

PRELIMINARY STUDY OF DECOLOURIZATION OF SOME TEXTILE EFFLUENTS BY HOMOGENOUS OXIDATIVE PROCESSES

BY

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Abstract. The paper presents a preliminary laboratory study of some homogenous oxidation processes with hydrogen peroxide (*i.e.* advanced oxidation with Fenton reagent) applied for wastewaters loaded with textile Orange 16 dye. The influence of different operational variables (*i.e.* stirring regime, temperature, pH, H₂O₂ concentration, ferrous ions concentration, dye concentration, oxidation time) was studied in order to find the most indicated values for high decolourization efficiency. A laboratory scale set-up decolourization experiment was performed for these proposed values in the case of an effluent loaded with 80 mg/L Orange 16 dye. The highest decolourization efficiency (> 97 %) was performed at pH (5.3), temperature of 19-20°C, continuous stirring regime (50 rpm), with 35.29 mM H₂O₂, 0.68 mM Fe²⁺, and after only 5 min of homogenous advanced oxidation.

Key words: textile effluent, decolourization, Orange 16 dye, homogenous advanced oxidation, Fenton reagent.

1. Introduction

The fulfillment of the stringent water quality regulations and demands for water reuse after treatment have stimulated strong research efforts aimed at the development of efficient routes to destroy toxic and/or bio-refractory organic compounds from aqueous streams [1], [2]. One of recognized and viable route is the oxidation (or mineralization) of these compounds to carbon dioxides and/or other harmless species. Progress in the removal of some refractory compounds has lead to the development of advanced oxidation processes (AOPs) [3],..., [14]. Among these processes, the advanced oxidation

using a Fenton reagent has proven an attractive treatment method for the effective decomposition of dyes [1], [8],..., [10]. The decolourization of the industrial effluent is essential for reuse of dyeing water resources or safe discharge into different receivers (*i.e.* urban sewerage or different emissaries) even when is released in small concentrations.

The use of different types of Fenton oxidation for dye or colour removal has advantages but also disadvantages that select sometimes the environmental options of management staff in fulfilment of environmental requirements on effluent quality and hourly loads. The main advantages of Fenton oxidation (FO) over other oxidative treatments are numerous including high efficiency, short oxidation times, simplicity in destroying the contaminants, stability to treat a wide range of substances, non-necessity of special equipment and relatively small quantities of precipitates and sludge. The principal disadvantages of FO are the chemical reagent consumption and the necessity of precipitates and sludge separation that requires coagulation-flocculation with separation of aggregates and sludge by sedimentation, filtration or other mechanical separation techniques and also application of Fenton Sludge Recycling System (FSR process, developed by peroxid-Chemie GmbH) [1],..., [10].

The objective of the present work is to find the specific variation limits for high efficiency of advanced Fenton oxidation (FO) applied for the commercial textile dye, Orange 16, selected as the test chemical to represent the azo dye group. All experiments were performed at laboratory scale set-up. The pH, H₂O₂ concentration, ferrous ions concentration and oxidation time are the basic chosen factors that are studied to find their influences against the FO treatment efficiency, in condition of delivering the treated effluent into aquatic environment or inside reuse.

Our previous studies were indicated higher dye removals when were used concentrations of 15-88 mM H₂O₂, 0.02-1.5 mM Fe(II), pH of 1-4, and an oxidation time of 1-30 min [3],..., [14]. This study of advanced Fenton oxidation will permit the comparison of authors' results concerning the Orange 16 removal from industrial textile effluents using different types of depollution treatments (*i.e.* chemical precipitation, coagulation-flocculation, chemical oxidation, ionic exchange, adsorption onto different types of solid materials, membrane process, ultra filtration, etc.).

2. Experimental

2.1. Materials and Reagents

The studied azo dye, Orange 16, is a commercially available textile dye used without further purification. The chemical formula of this azo dye is C₂₀H₁₆N₃O₁₁S₃Na₂ (C.I. 17757) and has the following properties: molecular

weight (MW) of 617.54 g/mol; solubility at 293K of 70 g/L; maximum absorbance (λ_{\max}) at 495 nm and purity of 80.90%. Working solutions (in concentrations of 20-150 mg/L) were prepared by appropriate dilution with bidistilled water of the stock dye solution (600 mg/L).

The hydrogen peroxide (30%) of analytical grade was obtained from S.C. Nordic Invest S.R.L. Company (Cluj Napoca, Romania).

The catalyst was prepared starting from commercially solid ferrous sulphate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, obtained from Fluka Analytical (Sigma-Aldrich Chemie GmbH, Germany). Thus, an aqueous stock solution containing 20 g/L was prepared with bidistilled water (adding 1-2 mL of concentrated or 2N sulphuric acid).

All the other solutions were used for pH adjustment (*i.e.* H_2SO_4 0.5N and NaOH 0.1N).

2.2. Apparatus and FO Procedures

The dye oxidation was carried out into a 300 mL glass reactor equipped with magnetic stirrer (AG-2). Different volumes of ferrous sulphate stock solution were introduced into 50 mL of aqueous dye solution, under continuous stirring. After temperature stabilization at selected value ($t = 19\text{-}20^\circ\text{C}$) and correction of pH, different volumes of 30% H_2O_2 solution were added to achieve the selected H_2O_2 concentrations, these being the basic conditions for the experimental tests. The moment when hydrogen peroxide was added into solution was considered the beginning of the FO experiment (zero time). Samples of ca 5 mL were collected from reactor at different specific time intervals and analysed in order to find the dye and colour removal progress. Into each collected sample, the hydrogen peroxide was removed by increasing pH value to basic interval (pH 9-10) with NaOH 2N solution and adding of solid MnO_2 (0.2 g MnO_2 for each sample of 5 mL).

The dye absorbance and colour were measured using a SP 830 Plus spectrophotometer, Metertech Inc. The visible light absorbance at the characteristic wavelength of dye, *i.e.* 495 nm, was measured to follow the progress of the dye removal during homogenous Fenton oxidation (FO). Colour determination was done by measuring the absorbance at $\lambda = 456$ nm using the distilled water as reference sample or at one of the standard wavelengths (*i.e.* 436, 525 and 620 nm; obligations are for absorbance measurement at 436 nm for all types of industrial wastewaters). The absorbance was converted in Hazen unit (HU), where 50 HU corresponds to an absorbance of 0.069 at 456 nm.

The pH measurements were performed at a HACH One-Laboratory pH-meter (Hach Company, USA).

The decolourization degree or dye removal (*i.e.* dye FO degree) was expressed with the general formula of a treatment degree for colour or dye (eq. 1).

$$(1) \quad DD = \frac{C_0 - C_t}{C_0} \cdot 100, [\%]$$

where: DD is the decolourization degree, [%]; C_0 – the initial dye concentration or color value into the initial effluent sample, [mg/L]; C_t – the dye concentration or color value at t oxidation time, [mg/L].

3. Results and Discussions

3.1. The Influence of pH in the FO Process

In Fenton process, the hydroxyl radicals with powerful oxidizing abilities to decompose dyes are formed as result of Fe^{2+} reaction with hydrogen peroxide. Hydroxyl radicals may react with ferrous ions to form ferric ions or react with organics. Hydroxyl radical generation is enhanced at low pH (2.5-4.5) [1],..., [5]. The oxidation products are usually low molecular weight oxygenated compounds that are easily biodegradable or, in some instances, the organic compounds reduce to carbon dioxide and water.

The pH values affect the FO process of dyes both directly and indirectly. The direct effect is the generation of hydroxyl radicals ($\text{HO}\bullet$) that influence the Fenton oxidation efficiency. Indirectly, the pH value influences the catalyst existence form and availability [1] (at pH value higher than 5.3 can precipitate ferric and ferrous hydroxides or other iron hydroxo complexes).

In the case of Orange 16 dye, the effect of pH is presented in Fig. 1 as a result of the kinetic studies of homogenous Fenton oxidation performed into solutions with 80 mg/L dye, 0.136 mM Fe(II), 0.178 M H_2O_2 , temperature of 19-20°C, under continuous stirring (50 rpm) for 120 min.

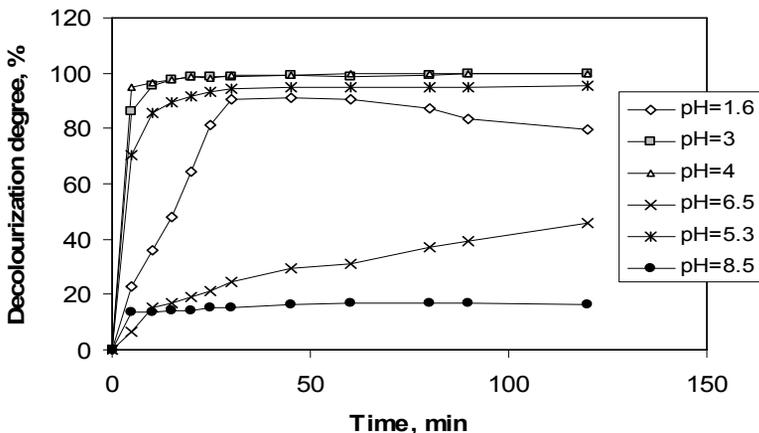


Fig. 1 – The influence of pH on dye FO process.

It is observing that in high acidic conditions (3-4), and also at pH of 5.3 there were performed high FO efficiencies for dye removal (*i.e.* > 90% after 20 minutes of Fenton oxidation, and > 80% after only 5 min). The dye oxidation rate decreased and may be even stopped at higher pH values than 5.3-6.0, appearing settleable iron precipitation aggregates and other hydroxo complexes.

The adequate pH range for Orange 16 decomposition by FO process is 3-4 (but it is necessary a neutralization step before direct discharge of treated effluent into different receiver basins), but can be chosen the pH of 5.3.

3.2. The Influence of H₂O₂ Concentration in the FO Process

There were performed kinetic experiments of homogenous Fenton oxidation into aqueous systems with 80 mg/L dye, 0.136 mM Fe(II), pH of 5.3, temperature of 19-20°C, under continuous stirring (50 rpm) for 120 min.

The experimental results were synthesized into Fig. 2 and indicate that competitive reactions take place in excess of hydrogen peroxide producing an inhibitory effect for the dye decomposition (*i.e.* higher H₂O₂ concentration than 88 mM H₂O₂).

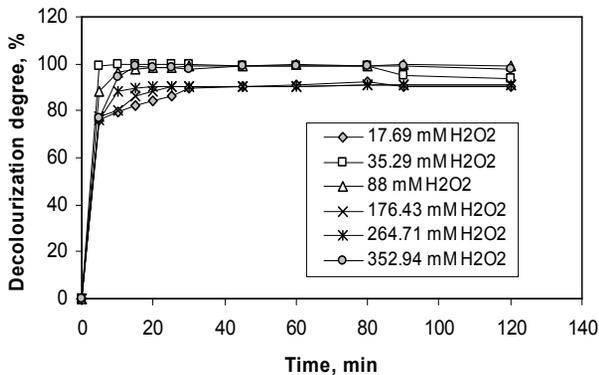


Fig. 2 – The influence of H₂O₂ concentration on dye FO process.

The adequate H₂O₂ concentration for Orange 16 decomposition by FO process must be between 20 - 40 mM H₂O₂ for an effluent loaded with 80 mg/L dye at pH of 5.3 and normal room temperature (*i.e.* the best H₂O₂ concentration value of 35.29 mM H₂O₂).

3.3. The Influence of Ferrous Ions Concentration in the FO Process

There were performed kinetic experiments of homogenous Fenton oxidation into aqueous systems with 80 mg/L dye, 35.29 mM H₂O₂, pH of 5.3, temperature of 19-20°C, under continuous stirring (50 rpm) for 120 min.

The experimental results were presented into Fig. 3 and indicate a reaction rate of dye oxidation that increases with catalyst concentration. Higher the ferrous ions concentration faster is the dye decomposition rate because more radicals are formed. When the concentration of Fe^{2+} ions is high the catalytic action is increasing in the first times of the reaction (5-10 min of dye FO).

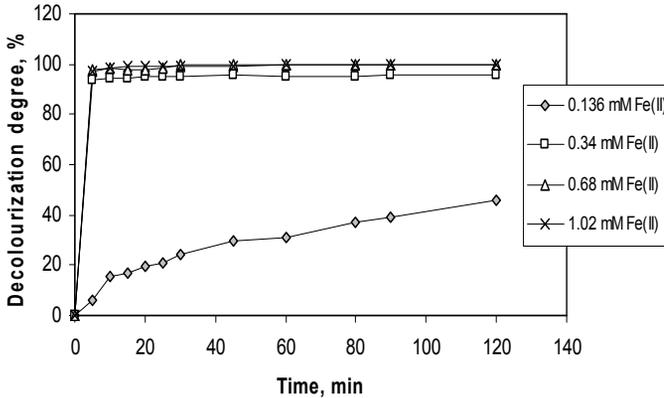


Fig. 3 – The influence of Fe^{2+} concentration on dye FO process.

The adequate ferrous ions concentration for Orange 16 decomposition by FO process after only 5 min must be between 0.34 – 1.02 mM Fe^{2+} for an effluent loaded with 80 mg/L dye at pH of 5.3 and normal room temperature (i.e. the best Fe^{2+} concentration value of 0.68 mM Fe^{2+} , decolourization degree of 98.03% after 5 min of dye FO). The treated effluent is possible and legal admissible into different receiving basins or urban sewerage system having admissible values of total iron concentration < 1 mg/L.

3.4. The Influence of Dye Concentration in the FO Process

The same operational methodology was applied for other kinetic experiments having as similar basic conditions the following: 80 mg/L dye, 35.29 mM H_2O_2 , 0.68 mM Fe^{2+} , pH of 5.3, temperature of 19-20°C, under continuous stirring (50 rpm), and final oxidation time of 120 min.

The results are summarized into Fig. 4. It is attempt that for constant $\text{Fe}(\text{II})$ and H_2O_2 concentrations, the dye oxidation degree decreases with the increasing of dye concentration.

It must be observed that the dye oxidation process, for all concentrations evolves in the same manner. Higher part of dye is rapidly destroyed in the first 10 min. The Fenton oxidation degree is lower for an effluent with a high dye load.

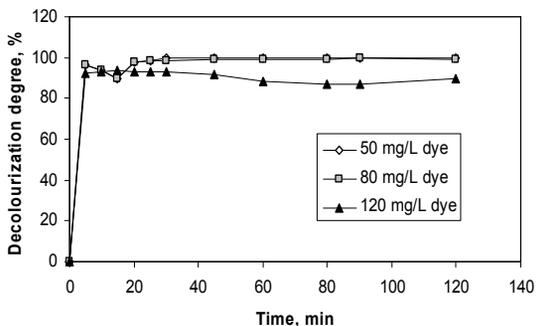


Fig. 4 – The influence of dye concentration on dye FO process.

3.5. The Influence of Oxidation Time in the FO Process

The effect of oxidation time vs. Fenton oxidation degree or dye removal can be observed into each of the Figs. 1,...,4. The higher part of dye is rapidly destroyed in the first 5-10 min. The remained concentration of dye is slowly transformed into the rest oxidation time, and generally can be concluded that the FO process of textile Orange 16 dye takes place with high efficiency into the first 30 min, and must be monitoring dye FO no more than a time period of 60 min.

The results of a kinetic FO process applied into the most indicated operational conditions presented above (*i.e.* pH of 5.3, 0.68 mM Fe^{2+} , 35.29 mM H_2O_2 , temperature of 19-20°C, under continuous stirring, final oxidation time of 120 min) were obtained and presented into Fig. 5. After only 5 min of FO process, there were performed dye FO degrees higher than 90%.

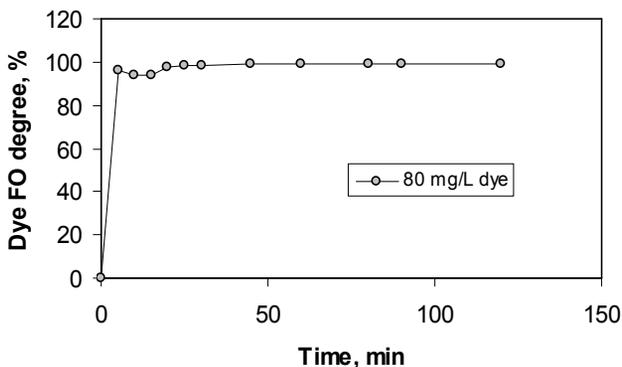


Fig. 5 – The variation of decolourization degree (*i.e.* dye Fenton oxidation degree). Operational conditions: pH=5.3, 80 mg/L dye, 0.68 mM Fe^{2+} , 35.29 mM H_2O_2 , $t=20^\circ\text{C}$.

4. Conclusions

The experimental results of this study indicate that the rate of the Orange 16 decomposition is important in the case of Fenton oxidation process (*i.e.* dye FO efficiency > 90% for specific adequate operational conditions).

A direct dependence between the H₂O₂ concentration and also the ferrous ions concentration and the Fenton oxidation rate of Orange 16 textile dye was observed. The most indicated values for H₂O₂ and Fe²⁺ concentrations are 20 - 40 mM H₂O₂ and 0.34 – 1.02 mM Fe²⁺ for an effluent loaded with no more than 80 mg/L dye at a pH of 5.3 and temperature of 19-20°C.

The dye Fenton oxidation is indicated to be performed in more acidic conditions (*i.e.* 3-4). At higher pH values than 5.3, the dye oxidation rate diminished or even stopped.

The higher values of dye FO efficiencies were obtained for dye effluent load lower than 80 mg/L (*i.e.* > 90% after only 5 min).

The Fenton oxidation can be a suitable treatment procedure for decolorization of textile effluents, once the optimal operational conditions were established.

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STUDIUL PRELIMINAR DE DECOLORARE A UNOR EFLUENȚI TEXTILI PRIN PROCESE OXIDATIVE OMOGENE

(Rezumat)

Lucrarea prezintă un studiu preliminar de laborator a unor procese de oxidare omogenă cu apă oxigenată (*i.e.* oxidare simplă și avansată cu reactiv Fenton) aplicate pentru ape uzate încărcate cu colorant textil Orange 16. A fost studiată influența diferitelor variabile operaționale (*i.e.* regimul de agitare, temperatură, pH, concentrația de H_2O_2 , de ioni feroși, de colorant, timpul de oxidare) în vederea găsirii celor mai bune valori pentru obținerea unor eficiențe mari de decolorare. Un experiment de decolorare la scară de laborator a fost realizat pentru aceste valori propuse în cazul unui efluent încărcat cu o medie de 80 mg/L colorant Orange 16. Cea mai mare eficiență de decolorare (> 97%) a fost obținută la pH (5,3), temperatură de 19-20°C, agitare continuă (50 rpm), cu 35.29 mM H_2O_2 , 0.68 M Fe^{2+} și după numai 5 minute de oxidare avansată.