

Fenton reagent in combination with UV light and ultrasound waves applied for caffeine oxidation

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Abstract

The oxidation of aqueous caffeine solutions ($[Ca]_0=100.0$ mg L⁻¹) was analyzed, operating at pH=3.0 and 25°C using different AOPs, which combine the Fenton reagent ($[H_2O_2]_0=15.0$ mM and $[Fe^{2+}]_0=20.0$ mg L⁻¹) with low power UV light (15W), medium (150W), and high (720 W). The Fenton reagent, combined with 150W UV light, was the most energetic treatment, proving that at 20 min it completely degrades caffeine and 80% of the water aromaticity. This hard oxidative process is accompanied by a high oxygen consumption, up to concentrations of $[DO]=0.9$ mg L⁻¹ at the time when the caffeine contained in the water is completely degraded. On the other hand, 150W UV light is the only treatment capable of decreasing the concentration of total solids dissolved in water, according to a ratio of 0.0035 min⁻¹. US waves allow degrading caffeine by 35%. This treatment leads to the emission of high oxygen concentrations ($[DO]=20.0$ mg L⁻¹), which subsequently decreases along time. The UV lamp of 15W allows degrading caffeine by 12%, but does not affect the rest of the parameters analyzed.

Keywords: AOPs; caffeine; Fenton reagent; ultrasounds waves; ultraviolet light

1. Introduction

Caffeine is an emerging contaminant that is detected both in various aquatic environments systems (superficial and underground) and in wastewater treatment plants (both in secondary and tertiary treatments), as it is a common component of various pharmaceutical products, processed food and soft drinks (Grandclement et al., 2017). The average global consumption of caffeine ranges around 70 mg/person/day (Anis and Sajjad, 2019). It should be considered that the effects of caffeine are not limited to the aquatic environment, but also affect the reuse of wastewater treated in WWTPs, since its accumulation can cause contamination of the entire food chain.

This situation has stimulate the study of effective treatments to degrade the emerging contaminants, where advanced oxidation processes (AOP) arise, based on the Fenton reaction, ultraviolet UV and US ultrasound radiation. In accordance with European Union directives 2013/39/EU, the processes based on the Fenton reagent

are considered the main treatment to carry out the degradation of these pollutants.

2. Materials and Methods

The oxidation of aqueous solutions containing 100.0 mg L⁻¹ of caffeine (Guinama, 99.97%) were conducted testing different AOPs, combining initial H₂O₂ dosages of 15.0 mM (Panreac, 30% w/v), and ferrous iron concentrations of 20.0 mg L⁻¹ (FeSO₄ 7H₂O Panreac, 99.0%) with 720 W ultrasonic power in a sonolytic reactor (Bandelin Electronic DK 156 BP), as well as the ultraviolet light action in a photocatalytic reactor that allows to operate with UV lamps of low pressure 15W (Heraeus, monocromatic 254 nm) and Hg medium pressure 150W (Heraeus, with 95% transmission between 300 and 570 nm). pH was kept steady at 3.0 and temperature at 25.0°C.

3. Results and Discussion

Fig. 1a) shows the results obtained by using different AOPs to degrade caffeine ($[Ca]$, mg L⁻¹). The low power UV light 15W and the US waves do not achieve degrading completely caffeine, obtaining yields around 12% and 40% respectively. The rest of treatments lead to their complete degradation, but they differ in the necessary reaction time. The best results are accomplished by combining Fenton reagent with UV 150W, which allows to obtain almost 100% outputs after 20 minutes of reaction. The combination of the Fenton reagent with the US waves requires much extended reaction times, longer than two hours. The rest of the treatments require order times around two hours.

Fig. 1b) displays that the only treatment capable of degrading the aromaticity of water is the UV 150W, obtaining yields of 80% at 90 min. When combined with the Fenton reagent, the reaction rate increases, achieving these results at 20 min. The plain Fenton reagent induces much slower kinetics. Fig. 1c) shows that only UV 150W decreases the concentration of total dissolved solids in the water. After an induction time of 30 min, the concentration of TDS diminishes linearly, according to a ratio of 0.0035 min⁻¹.

Fig. 1d) shows the concentration of oxygen contained in the water ([DO], mg L⁻¹). Using Fenton reagent and low power UV light 15W, oxygen is produced according to a ratio $R_{\text{Fenton/UV 15W}}=0.0582 \text{ mg L}^{-1} \text{ min}^{-1}$; $R_{\text{Fenton}}=0.0278 \text{ mg L}^{-1} \text{ min}^{-1}$. The UV light of 15W does not affect the reactions in which oxygen participates. By increasing the UV power to 150W, oxygen consumption occurs, depending on the loss of aromaticity of the water. Oxygen exhaustion is enhanced by combining UV 150W with the Fenton reagent. Thus, the highest rate of oxygen consumption occurs up to concentrations of [DO]=0.9 mg L⁻¹, at the time when caffeine is completely degraded. The ultrasound waves produce the emission of high oxygen levels during the first 15 min of reaction, until reaching a maximum value ([OD] = 20.0 mg L⁻¹), which

subsequently decreases along time.

4. Conclusions

Fenton reagent combined with UV=150W, allows to completely degrade caffeine and 80% of the aromaticity of water with reaction times shorter than 30 min. This process happens simultaneously with 91% consumption of the initial oxygen contained in the water. UV=150W is the only treatment capable of decreasing total dissolved solids in water, according to a ratio of 0.0035 min⁻¹. The US waves produce the emission of high DO rates about 0.042 mol O₂ mol⁻¹ H₂O₂.

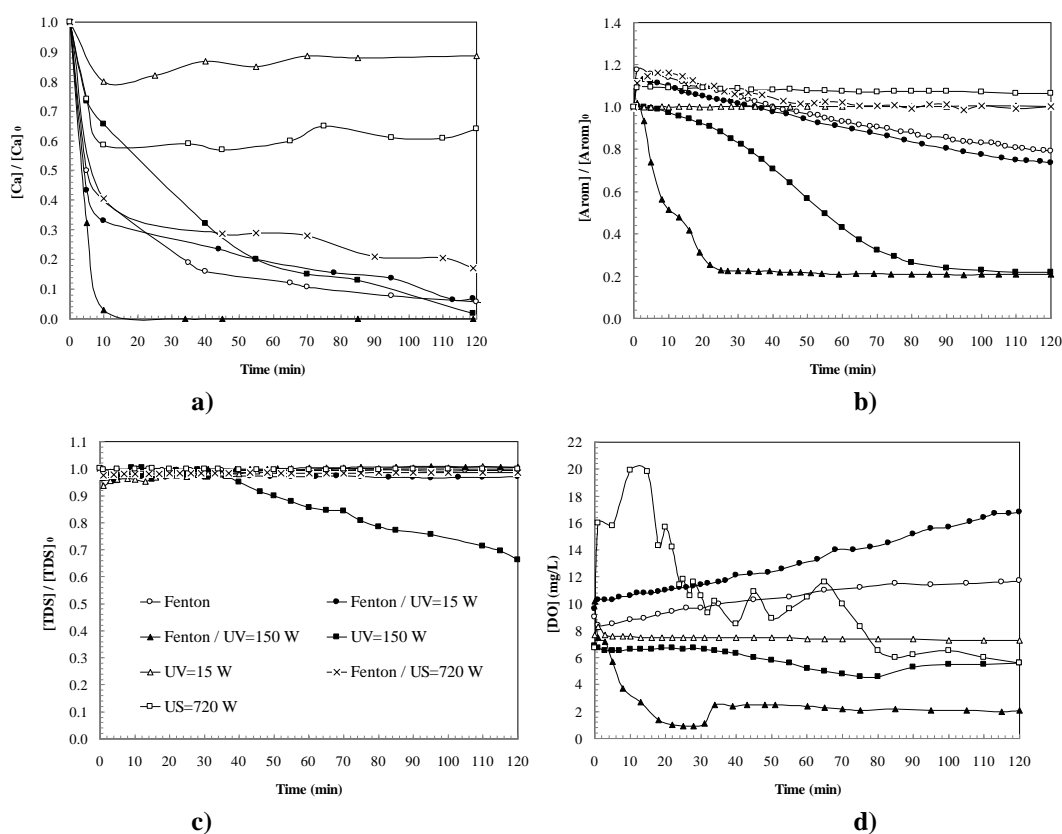


Figure 1. Effect of AOPs on **a)** caffeine oxidation ([Ca], mg L⁻¹) **b)** Water-aromaticity ([Arom], AU) **c)** Total dissolved solids ([TDS], mg L⁻¹) **d)** Dissolved oxygen ([DO], mg L⁻¹). Experimental conditions: [Ca]₀=100.0 mg L⁻¹; pH=3.0; [H₂O₂]₀=15.0 mM; [Fe²⁺]₀=20.0 mg L⁻¹; T=25.0°C.

References

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