Journal of Molecular Catalysis A: Chemical 301 (2009) 93–97

Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

journal homepage: www.elsevier.com/locate/molcata

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

Cleci Teresinha Fragoso, Rodrigo Battisti, Crisleide Miranda, Paulo Cesar de Jesus*

Departamento de Química, Universidade Regional de Blumenau, Antonio da Veiga 140, Blumenau-SC 89019-917, Brazil

ARTICLE INFO

Article history:
Received 10 September 2007
Received in revised form
12 November 2008
Accepted 13 November 2008
Available online 21 November 2008

Keywords:
Decolourisation
Hydrogen peroxide
Food Yellow 4
Food Yellow 3

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.

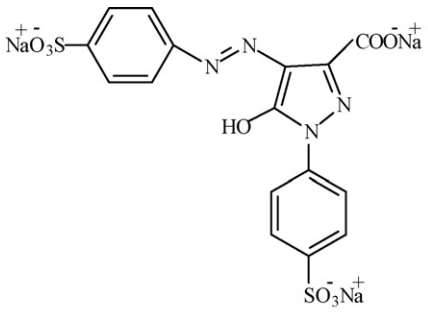
2. Experimental

2.1. Materials

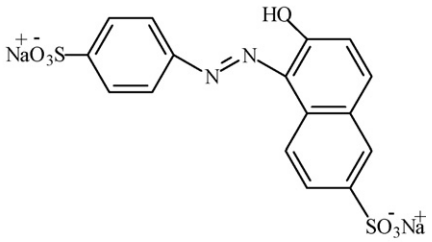
The hydrogen peroxide (H_2O_2) 30% and sodium hydroxide (NaOH) were acquired from Vetec. The azo dye Food Yellow 4 (named Tartrazine Yellow) batch No. 0A1881 and Food Yellow 3 (commercialized as Sunset Yellow) batch No. 9k8808 were donated by Duas Rodas Industrial, with commercial purity degree (90%).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

* Corresponding author. Tel.: +55 47 3221 6090; fax: +55 47 3221 6001.
E-mail address: pcj@furb.br (P.C. de Jesus).

1381-1169/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2008.11.014



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 λ_{max} in 427 nm, while the Food Yellow 3 has molecular weight of 452.4 g and λ_{max} in 485 nm.

The experiments done with different pH solutions were adjusted using buffer solution of McIlvaine (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 1.8×10^{-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 McIlvaine 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]:

$$\ln C_t = -kt + \ln C_0 \quad (1)$$

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

$$\ln k = \ln A - \frac{E_a}{RT} \quad (2)$$

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

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

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

$$\Delta G^{\#} = \Delta H^{\#} - T\,\Delta S^{\#} \quad (4)$$

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

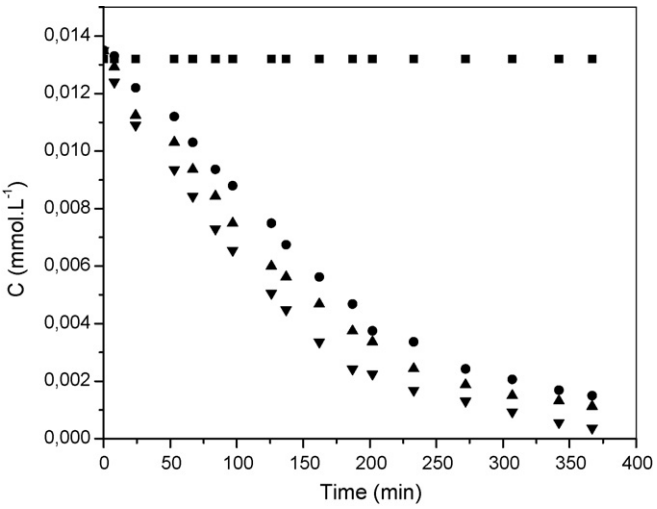


Fig. 2. Food Yellow 4 dye degradation at 60 °C. Initial dye concentration 0.013 mmol L^{-1}; H_2O_2 30%. NaOH concentration: (■) without NaOH, (●) 1.0 mol L^{-1}, (▲) 1.5 mol L^{-1} and (▼) 2.0 mol L^{-1}.

two simultaneous stages. The first is directly proportional to the concentration of the non-dissociated molecules of hydrogen peroxide. The second is not clearly defined, but it is independent of the concentrations of the individual components of the reaction (H_2O_2, HO_2^-, and OH^-). According to Muruganandham and Swaminathan [21] an increase in the peroxide concentration can act as a hydroxyl radical quencher and consequently reduce the concentration of hydroxyl radicals available. In other words, the free peroxide has to be present within an ideal concentration range so that the degradation can happen. As a result, we can infer that the sodium hydroxide prefers this balance causing the peroxide radical to be formed in the ideal concentration in the medium. The peroxide can still react with the base to form sodium peroxide. The sodium peroxide can become dissociated in the radical form, which can be also effective for the azo dyes.

3.2. Effect of temperature

Kinetic studies were conducted at different temperatures. Figs. 3 and 4 show the results obtained for the kinetics carried out with the FY4 and FY3 dyes, respectively.

Figs. 3 and 4 show the dependence of the decolourisation and degradation process on the increase of temperature. It was observed that at 25 °C, variation in the concentration of the FY4 dye did not happen. Significant variation in the absorbance of the dye solution began to happen only when raising the temperature to 35 °C. As the temperature rises the time necessary for the system to reach the equilibrium decreases significantly (Fig. 3). The FY3 dye demonstrated larger easiness for the degradation under low temperatures (Fig. 4). This result suggests that in spite of the possibility to form similar fragments during the process of degradation of the two dyes, the mechanism involved in both should be carried through different ways. The kinetic treatment for the performance of the curves observed in Figs. 3 and 4 follow pseudo-first order kinetics. Therefore, having applied Eq. (1), the rate constants (k_{obs}) were calculated for the kinetics of the degradation at different temperatures. Figs. 5 and 6 show $\ln C_t$ versus time plot, according to the kinetic equation (1) for the FY4 and FY3 dyes, respectively.

The k_{obs} values and degradation percentages are shown in Table 1. Table 1 shows that the k_{obs} increase as the temperature does. The times of half-life demonstrate the increase of the rate

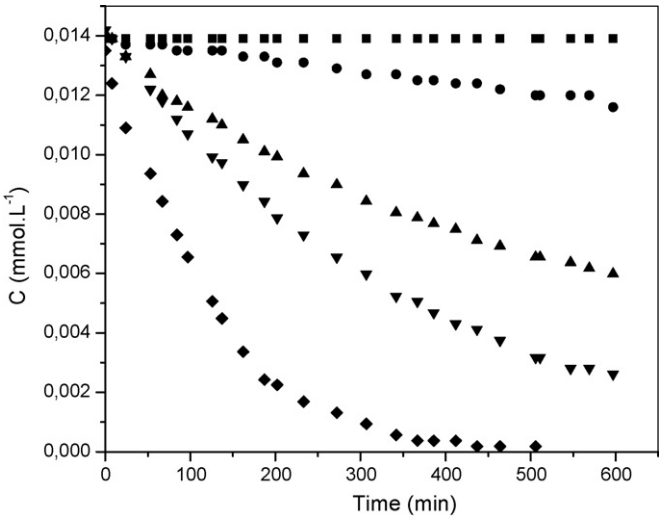


Fig. 3. Record of the oxidative degradation of FY4 under different temperatures: 25 °C (■), 35 °C (●), 40 °C (▲), 50 °C (▼) and 60 °C (♦). Initial dye concentration 0.014 mmol L^{-1}, 3 mL of H_2O_2 30%, and 0.30 μL of [NaOH] = 2.0 mol L^{-1}.

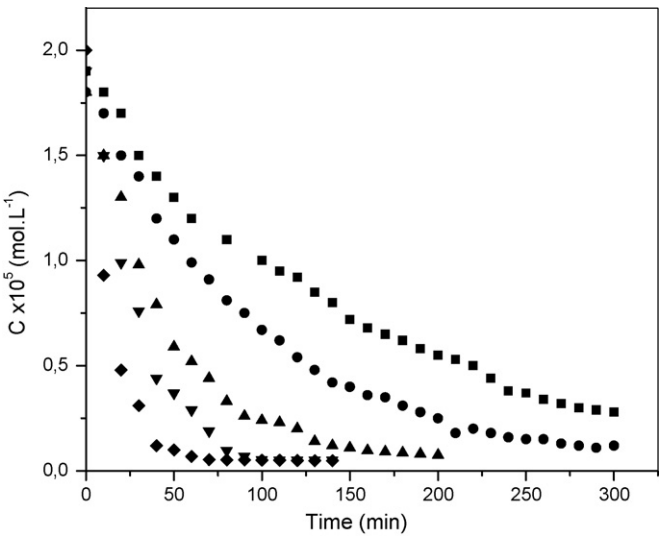


Fig. 4. Record of the oxidative degradation of FY3 under different temperatures: 25 °C (■), 35 °C (●), 40 °C (▲), 50 °C (▼) and 60 °C (♦). Initial dye concentration 0.2 mmol L^{-1}, 3 mL of H_2O_2 30%, and 0.30 μL of [NaOH] = 2.0 mol L^{-1}.

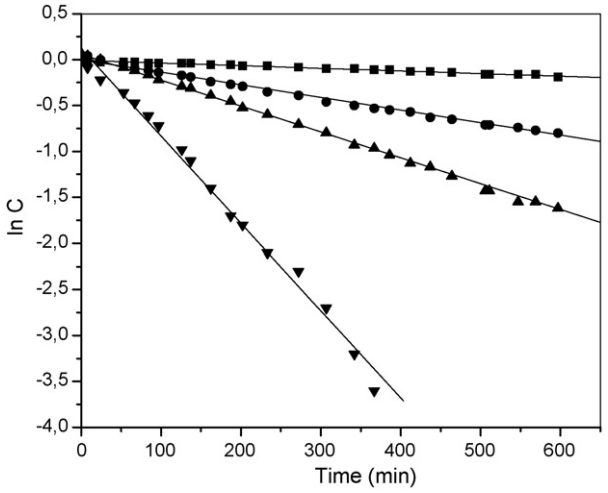


Fig. 5. The first order rate representation of FY4 versus time under various temperatures 35 °C (■), 40 °C, (●) 50 °C, (▲) and 60 °C (▼).

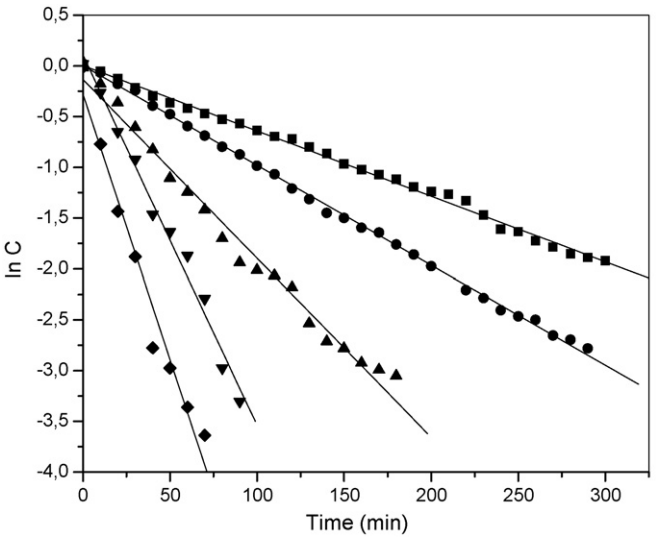


Fig. 6. The first order rate representation of FY3 versus time under various temperatures 25 °C (■), 35 °C (●), 40 °C (▲), 50 °C (▼) and 60 °C (♦).

Table 1
Rate constant and degradation percentage of the Food Yellow 4 and Food Yellow 3 dyes catalyzed by hydrogen peroxide at different temperatures.[a].

T (°C)	Food Yellow 4			Food Yellow 3		
	k_{obs} ($\times 10^3$ min^{-1})	$t_{1/2}$ (min)	Degradation (400 min) (%)	k_{obs} ($\times 10^2$ min^{-1})	$t_{1/2}$ (min)	Degradation (60 min) (%)
25	–	–	0	0.640	108.2	62
35	0.284	2440.1	15	0.980	70.7	79
40	1.39	498.5	70	1.80	38.5	94
50	2.93	236.5	93	3.70	18.7	96
60	9.84	70.4	99	4.80	14.4	99

[a] Correlation coefficient (r^2) ≥0.99.

Table 2
Activation parameters determined for the Food Yellow 3 (FY3) and Food Yellow 4 (FY4) dyes.[a].

Dye	E_a (kJ/mol)	$\Delta H^{\#}$ (kJ/mol)	$\Delta G^{\#}$ (kJ/mol)	$\Delta S^{\#}$ (kJ/(K mol))
FY4	101	103	15.5	+0.27
FY3	51	54	10.3	+0.14

[a] Correlation coefficient (r^2) ≥0.99.

constant in the degradation of the dye favored by the increase of temperature.

Based on the rate constants obtained from the different temperatures it was possible to calculate the activation energy (E_a), activation enthalpy ($\Delta H^{\#}$) and activation entropy ($\Delta S^{\#}$) and activation free energy ($\Delta G^{\#}$) for the kinetics of degradation of the FY4 and FY3 dyes, using Eqs. (2)–(4). These results are shown in Table 2.

The positive values of the activation energy, enthalpy, entropy and free energy, indicate that the oxidative process demands low amount of energy and it is of endothermic nature with little change in the three-dimensional arrangement of the state of transition of the molecule. Table 2 shows the difference in energy required in the degradation of the dyes, in which the FY4 dye requires twice the energy in relation to the FY3 dye to degrade. This explains the behavior observed in Fig. 3 for the kinetics of degradation of the FY4 dye in the temperatures of 25 °C and 35 °C. By the characteristic of the dyes, we can predict that possibility of some fragments are being formed in the process of degradation of the Food Yellow 3 and Food Yellow 4 dyes. Thus, we can propose a route to the fragmentation of the dyes, based on their structures and routes proposed by the literature [17], symmetrical azo bond cleavage and an asymmetrical azo bond cleavage. Figs. 7 and 8 show the routes proposed for the degradation of the azo dyes.

It is observed from the fragments that the 4-aminobenzenesulfonate and benzenesulfonate must be some of the intermediates present in the degradation of the two dyes. Another interesting observation is the presence of the OH group linked to the chain in ortho position to the azo group. The OH group, depending on the pH, can take the ionized form and by the conjugation of the connection with the chain can facilitate the

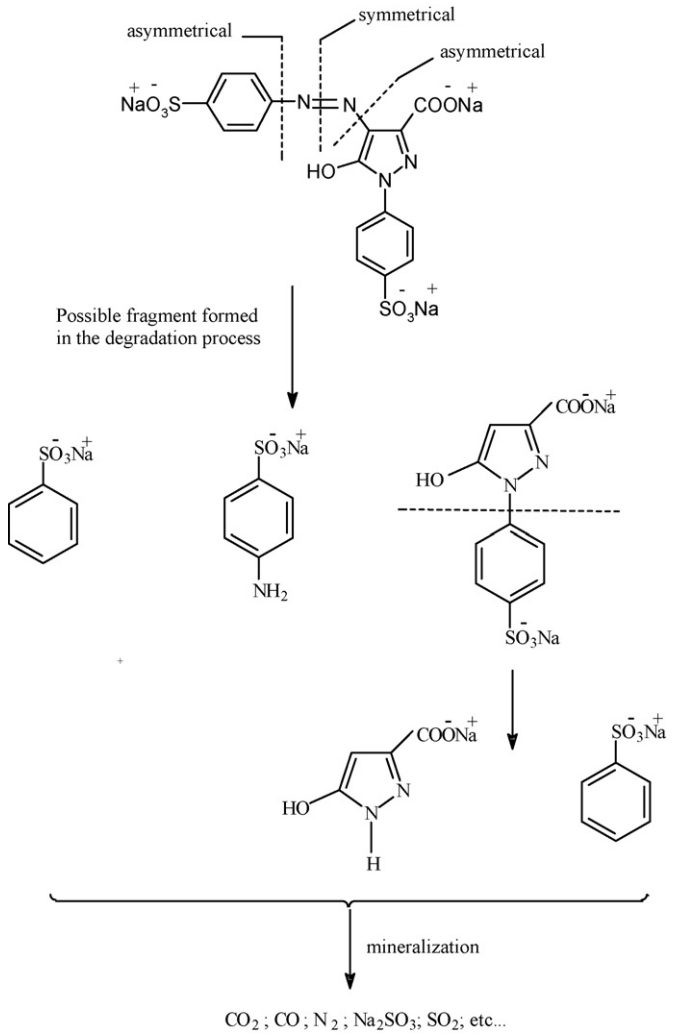


Fig. 7. Possible route to the fragments of the FY4 dye.

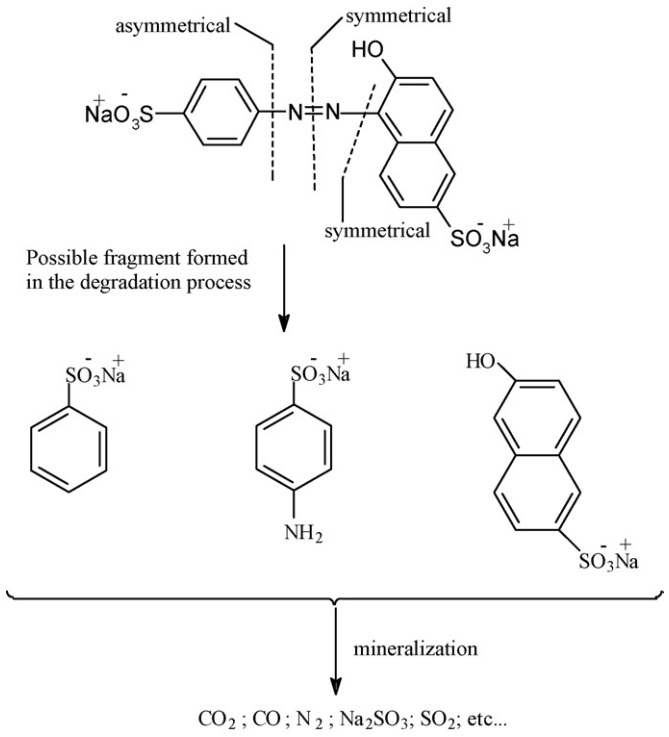


Fig. 8. Possible route to the fragments of the FY3 dye.

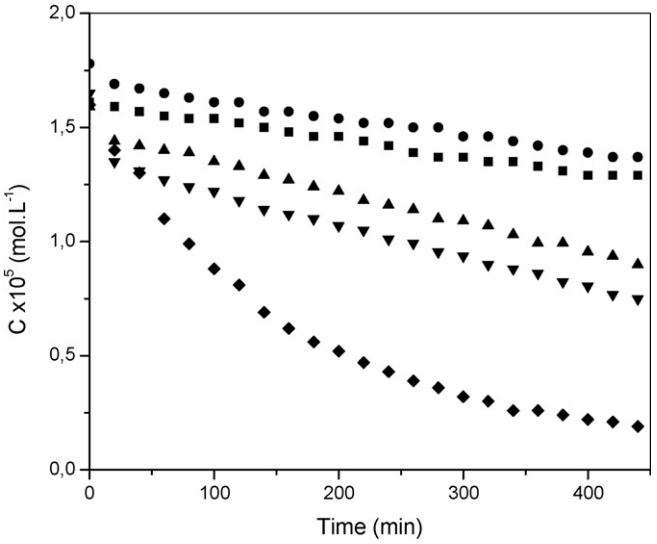


Fig. 9. The pH behavior of the degradation of FY4 dye at 60 °C: 4.0 (●); 5.0 (■); 6.0 (▲); 7.0 (▼); 8.0 (♦). Buffer Mcllvaine, initial dye concentration 0.2 mmol L^{-1}, 3 mL of H_2O_2 30%, and 0.30 μL of [NaOH] = 2.0 mol L^{-1}.

rupture of the azo bond. It is possible that other fragments like aniline, naftalene, benzene, ionic and radical forms of intermediates are being formed. In order to confirm the degradation, a reading in the UV–vis from 200 nm to 600 nm, was taken after each kinetic race, to detect any fragment with chromophore groups that could be formed from the degradation of the dye. The baseline in the spectrophotometer with hydrogen peroxide solution was carried out before each reading was taken, to eliminate possible interference of its absorption in the reading of the absorbance. No absorption was observed in the solution after each kinetic race.

According to Oakes et al. [22] the reaction between the perhydroxy anion and arylazonaphthol dyes in alkaline media is extremely complex, with initial reaction products degrading still further to smaller fragments. The same authors have postulated a mechanism for the oxidation by hydrogen peroxide for compounds with similar structure to Food Yellow 3 dye.

3.3. Effect of pH

Concerning the effect of the pH variation, it was observed that the degradation of FY4 and FY3 is favored by the increase of it. Fig. 9 shows the behavior of the FY4 dye under the pH variation. The percentage of degraded dye at pH 8 in 400 min reaches 90%.

4. Conclusion

The kinetic studies of the oxidative degradation of the Food Yellow 3 and Food Yellow 4 dyes lead into the following conclusions: the presence of sodium hydroxide in low concentration and amount works positively in the process. The rate constants and the degradation percentage are favored with the increase of temperature. The energy, enthalpy, entropy and free energy activation data demonstrate that the process depends on the molecular structure of the dye. The process using hydrogen peroxide proved to be viable once the decolourisation and consequent degradation of the Food Yellow 3 and Food Yellow 4 dyes happened.

Acknowledgements

The author would like to thank Duas Rodas Industrial for the donation of the dyes and the CNPq for the financial support.

References

[1] C.C.I. Guaratini, M.V.B. Zanoni, Quím. Nova 23 (2000) 71–78.
[2] M. Catanho, G.R.P. Malpass, A.J. Motheo, Quím. Nova 29 (2006) 983–989.
[3] M.S. Khehra, H.S. Saini, D.K. Sharma, B.S. Chadha, S.S. Chimni, Dyes Pigments 70 (2006) 1–7.
[4] M. Muruganandham, N. Shobana, M. Swaminathan, J. Mol. Catal. A: Chem. 246 (2006) 154–161.
[5] A.C. Serra, C. Docal, A.M.A.R. Gonçalves, J. Mol. Catal. A: Chem. 238 (2005) 192–198.
[6] M.A. Rauf, S.S. Ashraf, S. Alhadrami, Dyes Pigments 66 (2005) 197–200.
[7] N. Azbar, T. Yonar, K. Kestioglu, Chemosphere 55 (2004) 35–43.
[8] S.F. Kang, C.H. Liao, S.T. Po, Chemosphere 41 (2000) 1287–1294.
[9] S.S. Ashraf, M.A. Rauf, S. Alhadrami, Dyes Pigments 69 (2006) 74–78.
[10] A. Bhattacharyya, S. Kawi, M.B. Ray, Catal. Today 98 (2004) 431–439.
[11] J.H. Ramirez, C.A. Costa, L.M. Madeira, Catal. Today 108 (2005) 68–76.
[12] H.Y. Shu, M.C. Chang, Dyes Pigments 65 (2005) 25–31.
[13] S.V. Mohan, K.K. Prasad, N.C. Rao, P.N. Sarma, Chemosphere 58 (2005) 1097–1105.
[14] N.K. Pazarlioglu, R.O. Urek, F. Ergun, Process Biochem. 40 (2005) 1923–1929.
[15] E. Abadulla, K.H. Robra, G.M. Gübtiz, Text. Res. J. 70 (2000) 409.
[16] M.A. Ai-Ghouti, M.A.M. Khraisheh, S.J. Allen, M.N. Ahmad, J. Environ. Manage. 69 (2003) 229–238.
[17] C. Lopez, A.G. Valade, B. Combourieu, I. Mielgo, B. Bouchon, J.M. Lema, Anal. Biochem. 335 (2004) 135–149.
[18] T. Morita, R.M.V. Assunpção, Manual de soluções reagentes e solventes, second ed., Edgard Blücher Ltda., São Paulo, 1976, p. 275.
[19] P.W. Atkins, in: E.C. Silva, M.J.E.M. Cardoso, O.E. Barcia (Eds.), Físico-Química–Fundamentos, LTC Livros Técnicos e Científicos, Rio de Janeiro, 2003, pp. 188–210.
[20] T. Sismanoglu, A. Ercag, S. Pura, E. Ercag, J. Brazil. Chem. Soc. 15 (2004) 669–675.
[21] M. Muruganandham, M. Swaminathan, Dyes Pigments 62 (2004) 269–275.
[22] J. Oakes, P. Gratton, R. Clark, I. Wilkes, J. Chem. Soc., Perkin Trans. 2 (1998) 2569–2575.