

Induction of color in wastewaters oxidized by sono-Fenton technology

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Abstract Color induction in oxidized phenolic waters with Fenton-like reagent is favored by working at pH=3.0, similarly to the case of UV or dark Fenton operation. In this condition, FeOH^{2+} species is predominant and its presence would generate an additional supply of hydroxyl radicals, which would increase the degradation yield of phenol to colored by-products (quinones). The maximum intensity of color created in the water is obtained when carrying out the treatment with 4 mol H_2O_2 /mol phenol and 40 mg Fe^{2+} /L. When using UV or dark Fenton light, the highest degree of color is achieved with 20 mg Fe^{2+} /L. This difference may indicate a change in the reaction stoichiometry of iron species with the organic matter. By operating with ultrasound waves, the formation of (hydro)peroxo iron complexes may occur, due to the interaction of the $\text{Fe}(\text{OOH})^{2+}$ species with catechol or with carboxylic acids like 2,5-dioxo-3-hexenedioic, which would generate color in the water. The rate of decomposition of FeOH^{2+} and $\text{Fe}(\text{OOH})^{2+}$ species to ferrous ions is increased by using ratios around 0.025 kW L/mg Fe, observing an increase in the kinetics of color formation and degradation.

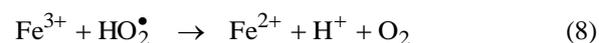
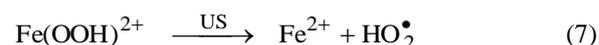
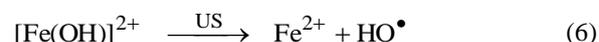
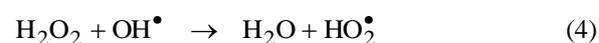
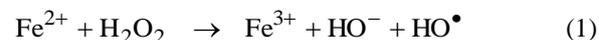
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1. Introduction

During the decomposition of organic pollutants using Fenton reagent, high color appears in the treated wastewaters (Mijangos *et al.*, 2006). This phenomenon occurs in a similar way when combined with UV light or ultrasound waves (Villota *et al.*, 2016a; Villota *et al.*, 2016b). However, the intensity of the color varies depending on the activator used to carry out the treatment. Phenol has been considered as a model compound for studying the nature of color-causing species in waters degraded with ultrasonic irradiation. Phenol is decomposed through species of strongly colored nature (quinones) and intermediates that may react with the iron species present in solution (Villota *et al.*, 2007). Finally, the mechanism leads to the formation of colorless carboxylic acids, which degrade to CO_2 (Devlin and Harris, 1984). These species, generated during the early stages of the mechanism, cause high toxicity to the water (Zazo *et al.*, 2007; De Luis *et al.*, 2001), so that color could be considered an indicator of the purification degree of the

treated effluent. In addition, it is a parameter included within the European Water Framework Directive.

Simultaneously, a cyclic mechanism of regeneration of the iron catalyst occurs, where the ferrous ions are oxidized to ferric ones during the production of hydroxyl radicals (Eq. 1). These ferric ions react with the residual hydrogen peroxide (Eq. 2) and with water molecules (Eq. 5), generating metal complexes (Eqs. 2 and 5), which can interact with the organic matter present in the system. These complexes are degraded under the action of ultrasonic waves to ferrous ions (Bagal and Gogate, 2014), which reactivate again the Fenton reaction (Eqs. 6 and 7). By combining Fenton reactions with ultrasonic waves there is an additional contribution of radicals, due to the self-decomposition of hydrogen peroxide (Eq. 3). This phenomenon increases the oxidation output (Grčić *et al.*, 2012).



2. Materials and methods

2.1. Reaction system

Oxidation of contaminated water with $\text{C}_0=100.0$ mg/L phenol (Scharlau 90%) is carried out using sono-Fenton technology. The tests are run in a sonolytic reactor consisting of a 1L stirred tank that is immersed in a 6L

capacity ultrasonic bath (Bandelin electronic DK 156 BP). The equipment has an ultrasonic output of 720W, heat power of 600W, frequency of 35kHz, a current consumption of 3.4 A and a nominal voltage of 230V. The reactor is connected with a digital controller to regulate the temperature and the irradiation power of the ultrasonic waves (US=0-0.72 kW).

To get started, 500 mL of contaminated water is poured into the reactor, agitated at 175 rpm with an electronic rod stirrer (Heidolph RZR 2101 electronic). The pH is maintained constant by rationing 0.05M NaOH with an automatic pump (Watson Marlow 400) connected to an electronic pH meter (Kent EIL 9142). The temperature is kept uniform at 25.0°C using a cryo-thermostat bath of 1150 watts (Selecta Frigiterm-10). The catalyst (FeSO₄ 2H₂O, Panreac 80%) is added in the form of ferrous ions Fe 0-50.0 mg/L. Once the mixture is homogenized, the oxidant is added (Foret 30%), starting the reaction. The oxidant dosage is expressed as an oxidizing molar ratio to phenol, R=0-14 mol H₂O₂/mol C₆ H₆O. Next, samples are analyzed during the first 120 min of reaction. Finally, the samples are stored for seven days to measure their corresponding steady state values.

2.2. Analytical methods

The concentration of phenol and its degradation intermediates is analyzed using a High Resolution Liquid Chromatography (Agilent Technologies 1200 Series) equipment, coupled to a UV/Vis spectrophotometer that detects compounds of aromatic nature at $\lambda=210$ nm, 242 nm and 280 nm. A Phenil C18 column 5.0 μ m in diameter (Waters) is utilized, through which an eluent is circulated, that consists of a mixture of MeOH/H₂O (20/80) with a flow rate of 1.0 mL/min. A sample volume of 25.0 μ L is injected at a pressure of 3000-3300 psia, and 25°C. The color of the samples is measured with a UV/Vis (Uvikon Kontron) spectrophotometer at $\lambda=455$ nm.

3. Results and discussion

3.1. pH effect

Figure 1 shows the color that the oxidized waters acquire as a function of the operating pH. The tests were conducted

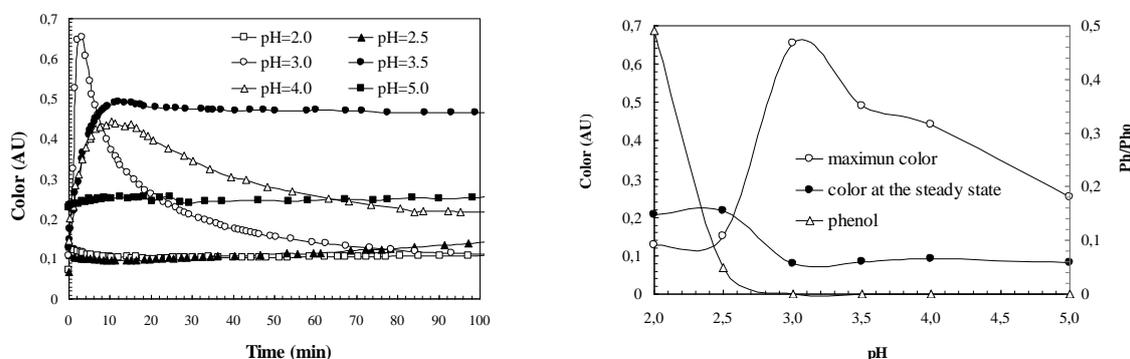


Figure 1. Effect of pH on the color induction of aqueous solutions of oxidized phenol with a sono-Fenton treatment. Experimental conditions: Ph₀=100.0 mg/L; R=14.0 mol oxidant/mol phenol; Fe=20.0 mg/L; T=25.0 °C; US=0.72 kW

using the stoichiometric ratio R=14.0, which allows degradation of the phenol to carbon dioxide and a concentration of catalyst Fe=20.0 mg/L, which favors the oxidation performance (Villota *et al.*, 2015; Villota *et al.*, 2007). When oxidation begins, the catalyst added in the form of ferrous ions evolves to higher oxidation states depending on pH. Operating at pH=2.0-2.5 the water does not undergo significant color variations, because the catalyst exists in the form of ferrous ions of a colorless nature.

By increasing the pH to 3.0, which favors the oxidation efficiency, the color induction shows the kinetic evolution of reaction intermediates. During the first 3 minutes of reaction, the water acquires color until reaching a maximum value (Color=0.65 AU). Then, the color slowly fades to steady state (Color=0.08 AU). This evolution would be associated to the regeneration cycle of iron where, in a first stage, the colorless ferrous ions would be oxidized to ferric ions, which in turn, would give rise to the FeOH²⁺ and Fe (OOH)²⁺ species that can react with the organic matter, resulting in the formation of strongly colored metal complexes. Next, in a second step, these species would be slowly reduced to colorless ferrous ions.

Operating at pH between 3.5 and 4.0, the water acquires color more slowly, until it reaches a maximum at 12 min, which decreases slowly for several days to steady state. In this case, the ferrous catalyst is oxidized to ferric species that decrease the activation of the Fenton reactions. On the other hand, at these levels of acidity, the regeneration of the catalyst is disfavored. Working at pH=5.0, iron is in its oxidized form and can induce formation and precipitation reactions of hydroxides (Bergendahl *et al.*, 2003).

When evaluating the color induced in the water, it is verified that at pH=3.0 a maximum is reached, similarly to the case of applying UV or dark Fenton (Neyens and Baeyens, 2003). This would be caused by an additional contribution of hydroxyl radicals from the decomposition of the FeOH²⁺ complex, which is the majority iron species formed at pH=3.0 (Pozdnyakov *et al.*, 2000). Considering the steady state, when operating with pH values greater than 3.0, phenol degrades completely, obtaining treated colorless water. At values below pH=3.0,

the output of phenol degradation decreases as the medium is acidified, with a residual color around 0.21 AU remaining.

3.2. Effect of oxidant dosage

Figure 2 displays the maximum and residual color induced in the waters as a function of the oxidant dosage used in the treatment. As the oxidant ratio increases to $R=4.0$, the color intensity in the water is intensified, reaching its highest value (0.76 AU). This concentration would lead to the degradation of phenol to muconic acid (Villota *et al.*, 2014a). Working with greater ratios, the maximum color generated diminishes linearly at the rate of 0.0115 A/mol oxidant. It is noteworthy that studies in photo-Fenton and dark Fenton systems have obtained similar results (Villota *et al.*, 2016b; Mijangos *et al.*, 2006). The residual color of the treated waters in the steady state shows that as the oxidant dosage is increased, degradation byproducts are generated, enlarging the color intensity of the water, presenting a maximum level at $R=4.0$. From this ratio, the color decreases progressively as the oxidant load enlarges.

Moreover, phenol degradation byproducts have been analyzed in order to identify the nature of the species that contribute color to the water. It is proved that operating at $R=4.0$, although none of the species identified have a maximum concentration, a notable presence of catechol is detected. This result could indicate that the formation of metallic complexes with the organic matter would determine the kinetics of the color evolution. Given the nature of the iron species generated by the action of ultrasound waves, it is proved to consider the formation of (hydro)peroxo iron (II) complexes by reacting $\text{Fe}(\text{OOH})^{2+}$ species with catechol, which would lead to the production of muconic acid (Kovaleva and Lipscomb, 2008). On the other hand, the creation of (hydro)peroxo iron (III) could

occur with carboxylic acids having an ortho-substituted keto group (type 2,5-dioxo-3-hexenedioic acid). Operating at ratios greater than $R=10$, which would lead to the formation of malonic acid, a colorless water is obtained.

3.3. Effect of catalyst dosage

Figure 3 presents the catalytic effect of the iron used in the treatment on the induction of color. The concentration of ferrous ions determines the kinetics constants of formation and color degradation. Furthermore, it intervenes in the reaction mechanism, establishing the color intensity that the water acquires. As the iron dosage increases, the color induction in the water increases by 0.0134 AU L/mg Fe min. The maximum color intensity that the water acquires increases with the iron concentration, showing that using $\text{Fe}=40.0$ mg/L the water reaches its highest color (0.736 AU). Nevertheless, the results obtained in studies performed with UV light or dark Fenton, obtain the peak color intensity using $\text{Fe}=20.0$ mg/L (Villota *et al.*, 2016b; Mijangos *et al.*, 2006). This fact may indicate a change in the nature of the iron species interacting with the organic load of the medium. Ferric ions would give rise to the formation of FeOH^{2+} and $\text{Fe}(\text{OOH})^{2+}$, which could react with the organic matter present in the system, resulting in the formation of complex (hydro)peroxides. The initial concentration of ferrous ions that generates the maximum color intensity in the water, 0.4 mg Fe^{2+} /mg phenol, could indicate the stoichiometric iron ratio that would participate in the formation of these structures. Once the maximum color intensity is reached, the water will fade following second-order kinetics until it gains a colorless appearance. It is verified that when carrying out the oxidation with $\text{Fe}=2.0$ mg/L a refractory color remains in the steady state, that can be produced by the presence of catechol.

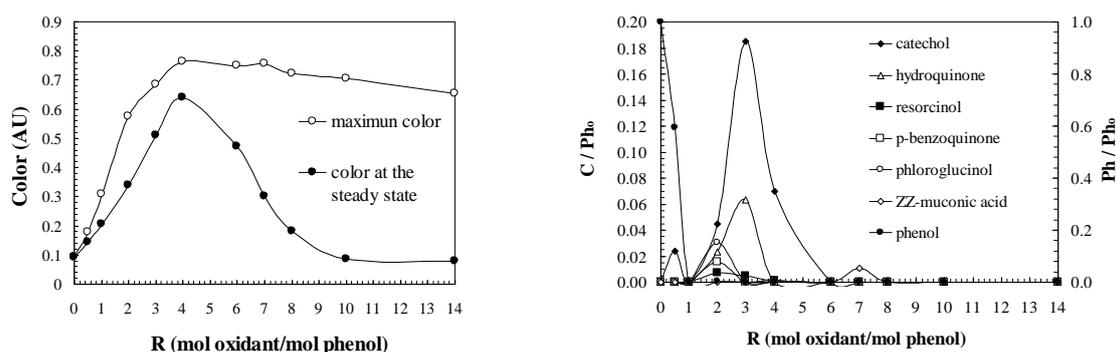


Figure 2. Effect of oxidant dosing on the color induction of oxidized waters with a sono-Fenton treatment. Experimental conditions: $\text{Ph}_0=100.0$ mg/L; $\text{pH}=3.0$; $\text{Fe}=20.0$ mg/L; $T=25.0$ °C; $\text{US}=0.72$ kW.

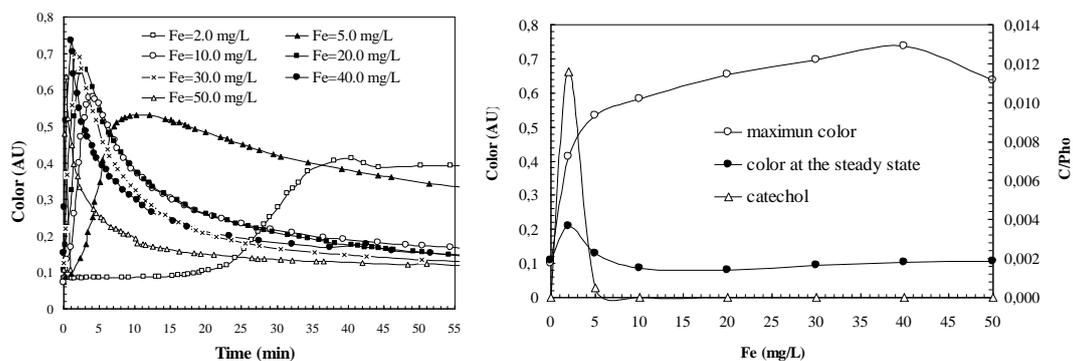


Figure 3. Effect of the catalyst dosage on the color induction of oxidized water using a sono-Fenton treatment. Experimental conditions: $Ph_0=100.0$ mg/L; $pH=3.0$; $R=14.0$ mol oxidant/mol phenol; $T=25.0$ °C; $US=0.72$ kW.

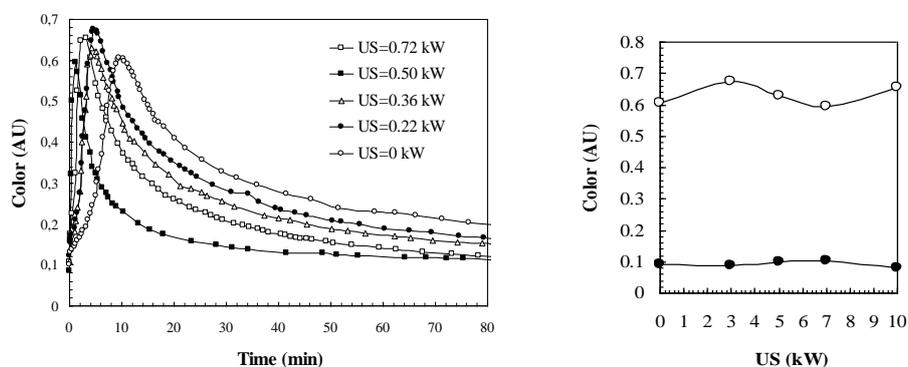


Figure 4. Effect of the ultrasonic irradiation power on the color induction of oxidized water with a sono-Fenton treatment. Experimental conditions: $Ph_0=100.0$ mg/L; $pH=3.0$; $R=14.0$ mol oxidant/mol phenol; $T=25.0$ °C; $Fe=20.0$ mg/L.

3.4. Effect of the irradiation power

Figure 4 shows that the irradiation power of the ultrasound waves exerts a catalytic effect on the color induction. Both the rate of color formation and water discoloration rise when using a higher irradiation power. It should be noted that, in the case of operating with $US=0.50$ kW, the celerity of color kinetics is increased. This fact would indicate that the power of the ultrasonic waves affect the reaction mechanism, proving that order ratios about 0.025 kW L/mg Fe can enlarge the rate of decomposition of iron species $FeOH^{2+}$ and $Fe(OOH)^{2+}$ to ferrous ions (Bagal and Gogate, 2014; Grčić *et al.*, 2012).

4. Conclusions

Color induction in oxidized waters with sono-Fenton technology is favored 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 the phenol to colored by-products (quinones). On the other hand, 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 color in the water. The rate of

decomposition of the $FeOH^{2+}$ and $Fe(OOH)^{2+}$ species to ferrous ions is enlarged by using ratios on the order of 0.025 kW L/mg Fe, presenting an increase in the kinetics of formation and color degradation. The maximum intensity of color created in the water is obtained when carrying out the treatment with 4 mol H_2O_2 /mol phenol and 40 mg Fe^{2+} /L.

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