

Research Article

Effect of the Fenton Technologies Applied to Oxidate Aqueous Solutions of Paracetamol

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***Corresponding author:** Natalia Villota Salazar, Department of Chemical and Environmental Engineering, University College of Engineering of Vitoria-Gasteiz, University of the Basque Country, Vitoria-Gasteiz, Spain**Received:** July 18, 2017; **Accepted:** August 21, 2017;**Published:** August 28, 2017**Abstract**

This work analyses the effects of the Advanced Oxidation Process (AOP) to oxidize paracetamol in the color and turbidity of the treated waters. Color induction kinetics is characterized by showing the evolution of a reaction intermediate. This fact allows the association of color with the formation of intermediates that include chromophore groups in their internal structure (i.e. pyrogallol, p-benzoquinone, hydroxyhydroquinone). Thus, by catalyzing the decomposition of hydroxide peroxide to radicals with more energetic activating agents, the effectiveness of the degradation of paracetamol to these species increases, generating intensive color and turbidity in the water. The results allow establishing that ultrasonic waves are usually catalysts more vigorous than ultraviolet light. On the other hand, when introducing iron ions in the system, we should consider the nature of the ferric species, since they can react with organic matter, generating highly colored complexes contributing turbidity to the water. The reactions were carried out at pH=3.0, which favors the oxidation performance by the presence of Fe (OH)²⁺ species. On the other hand, ferrous ions upon contact with UV light may lead to the creation of ferric hydroxides, which provide high turbidity and may precipitate, reducing the water color. This reaction is emphasised by increasing the intensity of the irradiation. US waves enhance the regeneration cycle of iron by inducing the formation of Fe (OOH)²⁺, which can lead to the formation of hydro (peroxo)-iron complexes.

Keywords: Color; Dark Fenton; Photo-Fenton; Paracetamol; Sono-Fenton; Turbidity**Introduction**

The so-called emerging pollutants (pesticides, petrol additives, pharmaceuticals and hygiene products, surfactants and surfactants, drugs, etc.) are compounds not regulated by current legislation (Directive 2013/39/UE, DMA Dir 2000/60/CE, Marine Strategy Dir. 2008/56/EC). The main characteristic of this kind of contaminants is that they do not need to persist in the environment to cause negative effects, since their elimination or transformation is compensated by their continuous contribution to the environment.

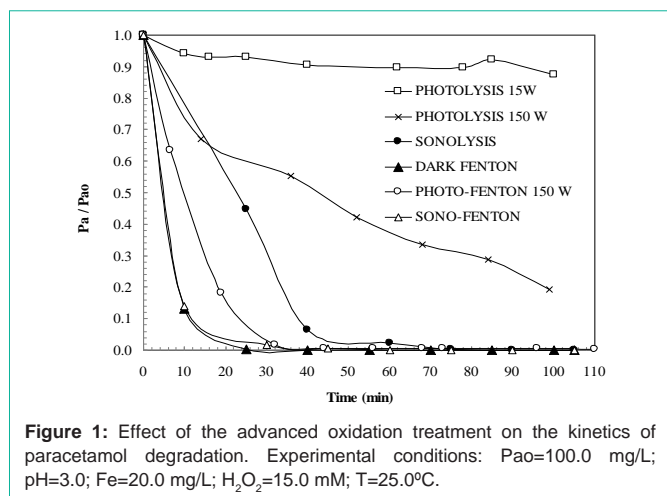
The presence of pharmaceutical chemicals in the aquatic environment has become a concern in developed countries. The main routes of these products in the environment are via human excrements, elimination of unused products and through agricultural use. A wide range of pharmaceuticals are detected in surface and groundwater, associated with wastewater disposal. These residues are transported to the water cycle through different routes. Moreover, wastewater treatment plants act as a gateway for these products to rivers, because many of these compounds are not actually retained in their processes. In addition, many veterinary pharmaceutical residues are discharged directly from farms into ditches or irrigation channels.

Finding of some of them (i.e. ibuprofen, paracetamol, diclofenac) in drinking water has raised a greater concern with these drugs. Depending on the physicochemical properties of these drugs, their metabolites, degradation products and soil characteristics that influence their transport and destination, these substances may

reach groundwater and contaminate aquifers, or are retained and accumulate, which can affect the ecosystem and humans through the food chain. Finding some of them (i.e. ibuprofen, paracetamol, diclofenac) in drinking water has raised a greater concern. The most widely used drugs in the world are analgesics, antihypertensive and antimicrobials. Among them, paracetamol stands out, detected in higher concentrations, 6-65 µg/L⁻¹ [1].

Currently, sewage treatment plants (WWTPs) are not designed to treat this type of compounds. Therefore, a high percentage of these materials and their metabolites reach the aquatic environment, making the effluents of the WWTPs one of the main emission sources. Consequently, notable concentrations of these pollutants are discharged daily into rivers, where their persistent presence may lead to damage. In addition, they can reach the water sources for consumption. For this reason, the focus of the studies carried out in recent years is to prevent these compounds from affecting drinking water.

An important characteristic of emerging pollutants is that there is still a great ignorance about their evolution in the aquatic environment, so as their long-term consequences. Sufficient data are not available for an appropriate assessment of their impact. Many of them are ubiquitous due to the wide use and, despite their evident bioactive nature; the effects of prolonged exposure to sub lethal levels are not estimated. Therefore, it is difficult to predict the effects they may have on health in human and aquatic organisms [2].

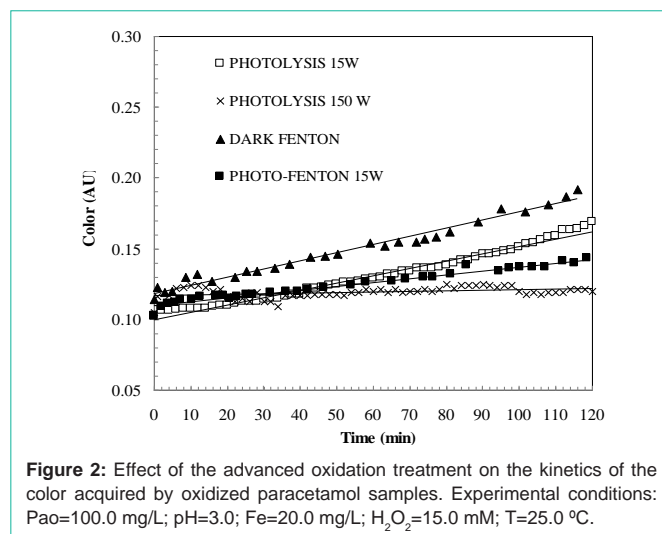


Development of efficient methods for the elimination of these pollutants is necessary, reducing the environmental contamination and the potential damage that they can exert on the living beings. The main challenge is to evaluate properly the different technologies to minimize the toxic risk to human health [3]. At present, Advanced Oxidation Processes (AOPs) are widely studied, applied in the elimination of these contaminants presented in both wastewater and drinking water [4,5].

The industrial implementation of these technologies is limited by the low levels of concentration of these pollutants. The evaluation of the risk induced by the discharge of wastewater in natural sources or irrigation channels is a challenge, since it presents the difficulty of identifying numerous contaminants, metabolites and transformation products. Therefore, it is necessary to modify current methods and to develop new systems to ensure the efficiency of POAs and the correct design of new processes [3,6,7].

Among AOPs, the Fenton reagent is considered a n interesting alternative applied in the treatment of wastewater from many industrial sectors [8,9]. This process is used to treat a wide spectrum of organic compounds of toxic nature to biodegradable compounds [10,11], due to its high efficiency generating hydroxyl radicals from the acidic decomposition of H_2O_2 by iron salts. The efficiency of the process can be improved by combining it with other agents such as sunlight, ultraviolet (UV) light, or ultrasound (US) waves. When irradiating UV/visible light between 300 and 650 nm, known as photo-Fenton process, the efficiency improves, creating a higher concentration of hydroxyl radicals and causing the regeneration of the catalyst [12,13].

One of the main disadvantages of this treatment comes from the need to use concentrations of dissolved iron salts higher than those established by the European Union Directives on water quality (EU Water Framework Directive, 2000/60/EC). This aspect requires the incorporation of physico-chemical coagulation-flocculation stages that eliminate or recover the iron salts. These processes generate as a waste large amounts of metal sludge that must be managed [14,15]. These issues have promoted new technologies based on the Fenton reagent [16,17], which allow minimizing the presence of iron species, without affecting the effectiveness of the treatment.



Between the available alternatives, the combination of Fenton process is proposed with low-frequency ultrasonic waves, known as sono-Fenton process [18-21]. This technology accelerates the regeneration of the iron species, which allows decreasing the dosage of catalyst. During the acoustic cavitation process, a large amount of energy is released, inducing the formation of oxidizing radicals. In turn, when using hydrogen peroxide as oxidizing agent, its sonolytic decomposition occurs, creating an additional amount of radicals [22]. Thus, the oxidation of the contaminants takes place via two mechanisms that run simultaneously: the thermal decomposition of the organic compound and the action of free radicals.

Based on this approach, the present work analyzes the oxidation of water contaminated with paracetamol, applying different treatments based on the Fenton reagent. Paracetamol concentration and several indicators of water quality are studied in order to characterize the effect of the different treatments on turbidity and color [23,24]. In this way, the oxidation mechanism of paracetamol can be related to the formation of species of colored nature and causing turbidity. The importance of establishing parameters indicative of the presence of these species is that they induce levels of toxicity in the water superior to the contaminant itself [25].

Materials and Methods

Reaction systems

The experimental essays utilizing the dark Fenton technology were carried out with 500mL of aqueous solutions of paracetamol ($C_8H_9NO_2$ Sigma-Aldrich, 99%), with an initial concentration $P_{a0}=100$ mg/L and iron catalyst $Fe=20.0$ mg/L added as ferrous ions ($FeSO_4 \cdot 2H_2O$, Panreac 80%). The reaction mixture was homogenized with a stirrer at 500rpm. Acidity was adjusted at $pH=3.0$ by dosing NaOH or HCl 0.2M (both Probus, 99.9%). Temperature was controlled at $T=25.0^\circ C$ using a cryo-thermostat bath of 1150 W (Selecta Frigiterm-10), pumping water through a cooling sheath. Oxidant (H_2O_2 , Foret 30%) was added at 15.0mM.

Experiments were carried out on a photo-Fenton system, performed by mixing the reactants under the same operating conditions in an 800 mL capacity photocatalytic reactor [25], provided

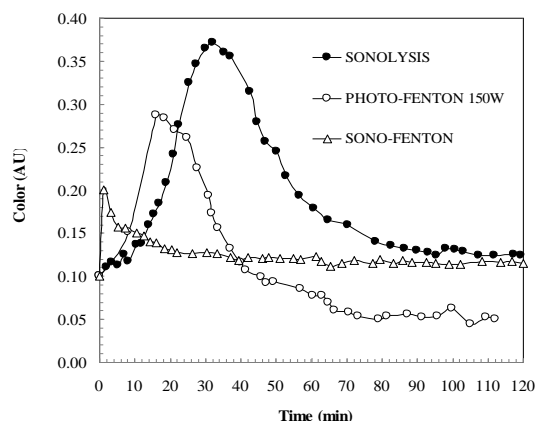


Figure 3: Effect of the advanced oxidation treatment on the kinetics of the color acquired by oxidized paracetamol samples. Experimental conditions: $P_{ao}=100.0$ mg/L; $pH=3.0$; $Fe=20.0$ mg/L; $H_2O_2=15.0$ mM; $T=25.0^\circ C$.

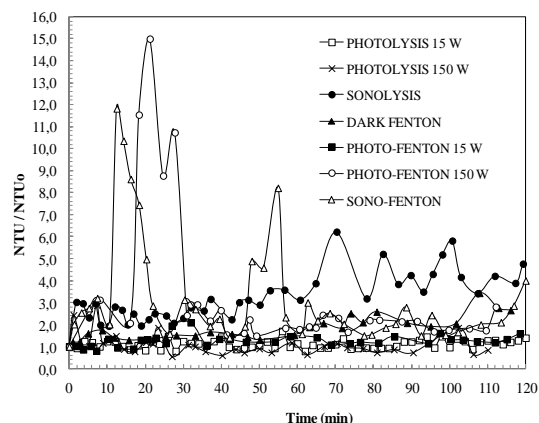


Figure 4: Effect of the advanced oxidation treatment on the turbidity kinetics of the oxidized paracetamol samples. Experimental conditions: $P_{ao}=100.0$ mg/L; $pH=3.0$; $Fe=20.0$ mg/L; $H_2O_2=15.0$ mM; $T=25.0^\circ C$.

with a cooled quartz sheath and an UV lamp. In order to compare the effect of the lamps power, tests were carried out using 150W and 15W UV lamps (Heraeus). Similarly, the tests were conducted in the absence of iron (photolysis).

On the other hand, the tests using the sono-Fenton technology were carried out in a sonolitic reactor [18] composed of a stirred tank of 1L, immersed in an ultrasonic bath of 6L (Bandelin electronic DK 156BP). The ultrasonic device had 720W US output power, 600W heat capacity and 35kHz frequency. A digital controller was coupled regulating the temperature and irradiation of the US waves (US power=0-0.72kW).

Operating methods

500mL of contaminated water was poured into the reactor, agitated at 175rpm with an electronic stirrer (Heidolph RZR 2101 electronic). All tests were performed in the absence of iron (sonolysis). The samples were analyzed during the first 120min of reaction and then they were stored during seven days, in order to measure the values corresponding to the steady state.

Analytical methods

Paracetamol concentration analysis was conducted with a High Resolution Liquid Chromatography equipment (Agilent Technologies 1200 Series), coupled to a spectrophotometer measuring at $\lambda=254$ nm. For this purpose, a Phenil C_{18} column 25cm long and 5.0 μ m diameter (Waters) was used, through which an eluent formed by a mixture of MeOH/ H_2O (20/80) passed with 1.0mL/min flow. A sample volume of 25.0 μ L was injected manually at a pressure of 3000-3300 psi and 25 $^\circ$ C. Solution turbidity (NTU) was monitored with a nephelometric turbidimeter (2100Qis Hach). The color was measured using a spectrophotometer UV/Vis (Uvikon Kontron) at $\lambda=455$ nm.

Results and Discussion

Effect of the advanced oxidation process on the kinetics of paracetamol degradation

Figure 1 shows the kinetics of paracetamol degradation when performing the different treatments under the same operating conditions. The results obtained show that when paracetamol is

degraded using the combination of UV light with hydrogen peroxide, in the absence of catalyst, oxidation takes place more slowly than in the rest of the treatments, requiring reaction times longer than two hours. It is noted the action of the power of the UV lamps, proving that when carrying out the treatment with the 15W lamp, degradation output is around 10%, whereas using the 150W lamp; output is near 80% after two hours of reaction. In the rest of the tests, paracetamol is completely degraded during the first hour of reaction. Moreover, it is observed that the combination of the ultrasonic waves with the Fenton reagent produces oxidation rates superior to ultraviolet light. Likewise, dark Fenton treatment allows obtaining high rates of paracetamol degradation. However, it is necessary to take into account the formation of oxidation paracetamol intermediates, since they are highly refractory species, demanding hard oxidizing conditions (combined with UV and US light) to decompose to biodegradable carboxylic acids [25].

Effect of AOP on the coloration of oxidized water

Figures 2 and 3 show the color kinetics analyzed during oxidation of paracetamol. The results present two clearly differentiated trends: On the one hand, when oxidizing paracetamol with low and high intensity photolysis, dark Fenton and low intensity photo-Fenton, the oxidized samples acquire a brown color that increases in a practically linear way during the course of the reaction (Figure 2).

The results allow confirming that the treatments producing less oxidizing capacity are the ones generating color in the water. This fact can be explained under the proposed mechanism for paracetamol degradation [25]. Analyzing its decomposition, the existence of minor oxidation pathways is verified, where the formation of colored species (benzoquinones) takes place. These compounds are created during the early stages of oxidation, and as they are minor species, they are formed only when applying treatments of low oxidative intensity.

When using greater oxidizing intensity of the AOPs, the decomposition of paracetamol occurs through pathways leading to the formation of highly refractory nitrogen intermediates, which degrade to colorless carboxylic acids. Therefore, these intermediates do not contribute significantly to the color of the oxidized samples. Moreover, the most notable of the analysis of the results is the

negligible effect of using iron in the treatment. Thus, iron itself does not determine the color of the treated water, but the color is conditioned by the oxidative efficacy of AOP.

On the other hand, there is another trend in the color evolution of the oxidized samples using ultrasonic waves and high-power ultraviolet light (Figure 3). These treatments generate high levels of color in the water. They have in common their color evolutions, which follow the corresponding to a degradation intermediate, where the water becomes colored during the first minutes of the reaction, until reaching a maximum intensity that depends on the type of treatment. Then, it decreases to steady state.

The interpretation for this behavior may be because US waves and UV light of 150W are agents that, in addition to degrading the organic pollutant load of the water, are intense enough to trigger parallel reactions of iron complexation. That is, they would provide the activation energy needed to give rise to the formation of metal complexes between the metal catalyst and the organic molecules present in the system [12,18]. In general, treatments with high power UV light lead to the formation of ferric hydroxide, which brings color and water turbidity. These species lead to precipitation reactions, causing that the treated water, once filtered, presents low level of color or even becomes colorless (Figure 3).

In the case of using ultrasonic waves, the H_2O_2 reacts with Fe^{2+} to generate OH^\bullet . The resulting Fe^{3+} can react with H_2O_2 to produce (hydro) peroxy iron complexes, which are subsequently dissociated by the effect of ultrasonic irradiation in Fe^{2+} and HO_2^\bullet . Given the molecular structure of the iron (hydro)peroxy species, it is natural to consider that they can react with the organic substrate containing ortho-substituted hydroxyl groups, so that the formation of colored metal complexes would occur [12].

The maximum color intensity in the waters appears when oxidizing paracetamol in the presence of hydrogen peroxide and ultrasounds, in the absence of iron. This result would indicate that the formation of condensation polymers of colored nature would occur, which would not happen when there are iron species. Iron, being quite active, reacts quickly with organic matter, generating metallic complexes, masking the organic substrate, thus preventing other reactions occurring from this matter. The color of those metal complexes would be of lesser intensity than the presented by the polymers generated through condensation reactions between the organic matter of the system itself. These molecules would have binding forces capable of resisting the action of the ultrasonic waves. Therefore, it seems suitable to analyze them indirectly through the measurement of the water color.

Effect of AOP on the turbidity of the oxidized water

Figure 4 shows the turbidity kinetics analyzed during paracetamol degradation, which follow a tendency similar to the obtained when analyzing the water color. In this way, turbidity hardly undergoes variations when using photolysis, dark Fenton and low-intensity photo-Fenton treatments. However, when performing oxidation using high-intensity photo-Fenton, sonolysis and sono-Fenton treatments, some isolated increases in water turbidity are detected. Moreover, by comparing the results, in the case of degrading acetaminophen-type contaminants, only color can be considered as

an indicative parameter of the output achieved with the treatment. On the other hand, studies performed with other organic compounds containing phenol-type contaminants [23,24], demonstrate that turbidity is a suitable parameter to detect, in a general way, the formation of species affecting the quality of treated water. However, in the case of paracetamol, turbidity monitoring is not indicative.

Conclusion

The combination of the ultrasonic waves with the Fenton reagent allows degradation rates of paracetamol higher than when using UV light. The combination of UV light with hydrogen peroxide, in the absence of catalyst, requires reaction times longer than two hours to achieve degradation outputs of 10% when using a 15W UV lamp, and 80% when using a 150W lamp. With the other treatments tested, paracetamol degrades completely during the first hour of reaction.

The kinetics of color analyzed during the oxidation of paracetamol allows observing two clearly differentiated trends. On the one hand, when oxidation is carried out using low-oxidative treatments, i.e. photolysis, dark Fenton and photo-Fenton of 15W, the samples acquire a brown color that increases linearly during the reaction. This is due to the formation of colored intermediate species (benzoquinones). As a remark, iron does not determine the color of the treated water, but the color is determined by the oxidative efficacy of AOP.

Oxidized samples with US waves and UV light of 150W present higher levels of color, which shows the evolution of degradation intermediate. This behavior may be due to agents capable of activating iron complexing reactions. The treatments with high power UV light give rise to the formation of ferric hydroxides, which contribute color and turbidity. These species lead to precipitation reactions, causing the treated water to become colorless. In the case of using ultrasound waves, (hydro) peroxides iron complexes can be generated, which can react with the organic substrate producing colored metal complexes.

The maximum color intensity happens by using hydrogen peroxide and ultrasound waves, in the absence of iron. This result could indicate the formation of condensation polymers of colored nature, which would not appear when there exist iron species in the system, since metal complexes appear and mask the organic matter.

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