

Textile wastewater discoloration by Fenton oxidation process

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Abstract

Treating industrial wastewater by advanced oxidation processes, is a recent **interest** primarily for decolorization of aqueous solutions containing dyes. The application of the Fenton reaction is one of these processes, bleaching liquid discharges after a textile dyeing unit in the city of Marrakech, Morocco, which are non-biodegradable, using oxidation by Fenton's reagent has shown its ability to degrade the dyes in water to carbon dioxide, water, and other harmless products. In this study a serie of pure dyes mineralization experiments used in the dyeing process, such as: the Bezaktiv BLUE-SR, the NOVACRON® Red FN-R, and the NOVACRON®SCALE TFN-6G, and a global liquid discharge containing dyes and chemical additives. Fenton's method is effective at pH = 3, as a result, we had a total discoloration for the three pure colors, and up to 47% to the overall rejection for 60 minutes at room temperature, and 100% when the temperature was increased to 60 °C. The presence of chemical additives disadvantage Fenton oxidation.

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1. Introduction:

The textile industry is a major source of environmental contamination, it contains non-biodegradable and toxic substances and their impact on wildlife is very harmful. Today facing a global awareness, especially in the context of Community policy, industrial liquid waste textiles are subject to control and regulations increasingly severe. The socio-economic actors should help to fight against this problem and save what can be saved. The objective of this work is to deal with an advanced oxidation process, Fenton reaction, applied to colored liquid discharges of a textile industry in the SIDI GHANEM industrial zone of the city of Marrakech, Morocco. Recently there are highly developed technologies to treat industrial wastewater especially those containing dyes. These effluents are loaded with dyes, which may be the main cause of some environmental problems especially for aquatic plants and living beings, (Ibrahim M et al 1996; Tim Robinson et al 2001); and can be toxic and carcinogenic to animals. (Reife 1993). Many conventional methods for the removal of dyes in textile effluents including physical, chemical and biological process, (Shahzad Ali et al 2012; Xiaojun Wang et al 2007), have been used. Biological treatment was used to remove most BOD and a part of the DCO, but most textile dyes are not biodegradable so tertiary treatment, such as adsorption on activated carbon derived from biomass, or chemical oxidation is added after to remove residual dyes (Eckenfelde 1989; B. Benguella et al 2009; V. Dulman et al 2009; B.H. Hameed et al 2009; P. Janoš et al 2009; P. Leechart et al 2009; A.E. Nemr et al 2009). Non-biodegradable and refractory coloring, can be completely mineralized in an aqueous solutions into carbon dioxide, water, and other harmless products, through the OH groups. Now, several methods exist for generating hydroxyl radicals, such as the classic Fenton reaction, (A.L. Barros et al 2006; N. Modirshahla et al 2007; J.-H. Sun et al 2007), ozonation, (M.A. Behnajady et al 2006; A. de O. Martins et al 2006; C.-H. Wu et al 2007), UV radiation and UV-based processes (I. Peternel et al 2006; W.A.-A. et al 2008; S.G. Schrank et al 2007; H.-Y. Shu et al 2006; L. Wojnárovits et al 2008), photocatalysts, (E.R. Bandala et al 2008; M.H. Habibi et al 2007; M. Muruganandham et al 2007), and electrochemical methods. (N. Bensalah et al 2009; E. Chatzisyneon et al 2007; C.A. Martínez-Huitle et al 2009; Z. Zainal et al 2007). However, Fenton's process remains the oldest and cheaper but requires some conditions. Removal of dyes can achieve between 70% and 100%. Hydroxyl radicals react rapidly and indiscriminately with most organic compounds, by addition to a double bond or by abstraction of a hydrogen atom from an aliphatic organic molecule. (Song Y.L et al 2009). And the optimal pH range of Fenton process was found between 2 and 4, (I. Arslan-Alaton et al 2008; H.-J. Hsing et al 2007; H. Kušić et al 2007). Then chemical oxidation reactions occurred in aqueous solution between the organic radicals and oxygen, which ultimately lead to mineralized products carbon dioxide and water, (Sun S.P et al 2009; Talinli I et al 1992).

In our study, we examined the pure dyes used in dyeing to get an idea on the degradation of dyes in the absence of chemical additives, as a model, and a dyeing liquid rejection to study the effect of the presence of chemical additives on the final effluent, in the output of the industry.

2. Methods and materials :

2.1. Materials:

2.1.1. Chemical products and reagents:

Dyes studied are the Bezaktiv BLUE-SR, the NOVACRON® Red FN-R, and the NOVACRON®SCALE TFN-6G, widely used in the dyeing process, and a representative overall rejection which is a mixture of several dyes and chemical additives (acids, bases, oxidizing agents, and reducing agents, shampoos, detergents, emulsifiers, wetting agents and dispersants, etc). Chemical reagents used in the Fenton reaction are the pure iron sulphate FeSO_4 and hydrogen peroxide 50% H_2O_2 , gotten from the textile industry and highly used in fabrics bleaching, the acid sulfuric H_2SO_4 to acidify the reaction and keep the pH near 3 in order to have the Fenton reaction.

2.1.2. Procedure:

The colored solution is prepared at a concentration of 10 mg of pure dye per liter of distilled water for those three dyes: Bezaktiv BLUE-S-R, the NOVACRON® Red FN-R, and the NOVACRON®SCALE TFN-6G. Previous studies indicated that wastewater from the textile industry contains different dyes and their concentrations vary from 10 to 200 mg/L.^[37] In addition to the three pure dyes, we had studied a real liquid discharge of the dyeing unit at the exit, a global rejection of liquid sample in the middle of the week, is more representative, the sample contains different dyes and chemical additives, due to the variation of effluent components in the production process. A volume of 1 liter is then placed in glass vials, at ambient temperature, and mixed with iron sulphate FeSO_4 and H_2O_2 50%, for one hour. The pH of each solution was adjusted to the appropriate value by addition of sulfuric acid, H_2SO_4 . The reaction was initiated by adding different amounts of hydrogen peroxide and iron sulfate in the reactor after the pH adjusted, the speed of agitation was adjusted in 30 rpm samples were periodically removed from the reactor, every 15 minutes, using a pipette, and then the absorbance of the reaction solution was measured immediately, of course after the determination of the maximum wavelength of each sample by performing a UV-visible scanning.



Figure: Tenmar dye patterns and the Fenton reaction process

3. Results and discussion

3.1. Degradation of pure dye textile by Fenton catalytic:

The Fenton oxidation treatment has shown its ability to degrade completely the pure dyes in water. The efficiency of degradation is depending on the concentration of H_2O_2 and Fe^{2+} and was defined by measuring the absorption intensity at 610 nm, at 541 nm, and 504 nm max, respectively for the Bezaktiv BLUE-SR, the NOVACRON®Red FN-R, and the NOVACRON®SCALE TFN-6G from the UV-visible scanning curve for periodically withdrawn samples from reaction mixture using a pipette every 15 minutes. The rate of oxidation dyes reached 100% after 60 minutes of the reaction using the following formula:

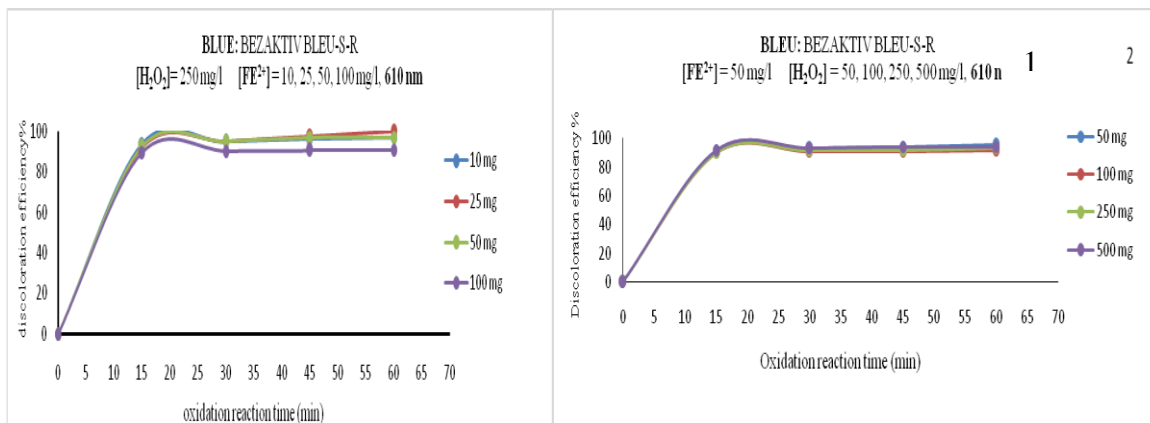
$$\% \text{ decoloration efficacy (X)} = [\text{Absi (x)} - \text{Absf (x)}] / \text{Absi (x)} \times 100$$

Absi (x) : Initial Absorbance , **Absf (x)**: Final Absorbance

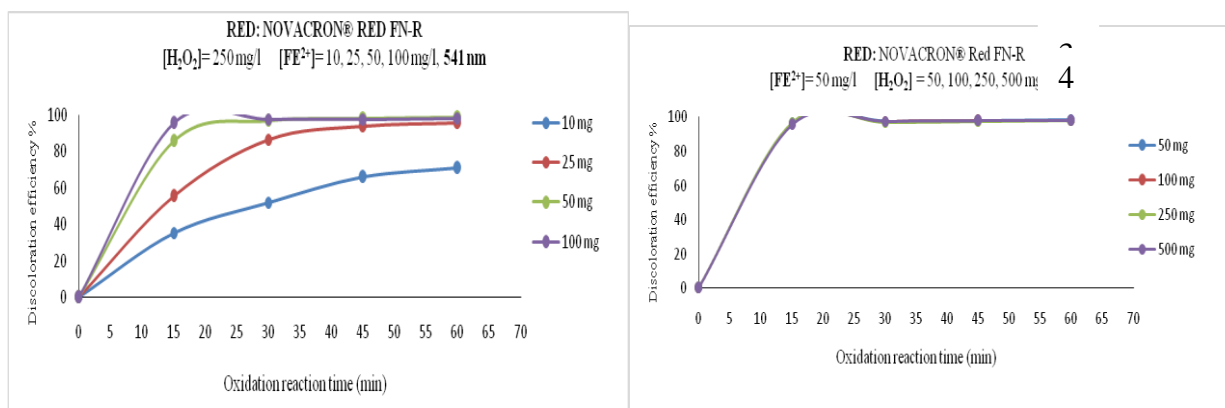
3.2. Effect of H_2O_2 concentrations on Fe^{2+} and the elimination of absorbance: For pure dyes [38].

When we are treating water by Fenton reaction, the ratio of $[\text{Fe}^{2+}]/[\text{H}_2\text{O}_2]$ or the reverse $[\text{H}_2\text{O}_2]/[\text{Fe}^{2+}]$, is very important to optimize the process conditions and the all the parameters are fixed in the room temperature and pH is maintained close to 3. Initially, we studied the effect of $[\text{Fe}^{2+}]$, on the efficiency of removal of the absorbance, the concentration of $[\text{H}_2\text{O}_2]$ was fixed at 250mg/l, and we used different concentrations of $[\text{Fe}^{2+}] = 10, 25, 50, 100 \text{ mg/l}$, we note that the effect of hydroxyl radicals react rapidly and indiscriminately with the dyes, either by addition to a double bond or by abstraction of a hydrogen atom from an organic molecule,^[31] and subsequently reacted with oxygen to

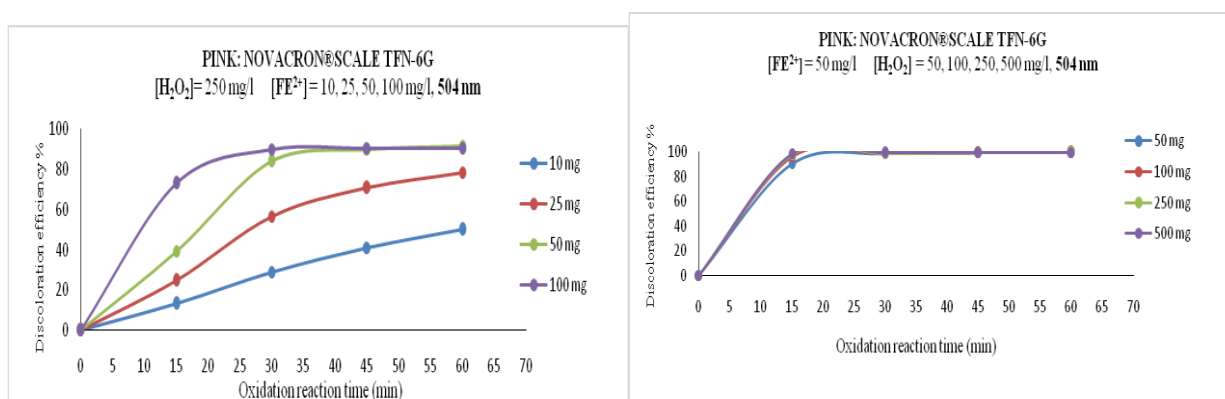
initiate a series of oxidation reactions that ultimately lead to a carbon dioxide mineralization and water.^{[35], [36]} It is noted that the discoloration reached 100% after 30min for the three pure dyes figures 1, 2, 3,4,5, and 6. The concentration of Fe^{2+} and H_2O_2 in the Fenton reagent, affected the efficiency of the degradation of dyes, the rate of kinetics, and hydroxyl ion generation. The ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ is found to be equal to 0.2, to obtain better results for the decolorization efficiency, as shown in the figures below.



Figures 1.2: Effect of concentration of $[\text{Fe}^{2+}]$, and $[\text{H}_2\text{O}_2]$ of the Fenton reaction time depending on the bleaching efficiency (%), case of Bezaktiv BLUE BLUE-S-R



Figures 3.4: Effect of concentration of $[\text{Fe}^{2+}]$ and $[\text{H}_2\text{O}_2]$ of the Fenton reaction time depending on the bleaching efficiency (%), case of NOVACRON® Red Red FN-R



Figures 5.6: Effect of concentration of $[\text{Fe}^{2+}]$, and $[\text{H}_2\text{O}_2]$ of the Fenton reaction time depending on the bleaching efficiency (%), case of PINK NOVACRON®SCALE TFN-6G



Figure: Discoloration of the three model dyes by Fenton reaction.

The Fenton process was effective at pH = 3, and the decolorization efficiency was 100% for the three dyes, these results being in agreement with similar work, the case of Reactive Yellow 84 reached 85% for 20 min of time of reaction, for an $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ratio is equal to 0.1, ^[39] Even for discoloration of the red peach azo dye, HF6 by Fenton reaction within a UV cell to allow rapid degradation of the dye, ^[40] And also the reduction of the organic matter content of the waste water produced from the textile. The results indicate that the oxidation process leads to a decrease in the concentration of the chemical oxygen demand (COD) of 45%, [41].

3.3. Physicochemical characteristics of a textile liquid waste:

The experimental study of this second part was carried on using the industrial wastewater from a dyeing unit textile located in the industrial zone of the city of Marrakech. Due to the variation in the composition of industrial wastewater from the dyeing factory, samples were taken in the middle of the week, the total liquid discharge is a mixture of several dyes and additives were analyzed. **Table 1** shows the characteristics of the liquid discharge, we notice that the parameters are not stable as the amount of chemicals used changes from day to day because of the activity of the plant and the command. The COD / BOD ratio is about 3, indicating that the organic matter in the discharge will be difficult to degrade by bacteria, which is a more or less difficultly biodegradable effluent, since a biological treatment must be incapable of eliminating most of the Pollution, from which the following systems - chemical oxidation, UV, ozone, bleach, peroxide, and Fenton, are able to eliminate a large part of COD. An analyzing by ICP was done, the inductively coupled plasma atomic emission spectroscopy showed that the inorganic chemical composition of the liquid discharge Table 1. The methods used for physicochemical measurements used in this study are essentially those described by AFNOR.



Figure: Appearance of Tenmar dye liquid rejection.

Table 1: Average characteristics of industrial wastewater of textile.

Parametersanalyzed	Value
Température whilesampling (°C)	38
pH	7.68
Conductivity (μS/cm)	3900
SuspendedMatter (mg/l)	200
Turbidity (FTU)	97
dry matter (g/l)	4.97
Ashes (g/l)	1.93
COD (mg/l)	991.67
BOD5 (mg/l)	348
COD/BOD5	2.84
N-NTK (mg/l)	32.67
SO ₄ ²⁻ (mg/l)	823
Na ⁺ (mg/l)	116

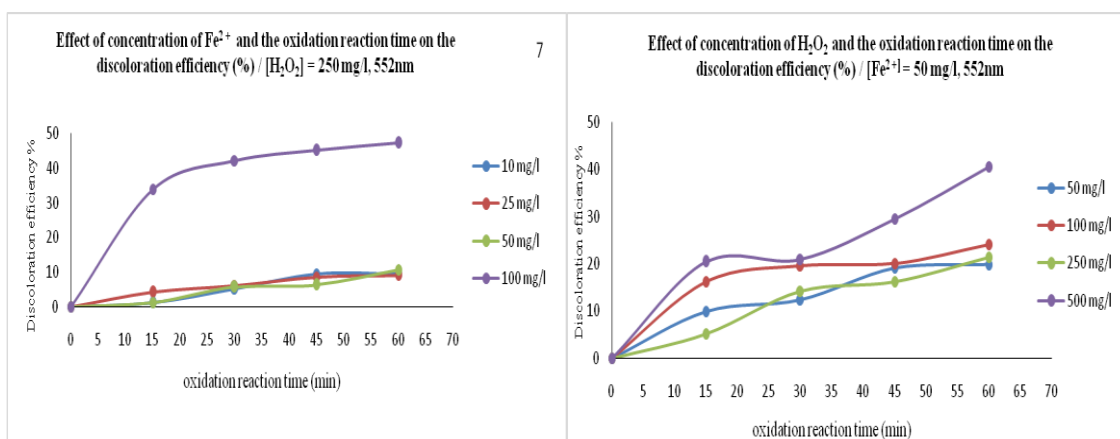
An analysis by plasma mass spectrometry ICP induced, showed the presence of several heavy metals but in low concentrations, Table2.

Table 2: Chemical composition of the textile liquid discharge.

Chemicalelement (ppm)	Amount	Chemicalelement (ppm)	Amount
Ag	0,211	Mn	0,0077
Al	0,4308	Mo	<1.9280
As	<0.0100	Na	1420,0856
B	0,0444	Ni	<0.0210
Ba	<0.0030	P	11,1497
Be	<0.0002	Pb	<0.0110
Bi	0,0513	Sb	<0.0210
Ca	44,4123	Se	<0.0570
Cd	<0.0040	Si	10,3459
Co	<0.0100	Sn	<0.0150
Cr	<0.0030	Sr	0,1226
Cu	<0.0036	Ti	<0.0062
Fe	0,0938	V	<0.0031
K	83,7252	W	0,0883
Li	0,0288	Zn	<0.0020
Mg	17,2095	Zr	0,0586

3.4. Effect of concentrations of H_2O_2 , Fe^{2+} and other parameters: T , pH in the elimination of absorbance: case of a textile liquid waste:

Fenton oxidation by treating a liquid discharge of the dyeing unit textile showed a limited degradation because of the presence of mineral components and which may be prevent the Fenton reaction, unlike in the case of dyes and in the absence of the mineral compounds or when the oxidation is complete. Previous works already shown that the existence of SO_4^{2-} , sulphate ions, Cl^- chloride ions, carbonate ions CO_3^{2-} , and phosphate ions PO_4^{3-} can inhibit the Fenton reaction.^{[42], [43], [44], [45], [46]} also the acidification of reaction medium with sulfuric acid, or acid chloride allows the sulphate and chloride ions to react with the ferrous ions required in the generation of hydroxyl radicals, ions, and discriminate the Fenton reaction. In addition the dissolution of textile dyes in water depends on their aggregation and their ionization. The aggregation increased by the inorganic salts can significantly limit the solubilization and ionization of dyes, especially those soluble on water. Thus, the possibilities that the dye molecules react with hydroxyl radicals is reduced.^{[47], [48]} The effect of the concentration of $[Fe^{2+}]$, and $[H_2O_2]$ on the textile effluent reaches an efficiency of discoloration of 47.12% and 40.63% respectively as shown in the figures below, figures 7 and 8. The concentrations 250 mg/L of $[H_2O_2]$, and 100 mg/l $[Fe^{2+}]$, are the optimal concentrations in the case of textile liquid discharge. However, the study will focus on the effects of the temperature T and pH .



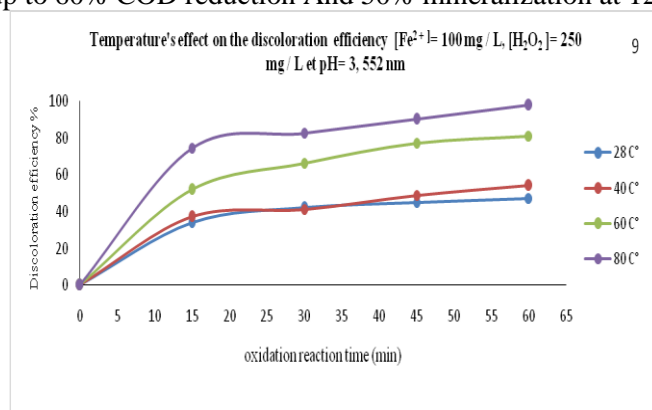
Figures 7.8: Effect of concentration of $[Fe^{2+}]$, and $[H_2O_2]$, of the Fenton reaction in function of time on the bleaching efficiency (%) case of textile liquid discharge.



Figure: Treatment of **Tenmar** liquid rejects by reaction of Fenton at ambient temperature.

The results of the study of the temperature parameter, liquid discharge mineralization increases, and the discoloration increased until the total degradation at a temperature of $80^{\circ}C$. So temperature is acting positively on the kinetics of the reaction,^{[49], [50]} and the optimum temperature for the best mineralization kinetics is about $60^{\circ}C$, with 81.09% of the degradation efficiency after 60 minutes as shown on following figures 9. Even in the case of sawmill wastewater

characterized by a moderate load of DOC about 3 g / l, a temperature increase significantly improved oxidation rate and degree of mineralization, up to 60% COD reduction And 50% mineralization at 120 ° C after one hour.^[51]

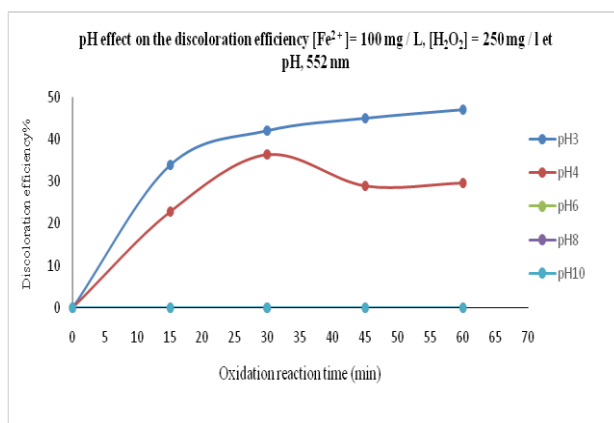


Figures 9: Effect of the temperature of the Fenton reaction in function of time on the bleaching efficiency (%) case of a textile liquid discharge.



Figure: Treatment of **Tenmar** liquid rejects by reaction of Fenton at 80 C °.

For pH, in the literature, the pH close to 3 remains always being the best as shown in the figure 10, for efficient degradation of organic pollutants.^{[52], [53], [54]} pH values very approximately acid to 2 promotes complexation of Fe^{2+} and Fe^{3+} , by H_2O_2 , and lead to a decrease in the concentration of these ions in the reaction medium. For the case of higher pH values greater than 4, the ferric ions are precipitated as iron hydroxide $\text{Fe}(\text{OH})_3$. The results of the study on pH effect on the degradation of components of the liquid discharge, show that a pH above 4 is assigned low production of OH, hydroxyl radicals.^[55] and a pH less than 2.8 due to the precipitation of ferric hydroxide into ferric iron which causes a decrease of the rate of decomposition of hydrogen peroxide H_2O_2 ,^[56]. We also noticed a coloration changes in basic pH, then the liquid became dark blue.



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Figures 10: pH Effect of the Fenton reaction in function of time on the bleaching efficiency (%) case of a textile liquid discharge.

4. Conclusion:

The treatment of textile liquid discharges, and textile dyes by advanced oxidation, using the Fenton reaction vector, shows that the presence of chemical additives in large quantity inhibits the Fenton reaction, thus mineralization dyes, so it is a method with drawbacks since the use of iron sulphate as a reagent is a pollution element for waste water. Also the need to operate in conditions a bit harsh (pH and concentration), sludge production, and consumption of OH[•] radicals by parasitic reactions. All this lead to look for more efficient methods for treating colored wastewater includes Fenton reaction process electro-Fenton, photo-Fenton, and which have an additional report of OH[•] Radicals, as the catalytic generation of Fe²⁺ ions, and the suppression of the formation of ferric hydroxide sludge.

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