



Kinetic modelling of water-color changes in a photo-Fenton system applied to oxidate paracetamol

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ABSTRACT

Paracetamol aqueous solutions are oxidized with a photo-Fenton technology. The analysis of the color generation shows that it is created by aromatic intermediates of paracetamol degradation, besides iron species. These appear due to the catalyst regeneration cycle, which consist of ferric hydroxides and organometallic compounds. The nature of these intermediates is a function of the dosage of hydrogen peroxide that determines the oxidation reached. Maximum water color happens when 4.8 mol of hydrogen peroxide react with 0.66 mol of paracetamol. The colored solutions consist of mixtures of intermediates such as pyrogallol, muconic acid, hydroquinone and resorcinol.

Paracetamol is degraded to intermediates that induce color in the water, reaching a maximum value (Color_{\max} , AU at t_{colormax} , min). Next, color decreases until a steady state around one hour. The catalyst is oxidized in the presence of UV light to ferric hydroxides, which increase the intensity of the maximum water color following a 0.16 reaction order, $\text{Color}_{\max} = \alpha_{\text{Fe,color}} (\text{Fe}^{2+})^{0.16}$. The catalytic effect of iron is revealed by reducing the time for water to acquire the maximum coloration, following a 0.72 order, $t_{\text{colormax}} = \alpha_{\text{Fe,t}} (\text{Fe}^{2+})^{-0.72}$. The temperature also causes a notable effect on the reaction, decreasing the time for maximum of color formation by a 0.5 order without affecting, however, the color intensity, $t_{\text{colormax}} = \alpha_{\text{T,t}} (\text{T})^{-0.5}$. Moreover, water color formation (k_f , $\text{AU}^{-1} \text{min}^{-1}$) and degradation (k_d , $\text{AU}^{-1} \text{min}^{-1}$) follow second order kinetics. The kinetic constant of color formation shows a dependence of order 0.7 with iron dosage, $k_f = \alpha_{\text{fFe}} (\text{Fe}^{2+})^{0.7}$. Nevertheless, iron effect is minor in the color degradation. Both kinetic constants for color formation, $k_f = \alpha_{\text{fT}} \text{T} + \varepsilon_{\text{fT}}$ and degradation, $k_d = \alpha_{\text{dT}} \text{T} + \varepsilon_{\text{dT}}$ reveal a linear dependence with temperature. This finding denotes that the catalytic effect of temperature is greater than that of iron.

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1. Introduction

Emerging pollutants (pesticides, pharmaceutical and personal hygiene products, surfactants, and narcotics), [1] are compounds that are not regulated by existing legislation (R.D. 817/2015, Directive 2013/39/UE) because there is no detailed understanding of their evolution in aquatic environments, and their long term consequences. No sufficient data are available to perform an appropriate assessment of their environmental impact [2]. Therefore it is difficult to predict the effects that they may have on the health of living organisms [3] although it is generally agreed that their main characteristic is their continuous introduction into the environment causing negative effects.

Among these contaminants, pharmaceuticals are noteworthy because of the high consumption of medical drugs in society. Once pharmaceuticals have been metabolized in the body they are excreted into the water and reach the sewage treatment plants [4]. Treatments in these plants do not completely degrade these metabolites which reach the natural ecosystem in the outflow water and slurries [5]. Also, cattle waste, fertilizers, and agricultural pesticides can reach and contaminate the underground aquifers [6,7]. Some of these substances (ibuprofen, paracetamol, diclofenac, carbamacepine) have been identified in potable waters. At the world level, the most consumed pharmaceuticals are analgesics, antihypertensives, and antimicrobials. Among all these substances paracetamol is outstanding since this compound has been most frequently detected and at the highest concentrations, 6–65 μgL^{-1} [8].

The development of efficient methods to eliminate these contaminants is absolutely essential to avoid environmental pollution and the potential damage that these compounds could

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Nomenclature

Color	Water color (AU)
Color _{max}	Maximum intensity of color generated in the water (AU)
Color _o	Color of the aqueous solution of paracetamol (=0.06 AU)
Color _∞	Color of water in the steady state (AU)
Fe ²⁺	Ferrous ion concentration (mg L ⁻¹)
H ₂ O ₂	Concentration of hydrogen peroxide (mM)
k _f	Second order kinetic constant for color formation (AU ⁻¹ min ⁻¹)
k _d	Second order kinetic constant for color degradation (AU ⁻¹ min ⁻¹)
m	Reaction order for color degradation (–)
n	Reaction order for color formation (–)
Pa _o	Initial concentration of the aqueous solution (mg L ⁻¹)
t	Time (min)
t _{colo max}	Time when the water acquires maximum color (min)
T	Temperature (°C)
α _T	Pseudo kinetic constants for color degradation (=2 10 ⁻⁵ °C ⁻¹ AU ⁻¹ min ⁻¹)
α _{Fe}	Pseudo kinetic constants for color formation (=0.001 L ^{0.7} mg ^{-0.7} AU ⁻¹ min ⁻¹)
α _T	Pseudo kinetic constants for color formation (=10 ⁻⁵ °C ⁻¹ AU ⁻¹ min ⁻¹)
α _{Fecolor}	Conversion factor between the units of maximum color generated and the iron concentration employed (=0.1743 AU L ^{0.163} mg ^{-0.163})
α _{Fet}	Conversion factor between time and iron concentration (=84.07 min mg ^{0.716} L ^{-0.716})
α _{Tt}	Conversion factor between time and temperature (=80.515 min °C ^{-0.482})
ε _T	Color contributed by the matrix when oxidating 100 mg of paracetamol with 15 mmol of H ₂ O ₂ and 20 mg of Fe ²⁺ during color degradation (=0.0001 AU ⁻¹ min ⁻¹)
ε _T	Color contributed by the matrix when oxidating 100 mg of paracetamol with 15 mmol of H ₂ O ₂ and 20 mg of Fe ²⁺ during color formation (=9 10 ⁻⁵ AU ⁻¹ min ⁻¹)

exert over living organisms [9]. Presently, the Advance Oxidation Processes (AOPs) are the most commonly studied technologies for the elimination of these emerging contaminants [10,11]. The industrial implementation of these technologies is limited by the low concentration levels in which these contaminants are present in the waters, making difficult the identification of metabolites and transformation products [12].

Among AOPs, Fenton technology is generally seen as a viable alternative to be applied to waste waters that contain a wide spectrum of organic compounds of toxic nature and low biodegradability [13–16]. The efficiency of the process can be improved when ultraviolet light is employed with a wavelength between 300 and 650 nm. This is known as the photo-Fenton process [17–19]. In this reaction, the photochemical regeneration of the Fe²⁺ ions occurs. The main parameters that influence the efficacy and speed of the oxidation process are the pH, the concentrations of Fe²⁺ ion and H₂O₂, and the temperature. Reaction velocity tends to reach the maximum at a pH around 3.0. At higher pH, the velocity decreases due to the precipitation of iron in the

form of Fe(OH)₃. At pH < 2.0, Fe(OOH)²⁺ is produced which reacts with H₂O₂ at a reduced rate thus slowing down the generation of hydroxyl radicals. Fe²⁺ strongly bears on the reaction kinetics whereas H₂O₂ on its efficacy. An increase in temperature produces a rise in the rate of the oxidation reactions.

The analysis presented in this work is conducted considering that the mechanism of paracetamol oxidation happens along pathways that lead to the formation of acetamide, hydroquinone, 3-hydroxyaminoacetaminophen, 4-aminophenol and formic acid [20,21]. This mechanism is characterized by the preponderant role of para-substituted intermediates, which reduce the possibility of iron compound formation with the organic species in the reaction system [22–24]. On this basis, we have analyzed the oxidizing effect of the dosage of hydrogen peroxide, as well as the catalytic effect of ferrous sulfate and temperature in the kinetics of the paracetamol degradation pathways, when using a photo-Fenton process. Thus, we have mathematically characterized and modeled their kinetic effect in terms of the color, which indicates the quality of the water treated.

2. Materials and methods

2.1. Reaction system

Tests were performed with 100.0 mg/L synthetic solutions of paracetamol (Sigma Aldrich ≥99.0%). Ferrous ion (FeSO₄ 2H₂O Panreac 80%) was added as catalyst, followed by the addition of oxidant (H₂O₂ Foret 30%). At this point the reaction starts. These reactants are mixed in an 800 mL photocatalytic batch reactor, agitated by a magnetic stirrer, and fitted with a refrigerated quartz sheath provided by a 150W UV lamp (Heraeus TQ-150, Hg medium pressure, 85.8 V, 148.8 W, 1.79 A), with 95% transmission between 300 and 570 nm. Whereas, pH is maintained constant at 3.0 by adding solved NaOH and HCl. Temperature remains constant throughout the test by using a cryo-thermostatic bath (Frigiterm-10 Selecta).

2.2. Analysis methods

Solution color was measured at λ = 455 nm with an UV/Vis Spectrophotometer (Jenway 6305 Uvikon). The quantitative analysis of the organic compounds was carried out by High Performance Liquid Chromatography (HPLC) (Agilent Technologies 1200 Series). The column was connected to an UV/Vis spectrophotometer that detects paracetamol at λ = 254 nm, hydroquinone, catechol, resorcinol and *p*-benzoquinone at λ = 280 nm, pyrogallol a λ = 210 nm, and muconic acid a λ = 242 nm. The analyses were performed by manually injecting 20 μL samples into the column at a carrier flow rate of 1.0 mL/min. The carrier consisted of a MeOH/H₂O 20/80 mixture, flowing in a 25 cm long, 4.6 mm diameter, C₁₈ column (Bridge Waters). Turbidity was measured using a nephelometric turbidimeter (2100Q-Hach) [25].

3. Results and discussion

3.1. Effect of oxidant dosage

Fig. 1 shows the kinetics of the resulting water color after paracetamol oxidation using different concentrations of hydrogen peroxide. The oxidant concentration range was 0.6–15.0 M to oxidize 100.0 mg/L of paracetamol. Color formation after treatment shows the evolution of a reaction intermediate. Water acquires color in the initial minutes of reaction to reach a maximum after approximately 20 min. This reveals that the oxidant determines the degree of oxidation obtained with the treatment but it has no catalytic effect. The maximum color

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