DEGRADATION OF TARTRAZINE IN WATER
BY ELECTRO-FENTON PROCESS

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ABSTRACT: An indirect electrochemical process which is very efficient for the degradation of organic pollutants in aqueous solution, is described. The process, named electro-Fenton, is based on *in situ* electrochemical generation of Fenton's reagent (H_2O_2, Fe^{2+}) which leads to the production of hydroxyl radicals °OH. Hydroxyl radicals are very powerful oxidizing agents. They react with organic pollutants and thus lead to their mineralization. In this study we have applied the electro-Fenton process to degrade an azo dye, the tartrazine, present in waste food industrial water. Degradation kinetics and chemical oxygen demand (COD) have been determinated. Here we show that the mineralization efficiency was around 80% for the tartrazine in case of a 0.05 mM aqueous solution at 5000 coulombs under our experimental conditions. The results display the efficiency of the electro-Fenton process to degrade organic matter present in water.

Key Words: Electro-Fenton process, Hydroxyl radicals, Tartrazine, Degradation, Mineralization.

RESUME: Une procédé électrochimique indirecte et très efficace pour la dégradation des polluants organiques présents en solution aqueuse est décrite. Ce procédé, appelé électro-Fenton, est basé sur la génération *in situ* par électrochimie du réactif de Fenton (H_2O_2, Fe^{2+}) qui conduit à la formation des radicaux hydroxyles °OH fortement oxydant. Ces radicaux réagissent rapidement sur les polluants organiques conduisant à leur dégradation jusqu'à la minèralisation. Dans cette étude nous avons appliqué le procédé électro-Fenton au traitement d'un colorant alimentaire présent dans les rejets liquides de l'industrie alimentaire. La cinétique de la dégradation de la tartrazine en solution et le taux d'abattement de la demande chimique en oxygène (DCO) ont été étudiés. Les mesures de la DCO montrent que l'efficacité de la minéralisation est de l'ordre de 80% dans le cas de traitement d'une solution aqueuse à la concentration de 0.05 mM et après passage d'une charge électrique de 5000 coulombs. Les résultats obtenus confirment l'efficacité du procédé électro-Fenton pour la dégradation des polluants organiques présents dans l'eau.

Mot clés : Procédé électro-Fenton, Radicaux hydroxyles, Tartrazine, Dégradation, Minéralisation.

1. INTRODUCTION

Synthetic organic dyes, the majority of which are recalcitrant in nature, are used universally in many different manufacturing processes. The dyes are released into the environment in industrial effluents and are highly visible even at low concentrations (<1 mg. L^{-t}) [1]. The colour is one of the most obvious indicators of wastewater pollution.

Azo dyes are important since at least half of all commercial dyes belong to the azo class. Azo dyes are water-soluble, synthetic organic colouring agents possessing the characteristic –N=N– (azo) bond and showing great structural diversity. Generally, azo dyes contain between one and three azo linkages, linking phenyl and/or naphthyl rings that are usually substituted with some combination of functional groups including: amino, chloro, hydroxy, methyl, nitro and sulphonate groups [1]. Azo dyes can be used to colour many different substrates, such as synthetic and natural textile fibres, plastics, leather, paper, mineral oils, cosmetics and foodstuffs.

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The current environmental concern with azo dyes revolves around the potential carcinogenic health risk that they, or their intermediate biodegradation products, present to humans [2]. Thus, appropriate treatment of dye wastewaters to remove both colour and the dye compounds is important for the protection of natural waters. Several chemical and biochemical methods have been proposed to eliminate the azo dyes. Chemical treatments are based on chemical oxidation [3], coagulation/floculation [4] and electrocoagulation process [5]. Biological treatments are based on anaerobic/aerobic degradations [6]. The recalcitrant nature of azo dyes, together with their toxicity to micro-organisms, makes biological treatment inefficient. The strong electron withdrawing character of the azo group stabilises these aromatic pollutants against conversions by oxygenases, and hence azo dyes are resistant to aerobic degradation by bacteria [1]. Nevertbeless, their degradation has been achieved under anaerobic conditions [7].

Further degradation of the intermediates, which are generally recalcitrant under anaerobic conditions, is readily achieved under aerobic conditions. In recent years, there has heen growing interest in finding better way to degrade those recalcitrant compounds. Several studies have shown that the oxidation of organic compounds like azo dyes can be achieved hy using Fenton's reagent (H_2O_2, Fe^{2+}) or electrochemically/photochemically assisted Fenton's reagent [8-12]. The Fenton's reagent is known as a precursor of the hydroxyl radical $°OH$, a highly strong oxidizing agent.

In this paper we describe an indirect electrochemical method for ecological treatment of wastewaters: the electro-Fenton process to degrade the azo dyes. This process is based on an in situ and catalytic production of Fenton's reagent (H_2O_2, Fe^{2+}) to produce hydroxyl radicals $°OH$ according to the Fenton's reaction [13]:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + °OH \tag{1}$$

Many studies [13] have shown that the hydroxyl radical whicb has a very sbort life time reacts efficiently with organic compounds, finally leading to their destruction. $°OH$ radicals are able to oxidise organic compounds by hydrogen abstraction reaction (equation 3), by electron transfer reaction (equation 4) or by electrophilic addition to π systems (equation 5) [14]:

$$RH + °OH \longrightarrow R° + H_2O \tag{2}$$
$$RX + °OH \longrightarrow RX^{+°} + OH^- \tag{3}$$

$$\tag{4}$$
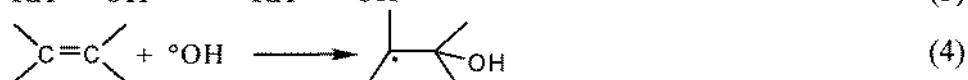
These reactions generate organic radicals, which by addition of molecular oxygen yield peroxyl radicals, which in turn initiate chain reactions of oxidative degradation, leading finally to CO_2 and H_2O [14].

In this work we selected the tartrazine ($C_{16}H_9N_4Na_3O_9S_2$), the trisodium 5-hydroxy-1-(4-sulfonatophenyl)-4-(4-sulfonatophenyllazo)-H-pyrazole-3 carboxylate (Figure 1) as an example of the azo dyes to treat because of its large production volume by the industrial dye manufacturers. It was classified among the priority pollutants of the waste food industrial water.
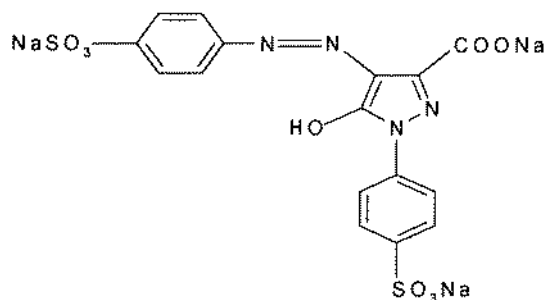

Figure 1: Chemical structure of tartrazine

The degradation of the tartrazine by the hydroxyl radicals °OH produced by the electro-Fenton process was followed by an UV-Visible analysis and chemical oxygen demand (COD) measures. The COD values permitted to evaluate the mineralization efficiency in function of electrical charge passed in the solution during electrolysis.

II. EXPERIMENTAL DETAILS

The azo dye tartrazine (Aldrich) was of the highest purity and was used without further purification. Iron (III) sulphate $Fe_2(SO_4)_3$, $5H_2O$ which was purchased from Prolabo was used to obtain ferrous ions. The cathode (working electrode) was a carbon plate which was obtained from Carbone-Lorraine.

A potentiostat/galvanostat type DEA 332 monitored by a personal computer, was used for electrochemical treatments and for measurements of consumed electrical charge. Electrolyses were performed in an electrochemical cell (200 cm^3) equipped with two electrodes (Figure 2). A platinum anode (0.5 cm^2) and a carbon plate cathode (15 cm^2) were used during the electro-Fenton treatment. Prior to the electrolysis, compressed air was bubbled for 10 minutes to saturate the aqueous solution with oxygen. During the electro-Fenton process, the pH of solutions is maintained at 3 by addition of 0.1 M H_2SO_4 solution. A ferrous iron salt (0.5×10^{-3} mol.L^{-1}) was added to the solution as catalyst. The solution was stirred with a magnetic bar to achieve the transport of electroactive matter toward the cathode. Under these electrolysis conditions, the current is kept constant (20 mA).
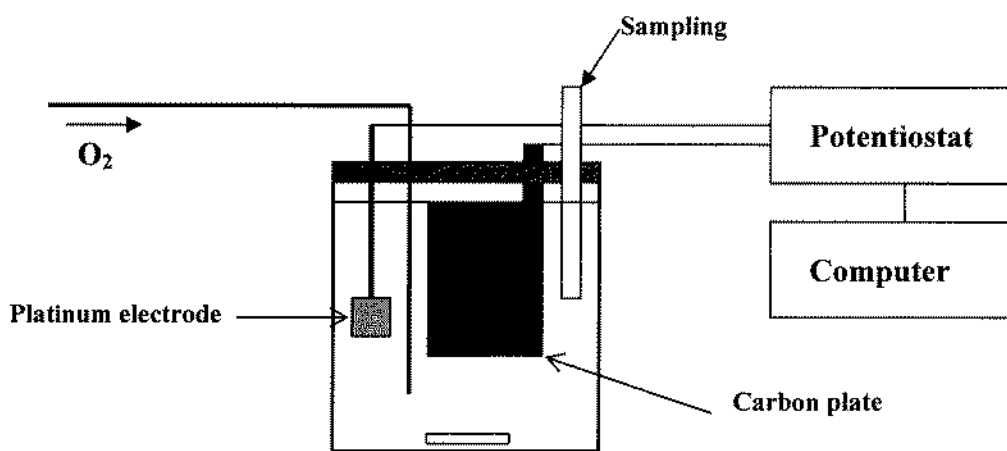

Figure 2: Schematic setup of the electrochemical cell used for electro-Fenton process.

The tartrazine concentrations in the solution were determined by an UV-Vis spectrophotometer (Backman). Chemical oxygen demand (COD) was measured using COD reactor and direct reading spectrophotometer (DR/2000, HACH, USA).

III. RESULTS AND DISCUSSION

I. Electrochemically hydroxyl radicals production

During the electro-Fenton process, the molecular oxygen and ferric ions present in the initial aqueous tartrazine solution are simultaneously reduced at the cathode to generate hydrogen peroxide and ferrous ions according to reactions (5) and (6):

$$O_2 + 2\,H^+ + 2e^- \longrightarrow H_2O_2 \tag{5}$$

$$Fe^{3+} + e^- \longrightarrow Fe^{2+} \tag{6}$$

The Fenton's reagent being thus electrochemically generated [14, 15], leads to the $^\circ OH$ radical production according to the Fenton's reaction (reaction 1).

Ferrous ions consumed by Fenton's reaction (reaction 1) are generated electrochemically at the cathode (reaction 6). At the anode, the oxidation of water takes place:

$$2\,H_2O \longrightarrow O_2 + 4\,H^+ + 4\,e^- \tag{7}$$

thus supplying oxygen for reaction (5) to produce H_2O_2.

The global chemical equation corresponding to the electro-Fenton process can obtained by the sum of the reactions (1) and (5) to (7):

$$0.5\,O_2 + H_2O \longrightarrow 2\,^\circ OH \tag{8}$$

This equation summarises the catalytic properties of the electro-Fenton process : the ferrous ion does not appear in equation [14]. The only reagents necessary for the production of two moles of $^\circ OH$ are half a mole of oxygen and energy from the electrical generator.

2. Tartrazine degradation kinetics

Hydroxyl radicals, which were produced in-situ by electro-Fenton process, react on tartrazine leading to its degradation. The UV-visible analysis at $\lambda = 430$ nm permits to follow the disappearance of tartrazine present in the initial solution at a concentration of $C_0 = 5 \times 10^{-5}$ M (25 mg/L) during the current controlled electrolysis. Figure 3 shows the rapid decay of tartrazine concentration in the aqueous solution with electrolysis time and its complete degradation at less than 12 min (700 seconds). The electrophilic addition of $^\circ OH$ on the azo double bond $-N=N-$ leads to its rapid breaking [11].

Our results show that the electro-Fenton process is efficient to degrade tartrazine in solution and remove solution colour. The tartrazine concentration decreases exponentially (Figure 3). The degradation curve exhibits a pseudo-first order kinetics for the hydroxylation of tartrazine molecules by hydroxyl radicals $^\circ OH$:

$$- d[Tart]/dt = k\,[Tart]\,[OH^\circ]$$

In the electro-Fenton process, the $^\circ OH$ formation rate is controlled by the electrical current applied to the cathode during electrolysis and the O_2 concentration in the solution. The current and O_2 concentration being kept constant during electro-Fenton process, the $^\circ OH$ production rate is also kept constant. Therefore, the degradation kinetics of tartrazine can be written:

$$- d[Tart]/dt = k_{app}\,[Tart]$$

where $k_{app} = k\,[^\circ OH]$ is the apparent rate constant accordingly to the pseudo-first order kinetics, k being the absolute rate constant. This kinetics consideration is in agreement with recent works concerning the reaction of hydroxyl radicals with organic compounds [11, 16, 17].

Assuming a first-order kinetics for the degradation of tartrazine molecules, the apparent rate constant was determined analytically from the slope of concentration vs. time plot in accordance with the equation Ln $[Tart]_0/[Tart] = k_{app} \times t$. The degradation apparent rate constant k_{app} for tartrazine in aqueous solution was found as 6.5×10^{-3} s^{-1}.
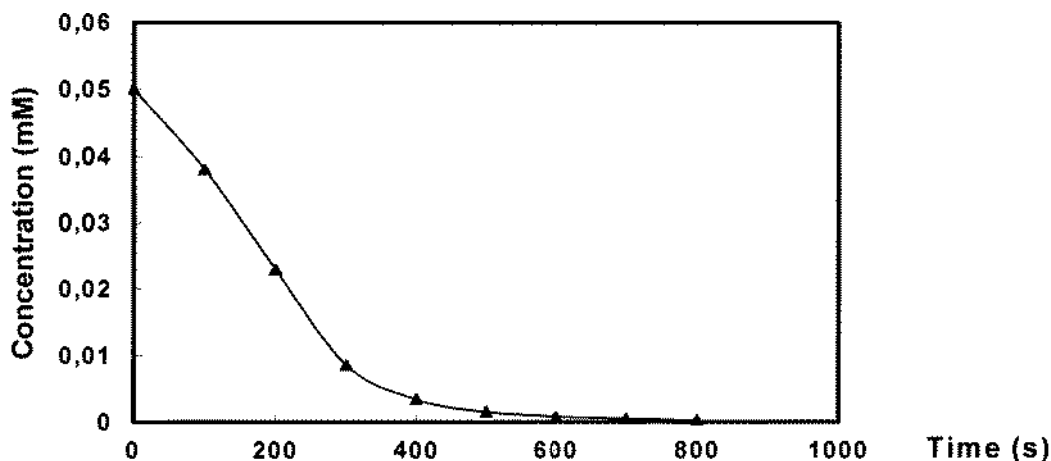
Figure 3: Evolution of aqueous tartrazine solution ($C_0 = 5 \times 10^{-5}$ M) during the electro-Fenton treatment. I = 20 mA, pH = 3, V = 200 cm³.

3. Mineralization efficiency

Mineralization of treated tartrazine solutions during electro-Fenton process are followed by measuring the chemical oxygen demand (COD) values to evaluate the organic carbon content of the solution. Electrolysis of initial tartrazine solution leads to a gradual decrease in chemical oxygen demand (COD) with electrical charge Q consumed, indicating the mineralization progress. Figure 4 shows the COD decrease as a function of total charge passed during the electro-Fenton treatment of 5×10^{-5} M tartrazine solution under conditions described in the experimental part.
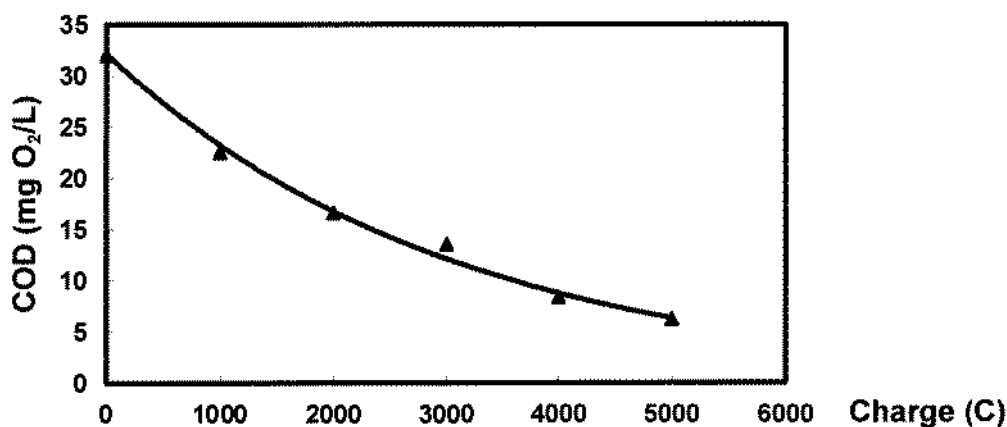

Figure 4: Chemical oxygen demand (COD) evolution of tartrazine solution ($C_0 = 5 \times 10^{-5}$ M) during the electro-Fenton process. I = 20 mA, pH = 3 and V = 200 mL.

The mineralization process reached a ratio of 80 % at 5000 coulombs. Figure 4 shows that the mineralization rate is higher at the beginning of the treatment. The COD decreases being slow since 3000 coulombs (after disappearance of the tartrazine and its aromatic intermediates) because of the presence of more stable intermediates (aliphatic compounds) formed by ring opening reactions. Because the medium is strongly oxidizing, aliphatic compounds are transformed into carboxylic acids, essentially oxalic acid which is the last end product before mineralization. It reacts slowly with hydroxyl radicals. Because it is a biodegradable compound the treatment can be stopped at this stage. This hypothesis was also reported by Oturan and al. [11]. Due to the inactivation of the electrophilic attack centres, carboxylic acids have a lower reactivity toward hydroxyl radicals than aromatic structures [11]. The degradation of the tartrazine is not only a breaking of the azo bond, but also degradation of the aromatic rings. Chen and al. [18] have shown that the infrared (IR)

characteristic peak of the phenyl group disappeared after reaction with $°OH$, proving that carboxylic intermediates were generated like acetic and formic acids [19, 20]. In this study, the COD measurements have shown that the successive oxidation reactions by hydroxyl radicals lead to the quasi-total mineralization of the aqueous solution. It is also to be mentioned that final degradation products were mineral ions such as NH_4^+, NO_3^- and SO_4^{2-} according to the substituent groups included in the initial molecule, as well as CO_2 and H_2O [17, 21].

IV. CONCLUSION

The degradation of the azo dye tartrazine by electrochemically generated hydroxyl radicals has been studied in aqueous medium. These radicals are produced in situ by electro-Fenton process in a catalytic way. The efficiency of this process is confirmed by dye concentration decrease, colour disappearance and COD abatement. Complete degradation at fixed current (I = 20 mA) of 100 mL of 0.05 mM of tartrazine was achieved in 10 min. The COD measurements indicate an efficient abatement (80% after the passage of a charge of 5000 C) of organic carbon during the electro-Fenton process. In this stage of treatment, the final solution contains only some carboxylic acids as oxalic or acetic acids which are biodegradables. These results show that the electro-Fenton process is able to mineralize an aqueous tartrazine solution The degradation kinetics of tartrazine hy hydroxyls radicals follows a pseudo-first order reaction kinetics. The apparent rate constant for degradation of tartrazine under our experimental conditions was found $k_{app} = 6.5 \times 10^{-3}$ s^{-1}.

As hydroxyl radicals are non-selective species, the electro-Fenton process can be generalized to the treatment of wastewater effluents containing synthetic dyes. Indeed this novel process can be considered ecologically friendly; simple to handle and economical since catalytical processes are involved and no chemical reagent needed except molecular oxygen from compressed air.

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