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Photo-Fenton process for the degradation of Tartrazine (E102) in aqueous medium

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ABSTRACT

The kinetics of Tartrazine decay through photo-Fenton process, which has not reported in literature, was explored. Tartrazine is a synthetic azo dye used in food colorants industry, cosmetic and textile industry. There are very few studies in the literature concerning Tartrazine degradation but they did not lead to a total mineralization.

Fotooxidative degradation of Tartrazine (E102) by UV/Fe^{2+}/H_2O_2 was investigated using a laboratory scale photoreactor equipped with a low pressure mercury lamp.

The degradation kinetics under irradiation (200–280 nm) was optimized in respect to H_2O_2 concentration (6×10^{-4} M) and Fe^{2+} concentration (8.28×10^{-5} M) at a constant Tartrazine concentration (1.035×10^{-5} M) at pH 3. The degradation rate was influenced by the temperature with an optimum value of 323 K and thermodynamic parameters were calculated.

Application of photo-Fenton system also assures total organic carbon removal with 80% efficiency after 2 h irradiation.

1. Introduction

Azo dyes are complex aromatic compounds characterized by one or more azo groups (R_1–N=N–R_2) Khehra *et al.* [1] used in the textile, cosmetic, pharmaceutical and food industries. These dyes are resistant to biodegradation, under aerobic conditions. A wide range of methods have been proposed for the removal of synthetic dyes from aqueous solutions such as physical adsorption, electrochemical oxidation [2], chemical oxidation and chemical coagulation/precipitation [3–5]. Degradation of organic pollutants like dyes in industrial wastewater has become increasingly significant during the last decade by using advanced oxidation processes (AOPs) [6–15]. Matsui *et al.* [16] show that the azo-dyes had a tendency to be easily decomposed with ozone and the decomposition of dyes was markedly accelerated when ozonation was accompanied by ultra-violet irradiation.

Used Tartrazine is a synthetic lemon yellow azo dye utilized in food colorants industry, cosmetic and textile industry. Tartrazine seems to cause most of the allergic and intolerance reactions of all the azo dyes, particularly among asthmatics patients and those with aspirin intolerance.

There are very few studies in the literature concerning Tartrazine degradation. Salem and Gemeay [17], examined oxidation kinetics of Tartrazine with peroxydisulfate in the presence and absence of Ag(I) and Fe(III) catalysts and observed higher conversion in alkaline medium. Faragoso *et al.* [18] investigated the degradation of Tartrazine by oxidation with hydrogen peroxide in alkaline solution. Mittal *et al.* [19] studied the removal of Tartrazine using waste material-hen feathers as adsorbed; Patel and Suresh [20] studied decolorization of azo dyes using magnesium–palladium system, Gupta *et al.* [21] and Tanaka *et al.* [22] removed the dye-Tartrazine by photodegradation on titanium dioxide surface.

Fenton's reagent was discovered about 100 years ago, but its application as an oxidizing process for destroying toxic organics was not applied until late 1960s [23]. Kitis *et al.* [24], Yoan *et al.* [25], Lu *et al.* [26] used the Fenton reagent, a mixture of hydrogen peroxide and ferrous ions, which generate the oxidative radicals through the reactions as follows:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-} \quad (1)$$

$$Fe^{3+} + H_2O \rightarrow Fe(HO)^{2+} + H^{+} \quad (2)$$

In photo-Fenton process, in addition to the above reactions, the formation of hydroxyl radicals also occurs by the following

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reactions:

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + HO^{\bullet} \quad (3)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow HO^{\bullet} + Fe^{2+} + H^{+} \quad (4)$$

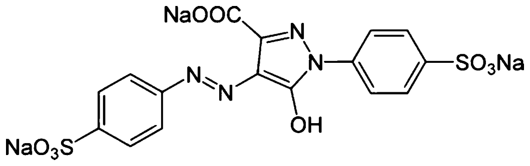
$$H_2O_2 + h\nu \rightarrow 2HO^{\bullet} \quad (5)$$

Studies of Tartrazine degradation kinetic by photo-Fenton have not found in literature. The objective of the present work was the optimization of photo-Fenton process in order to degrade Tartrazine at pH 3, to establish its degradation kinetics and degree of mineralization under specific experimental conditions. The method was based on monitoring the absorbance diminishes during irradiation times.

2. Materials and methods

2.1. Materials

Tartrazine (otherwise known as E number E102, C.I. 19140, or FD&C Yellow 5) and H_2O_2 (30%) were without further purification purchased from Merck. The purity of Tartrazine was tested by DSC (differential scanning calorimetry). The dye has the following structure:



Aqueous solutions (1×10^{-5} M) were prepared by dissolving the required quantity of the dye in double distilled water. The pH of the solution was adjusted using sulfuric acid. $[Fe(C_2O_4)_3]K_3{\cdot}3H_2O$ was synthesized in our laboratory for actinometry. $FeSO_4$ and H_2SO_4 were purchased from Merck.

2.2. Methods

The photodegradation of Tartrazine was carried out in a Laboratory-UV-Reactor system (Heraeus) with a low-pressure mercury lamp which emits in the UV range (λ = 200–280 nm). It is equipped with a quartz cooling jacket and immersed in the center of the reactor containing the dye solution. The total incident photon flow was 1.92×10^{-6} einsteins^{-1} as determined by ferrioxalate actinometry [27].

The UV–vis spectra of dye were recorded from 200 nm to 600 nm using a UV-vis spectrophotometer (Pye Unicam α Helios) with a spectrometric quartz cell (1 cm path length). The maximum absorbance wavelength (λ_{max}) of Tartrazine is 428 nm.

The pH data were recorded with a pH-meter (Radiometer Copenhagen).

The total organic carbon (TOC) was measured using a Analyzer Multi N/C 3100 (Analytic Jena).

2.3. Procedures

The photooxidation process was carried out using a constant solution volume of 400 mL. During reaction, the solution was agitated at a rate constant. The precise amount of ferrous sulfate or hydrogen peroxide was mixed with the dye solution. Ferrous sulfate was added to the dye solution before the addition of hydrogen peroxide. About 3 mL aliquot of the dye was taken after a specific time interval (varying from 3 min to 120 min) and analyzed spectrophotometrically. The rate of degradation with time was continuously monitored. The degradation rates of the dye monitored in the 428 nm spectral band (Fig. 1) fitted a first-order kinetic equation [28] presented in the corresponding inset panels for the first 15 min irradiation: $\ln(A_0/A_t) = k_{ap}t$, where k_{ap} (s^{-1}) is the rate constant, t (s) is the irradiation time and A_0 and A_t are the initial and the final absorbance values of the Tartrazine solution, respectively.

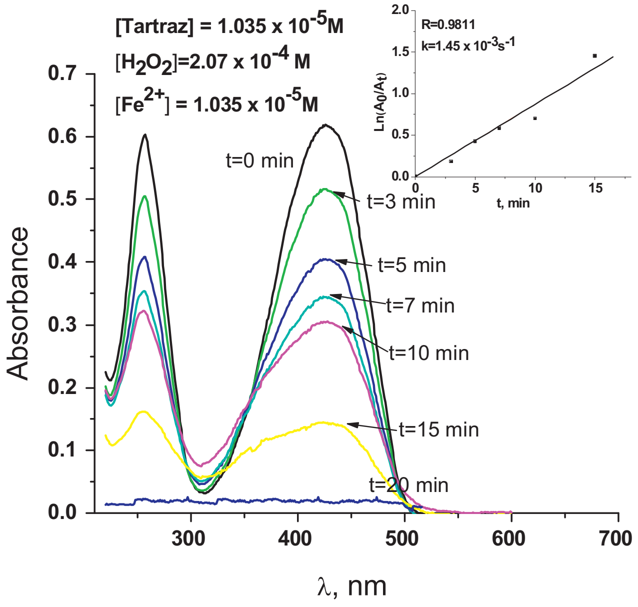


Fig. 1. UV–vis spectral change of dyes recorded during the Tartrazine degradation at different irradiation times. The inset panel present the first order reaction kinetic for the degradation of Tartrazine by $UV/Fe^{2+}/H_2O_2$.

3. Results and discussions

The absorption spectrum of azo dye Tartrazine (Fig. 1) presents two main bands, one in near UV (λ_{max} = 257 nm) and another one in the visible range (λ_{max} = 428 nm) responsible for the yellow color. The band at 428 nm can be assigned to n–π^* transition of N═N, C═N and C═O chromophore groups and the 257 nm band is characteristic to the individual aromatic rings.

The decreases of the absorption bands indicate a rapid degradation of the Tartrazine in solution. It is interesting to note that a new band started to 313 nm due to the modification of the π system delocalization. After 10 min irradiation this band decrease slowly indicating that the intermediates formed started to degrade. After 20 min the bands at 257 nm, 313 nm and 428 nm disappeared, what indicates that the dye and aromatic intermediates were degraded. The degradation of Tartrazine only with UV irradiation was of 30% in 60 min.

3.1. The effect of UV irradiation

In order to evaluate the effect of UV light, experiments were carried out in the absence and the presence of light employing the Fe^{2+}/H_2O_2 (Fenton reagent). According to the literature [28], pH was adjusted at 3. At pH 3, Fe^{3+} and $Fe(OH)^{2+}$ complex ions are found in equal proportion which have great light absorption coefficient and show high quantum yield for hydroxyl radical generation. The increasing of pH value to lead at decreasing the concentration of $^{\bullet}OH$ in the solution. This is due to the coagulation of Fe^{3+} and Fe^{2+} complex molecules formed in the reaction. Moreover, the higher pH value leads to precipitation of ferrous ions