Colour changes during the carbamazepine oxidation by photo-Fenton

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Abstract
Oxidation of waters containing 50.0 mg L^{-1} of carbamazepine was conducted by a photo-Fenton reagent employing a UV lamp of 150W, at pH=3.0 and T=40°C. The oxidising action of hydrogen peroxide was studied in a range between $[H_2O_2]_0$=0-15.0 mM. When applying stoichiometric ratios of 2 mol $C_{15}H_{12}N_2O$:20 mol H_2O_2:1.8 mol Fe^{2+}, the maximum formation of colour (0.381 AU) is promoted. The colour may be generated by by-products of degradation of carbamazepine that have chromophore groups in its internal structure, such as oxo and dioxo-carbazepines, which would generate colour during the first minutes of oxidation, while the formation of acridones would slowly induce colour to the water.
Keywords: acridone, carbamazepine, colour, oxo-carbazepine, photo-Fenton

1. Introduction

Carbamazepine is prescribed for the treatment of neurological diseases such as epilepsy, depression or bipolar disorder. It is a resistant contaminant detected in the effluents of wastewater treatment plants and in certain surface waters. Due to its potential effect on aquatic microorganisms and human health, there is a raising concern about its presence in those waters.

2. Materials and Methods

Samples of carbamazepine aqueous solutions ($[C]_0$=50.0 mg/L, Fagron 99.1%) were studied in a photocatalytic 1.0 L reactor provided with an UV-150W mercury lamp of medium pressure (Heraeus, 95% transmission between 300 and 570 nm). Reactions began adding the iron catalyst as ferrous ion $[Fe]_0$=10.0 mg/L ($FeSO_4$ $7H_2O$, Panreac 99.0%) and the oxidant dosage for each set of experiments, which varied between $[H_2O_2]_0$=0-15.0 mM, (Panreac, 30% w/v). All experiments were conducted at 40°C and pH=3.0.

3. Results and Discussion

During the oxidation process of aqueous samples of carbamazepine, it is found that the treated water acquires brown colour during the first 20 minutes of reaction (Fig. 1a). The intensity of colour depends on the dose of oxidant used in the treatment. It is verified that, when employing a stoichiometric ratio 2 mol $C_{15}H_{12}N_2O$:20 mol H_2O_2, colour appears in the water according to a ratio of 0.0086 AU min^{-1}, until reaching its maximum intensity 0.353 AU at 30 min of reaction. Then, the colour continues increasing, but much more slowly (0.0005 AU min^{-1}) until reaching the steady state.

This result would indicate the existence of two stages in the formation of colour based on the degradation mechanism of carbamazepine proposed in Fig. 1c. The first one would occur during the first steps of the degradation of carbamazepine, and would involve the formation of bright colour species. This phase would involve hydroxylation reactions, through the electrophilic attack of the hydroxyl radicals to the olefinic double bond in the central and lateral heterocyclic rings of carbamazepine. This hydroxylation leads to the formation of the corresponding hydroxylated carbamazepines. The action of the hydroxyl radicals can produce a new hydroxylation of the molecule, resulting in the formation of cis and trans-dihydroxy-carbamazepine (Lei et al., 2019). The formation of the uncommon cis isomer appears to be smaller than that of the trans (Golan-Rozen et al., 2015). The oxidation of these species would lead to the formation of colour precursors (oxo and dioxo-carbazepines) due to the presence of chromophore groups in their molecular structure. During the second stage, the creation of additional species that coexist with those generated in the previous step, which provide lower colour to water, would take place. In this case, the generation of degradation by-products of the carbazepine species can be considered, generating hydroxylated acridine species and the corresponding acridones, which cause the additional colour contribution.

By increasing the oxidant concentration between $[H_2O_2]_0$=5.0-15.0 mM, colour is formed during the first 20 min of the reaction, up to a maximum value. Then, it degrades until reaching a residual amount about 0.12 AU that lasts a long time. Both the maximum colour (Eq. 1) and the time (Eq. 2) in which the water acquires the maximum intensity of colour are a function of the oxidant dose used:

$$Colour_{max}=0.3759 - 0.011\ [H_2O_2]_0 \quad (r^2=0.9988) \qquad (1)$$

$$t_{max}=58.31\ [H_2O_2]_0 - 0.8813 \quad (r^2=0.9916) \qquad (2)$$

Fig. 1b shows the effect of the oxidant concentration used in some of the parameters that indicate the quality of the treated water. Thus, it is found that the oxidation of carbamazepine occurs through the formation of strongly coloured species when dosing $[H_2O_2]_0$=2.0 mM. When applying concentrations higher than $[H_2O_2]_0$=5.0 mM, a recalcitrant colour persists in the water about 0.13 AU, generated by degradation by-products that possess chromophoric groups in their internal structure. In the case of turbidity, the trend changes, verifying that the water treated with $[H_2O_2]_0$=2.0 mM presents high turbidity (19.5 NTU). Meanwhile, when dosing $H_2O_2]_0$=5.0 the process degrades the species causing the turbidity, presenting values about 1.3 NTU. Increasing the dose above $[H_2O_2]_0$=8.0 mM, the mechanism of degradation leads to the formation of new species producing turbidity, leaving a permanent residue of 5.1 NTU. On the other hand, the concentration of TDS (Total Dissolved Solids) remains practically steady in all the treated samples, because the tests were carried out with a constant iron concentration of 10.0 mg L^{-1} and pH=3.0. Moreover, it is proved that when dosing $[H_2O_2]_0$=11.0 mM, the reactions are induced, as well as the release of oxygen that remains dissolved in the water (DO).

4. Conclusion

Aqueous solutions of carbamazepine are oxidized by means of photo-Fenton reagent at pH=3.0 and UV power of 150 W. It is found that the oxidized samples acquire a strong colour when employing a stoichiometric ratio of 2 mol $C_{15}H_{12}N_2O$:20 mol H_2O_2:1.8 mol Fe^{2+}. The colour may be generated by by-products of degradation of carbamazepine that contain chromophoric groups in their internal structure, such as oxo and dioxo-carbazepines, which would be created in the first stages of oxidation and provide hue during the first 20 min of oxidation, as well as acridones that would generate the colour more slowly.

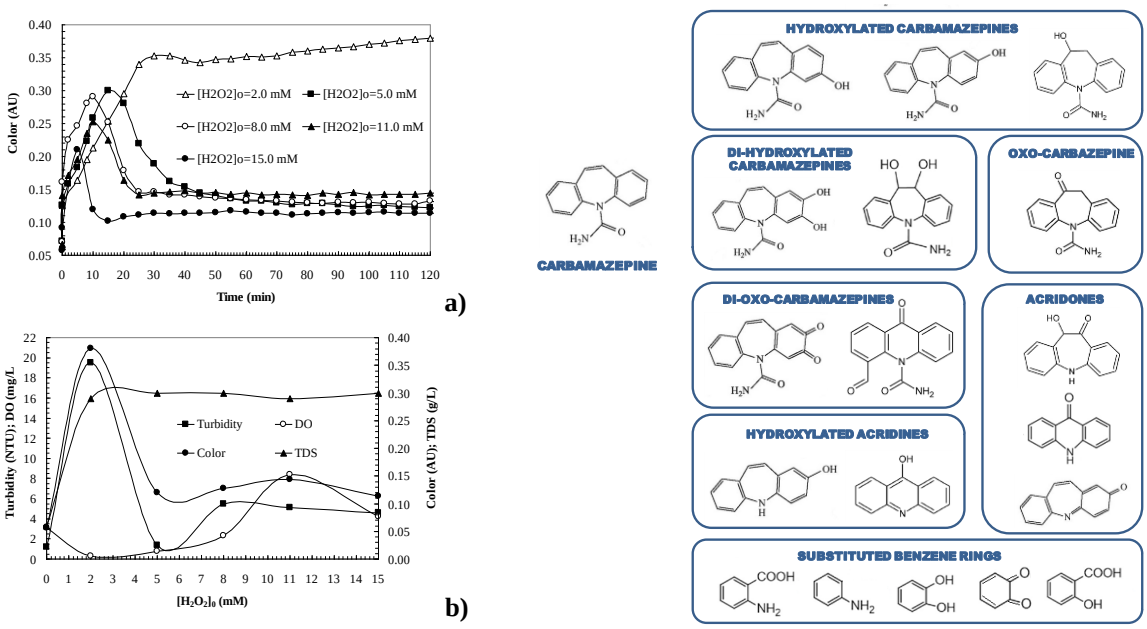

Figure 1. Effect of hydrogen peroxide concentration in a photo-Fenton system during the carbamazepine oxidation on **a)** Colour changes **b)** Indicator parameters of water quality analyzed at the steady state **c)** Reaction intermediates causing colour in oxidised carbamazepine solutions. $[C]_0$=50.0 mg/L; pH=3.0; $[Fe]_0$=10.0 mg/L; [UV]=150 W; T=40ºC.

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