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Oxidation of acetaminophen by ultrasound waves and H2O2 combined technology

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Abstract. This study analyses the colour acquired by oxidizing paracetamol aqueous samples through the combined US/H_2O_2 technology. When operating with only the action of the waves [US]=1.0 kWh/mmol $C_8H_9NO_2$, the water acquires progressively hue according to a ratio of 0.0004 AU/min, with a degradation output of 14%. Working under these conditions, the presence of hydroquinone, muconic acid and formic acid was evaluated. Colour formation presents a maximum intensity when water containing paracetamol is degraded using molar ratios of 1.5 mol H_2O_2/mol $C_8H_9NO_2$. This dosage leads to the formation of benzoquinone, as well as muconic and formic acids, reaching an efficiency of 30%. Oxidazing with 6.0 mol H_2O_2/mol $C_8H_9NO_2$, colour formation occurs slowly during the first hour of reaction, leading to the formation of benzoquinone, hydroquinone, acetamide, phoroglucinol and formic and muconic acids. This last one presents a molecular structure that is prone to reacting with other species that are present in the system forming complexes.

Keywords: Paracetamol, colour, hydrogen peroxide, reaction intermediates, ultrasounds waves

1. Introduction

Emerging water contaminants are arousing great interest due to their increasing consumption. This research focuses on the the degradation of paracetamol by US/H_2O_2. This medication is an anti-inflammatory and analgesic. When ingested, metabolites are generated in the body that are excreted along with their residual active ingredients. Although the human organism is capable of metabolizing up to 90%, it excretes between 3 and 5%, which allows to estimate that the amount of this pharmaceuticals reaching the water treatment plants worldwide is around 300-600 ton/year (Villota et al., 2019). These pollutants do not completely degrade in WWTPs, so they are discharged into rivers and accumulated in the environment (Villota et al., 2016). In order to decompose this kind of contaminants, the viability of the AOPs is currently studied (Villota et al., 2018).

2. Materials and methods

Wastewater solutions were prepared with paracetamol ($[Pa]_0$=100.0 mg/L). Tests were conducted at different oxidant dosages ($[H_2O_2]_0$=0-15 mM), operating in a sonolytic reactor that consists of an one-liter stirred tank reactor submerged in an ultrasonic bath with a 6.0 L capacity (Bandelin Electronic DK 156 BP). The US power was 720 W, heating 600 W and frequency 35 kHz. The equipment was fitted with a digital controller that permits regulating the bath temperature and the US radiation from 10 to 100%. Meanwhile, pH was kept constant at 3.0 and temperature at 25.0ºC.

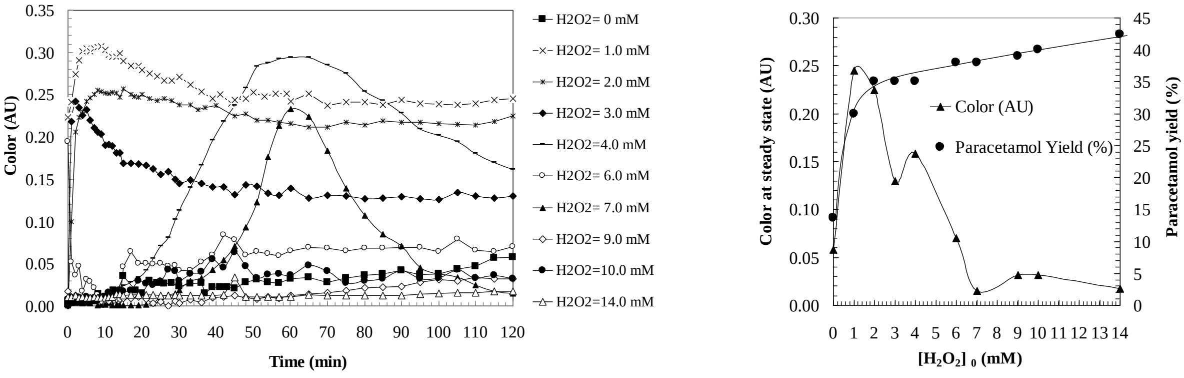
3. Results and discussion

Fig. 1a shows the tone acquired by aqueous samples of oxidized paracetamol using the combined technology US/H_2O_2. When operating in the absence of hydrogen peroxide, applying only the action of US waves, water gradually takes hue according to a ratio of 0.0004 AU/min. This effect is because US can degrade the paracetamol molecule to 14% of the initial concentration (Fig. 1b). This decomposition is sufficient for the formation of reaction intermediates of tinted nature (Villota et al., 2018). By combining the US waves with the action of H_2O_2, important alterations in the colour occur, verifying that the water acquires tone up to a maximum intensity. Then, it decreases until reaching a steady value. When dosing initial concentrations of $[H_2O_2]_0$=1.0 mM, the maximum induction of tint in the water happens during the first 5 min of reaction, lasting a recalcitrant residue of 0.245 AU. This dose of oxidant corresponds to a molar ratio of 1.5 mol H_2O_2/mol $C_8H_9NO_2$, leading to degradation outputs around 30%, which indicates the presence of a degradation pathway of paracetamol towards the formation of coloured intermediates.

It should be noted that there is no linear relationship between the formation of colour and the concentration of oxidant utilized. The experimental results allow to consider three types of tendencies in the kinetics of colour formation, refering to the reaction time in which the water shows the maximum intensity of hue. Operating with doses aroud $[H_2O_2]_0$=1.0-3.0mM, when increasing the oxidant dose, the intensity of the tone is lower, because the greater the oxidant action, the higher the degradation of the coloured intermediates to colourless species. On the other hand, conducting with $H_2O_2]_0$=6.0-14.0 mM generates smaller tint levels, whose formation progressively increase along time, according to ratios between 0.0003-0.0113 A/min. Otherwise, applying $[H_2O_2]_0$=4.0 and 7.0 mM, the colour formation happens during the first 60 min of reaction, reaching a maximum. Then, the water becomes discoloured, observing that with 7 mM of oxidant it follows a kinetics of quite symmetrical tendency to the formation stage. Conducting at 4.0 mM, a recalcitrant residue of 0.16 AU persists. This molar ratio corresponds to a 6 mol H_2O_2/mol $C_8H_9NO_2$, that leads to the degradation of 35% of paracetamol. This fact would indicate the stoichiometry of a second degradation pathway of paracetamol through coloured intermediates. Fig. 2 dysplays an analysis of these intermediates when operating with stoichiometric ratios of 1.5 y 6.0 mol H_2O_2/mol $C_8H_9NO_2$, which lead to colour creation.

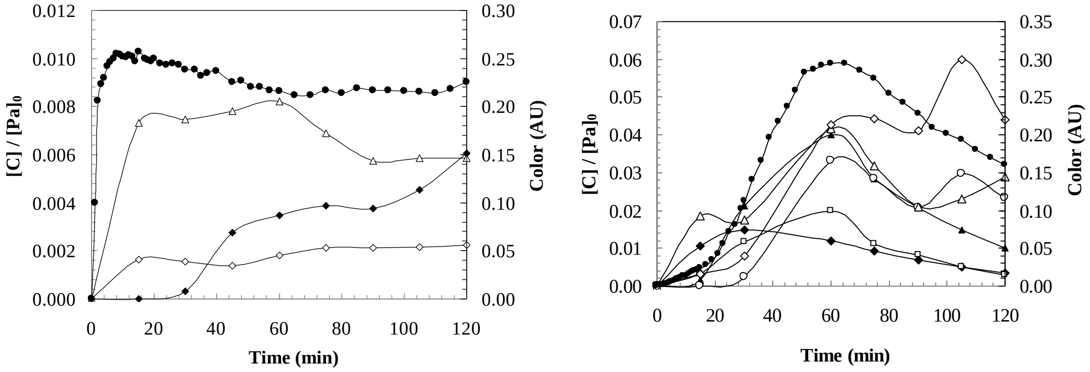
4. Conclusions

Colour generation presents its maximum intensity when water containing paracetamol is degraded using 1.5 mol H_2O_2/mol $C_8H_9NO_2$. This dosage leads to the formation of benzoquinone, as well as muconic acid and formic acids. A second molar ratio of H_2O_2/mol $C_8H_9NO_2$ is detected conducting to colour formation more slowly for approximately 60 minutes, creating benzoquinone, hydroquinone, acetamide and phloroglucinol, as well as formic and muconic acids.



a) **b)**

Figure 1. a) Effect of oxidant dosage on the colour changes during the paracetamol oxidation by US/H_2O_2. **b)** Effect of hydrogen peroxide on paracetamol yield (%) and colour of water treated. Experimental conditions: $[Pa]_0$=100.0 mg/L; pH=3.0; [US]=0.72 kWh; T=25.0ºC.



a) **b)**

Figure 2. Oxidation intermediates causing colour operating at **a)** $[H_2O_2]_0$=2.0 mM. **b)** $[H_2O_2]_0$=4.0 mM**.** Experimental conditions: $[Pa]_0$=100.0 mg/L; pH=3.0; [US]=0.72 kWh; T=25ºC. Legend: ● colour; ♦ benzoquinone; ▲ hydroquinone; ○ acetamide; Δ formic acid; □ phloroglucinol; ◊ muconic acid.

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