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# Kinetic of the degradation of C.I. Food Yellow 3 and C.I. Food Yellow 4 azo dyes by the oxidation with hydrogen peroxide

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ABSTRACT

The kinetic of the degradation of Food Yellow 3 (FY3) and Food Yellow 4 (FY4) dyes by oxidation using hydrogen peroxide 30% in alkaline solution was studied. The kinetics were measured spectrophotometrically by UV–vis at 427 nm for FY4 and 485 nm for FY3 and under a temperature range of 25–70 °C. The addition of sodium hydroxide was necessary for the beginning of the process, which resulted in an easier degradation for the FY3 dye. Kinetic studies showed that degradation and rate constants were favored by the temperature and pH increase. The kinetic activation parameters ($E_a$, $\Delta H^{\#}$, $\Delta G^{\#}$ and $\Delta S^{\#}$) were calculated by the Arrhenius and Eyring equations. The following results were obtained for the FY4: $E_a$ 101 kJ/mol, $\Delta H^{\#}$ 103 kJ/mol, $\Delta G^{\#}$ 15.5 kJ/mol and $\Delta S^{\#}$ 0.27 kJ/(K mol). For the FY3 dye the results were as follows: $E_a$ 51 kJ/mol, $\Delta H^{\#}$ 54 kJ/mol, $\Delta G^{\#}$ 10.3 kJ/mol and $\Delta S^{\#}$ 0.14 kJ/(K mol). The degradation of the FY4 azo dye was processed using twice the energy required for the degradation of the FY3 azo dye.

## 1. Introduction

Dyes are usually highly structured organic substances rather difficult to degrade. These complex aromatic compounds are normally used to color fibers, utensils, plastics, food among others. Up to the first half of the XIX century, all of the dyes were derived from leaves, roots, fruits and flowers of different plants [1,2]. The azo dyes are the largest class of dyes used in the textile industry, constituting 60–70% of all the synthetic-dyes produced. They are characterized by having one or more azo groups ($R_1{-}N{=}N{-}R_2$) [3]. They belong to a numerous family of synthetic dyes, quite resistant to natural degradation and with a proven carcinogenic and mutagenic character [3,4]. The presence of dyes in effluents, if not adequately treated, can cause serious problems for the environment, contaminating rivers and groundwater, particularly the azo dyes, due to their resistance to microbiological degradation [5]. The presence of dyes in effluents is easily perceptible, even in low concentrations. Aside from the visual aspect, the coloration of the water can inhibit the photosynthesis and affect the balance of the aquatic ecosystem. Some dyes can be very persistent (xenobiotic), and many of them contain heavy metals. An efficient treatment would make possible the water to be reused for other industrial processes, resulting in substantial economy [6–8].

The need for removal of the color in colored effluents is evident, and has been encouraging the search for treatments for this purpose. There are many methods of dyes degradation, including advanced oxidation processes (AOPs) that have been proven to be an excellent alternative for the treatment of residues, mainly in regard to the degradation of organic compounds. Among the advanced oxidation processes, the most used ones are ozonation ($O_3$/UV, $O_3/H_2O_2$/UV, $O_3/H_2O_2$, $O_3/OH^-$), photolysis of hydrogen peroxide ($H_2O_2$/UV), Fenton ($H_2O_2/Fe^{2+}$), photo-Fenton ($H_2O_2/Fe^{2+}$/UV) and heterogeneous photo catalysis ($TiO_2$/UV) [9–12]. Adsorption processes using chitosane, alumine and activated coal, precipitation and biodegradation using mushrooms have been investigated as well [13–17].

In this study, the kinetics of degradation of the azo dyes, Food Yellow 4 (FY4) and Food Yellow 3 (FY3), by the use of hydrogen peroxide in alkaline solution was investigated. We evaluated the effect of the dye concentration and catalyst in solution, effect of addition of solution of NaOH in different concentrations, pHs and temperatures. These dyes are widely used by the food industry.

## 2. Experimental

### 2.1. Materials

The hydrogen peroxide ($H_2O_2$) 30% and sodium hydroxide (NaOH) were acquired from Vetec. The azo dye Food Yellow 4 (named Tartrazine Yellow) batch No. 0A1881 and Food Yellow 3 (commercialized as Sunset Yellow) batch No. 9k8808 were donated by Duas Rodas Industrial, with commercial purity degree (90%). The chemical structures of the two azo dyes are shown in Fig. 1. The

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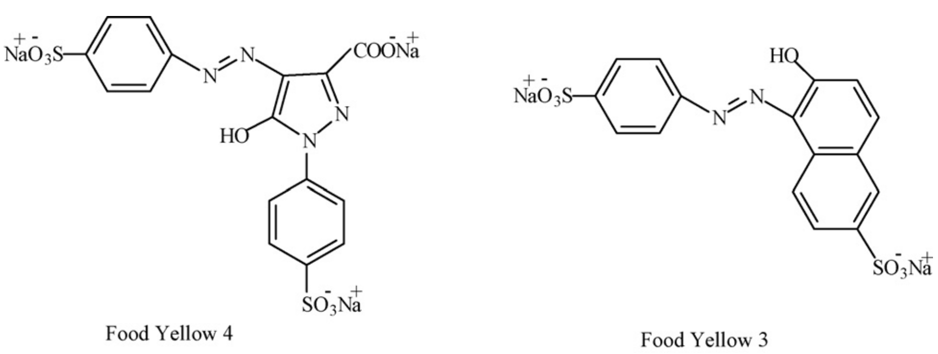

Food Yellow 4

Food Yellow 3

**Fig. 1.** Chemical structure of the azo dyes Food Yellow 4 and Food Yellow 3.

azo dye Food Yellow 4 has molecular weight of 534.4 g and $\lambda_{\max}$ in 427 nm, while the Food Yellow 3 has molecular weight of 452.4 g and $\lambda_{\max}$ in 485 nm.

The experiments done with different pH solutions were adjusted using buffer solution of Mcllvaine (sodium dihydrogenphosphate ($Na_2HPO_4$) and citric acid ($C_6H_8O_7$)) both acquired from Vetec [18].

The kinetic experiment was monitored by absorbance of the dyes using a CARY 50 BIO UV/VIS spectrophotometer from Varian® equipped with a thermostat for the studies in controlled temperature.

### 2.2. Procedure

In a 4-mL quartz cell, 250 μL of aqueous dye solution $1.8 \times 10^{-4}$ mol L$^{-1}$, 0.30 μL of sodium hydroxide (1 mol L$^{-1}$, 1.5 mol L$^{-1}$ and 2 mol L$^{-1}$) and 3 mL of $H_2O_2$ 30% were combined. The mixture was magnetically stirred in the quartz cell and the degradation or decolourisation of the Food Yellow 3 and Food Yellow 4 dyes were monitored spectrophotometrically at different temperatures (25 °C, 35 °C, 40 °C, 50 °C, 60 °C and 70 °C), using the software Cary WinUV to collect data. The influence of the pH in the process was evaluated using Mcllvaine buffer solutions in the 4, 5, 6, 7 and 8 pHs.

The kinetics showed first order behavior and the equation used to determine the rate constants was Eq. (1), in which $C_0$ = initial concentration of dye; $C_t$ = concentration in the time $t$; $k$ = rate constant and $t$ = time [19]:

$$\ln C_t = -kt + \ln C_0 \tag{1}$$

The linearised Arrhenius equation was used to calculate the activation energy:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{2}$$

in which $k$ = rate constant; $A$ = frequency factor; $E_a$ = activation energy; $R$ = gas constant; $T$ (K) = absolute temperature [19,20].

Activation enthalpy and activation entropy were calculated using the Eyring equation (Eq. (3)), where $k_b$ and $h$ are the Boltzmann's and Planck's constants, respectively

$$\ln\left(\frac{k_{\text{obs}}}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^{\#}}{R} - \frac{\Delta H^{\#}}{RT} \tag{3}$$

The free activation energy ($\Delta G^{\#}$) was determined using Eq. (4), at a $T$ value which is equal to 298.15 K [19,20]:

$$\Delta G^{\#} = \Delta H^{\#} - T\,\Delta S^{\#} \tag{4}$$

## 3. Results and discussion

### 3.1. Effect of the concentration of sodium hydroxide

Experiments were accomplished varying the concentration of the solution of sodium hydroxide (1.0 mol L$^{-1}$, 1.5 mol L$^{-1}$ and 2.0 mol L$^{-1}$). Fig. 2 shows the results obtained in the kinetics with the different concentrations of sodium hydroxide for the FY4 dye under the temperature of 60 °C. Similar performance was observed for the FY3 dye.

It is observed from Fig. 2 that if only hydrogen peroxide is added the degradation does not happen. Fig. 2 also shows that the degradation is favored by the increase of the sodium hydroxide concentration. This confirms that the mechanism of action of the peroxide is not spontaneous and that is not catalyzed by the impurities present. Consequently, although $H_2O_2$ is responsible for the degradation, NaOH can still play an important role in assisting the dye degradation. Muruganandham and Swaminathan [21] demonstrated that the degradation of the Reactive Orange 4 dye is inhibited when sodium hydroxide is added into the photochemical oxidation by UV–$H_2O_2$ process. The oxidative process is based on the production of hydroxyl radicals (•OH), considering that these are the radicals that accomplish the dissociation of the dye molecule, allowing its own degradation and consequently the elimination of the color of the solution. In the alkaline medium, $H_2O_2$ ionizes producing perhydroxyl ions. This degradation is divided into

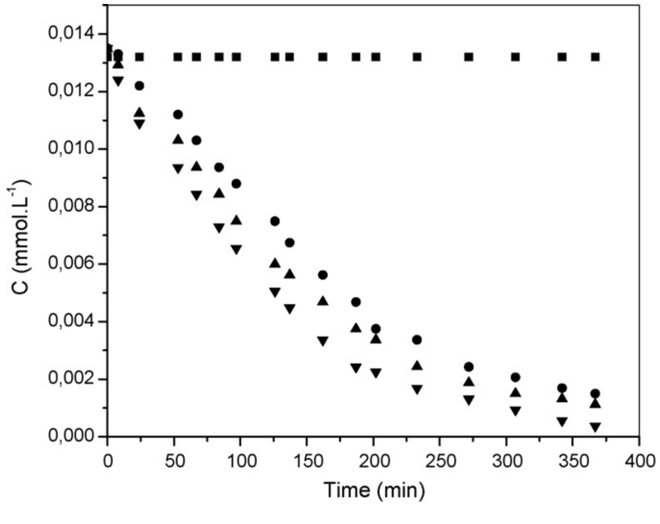

**Fig. 2.** Food Yellow 4 dye degradation at 60 °C. Initial dye concentration 0.013 mmol L$^{-1}$; $H_2O_2$ 30%. NaOH concentration: (■) without NaOH, (●) 1.0 mol L$^{-1}$, (▲) 1.5 mol L$^{-1}$ and (▼) 2.0 mol L$^{-1}$.