

Caffeine oxidation by sono-Fenton treatment

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Abstract. Oxidation of waters containing caffeine was conducted by a sono-Fenton treatment employing an ultrasound power of 720 W at pH=3.0 and T=25°C. The catalytic action of ferrous ion was studied in a range of [Fe]=0-100.0 mg/L and oxidant concentrations between [H₂O₂]=0-250.0 mM. The oxidation of caffeine was fitted to second order kinetic model, with the oxidation kinetic constant showing a linear dependence with iron dosage, obtaining removals of 98% when dosing 485 mol H₂O₂/mol C₈H₁₀N₄O₂. 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, being 116 mol H₂O₂/mol C₈H₁₀N₄O₂, the relationship that induced colour and aromaticity, while the formation of turbidity was favoured by using 29 and 116 mol H₂O₂/mol C₈H₁₀N₄O₂.

Keywords: aromaticity, caffeine, color, turbidity, sono-Fenton

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]₀=100.0 mg/L, Guinama, 99.97%) with iron concentration [Fe]₀=0-100.0 mg/L (FeSO₄·7H₂O, 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=3.0. The reaction was started when

hydrogen peroxide was added in a range of [H₂O₂]=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 C₁₈ phenyl (Waters) is employed, using a MeOH/H₂O (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

3.1. Effect of hydrogen peroxide

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⁻¹), t is the time (min) and k_{ca} is the second order kinetic constant for caffeine degradation (L mg⁻¹ min⁻¹). 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 Fe²⁺/mol C₈H₁₀N₄O₂, 98% removals were obtained operating with oxidant ratios of 485 mol H₂O₂/mol C₈H₁₀N₄O₂. 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 10⁵ mol H₂O/mol C₈H₁₀N₄O₂ an oxidizing potential similar to hydrogen peroxide.

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

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

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

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

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

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

3.2. Effect of iron catalyst

The oxidation of caffeine was fitted to second order kinetics, as shown in Eqs. 5-7, where the oxidation kinetic constant is function of the iron dosage used to carry out the treatment (Eq. 7). This result let to quantify the catalytic effect of iron.

$$-\frac{d[\text{C}]}{dt} = k_{\text{Ca}} [\text{C}]^{n=2} \quad (5)$$

$$[\text{C}] = \frac{[\text{C}]_0}{1 + [\text{C}]_0 k_{\text{Ca}} t} \quad (6)$$

$$k_{\text{Ca}} = 4.0 \times 10^{-5} + 5.0 \times 10^{-6} [\text{Fe}]_0 \quad (r^2=0.9899) \quad (7)$$

During oxidation of caffeine solutions treated by sono-Fenton ($\text{H}_2\text{O}_2/\text{US}/\text{Fe}^{2+}$), it was observed that the water acquired a yellow-brown colour, along with the turbidity increased and aromaticity degree. Fig. 1b shows the turbidity formation kinetics, mathematically modelled according to the Eqs. 8-9. The estimated kinetic parameters are shown in Table 2. Analyzing the kinetic reaction orders it was verified that depended on the

concentration of iron used. This is due to iron would participate in the mechanism of caffeine degradation, reacting with the organic load present in the system through the formation of (hydro)peroxide iron complexes. (Villota et al., 2017). These reactions would determine the number of species of different nature that would form as degradation byproducts.

$$-\frac{d[\text{NTU}]}{dt} = k_{\text{NTU}} [\text{NTU}]^{n_{\text{NTU}}} \quad (8)$$

$$[\text{NTU}] = [\text{NTU}]_0 \left[\frac{k_{\text{NTU}}}{(1 - n_{\text{NTU}}) t} \right]^{\frac{1}{(1 - n_{\text{NTU}})}} \quad (9)$$

Table 2. Kinetic parameters estimated for caffeine oxidation by sono-Fenton treatment.

$[\text{Fe}^{2+}]_0$ mM	k_{Ca} min ⁻¹	k_{NTU} min ⁻¹	n_{NTU} -
2.0	3.2×10^{-5}	75.2	-3
5.0	8.5×10^{-5}	1.06	-2
10.0	1.0×10^{-4}	0.470	-1
20.0	1.1×10^{-4}	5.2×10^{11}	-12
100.0	5.0×10^{-4}	5.6×10^{11}	-6

Fig. 3 shows the effect of different iron concentrations on caffeine removal, aromaticity, turbidity and colour. Using a molar ratio of 1 mol Fe^{2+} : 0.5 mol $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$: 250 mol H_2O_2 : 720W the oxidation of caffeine was promoted towards the formation of coloured species, highly aromatic, that was provided high turbidity to water. Operating under these conditions, caffeine was degraded a 96.5%. With an iron dosage of 100 mg L⁻¹, high levels of turbidity were formed in the water during the reaction first two hours. However, turbidity decreased in the stationary state because excess iron induced by precipitation reactions.

4. Conclusions

The evolution of caffeine oxidation by sono-Fenton treatment ($\text{H}_2\text{O}_2/\text{US}/\text{Fe}^{2+}$) was fitted to second order kinetics, where it was found that oxidation kinetic constant was function of the iron dosage. During oxidation, the water became yellow-brown in colour, at the same time that increased turbidity and the aromaticity degree. Iron catalyst could give rise to reaction mechanism with organic matter through the formation of (hydro)peroxide iron complexes. A molar ratio of 1 mol Fe^{2+} : 0.5 mol $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$: 250 mol H_2O_2 : 720W promoted the formation of coloured species that generated high turbidity in water.

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 H_2O_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 H₂O₂/mol C₈H₁₀N₄O₂ ([H₂O₂]₀=15.0 and 60.0 mM).

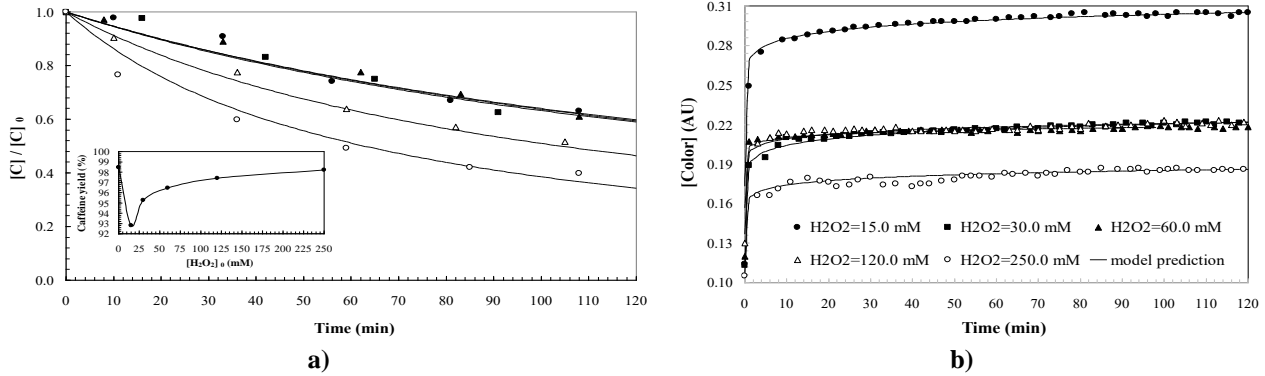


Figure 1. Model predictions for caffeine oxidation by sono-Fenton treatment for: **a)** Caffeine degradation **b)** Colour changes. [C]₀=100.0 mg/L; pH=3.0; [Fe]₀=20.0 mg/L; [US]=720W; T=25°C.

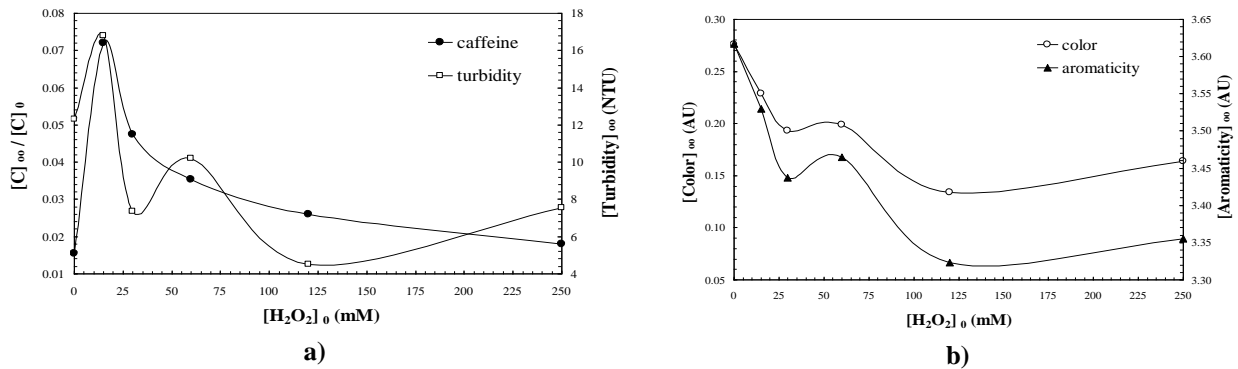


Figure 2. Effect of hydrogen peroxide on **a)** caffeine concentration and turbidity **b)** Colour and aromaticity. [C]₀=100.0 mg/L; pH=3.0; [Fe]₀=20.0 mg/L; [US]=720W; T=25°C, t=5 days.

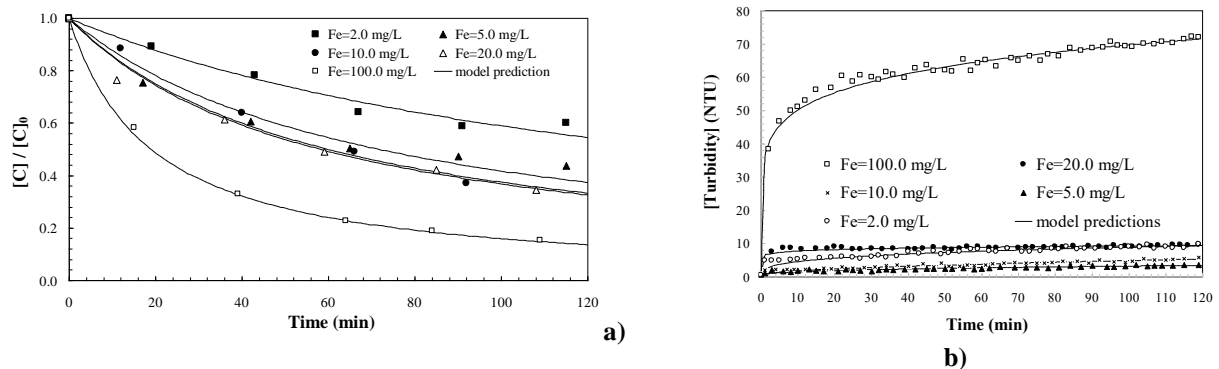


Figure 3. Model predictions for caffeine oxidation by sono-Fenton treatment for: **a)** Caffeine degradation **b)** Turbidity changes. [C]₀=100.0 mg/L; pH=3.0; [H₂O₂]₀=250.0 mM; [US]=720W; T=25°C.

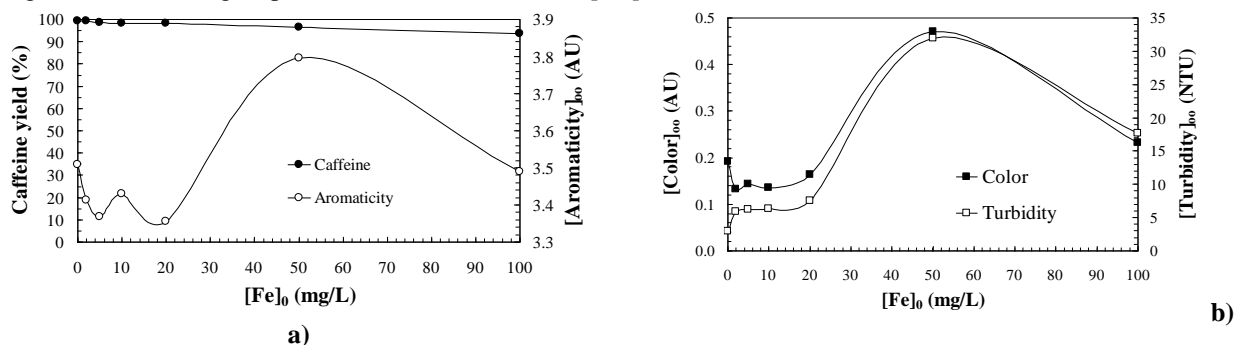


Figure 4. Effect of ferrous ion catalyst on **a)** caffeine yield (%) and water aromaticity **b)** Colour and turbidity. $[C]_0=100.0$ mg/L; pH=3.0; $[H_2O_2]_0=250.0$ mM; [US]=720W; T=25°C, t=7 days.

References

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