ph_0 = 100.0 mg/L; pH = 3.0; Fe^{2+} = 20.0 mg/L; *T* = 25.0°C; US = 0.72 kW; 35 kHz.



a) b)

Fig. 4. (a) Effect of the catalyst dosage on the kinetics of colour during the oxidation of phenol solutions by sono-Fenton. (b) Effect of the catalyst dosage on the colour levels in wastewaters oxidized. Experimental conditions: Ph_o = 100.0 mg/L; pH = 3.0; R = 14.0 mol oxidant/mol phenol; T = 25.0°C; US = 0.72 kW; 35 kHz.

system contains an excess of catalyst and iron precipitates as hydroxide.

The maximum colour that the water acquires increases along the iron concentration, showing that at Fe^{2+} = 40.0 mg/L it reaches its peak (0.736 AU). Nevertheless, the data from studies performed with UV light or dark Fenton obtain the highest colour at Fe^{2+} = 20.0 mg/L [9,19]. This fact may indicate a change in the nature of the iron species interacting with the organic load of the medium. In this way, ferric ions would give rise to the formation of $FeOH^{2+}$ and $Fe(OOH)^{2+}$, which react with the organic matter, resulting in the formation of complex (hydro)peroxides. The initial concentration of ferrous ions generating the maximum colour intensity, 0.4 mg Fe^{2+}/mg phenol, could indicate the stoichiometric iron ratio that lead to the formation of these structures.

Once the maximum colour intensity is reached, the water will fade until showing a colourless appearance at the steady state with average values around 0.1 AU. This performance is because iron added as ferrous ions is oxidized to ferrous species that precipitate as hydroxides. In turn, the conditions conducting the experiments lead to the complete degradation of phenol into colourless carboxylic acids. Moreover, when carrying out the oxidation with Fe^{2+} = 2.0 mg/L, a recalcitrant colour remains in the steady state that can be produced by catechol.

A kinetic model of the catalytic effect induced by the dosage of iron in colour kinetics is proposed. The model itemizes the colour changes experienced by the oxidized water in two stages (Eq. (3)). The first stage considers the kinetic adjustment of the colour induction, while the second one analyses the colour degradation. Both stages are distinguished by intermediate degradation species of different nature, whose formation affects the kinetic order of the reaction in each stage.

In the proposed reaction scheme, phenol, which is colourless (Colour_0, AU), is degraded to very coloured species, at a reaction rate defined by the kinetic constant of zero order k_f (AU/min), until the oxidized water reaches its maximum intensity ($\text{Colour}_{\text{max}}$, AU). Then, the coloured species are degraded depending on the concentration of the treatment oxidant, leading to the formation of colourless species (carboxylic acids). Finally, the colour stabilizes, reaching a stationary value that lasts in the water (Colour_∞, AU).

$$\text{Phenol} \xrightarrow{k_f} \text{Colour} \xrightarrow{k_d} \text{Uncolourless-species} \tag{3}$$

being k_f: kinetic constant of colour formation (AU/min); k_d: kinetic constant of colour degradation (AU^2/min)

Eqs. (4) and (5) are obtained by raising the mass balances for this reaction system:

$$\frac{d\text{Colour}}{dt} = k_f\ \text{Colour}^{n=0} \quad \Big]_{\text{Colour}_0}^{\text{Colour}_{\text{max}}} \tag{4}$$

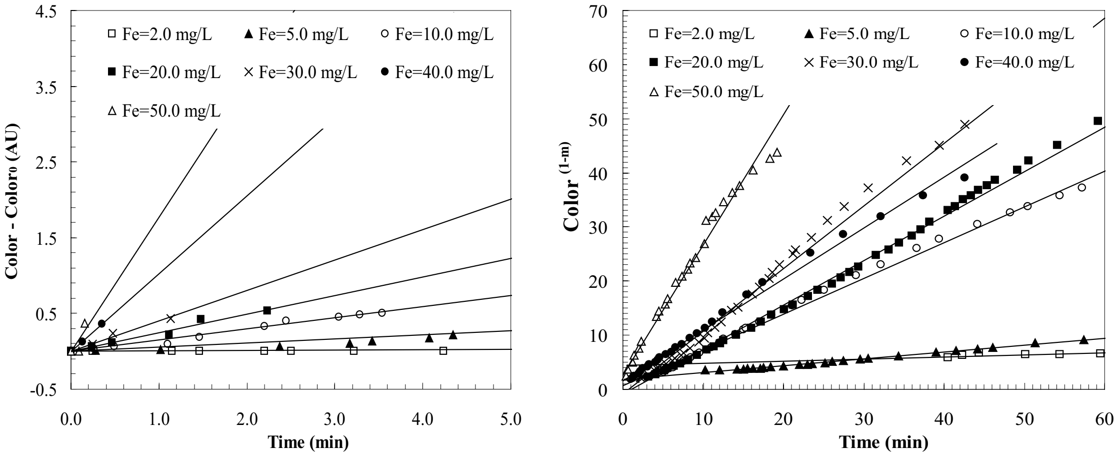
$$-\frac{d\text{Colour}}{dt} = k_d\left(\text{Colour} + \text{Colour}_\infty\right)^{m=3.0} \quad \Big]_{\text{Colour}_{\text{max}}}^{\text{Colour}_\infty} \tag{5}$$

where Colour_0: colour of the aqueous solution of phenol (AU); $\text{Colour}_{\text{max}}$: maximum colour intensity of the water(AU); Colour_∞: colour of water in steady stage (AU).

Fig. 5 indicates that the induction of colour in the water occurs rapidly and linearly during the first 10 min of oxidation. This approach allows considering a zero-order reaction (n = 0). However, the colour degradation follows a decrease, whose tendency approaches a kinetics of third order (m = 3.0). By integrating the mass balances, as shown in Eqs. (6) and (7), the kinetic equations for the formation of colour (Eq. (8)) and its degradation are obtained (Eq. (9)).

$$\int_{\text{Colour}_0}^{\text{Colour}} d\text{Colour} = k_f \int_{t=0}^{t} dt \tag{6}$$

$$\int_{\text{Colour}_{\text{max}}}^{\text{Colour}} \frac{d\text{Colour}}{\left(\text{Colour} - \text{Colour}_\infty\right)^{3.0}} = -k_d \int_{t_{\text{max}}}^{t} dt \tag{7}$$



a) **b)**

Fig. 5. (a) Zero-order kinetics estimated for the formation of colour depending on the dosage of iron used in the treatment. (b) Third-order kinetics for colour degradation Experimental conditions: Ph_o = 100.0 mg/L; pH = 3.0; R = 14.0 mol oxidant/mol phenol; T = 25.0°C; US = 0.72 kW; 35 kHz.

$$\text{Colour} = \text{Colour}_0 + k_f\, t \qquad (8)$$

$$\text{Colour} = \frac{\left(\text{Colour}_{\max} - \text{Colour}_\infty\right)}{\left[1 + 2k_d\left(\text{Colour}_{\max} - \text{Colour}_\infty\right)^2\left(t - t_{\max}\right)\right]^{0.5}} + \text{Colour}_\infty \qquad (9)$$

where $t_{\max}$: time when the oxidized water shows its maximum level of colour (min).

By adjusting the experimental results, the kinetic constants of colour formation (Eq. (10)) and degradation (Eq. (11)) were estimated, according to the catalyst concentration dosed in the reaction (mg Fe^{2+}/L). The assessed kinetic parameters are presented in Table 1. The predictions of the model have been represented in Fig. 4 together with the experimental results.

Here, the iron exerts a great catalytic effect during the reaction of colour induction, enhancing the colour of the oxidized water. Meanwhile, during the stage of colour degradation, although its effect is low, iron linearly increases the rate of water discolouration when operating with concentration of Fe^{2+} = 0–10.0 mg/L. On the other hand, applying the treatment at Fe^{2+} = 10.0–30.0 mg/L does not alter the discolouration rate. However, when using Fe^{2+} = 30.0 mg/L, there is a decrease in the colour fading rate. This fact is due to operate with an excess of catalyst, because a part of the added iron persists as ferric ion, with coloured nature.

$$k_f = 0.0131\ \text{Fe}^{2+} \quad \left(r^2 = 0.9883\right) \qquad (10)$$

$$k_d = 0.0224\ \text{Fe}^{2+} \quad \left(r^2 = 0.9307\right) \qquad (11)$$

Table 1
Kinetic parameters estimated for colour changes during the phenol oxidation by sono-Fenton technology

Fe^{2+} (mg/L)	US (kW)	k_f (AU/min)	k_d (AU^2/min)	$\text{Colour}_{\max}$ (AU)	Colour_∞ (AU)	$t_{\max}$ (min)	r^2
2.0	0.72	0.005	0.025	0.412	0.02	40.5	0.9975
5.0	0.72	0.054	0.070	1.460	0.02	10.0	0.9121
10.0	0.72	0.146	0.380	1.187	0.02	4.0	0.9825
20.0	0.72	0.245	0.400	1.299	0.00	2.7	0.9851
30.0	0.72	0.402	0.700	1.074	0.03	1.8	0.9622
40.0	0.72	1.028	0.900	0.750	0.05	1.0	0.9741
50.0	0.72	1.774	3.500	0.424	0.07	0.4	0.9846
20.0	0.00	0.049	0.160	0.605	0.00	9.50	0.9756
20.0	0.22	0.117	0.210	0.676	0.00	4.59	0.9685
20.0	0.36	0.119	0.250	0.630	0.00	4.25	0.9747
20.0	0.50	0.652	1.600	0.595	0.05	1.23	0.9862
20.0	0.72	0.245	0.380	0.654	0.00	3.19	0.9896

Experimental conditions: Ph_o = 100.0 mg/L; pH = 3.0; R = 14.0 mol oxidant/mol phenol; T = 25.0°C; 35 kHz.

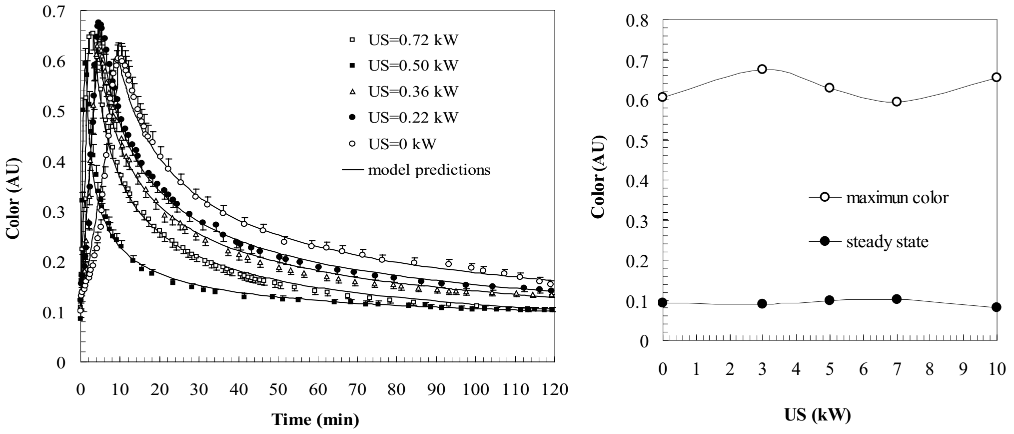
The results allow verifying that the iron exerts a catalytic effect on the induction and degradation of the colour, where the time in which the water reaches its maximum colour diminishes in a potential way when increasing the dosage of iron (Eq. (12)).

$$t_{\max} = 93.423\left(\mathrm{Fe}^{2+}\right)^{-1.28} \quad \left(r^2 = 0.9515\right) \tag{12}$$

3.4. Kinetic study of the US irradiation on the catalytic effect

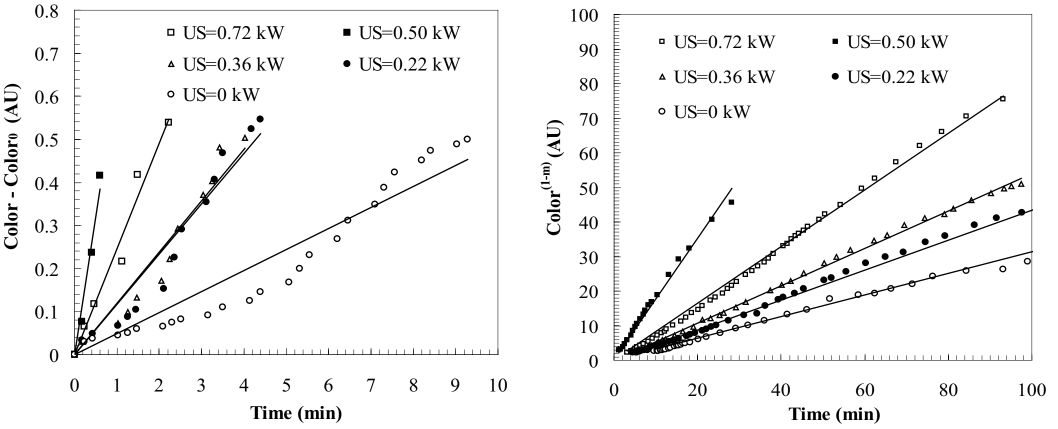
Fig. 6(a) shows that the irradiation of the US waves exerts a catalytic effect on the colour induction. Both the rates of colouring and discolouring the water rise when increasing irradiation. It should be noted that, in the case of operating with US = 0.50 kW, the rate of colour kinetics increases. This fact would indicate that the power of the US waves affects the reaction mechanism, proving that ratios about 20.0 mg Fe^{2+}/kW can increase the rate of decomposition of iron species FeOH^{2+} and $\mathrm{Fe(OOH)}^{2}$ to ferrous ions [39,40]. On the other hand, Fig. 6(b) shows the colour values analysed in the oxidized samples, verifying that the US waves do not determine the colour levels of the water. Nevertheless, its effect would alter the reaction rate, both in the colour induction and in the discolouration stages.

The kinetic model proposed considers the catalytic effect of the irradiation of the US waves in the colour changes. The analysis conducted indicates that the reaction kinetic orders are in line with the estimated ones for the iron catalyst (Fig. 7). Then, the colour induction would be adjusted to zero-order kinetics (Eq. (8)). Meanwhile, the rate of colour degradation can be estimated from Eq. (9), which considers a kinetics of third order. On the other hand, Table 1 displays the kinetic parameters calculated.



a) b)

Fig. 6. (a) Effect of the ultrasonic irradiation power on the kinetics of colour during the oxidation of phenol solutions by sono-Fenton. (b) Effect of ultrasounds power on the colour levels of wastewaters oxidized. Experimental conditions: $\mathrm{Ph_o}$ = 100.0 mg/L; pH = 3.0; R = 14.0 mol oxidant/mol phenol; Fe^{2+} = 20.0 mg/L; T = 25.0°C.



a) b)

Fig. 7. (a) Zero-order kinetics estimated for the formation of colour depending on the ultrasonic irradiation used in the treatment. (b) Third-order kinetics for colour degradation. Experimental conditions: $\mathrm{Ph_o}$ = 100.0 mg/L; pH = 3.0; R = 14.0 mol oxidant/mol phenol; Fe^{2+} = 20.0 mg/L; T = 25.0°C; 35 kHz.

Working at US = 0.50 kW, the rate of water colouring shows an important increase. This effect may be due to the fact that the ratio between iron and ultrasound waves 20.0 mg Fe^{2+}/kW may lead to the formation of (hydro)peroxo-iron(II) complexes. The creation of iron complexes, due to the interaction of the $Fe(OOH)^{2+}$ species with catechol or carboxylic acids, like 2,5-dioxo-3-hexenodioic, would induce colour in the water. The rate of decomposition of the $FeOH^{2+}$ and $Fe(OOH)^{2+}$ species to ferrous ions is enlarged by using ratios around 20.0 mg Fe^{2+}/kW [20], causing an increase in the kinetics of colour formation. This effect is more prominent in the discolouring phase.

These results indicate that the US waves affect the reaction kinetics taking place during the first minutes of the reaction, when a high formation of radical species occurs. Besides, the obtained estimations let verifying that the iron exerts a catalytic effect higher to the US waves in the induction rate of colour. However, both parameters obtain similar increases in the discolouration rate of the oxidized rates.

4. Conclusions

Colour induction in oxidized waters with sono-Fenton technology is favoured by operating at pH = 3.0, similarly to the treatment with UV or dark Fenton. This fact would be justified by the additional contribution of hydroxyl radicals generated by the decomposition of $FeOH^{2+}$ species, which would degrade phenol to coloured by-products (quinones). Operating at $R = 4.0$, although none of the intermediate species identified presents a maximum concentration, a notable presence of catechol is detected, that lets to consider the formation of (hydro)peroxo iron (II) complexes, which would lead to the creation of muconic acid. Applying ratios over $R = 10$, which would conduct to the formation of malonic acid, a colourless water is obtained.

A kinetic modelling of the catalytic effect exerted by the dosing of iron and the irradiation of US waves in colour kinetics is proposed. The colour induction is adjusted to zero-order kinetics, while the discolouration evolves in a kinetics of third order. The maximum colour intensity in the water increases with the iron concentration, showing that at Fe^{2+} = 40.0 mg/L the colour reaches its peak (0.736 AU). This fact may indicate that ratios around 20.0 mg Fe^{2+}/kW can enlarge the decomposition rate of iron species $FeOH^{2+}$ and $Fe(OOH)^{2}$ into ferrous ions. The formation of iron complexes, due to the interaction of the $Fe(OOH)^{2+}$ species with catechol or carboxylic acids, like 2,5-dioxo-3-hexenodioic, would induce colour in the water. The estimations allow verifying that iron exerts a catalytic effect greater to US waves.

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References

[1] X. Wei, H. Wu, F. Sun, Magnetite/Fe-Al-montmorillonite as a Fenton catalyst with efficient degradation of phenol, J. Colloid Interface Sci., 504 (2017) 611–619.

[2] J. Jiang, H. Wang, X. Chen, S. Li, T. Xie, D. Wang, Y. Lin, Enhanced photocatalytic degradation of phenol and photogenerated charges transfer property over BiOI-loaded ZnO composites, J. Colloid Interface Sci., 494 (2017) 130–138.

[3] Y. Park, G.A. Ayoko, E. Horváth, R. Kurdi, J. Kristof, R.L. Frost, Structural characterisation and environmental application of organoclays for the removal of phenolic compounds, J. Colloid Interface Sci., 393 (2013) 319–334.

[4] S. Ahmed, M.G. Rasul, W.N. Martens, R. Brown, M.A. Hashib, Heterogeneous photocatalytic degradation of phenols in wastewater: a review on current status and developments, Desalination, 261 (2010) 3–18.

[5] N.B. Turan, H.S. Erkan, G.O. Engin, Process safety and environmental protection, Process Saf. Environ. Prot., 109 (2017) 203–213.

[6] H.P. Devlin, I.J. Harris, Mechanism of the oxidation of aqueous phenol with dissolved oxygen, Ind. Eng. Chem. Fundam., 23 (1984) 387–392.

[7] N. Villota, L.M. Camarero, J.M. Lomas, J. Pérez, Changes of turbidity during the phenol oxidation by photo-Fenton treatment, Environ. Sci. Pollut. Res., 21 (2014) 12208–12216.

[8] N. Villota, J.M. Lomas, L.M. Camarero, Nature of the degradation products of phenol which produce high levels of colour in the wastewater oxidized in a photo-Fenton system, Desal. Wat. Treat., 57 (2016) 28784–28793.

[9] F. Mijangos, F. Varona, N. Villota, Changes in solution colour during phenol oxidation by Fenton reagent, Environ. Sci. Technol., 40 (2006) 5538–5543.

[10] A. Santos, P. Yustos, S. Rodriguez, F. Vicente, A. Romero, Kinetic modelling of toxicity evolution during phenol oxidation, Ind. Eng. Chem. Res., 48 (2009) 2844–2850.

[11] J.A. Zazo, J.A. Casas, C.B. Molina, A. Quintanilla, J.J. Rodriguez, Evolution of ecotoxicity upon Fenton's oxidation of phenol in water, Environ. Sci. Technol., 41 (2007) 7164–7170.

[12] A.M. De Luis, J.I. Lombraña, A. Menéndez, J. Sanz, Analysis of the toxicity of phenol solutions treated with H_2O_2/UV and H_2O_2/Fe oxidative systems, Ind. Eng. Chem. Res., 50 (2001) 1928–1937.

[13] J. Habicht, U. Mäeorg, Coupling of resorcinols in retorted kukersite semi-coke, Environ. Chem., 63 (2014) 75–85.

[14] M.C. Lu, H. Zhang, Y.Y. Huang, S.Y. Wang, Influence of inorganic ions on the mineralization of 2, 4-dinitrophenol by the Fenton reaction, Fresenius Environ. Bull., 14 (2005) 101–104.

[15] A. Babuponnusami, K. Muthukumar, Degradation of phenol in aqueous solution by Fenton, sono-Fenton and sono-photo-Fenton methods, Clean – Soil Air Water, 39 (2011) 142–147.

[16] A. Mehrdad, R. Hashemzadeh, Ultrasonic degradation of rhodamine B in the presence of hydrogen peroxide and some metal oxide, Ultrason. Sonochem., 17 (2010) 168–172.

[17] Y.S. Ma, C.F. Sung, J.G. Lin, Degradation of carbofuran in aqueous solution by ultrasound and Fenton processes: effect of system parameters and kinetic study, J. Hazard. Mater., 178 (2010) 320–325.

[18] M. Rivera, M. Pazos, M.A. Sanroman, Improvement of dye electrochemical treatment by combination with ultrasound technique, J. Chem. Technol. Biotechnol., 84 (2009) 1118–1124.

[19] N. Villota, J.M. Lomas, L.M. Camarero, Study of the paracetamol degradation pathway that generates colour and turbidity in oxidized wastewaters by photo-Fenton technology, J. Photochem. Photobiol., A329 (2016) 113–119.

[20] N. Villota, J.M. Lomas, L.M. Camarero, Effect of ultrasonic waves on the water turbidity during the oxidation of phenol. Formation of (hydro)peroxo complexes, Ultrason. Sonochem., 39 (2017) 439–445.

[21] C. Özdemir, M.K. Öden, S. Sahinkaya, E. Kalipci, Colour removal from synthetic textile wastewater by sono-Fenton process, Clean – Soil Air Water, 39 (2011) 60–67.

[22] D. Cailean, C. Teodosiu, A. Friedl, Integrated sono-Fenton ultrafiltration process for 4-chlorophenol removal from aqueous effluents: assessment of operational parameters (Part 1), Clean Technol. Environ. Policy, 16 (2014) 1145–1160.

[23] E. Basturk, M. Karatas, Advanced oxidation of reactive blue 181 solution: a comparison between Fenton and sono-Fenton process, Ultrason. Sonochem., 21 (2014) 1881–1885.

[24] D.G. Aseev, M.R. Sizykh, A.A. Batoeva, Oxidative degradation of phenols in sono-Fenton-like systems upon high-frequency ultrasound irradiation, Russ. J. Phys. Chem. A, 91 (2017) 2331–2336.

[25] D.H. Bremner, R. Molina, F. Martinez, J.A. Melerob, Y. Segurab, Degradation of phenolic aqueous solutions by high frequency sono-Fenton systems (US–Fe_2O_3/SBA-15–H_2O_2), Appl. Catal., B, 90 (2009) 380–388.

[26] M. Abbasi, A.N. Razzaghi, Sonochemical degradation of Basic Blue 41 dye assisted by nanoTiO_2 and H_2O_2, J. Hazard. Mater., 153 (2008) 942–947.

[27] M. Li, J.T. Li, H.W. Sun, Sonochemical decolourization of acid black 210 in the presence of exfoliated graphite, Ultrason. Sonochem., 15 (2004) 37–42.

[28] H. Zhang, J. Zhang, C. Zhang, F. Liu, D. Zhang, Degradation of C.I. Acid Orange 7 by the advanced Fenton process in combination with ultrasonic irradiation, Ultrason. Sonochem., 16 (2009) 325–330.

[29] T. Sivasankar, V.S. Moholkar, Physical insights into the sonochemical degradation of recalcitrant organic pollutants with cavitation bubble dynamics, Ultrason. Sonochem., 16 (2009) 769–781.

[30] M. Goel, H. Hongqiang, A.S. Mujumdar, R.M. Bhowmick, Sonochemical decomposition of volatile and non-volatile organic compounds: a comparative study, Water Res., 38 (2004) 4247–4261.

[31] A. De Visscher, P. Van Eenoo, D. Drijvers, H.V. Langenhove, Kinetic model for the sonochemical degradation of monocyclic aromatic compounds in aqueous solution, J. Phys. Chem., 100 (1996) 11636–11642.

[32] T. Sivasankar, V.S. Moholkar, Physical features of sonochemical degradation of nitroaromatic pollutants, Chemosphere, 72 (2008) 1795–1806.

[33] T. Sivasankar, V.S. Moholkar, Mechanistic approach to intensification of sonochemical degradation of phenol, Chem. Eng. J., 149 (2009) 57–69.

[34] N. Villota, L.M. Camarero, J.M. Lomas, J. Perez-Arce, The role of iron species on the turbidity of oxidized phenol solutions in a photo-Fenton system, Environ. Technol., 36 (2015) 1855–1863.

[35] J. Bergendahl, S. Hubbard, D. Grasso, Pilot-scale Fenton's oxidation of organic contaminants in groundwater using autochthonous iron, J. Hazard. Mater., 99 (2003) 43–56.

[36] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater., 98 (2003) 33–50.

[37] I.P. Pozdnyakov, E.M. Glebov, V.F. Plyusnin, V.P. Grivin, Y.V. Ivanov, D.Y. Vorobyev, N.M. Bazhin, Mechanism of $Fe(OH)(^{2+})(aq)$ photolysis in aqueous solution, Pure Appl. Chem., 72 (2000) 2187–2197.

[38] E.G. Kovaleva, J.D. Lipscomb, Versatility of biological non-heme Fe(II) centers in oxygen activation reactions, Nat. Chem. Biol., 4 (2008) 186–193.

[39] M.V. Bagal, P.R. Gogate, Wastewater treatment using hybrid treatment schemes based on cavitation and Fenton chemistry: a review, Ultrason. Sonochem., 21 (2014) 1–14.

[40] I. Grčić, A. Šipić, N. Koprivanac, D. Vrsaljko, Global parameter of ultrasound exploitation (GPUE) in the reactors for wastewater treatment by sono-Fenton oxidation, Ultrason. Sonochem., 19 (2012) 270–279.