

Development and optimization of dark Fenton oxidation for the treatment of textile wastewaters with high organic load

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Abstract

The examination of the effectiveness of the chemical oxidation using Fenton's reagent ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$) for the reduction of the organic content of wastewater generated from a textile industry has been studied. The experimental results indicate that the oxidation process leads to a reduction in the chemical oxygen demand (COD) concentration up to 45%. Moreover, the reduction is reasonably fast at the first stages of the process, since the COD concentration is decreased up to 45% within four hours and further treatment time does not add up to the overall decrease in the COD concentration (48% reduction within six hours). The maximum color removal achieved was 71.5%. In addition, the alterations observed in the organic matter during the development of the process, as indicated by the ratios of COD/TOC and BOD/COD and the oxidation state, show that a great part of the organic substances, which are not completely mineralized, are subjected to structural changes to intermediate organic by-products. © 2007 Elsevier B.V. All rights reserved.

Keywords: Advanced chemical oxidation; Fenton's reaction; Organic load; Textile wastewater

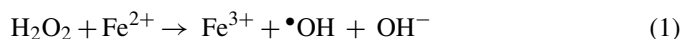
1. Introduction

Conventional biotreatment methods are not effective for the most of the synthetic dyestuffs due to the complex polyaromatic structure and recalcitrant nature of dyes. Textile wastewaters exhibit low BOD to chemical oxygen demand (COD) ratios (ca. 0.1) indicating the non-biodegradable nature of dyes.

Advanced oxidation processes (AOPs) have been proven particularly effective for the treatment of a wide variety of wastewater containing refractory organic contaminants. These methods include among others, the use of UV, O_3 , H_2O_2 , TiO_2 and their combinations [1–6], photocatalysis [7–9], sonolysis [10–13] and supercritical oxidation [14–16]. These methods employ chemical, photochemical, sonochemical or radiolytic techniques to bring about chemical degradation of pollutants.

The common feature of these techniques is the generation of free hydroxyl radicals ($\cdot\text{OH}$), which are very reactive since they have a high oxidation potential. The oxidation potential of the hydrogen peroxide has been reported to be 1.9 V [17]

while the oxidation potential for the hydroxyl radicals is approximately 2.8 V. Using H_2O_2 , the production of hydroxyl radicals is enhanced by the presence and action of ferrous ion (Fe^{2+}), as a catalyst. In this case, hydrogen peroxide is decomposed to hydroxyl radical and hydroxyl ion, while ferrous ion is transformed into ferric ion. This reaction is known as Fenton's reaction:

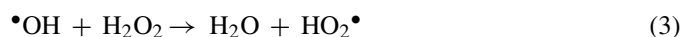


The Fenton's reaction is complex and it involves individual elementary reactions between initial reactants and generated radicals. A mechanism that describes the entire process includes the following reactions [18–20]:

Hydroxyl radicals might react with ferrous ions leading to the production of hydroxyl and ferric ions:



Hydroxyl radicals can react with hydrogen peroxide to form hydroperoxyl radicals and may also combine with each other to produce hydrogen peroxide:



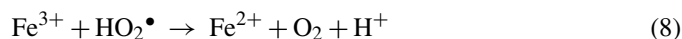
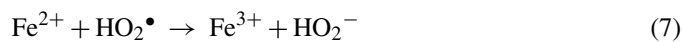
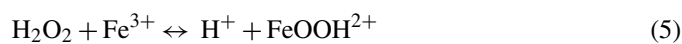
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Also, ferrous ion and radicals are formed during the following reactions:



The Fenton's reaction takes place in pH values ranging between 3 and 3.5. In these pH values, the formation of the free hydroxyl radicals is activated. In addition, the low pH values inhibit the formation and precipitation of the insoluble ferric hydroxide, $\text{Fe}(\text{OH})_3$.

Moreover, the reaction rate in reactions (5) and (6) is lower than that in reaction (1). As a result, ferrous iron is consumed quickly and reproduced slowly. Several researchers examined the applicability of the Fenton reaction process for the treatment of wastewater generated at textile and dye industries.

Perkowski and Kos [21] investigated the applicability of Fenton reagent for the treatment of textile dyeing wastewater. The optimum conditions and efficiency of the method were determined, taking as an example three types of wastewater produced while dyeing cotton, polyacrylonitrile, and polyester. Two types of iron(II) salt were used: sulphate ($\text{FeSO}_4 \times 7\text{H}_2\text{O}$) and chloride ($\text{FeCl}_2 \times 4\text{H}_2\text{O}$). To adjust the pH of the wastewater, a 1% solution of calcium oxide (CaO) was used. The process of pollutant decomposition which took place in the wastewater under the influence of hydrogen peroxide alone at different concentrations was investigated. When the Fenton reagent was used both for iron sulphate and iron(II) chloride, the optimum doses of the two salts and hydrogen peroxide were determined. It was found that the tested dyeing wastewater showed high susceptibility to treatment using a combined action of ferrous salts and hydrogen peroxide. The main parameters of wastewater, that is the color threshold number, chemical oxygen demand, and anionic surfactants, were greatly reduced. Investigations of the wastewater after treatment showed a remarkable increase in susceptibility to biodegradation.

The efficiency and cost-effectiveness of $\text{H}_2\text{O}_2/\text{UV}$ for the complete decolorization and mineralization of wastewater containing high concentrations of the textile dye Reactive Black 5 was examined by El-Deim et al. [22]. Oxidation until decolorization removed 200–300 mg/g of the dissolved organic carbon (DOC). Biodegradable compounds were formed, so that DOC removal could potentially be increased by 30% in a following biological stage. It was found that in order to attain 800 mg/g overall mineralization, 500 mg/g of the DOC had to be oxidized in the $\text{H}_2\text{O}_2/\text{UV}$ stage.

The aim of the study performed by Solmaz et al. [23] was to compare the performance of coagulation, Fenton's oxidation ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and ozonation for the removal of COD and color from biologically pre-treated textile wastewater. FeSO_4 and FeCl_3 were used as coagulants at varying doses and varying color removal efficiency was measured. For the Fenton process,

COD and color removal efficiencies were found to be 78 and 95% and 64 and 71% for the Fenton-like process ($\text{Fe}^{3+}/\text{H}_2\text{O}_2$). Ozonation resulted in 43% COD and 97% color removal whereas these rates increased to 54 and 99% when 5 mg/l hydrogen peroxide was added to the wastewater before ozonation at the same dose.

Reuse of effluent obtained from the biological wastewater treatment plant of a textile dyeing facility has been investigated by Gonder and Barlas [24]. Effluent has been further treated by Fenton process, chemical precipitation, adsorption and demineralisation, respectively. Optimum molar ratio of ferrous sulfate to hydrogen peroxide ($\text{FeSO}_4/\text{H}_2\text{O}_2$) was determined to be 0.025 (0.25/10). Under these circumstances the wastewater COD has been decreased by 39%.

In a study carried out by Azbar et al. [25], a comparison of various advanced oxidation processes (AOPs) (O_3 , O_3/UV , $\text{H}_2\text{O}_2/\text{UV}$, $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$, $\text{Fe}^{2+}/\text{H}_2\text{O}_2$) and chemical treatment methods using $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, FeCl_3 and FeSO_4 for the COD and color removal from a polyester and acetate fibre dyeing effluent was undertaken. AOPs showed a superior performance compared to conventional chemical treatment. For the latter the maximum achievable color and COD removal for the textile effluent used in this study was 50 and 60%, respectively. Although $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ combination among other AOPs methods studied was found to give the best result (99% removal for COD and 96% removal for color), the use of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ gave a satisfactory COD and color removal performance (90% removal) and the method was proved to be economically the most viable choice for the acetate and polyester fibre dyeing effluent.

The research undertaken by Bae et al. [26] evaluated quantitatively the predominant reactions in a large-scale Fenton process that treated dyeing wastewaters and suggested an economical and effective treatment process. Through plant analysis, it was found that a great part of the COD was removed by ferric coagulation. The comparative evaluation of Fenton oxidation and ferric coagulation revealed that ferric coagulation was the predominant mechanism to remove COD. In Fenton oxidation, the removal efficiency of COD was 67.7% and in ferric coagulation, 60.8%. A combined process with iron coagulation/precipitation and Fenton oxidation reduced the hydrogen peroxide dosage by over 40% compared to a conventional dosage.

Finally, the oxidative treatment characteristics of biotreated textile-dyeing wastewater and typical chemicals such as desizing, scouring, dispersing, and swelling agents used in the textile-dyeing process by advanced oxidation processes were experimentally studied by Lim et al. [27]. The refractory organic matters remained in the effluent of biological treatment process were degraded to CO_2 by combined ozonation with and without hydrogen peroxide. As a result, AOPs, followed by biological treatment were proposed for the treatment of the refractory organics of the wastewater from the textile-dyeing process. On the other hand, the refractory chemicals contained in the scouring and swelling agent were not mineralized and their biodegradability was not improved by applying AOPs.

2. Methods

2.1. Wastewater sampling and characterization

Textile wastewater samples were taken in polyethylene bottles from an industry located in the greater area of Athens, Greece. Samples taken were preserved in the refrigerator at 4 °C in accordance with the standard methods for the Examination of Water and Wastewater [28]. Textile wastewater samples were characterized in terms of the pH value as well as of BOD, COD, and TOC concentrations [28]. All solutions were prepared with ultra pure water prepared by Milli-Q system. The detection of the color value was determined using a UV–Vis spectrophotometer (Jasco V-530) according to Method 2120 C in standard methods [28]. The initial value of color was 0.270 [absorbance at wavelength (λ_{max}) = 600 nm, number of selected ordinates = 10].

2.2. Development of the chemical oxidation process

For the development of the chemical oxidation method, batch experiments were performed in triplicate, using hydrogen peroxide (H_2O_2) in the presence of ferrous iron (Fe^{2+}), as a catalyst. The chemical oxidation took place using an appropriate 2 l reactor made by borosilicate glass, with baffles to minimize vortexing and rotational flow. The opening of the bottle was equipped with a sampling port by fitting a mini-nert valve. A magnetic stir bar was placed in each bottle and the entire reactor assembly, bottle and sampling ports, was placed on a magnetic stir plate. The reactors were filled with 2 l of wastewater and then the pH of the solution was adjusted to 3 using 1 M sulfuric acid. The reactor temperature was maintained by a water circulator at room temperature.

Initially, hydrogen peroxide solution (perhydrol containing 30% w/w of H_2O_2 , Merck) was added in various dosages to known wastewater samples volumes (2 l) with the addition of various dosages of Fe^{2+} (in the form of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solution), in order to select the optimum quantities of the reagents for the development of the method (jar-tests experimental series).

The initial development of the process lasted 24 h; a time period that may be considered adequate for the completion of the chemical oxidation action. In addition, the reaction was suppressed with NaOH in order to increase the pH above 10. At such high pH the removal efficiency of organics via oxidation stops. Not only decomposition of hydrogen peroxide but also deactivation of ferrous catalyst by formation of ferric hydroxide, $\text{Fe}(\text{OH})_3$ or/and ferric hydroxo complexes e.g. $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, $\text{FeO} \cdot \text{OH} \cdot \text{H}_2\text{O}$ is the reason. Furthermore, at high pH any interference of any residual H_2O_2 during the COD measurement is avoided. Then, a portion of the treated samples was taken using appropriate glass syringes and the treated wastewater was analyzed for COD concentration [28].

Four different dosages of oxidant (perhydrol solution from 50 to 200 ml/l of wastewater containing corresponding quantities of pure H_2O_2 in the range from 0.440 to 1.764 mmole/l) were used in combination with four different dosages of catalyst (20 to 50 mg Fe^{2+} /l or 0.358 to 0.895 mmole Fe^{2+} /l). For the sixteen

combinations of oxidant and catalyst, the respective $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio dosages ranged from 0.492 to 4.927.

Under the same experimental conditions, as described above, a more detailed study was performed in order to assess the efficiency of the method, as well as to determine the variations in the organic matter form through the development of the process. In particular, the selected optimum hydrogen peroxide dosage was added in wastewater samples over a six-hour reaction time period. During the course of the reaction, treated samples were taken at specific pre-selected time intervals (0.5, 1, 2, 3, 4, 5, and 6 h). The treated wastewater was then analyzed for the determination of the BOD, COD, and TOC concentrations [28].

3. Results and discussion

The reduction in the COD concentrations, using various quantities of hydrogen peroxide solution and ferrous sulfate is given in Table 1. It is evident that the highest reduction, up to 50%, was achieved by using 100 ml perhydrol (corresponding to 0.882 mmole hydrogen peroxide) per liter of wastewater, while the catalyst dosage was 40 and 50 mg Fe^{2+} per liter of wastewater.

By doubling the quantity of oxidant (200 ml perhydrol or 1.764 mmole H_2O_2 per liter of wastewater), the further reduction that was achieved is considered negligible (49 to 50% and 50 to 51%, for 40 and 50 mg catalyst/l, respectively). Moreover, the same pattern was observed by increasing the amount of catalyst from 40 to 50 mg/l (49 to 50% and 50 to 51%, for 100 and 200 ml perhydrol/l - corresponding to 0.882 and 1.764 mmole of H_2O_2 /l, respectively).

Comparing the results obtained by the use of specific amount of catalyst and different quantities of oxidant in increasing dosages, the following can be derived: For the two experimental series using 50 and 70 ml perhydrol/l (0.440 and 0.617 mmole of H_2O_2), the reduction in the COD concentration varied slightly. This is due to the fact that the catalyst was present in excessive quantity as the dosage of catalyst increased and/or the oxidant was present in scant quantity (as indicated by comparing the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio dosages between the two experimental series). Using 100 ml perhydrol/l (0.882 mmole of H_2O_2 /l), the reduction in the COD concentration was increased sufficiently, leading to a significant removal of organics from the wastewater. By doubling the amount of oxidant (200 ml perhydrol/l or 1.764 mmole of H_2O_2 /l), there was only excess of the oxidant in the solution for all the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio dosages used (the oxidation actions had already been completed).

Table 1
Percent of COD reduction for various oxidant and catalyst dosages

Perhydrol dosage (ml/l)	50	70	100	200
H_2O_2 dosage (mmole/l)	0.440	0.617	0.882	1.764
Dosage of Fe^{2+}				
20 (mg/l) or 0.358 mmole/l	17.5	18	25.5	27
30 (mg/l) or 0.537 mmole/l	25.5	26.5	32	33.5
40 (mg/l) or 0.716 mmole/l	28	29.5	49	50
50 (mg/l) or 0.895 mmole/l	29	31	50	51

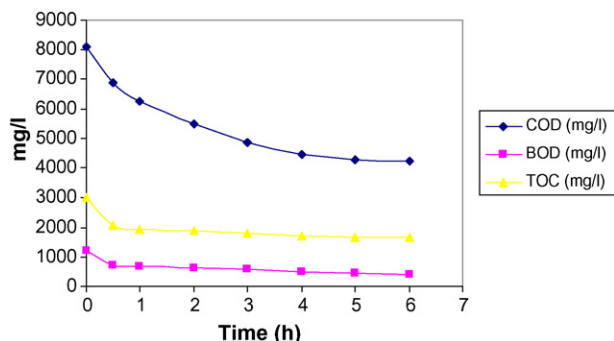


Fig. 1. COD, BOD, and TOC concentration during the chemical oxidation process.

Referring to the results obtained by the use of specific amounts of oxidant and various quantities of catalyst in increasing dosages, the following are observed: For all catalyst dosages (20–50 mg Fe^{2+}/l), the COD concentration was reduced in decreasing rate, when 50 and 70 ml perhydrol/l were used. On the contrary, when 100 and 200 ml perhydrol/l were added, the pattern was different: By adding up to 40 mg Fe^{2+}/l , the reduction in COD followed an increasing rate, while the use of 50 mg Fe^{2+}/l , as mentioned previously, did not lead to further reduction in the COD concentration. This indicates that the catalyst was present in excessive quantity for the dosage of 100 ml perhydrol/l or 0.882 mmole of $\text{H}_2\text{O}_2/\text{l}$ while both catalyst and oxidant quantities were in excess, for the dosage of 200 ml perhydrol/l or 1.764 mmole of $\text{H}_2\text{O}_2/\text{l}$.

As a result, the optimum dosages of oxidant and catalyst for the development of the process were 100 ml perhydrol (0.882 mmole of $\text{H}_2\text{O}_2/\text{l}$) and 40 mg Fe^{2+} , respectively. These quantities were selected for further experimental series, the results of which are presented and assessed below.

Fig. 1 shows the results obtained during the six-hour reaction period, concerning the concentrations of BOD, COD, and TOC, while Fig. 2 illustrates their reduction through the oxidation process. The percent of the color removal is shown in Fig. 2 as well. The maximum color reduction achieved was 71.5%.

The oxidation process was reasonably fast at the beginning and most of the reduction in COD was observed within the first few hours. In particular, the concentration of COD was reduced up to 45%, during the first four hours of the process, while further

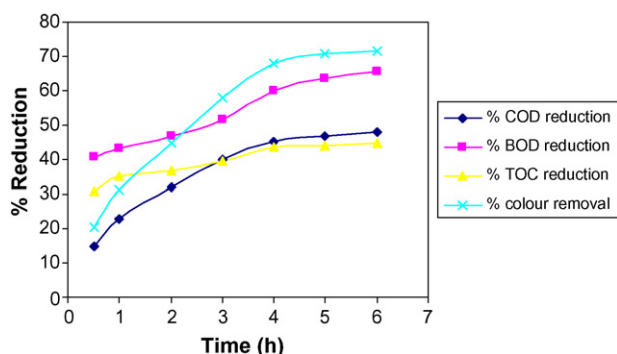


Fig. 2. Percent of reduction in COD, BOD, TOC, and color during the chemical oxidation process.

Table 2

BOD/COD, COD/TOC ratio, and oxidation state during the chemical oxidation process using the optimum dosages of oxidant and catalyst, 100 ml/l perhydrol and 40 mg Fe^{2+}/l , respectively

Time (h)	BOD/COD	COD/TOC	Oxidation state
0	0.148	2.691	-0.04
0.5	0.103	3.310	-0.97
1	0.109	3.200	-0.80
2	0.116	2.892	-0.34
3	0.119	2.677	-0.02
4	0.108	2.614	+0.08
5	0.101	2.556	+0.17
6	0.097	2.528	+0.21

oxidation time period did not lead to significant reduction in the COD concentration (48% for six hours of treatment). The same pattern was followed with respect to the decrease of BOD and TOC concentrations, which reached 60 and 40% for four hours and 66 and 45% for six hours, respectively.

As described previously, the main parameter for the development of the process is the presence of ferrous ions. In the first stages of the process, the oxidation rate of organic compounds is fast because sufficient amount of ferrous ions that react quickly with hydrogen peroxide is present and as a result, high amount of hydroxyl radicals are formed, (reaction (1)). In the following stages, while ferrous ions are consumed, their reproduction takes place in low rates, as depicted in reactions (5) and (6). This is confirmed by the fact that the reaction rate constant ($\text{M}^{-1} \text{s}^{-1}$) of ferrous ions reacting with hydrogen peroxide to form hydroxyl radicals is between 53 and 76 [8], while the reaction rate constant of ferric ions reacting with hydrogen peroxide to produce ferrous ions is only 0.01. In addition, ferrous ions can also be rapidly destroyed by hydroxyl radicals with the rate constant in the range of $3.2\text{--}4.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ (reaction (2)). As a result, lower amount of hydroxyl radicals is available for the oxidation of the organics present in the wastewater.

Moreover, Table 2 and Fig. 3 present the results regarding the variations of BOD/COD and COD/TOC ratios as well as of the oxidation state during the development of the process. From the results, the following information is derived:

The organic content of the wastewater under examination, as expressed by the parameters of BOD, COD, and TOC

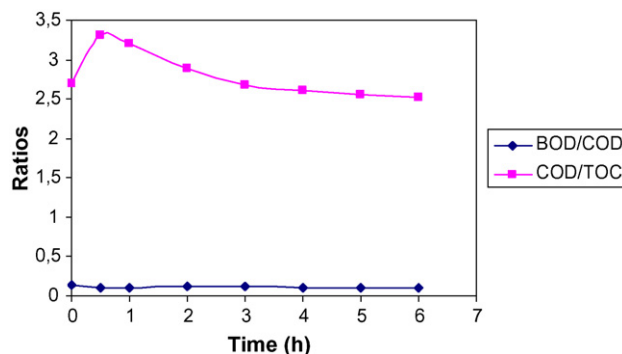


Fig. 3. BOD/COD and COD/TOC ratio during the chemical oxidation process.

is quite high (1200, 8100, and 3010 mg/l, respectively). The low BOD/COD ratio, 0.148, indicates that this organic matter is mainly not biodegradable. In addition, the wastewater is neutral to alkaline, since the pH value was found to be 7.9.

It must be mentioned that the COD test is based on the assumption that all the organic materials can be oxidized by a strong oxidizing agent under acidic conditions. However, the COD test has some restrictions. Some reduced substances such as sulfides, sulfites, ferrous iron can be oxidized too and this contributes to the determination of COD. In addition, some aromatic compounds are not oxidized completely within the COD test procedure. As a result, the oxygen demands that were determined do not reflect the actual oxygen requirements for oxidation. TOC is a more convenient and direct expression of total organic content than COD. TOC is independent of the oxidation state of the organic matter and does not measure other organically bound elements such as nitrogen, hydrogen, and inorganics that can contribute to the oxygen demand measured by COD. Additionally, the TOC measurements are not affected by the presence of organics that are difficult to be oxidized completely. Using COD and TOC as well as their relationship, the efficiency of the chemical oxidation and the state of oxidation can be interpreted. The average oxidation state of organics in the wastewater can be expressed as: oxidation state (O.S.) = $4(\text{TOC} - \text{COD})/\text{TOC}$ or $4(1 - \text{COD}/\text{TOC})$, where COD is expressed in moles of O_2/l and TOC in moles C/l .

The amount of carbon converted to carbon dioxide can be determined directly by measuring the TOC, while the ratio COD/TOC can be related to the degree of change in the structure of the organic compounds after oxidation.

Concerning the variations in BOD/COD ratio, the results show that during the process, this ratio was reduced from an initial value of 0.148 to 0.097 after the completion of the oxidation action. In addition, the COD/TOC ratio was decreased from 2.691 to 2.528 during the same time period, while the oxidation state decreased in the first stages from (-0.04) (initial value) to (-0.97) and then it increased to a final value of $(+0.21)$. It must be also noticed that during the first two hours of the process, the COD/TOC ratio was decreased significantly since its value was 3.310, 3.200, and 2.892 for 0.5, 1, and 2 h of treatment, respectively.

The initial increase in the COD/TOC ratio is mainly a result of TOC reduction due to the complete decomposition of organics to CO_2 . In this case, COD is decreased, due to the formation of partially oxidized organic by-products and complete degradation of other organics to CO_2 . The reduction in COD/TOC ratio after two hours of oxidation action is a result of the high decrease in both COD and TOC. COD is reduced significantly due to the formation of organic by-products with higher oxidative level and the complete degradation of organics to CO_2 in higher levels than in the initial stages of the process. This degradation to CO_2 is reflected also in the decrease of TOC as well.

The overall results show that the application of the Fenton's reaction for the oxidation of the wastewater under study is completed after four hours, since longer treatment time period

did not lead to significant additional reduction in the organic load concentration, as expressed by the parameters of COD and TOC.

Moreover, the changes in the concentrations of the COD values (that indicate the degree of oxidation) and TOC values (that indicate the degree of ultimate conversion) as well as the variations in ratios of BOD/COD, COD/TOC and oxidation state level that were observed during the development of the process show that the organics in the wastewater react with the chemical oxidant, following two main paths of degradation: primary degradation (a structural change in the parent compound resulting in the formation of intermediate organic by-products) and ultimate degradation (complete oxidation of a portion of these organic by-products to carbon dioxide, water and other inorganic substances, i.e. mineralization).

Comparing the overall results that were obtained through this work to those achieved by other researchers who examined the treatment of similar wastewaters applying the Fenton process, it is apparent that the removal of COD that was achieved is at satisfactory levels and similar to those reported in the literature [21–27]. Furthermore, in all cases, the application of the Fenton process alone, did not lead to complete degradation of the organics contained in the textile wastewaters and additional treatment (pretreatment or post treatment) or combination of AOPs were required for the total removal of the organic load from this type of wastewater.

4. Conclusions

The development of the chemical oxidation based on the Fenton's reaction, leads to significant reduction in the organic matter of the wastewater generated from a textile industry. This reduction is reasonably fast at the first stages of the process, since COD concentration is decreased up to 45% within four hours and further treatment time does not add up to this reduction (48% reduction within 6 h). The color removal achieved by the application of the method was found to be up to 71.5%. The results indicate the possibility of application of this method as a pretreatment or as a post treatment process (after chemical precipitation – coagulation) for the removal of the organics from the wastewater under examination. Furthermore, combination of AOPs (e.g. photo Fenton) should also be investigated since it is expected to further enhance the production of hydroxyl radicals and therefore strengthen the oxidation process.

Finally, the alterations observed in the organic matter during the development of the process indicate that the organic substances, which are not destructed completely to CO_2 , are subjected to structural changes to intermediate organic by-products of a lower molecular weight. This fact underlines the potential for development of further research on this topic in order to identify the pH influence on the process, the organic by-products that are formed, determine the kinetics of the Fenton's reaction and specify the mechanisms of the individual chemical reactions that take place during the development of the entire process.

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