

# Effect of iron catalyst 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 catalytic action of ferrous ion was studied in a range of [Fe<sup>2+</sup>]<sub>0</sub>=0-100.0 mg L<sup>-1</sup>, using oxidant ratios of [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>=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. During oxidation, the water acquired yellow-brown colour, along with an increase of turbidity and aromaticity degree. This is due to byproducts formation of uric acid-derived that has strongly aromatic structures that contain chromophore groups. Iron could give rise to a reaction mechanism with organic matter through the formation of (hydro)peroxo iron complexes. The molar ratio of 1 mol Fe<sup>2+</sup>: 0.5 mol C<sub>8</sub>H<sub>10</sub>N<sub>4</sub>O<sub>2</sub> : 250 mol H<sub>2</sub>O<sub>2</sub> : 720W promotes the formation of coloured species that generate high turbidity in the water.

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

## 1. Introduction

Caffeine is an alkaloid from the xanthenes group that found of natural form in coffee beans, tea leaves, cola nuts, which are used to flavour cola drinks and cocoa pods, which are used to make chocolate products. Also, synthetic caffeine is added to some medicines (analgesics), foods and beverages (energy). Only 1% is excreted in the urine, and its main metabolites are methyl derivatives of uric acid, such as 1,3,7-trimethyluric acid, 1-methyluric acid and 1,3-dimethyluric acid, as well as theobromine, paraxanthine and theophylline. (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 established for each assay [Fe]<sub>0</sub>=0-100.0 mg L<sup>-1</sup> (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 [H<sub>2</sub>O<sub>2</sub>]<sub>0</sub>=250.0 mM (Panreac, 30% w/v). Caffeine concentration is determined by High Resolution Liquid Chromatography (Agilent Technologies 1200 Series) measuring at 254 nm, using a C<sub>18</sub> phenyl column (Waters) by MeOH/H<sub>2</sub>O (60/40). Solution turbidity is measured with a nephelometric turbidimeter (2100Qis Hach). Colour and aromaticity are measured at 455 nm and 254 nm by a spectrophotometer UV/Vis (Uvikon Kontron).

## 3. Results and Discussion

The oxidation of caffeine was fitted to second order kinetics, as shown in Eqs. 1-2, where the oxidation kinetic constant is function of the iron dosage used to carry out the treatment (Eq. 3). This result let to quantify the catalytic effect of iron.

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

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

$$k_{Ca} = 4.0 \times 10^{-5} + 5.0 \times 10^{-6} [Fe]_0 \quad (r^2=0.9899) \quad (3)$$

During oxidation of caffeine solutions treated by sono-Fenton (H<sub>2</sub>O<sub>2</sub>/US/Fe<sup>2+</sup>), 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 Eqs. 4-5. Estimated kinetic parameters are shown in Table 1. 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)peroxo iron complexes. (Villota et al., 2017). These reactions would determine the number of species of different nature that would form as degradation byproducts.

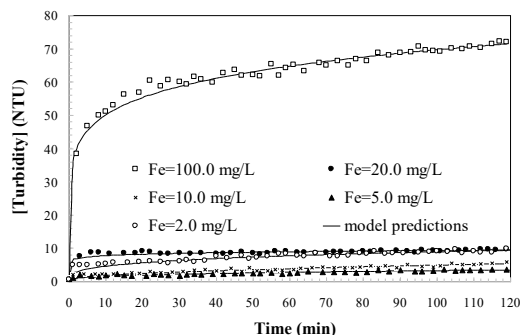
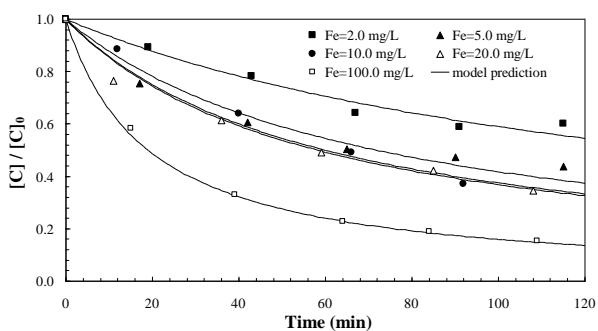
$$-\frac{d[\text{NTU}]}{dt} = k_{\text{NTU}} [\text{NTU}]^n \quad (4)$$

$$[\text{NTU}] = [\text{NTU}]_0 \left[ \frac{k_{\text{NTU}}}{(1-n_{\text{NTU}})t} \right]^{\frac{1}{(1-n_{\text{NTU}})}} \quad (5)$$

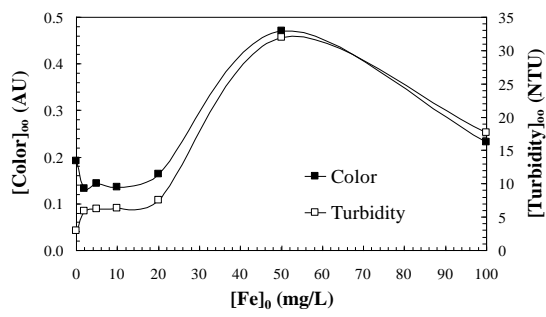
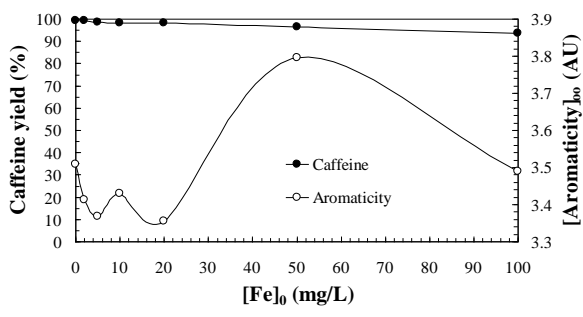
**Table 1.** Kinetic parameters estimated for caffeine oxidation by sono-Fenton treatment.

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

Fig. 2 shows the effect of different iron concentrations on caffeine removal, aromaticity, turbidity and colour. Using a molar ratio of 1.0 mol  $\text{Fe}^{2+}$  : 0.5 mol  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$  : 250.0 mol  $\text{H}_2\text{O}_2$  : 720W the oxidation of caffeine was promoted towards the formation of coloured species, highly



**Figure 1.** Model predictions for caffeine oxidation by sono-Fenton treatment for: **a)** Caffeine degradation **b)** Turbidity changes.  $[\text{C}]_0=100.0$  mg/L;  $\text{pH}=3.0$ ;  $[\text{H}_2\text{O}_2]_0=250.0$  mM;  $[\text{US}]=720\text{W}$ ;  $T=25^\circ\text{C}$ .



**Figure 2.** Effect of ferrous ion catalyst on **a)** caffeine yield (%) and water aromaticity **b)** Colour and turbidity.  $[\text{C}]_0=100.0$  mg/L;  $\text{pH}=3.0$ ;  $[\text{H}_2\text{O}_2]_0=250.0$  mM;  $[\text{US}]=720\text{W}$ ;  $T=25^\circ\text{C}$ ,  $t=7$  days.

## References

Telo J.P. and Vieira A.J.S.C. (1997), Mechanism of free radical oxidation of caffeine in aqueous solution. *Journal of the Chemical Society, Perkin Transactions 2*, **9**, 1755-1757.

aromatic, that was provided high turbidity to water. Operating under these conditions, caffeine was degraded a 96.5%. With an iron dosage of  $100.0$  mg  $\text{L}^{-1}$ , 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)peroxo iron complexes. A molar ratio of 1 mol  $\text{Fe}^{2+}$ :0.5 mol  $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2$ :250 mol  $\text{H}_2\text{O}_2$ :720W promoted the formation of coloured species that generated high turbidity in water.