

# Effect of hydrogen peroxide on caffeine oxidation by sono-Fenton technology

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## Abstract

Oxidation of waters containing 100.0 mg L<sup>-1</sup> of caffeine was conducted by a sono-Fenton treatment employing an ultrasound power of 720W at pH=3.0 and T=25°C. The oxidizing action of hydrogen peroxide was studied in a range between [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>=0-250.0 mM, using iron ratios of 0.7 mol Fe<sup>2+</sup>/mol C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>. The oxidation of caffeine was fitted to second order kinetics, obtaining removals of 98% when dosing 485 mol H<sub>2</sub>O<sub>2</sub>/mol C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>. During the oxidation, the water acquired a strong brown colour at the same time as there was a strong increase in turbidity and degree of aromaticity. The interaction of (hydro)peroxo-iron complexes with the byproducts of caffeine degradation (1,3,7-trimethyluric acid, theobromine, paraxanthine, theophylline) generated supramolecular structures responsible for this phenomenon, being 116 mol H<sub>2</sub>O<sub>2</sub>/mol C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>, the relationship that induced colour and aromaticity, while the formation of turbidity was favoured by using 29 and 116 mol H<sub>2</sub>O<sub>2</sub>/mol C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>.

**Keywords:** aromaticity, caffeine, colour, sono-Fenton, turbidity

## 1. Introduction

Caffeine is a natural purine that is found in coffee, tea, cocoa and cola nuts. Caffeine has antimutagenic, antifungal, antiviral and antioxidant properties. The main degradation by-product is 1,3,7-trimethyluric acid (8-hydroxycin), although byproducts such as theobromine, paraxanthine and theophylline have been detected. The demethylation and hydroxylation reactions of caffeine mainly produce 1-methyluric acid and 1,3-dimethyluric acid (Telo and Vieira 1997).

## 2. Materials and Methods

Samples of caffeine aqueous solutions ([C]<sub>0</sub>=100.0 mg/L, Guinama, 99.97%) with iron concentration [Fe]<sub>0</sub>=20.0 mg/L (FeSO<sub>4</sub>·7H<sub>2</sub>O, Panreac 99.0%) were added to a 1 L jacketed agitated reactor introduced in a sonolytic tank irradiated by US-720W (Bandelin Electronic DK 156 BP). All assays were carried out

under a constant temperature of 25°C and a pH=3. The reaction was started when hydrogen peroxide was added in a range of [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>=0-250.0 mM, (Panreac, 30% w/v). The concentration of caffeine is determined by High Resolution Liquid Chromatography (Agilent Technologies 1200 Series) measuring at 254 nm. A C<sub>18</sub> phenyl (Waters) is employed, using a MeOH/H<sub>2</sub>O (60/40) at a flow of 1.0 mL/min. Solution turbidity is measured with a nephelometric turbidimeter (2100Qis Hach), whereas colour and aromaticity are measured with a spectrophotometer UV/Vis (Uvikon Kontron) at 455 nm and 254 nm.

## 3. Results and Discussion

Fig. 1a shows that the oxidation reaction of caffeine using the sono-Fenton reagent fits to second order kinetic model (Eq. 1), where [C] is the caffeine concentration (mg L<sup>-1</sup>), t is the time (min) and k<sub>Ca</sub> is the second order kinetic constant for caffeine degradation (L mg<sup>-1</sup> min<sup>-1</sup>). The integration of matter balance, led to the kinetic equation of caffeine oxidation (Eq. 2). Table 1 shows the estimated values. The oxidation of caffeine elapsed slowly until it reaches to stationary state. It was proven that using iron ratios of 0.7 mol Fe<sup>2+</sup>/mol C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>, 98% removals were obtained operating with oxidant ratios of 485 mol H<sub>2</sub>O<sub>2</sub>/mol C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub>. Similar removals were obtained by carrying out the treatment under the same conditions, but without using oxidant. This effect would indicate that the water of the solution would give rise to cavitations phenomena, obtaining with 1.08 x 10<sup>5</sup> mol H<sub>2</sub>O/mol C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub> an oxidizing potential similar to hydrogen peroxide.

$$-\frac{d[C]}{dt} = k_{Ca} [C]^{n=2} \quad (1)$$

$$[C] = \frac{[C]_0}{1 + [C]_0 k_{Ca} t} \quad (2)$$

$$-\frac{d[\text{Color}]}{dt} = k_{\text{color}} [\text{Color}]^{n_{\text{color}}} \quad (3)$$

$$[\text{Color}] = [\text{Color}]_0 \left[ \frac{k_{\text{color}}}{(1 - n_{\text{color}}) t} \right]^{\frac{1}{(1 - n_{\text{color}})}} \quad (4)$$

**Table 1.** Kinetic parameters estimated for caffeine oxidation by sono-Fenton treatment.

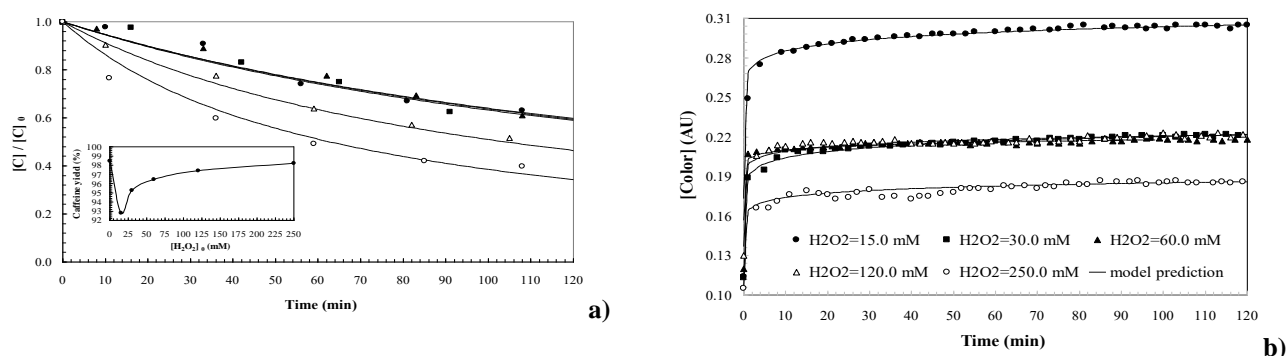
$[\text{H}_2\text{O}_2]_0$ mM	$k_{\text{Ca}}$ $\text{min}^{-1}$	$k_{\text{color}}$ $\text{min}^{-1}$	$n_{\text{color}}$ -
15.0	$3.3 \times 10^{-5}$	$2.59 \times 10^{-20}$	-36
30.0	$2.7 \times 10^{-5}$	$6.00 \times 10^{-21}$	-29
60.0	$2.5 \times 10^{-5}$	$1.26 \times 10^{-42}$	-62
120.0	$5.0 \times 10^{-5}$	$2.58 \times 10^{-29}$	-42
250.0	$1.1 \times 10^{-4}$	$2.96 \times 10^{-28}$	-36

During the oxidation of caffeine, the water acquires a strong brown colour (Fig. 1b). Colour formation is a consequence of an oxidation complex system involves both species of inorganic nature as (hydro)peroxo iron complexes) generated by the sono-Fenton process (Villota et al., 2017) and by-products of caffeine degradation (Telo and Vieira, 1997). During caffeine degradation it was experienced an increase in the degree of aromaticity, which could indicate that it degrades to

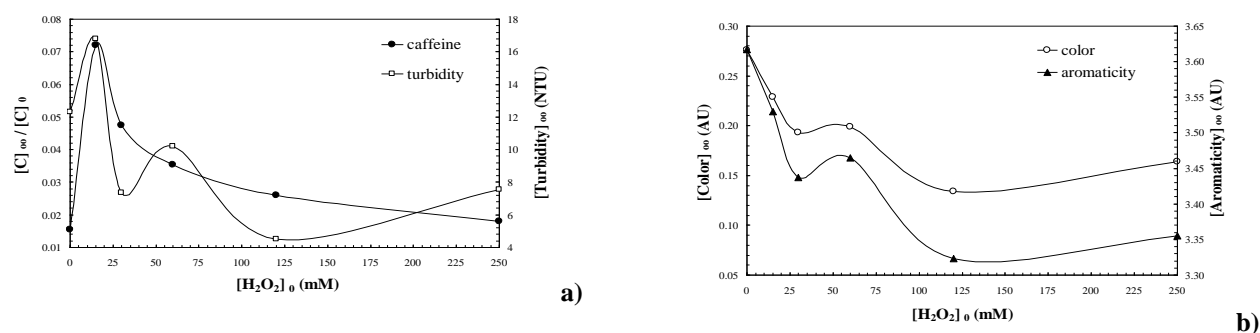
species of aromatic nature that would contain chromospheres groups in their internal structure. The interaction of these species with (hydro)peroxo complexes would generate supramolecular structures that would contribute to a greater water coloration. This complex reaction system would be fitted to high kinetic orders (Table 1) and of negative value, due to the fact that each caffeine molecule ( $[\text{Color}]_0=0.12$  AU) produces the generation of a high number of coloured intermediates species, according to Eqs. 3-4.

#### 4. Conclusions

It was found that an increase in the concentration of oxidant in the caffeine oxidation increased the degradation efficiency. The oxidant stoichiometric ratio for colour formation in oxidized waters, corresponds to 116 mol  $\text{H}_2\text{O}_2$ /mol  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$  ( $[\text{H}_2\text{O}_2]_0=60.0$  mM). This relationship favours the oxidation of caffeine through the formation of species with aromatic nature. Two stoichiometric relationships have been estimated that lead to oxidation through the formation of species that produce turbidity in water: 29 and 116 mol  $\text{H}_2\text{O}_2$ /mol  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$  ( $[\text{H}_2\text{O}_2]_0=15.0$  and 60.0 mM).



**Figure 1.** Model predictions for caffeine oxidation by sono-Fenton treatment for: **a)** Caffeine degradation **b)** Colour changes.  $[\text{C}]_0=100.0$  mg/L;  $\text{pH}=3.0$ ;  $[\text{Fe}]_0=20.0$  mg/L;  $[\text{US}]=720\text{W}$ ;  $T=25^\circ\text{C}$ .



**Figure 2.** Effect of hydrogen peroxide on **a)** caffeine concentration and turbidity **b)** Colour and aromaticity.  $[\text{C}]_0=100.0$  mg/L;  $\text{pH}=3.0$ ;  $[\text{Fe}]_0=20.0$  mg/L;  $[\text{US}]=720\text{W}$ ;  $T=25^\circ\text{C}$ ,  $t=5$  days.

#### References

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