International Journal of Scientific Research & Engineering Technology (IJSET)
ISSN: 2356-5608, Vol.3, issue 2

Treatment of Water Soluble Dyes in Real Textile Wastewater by Fenton's Process

Wafa Miled, Sihem Soula and Neji Ladhari
Textile engineering laboratory, Monastir University, TUNISIA
w.miled@yahoo.fr

***Abstract*— In this study, synthetic and real wastewaters mainly polluted with direct and reactive dyes were treated by Fenton process. The real wastewater was coming from a dyeing and finishing factory. The synthetic wastewater was stimulated in order to compare degradation results. Azoic and Vinylsulfonic dyes and other finishing reagents were selected as model pollutants. The study was performed in a systematic approach searching optimum values of H_2O_2 and $FeSO_4$ concentrations, pH, temperature and composition of each tested wastewater. Results showed that the oxidation behavior of synthetic and real wastewater was very similar especially during the first stage were the breakage of the chromophores groups allowed fast color removal of the sample. However, the COD removal of the real wastewater was visibly smaller than synthetic wastewater. The H_2O_2 optimum concentration seems to be related to initial COD of the sample. Instability of the composition of the real wastewater and the unknown chemical and physical interferences between its compounds made big differences in the $[H_2O_2]/[FeSO_4]$ optimum ratios for both tested wastewaters. Considering the very powerful oxidant involved in the oxidation mechanism and the possibility to use this process as a final treatment (after coagulation and sedimentation) a much better final wastewater quality can be discharged by the concerned textile factory.**

Keywords*— *Fenton process; real wastewater; color removal; COD removal; reactive dye; direct dye.

I. INTRODUCTION

The textile industry is one of the most polluting sectors when discharge volume and effluent composition were considered [1]. Dyeing washing and finishing industries use large amount of water of very good quality and chemicals with complex structures. Such industries impose serious environmental problems because of the high color, high chemical oxygen demand, low biodegradability, fluctuating pH and high temperature of its wastewater [1, 2, 3]. The treatment of such effluent is commonly carried out using biological and physicochemical methods [2, 3]. However, many of the commercially used dyes are resistant to biodegradation [1, 4]. In addition coagulation process followed by sedimentation or adsorption are widely used but not promising in terms of performance because the secondary pollution arising from the residual sludge [4]. Biological treatments are very employed in the Tunisian textile wastewater stations but with low efficiency for synthetic dyes. This problematic is originally due to the toxicity of some by-products [1, 2, 3]. The most commonly used textile dyes consists of direct and reactive dyes which are anionic and very soluble. Such dyes have also a high chemical and photolytic stability. Also, the conventional textile effluent treatment in aerobic conditions does not degrade these textile dyes, and are presented in high quantities into natural water resources in absence of some tertiary treatments [1, 5]. In order to meet legislative requirements many chemical treatment processes have been used extensively to treat textile wastewaters. Among all these proposed systems oxidative treatments seem to be promising because they really involve a degradation process of the pollutant although never complete [4, 6].

There are a number of advanced oxidation processes currently being evaluated for the destruction of dyes in effluents. Fenton is one of the oldest advanced oxidation processes which is used successfully, as it is comparatively low cost and uses easy to handle reagents. It allows the production of highly active hydroxyl radicals as a result of the reaction of hydrogen peroxide with iron II ions. Undoubtedly, the process efficiency can be much improved and intensified because the oxidation of organic compounds by the hydroxyl radical generated insitu is much faster [7, 8, 9, 10]. The chemistry of Fenton process is initiated by the hydroxyl radical as follows [11].

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

The formed oxidizing and propagating agent initiates the chemical oxygen demand (COD) and color removal reactions of organics (RH).

$$OH^\bullet + RH \rightarrow H_2O + R^\bullet \quad (2)$$

$$R^\bullet + H_2O_2 \rightarrow ROH + OH^\bullet \quad (3)$$

$OH^\bullet$ radicals also decompose H_2O_2 producing $HO_2^\bullet$ radicals.

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \quad (4)$$

The kinetic chain is finished by reactions between radicals as follows:

$$OH^\bullet + OH^\bullet \rightarrow H_2O_2 \quad (5)$$

$$Fe^{2+} + HO^\bullet \rightarrow Fe^{3+} + HO^- \quad (6)$$

$$Fe^{2+} + HO_2^\bullet \rightarrow Fe^{3+} + HO_2^- \quad (7)$$

In this study the use of Fenton process were explored for the decolorization of synthetic and real wastewaters coming from a dyeing and finishing factory. The purpose was to investigate the effectiveness of Fenton process for the decolorization of such wastewaters with different complexity and chemical stability behavior. The real wastewater was a mixture of direct and reactive dyes with other finishing

reagents. The synthetic wastewater was stimulated in manner to have a known composition easier to define. The investigation covered the determination of parameters affecting the process efficiency to find out optimum values and to make comparisons with the literature values. The performance of Fenton process was evaluated especially in terms of color and COD removals but also using many other pollution parameters such as suspended solids, biodegradability and turbidity.

II. EXPERIMENTAL

A. Materials

All chemicals employed in this study were commercial grade. Solutions of the synthetic wastewater were prepared in one time distilled water. Glassware used was washed with detergent, rinsed with tap water and rinsed with distilled water prior to drying. Reagent grade H_2O_2 35% (Chimitex) was standardized using iodometric titration and used as purchased. Iron sulfate $FeSO_4.7H_2O$ was standardized just before Fenton's experiments. Solutions of NaOH and H_2SO_4 were used for pH adjustments.

Commercially direct (azoic structure) and reactive dyes (vinylsulfonic structure) were used as received without any purification in order to make similar preparation conditions of both synthetic and real wastewaters.

B. Samples preparation

The real wastewater used in the present research was obtained from dyeing and finishing cotton goods and supplied by a Tunisian textile manufacturer located in Monastir. It was collected from the wastewater station just before treatment. Taken samples were preserved in the refrigerator at 4° C in accordance with the standard methods for the examination of Water and Wastewater [12]. The real wastewater consists of a mixture of dyeing and finishing steps. The characteristics of this textile wastewater are showed in Table 1.

TABLE I. CHARACTERIZATION OF TESTED WASTEWATERS

Parameter	Synthetic wastewater	Real wastewater
Color (at λmax)	3.55 (diluted 10 times)	4.01 (diluted 10 times)
COD (mg O2/L)	1785	19900
BOD (mg O2/L)	820	1100
MES (g/L)	200	672
Turbidity (NTU)	78	138
Conductivity (mS/cm)	18.07	24.24

C. Fenton's experimental procedure

Fenton oxidation assays were carried out in laboratory scale batch reactor. In every essay the reactor were filled with 100 mL of either synthetic or real wastewater. Then the iron dose were added under stirring and the pH of the initially basic sample was adjusted with adding sulfuric acid. In every case the reaction was started by adding the dose of hydrogen peroxide.

Several preliminary experiments were carried out to determine the range of hydrogen peroxide and iron sulfate doses, time temperature and pH needed to obtain depollution results.

The molar fraction of $[H_2O_2]/[FeSO_4]$ was varied from 20 to 100. The pH of the solution was measured with a calibrated pH meter of Jenway type and varied from 2 to 4.5. Experiments were conducted on the dye solutions at 40°C, 60°C and 90°C temperature ranges. The temperature range was chosen for representing conditions occurred in the industry of dyeing and finishing [**Erreur ! Signet non défini.**].

D. Analytical procedure

Absorbance measurements were carried out with a UV-Visible spectrophotometer (Shimadzu UV-256) recording the spectra over the 190-900 nm range. Different dyes with different absorbance peaks were presented in the studied wastewaters. The maximum of absorbance of the real wastewater is non stable. So, prior to each experiment, UV-Vis spectra of dye solutions were obtained to establish their maximum.

The disappearance of the absorbance peaks of the solution was monitored and the Color removal ratio was calculated as follows:

$$abs(\%) = \frac{abs(\lambda_{\max})_{ini} - abs(\lambda_{\max})_t}{abs(\lambda_{\max})_{ini}} \qquad (8)$$

Where abs $(\lambda max)_{ini}$ is the average value of absorbency at λmax of the concerned wastewater. abs $(\lambda max)_t$ is the value obtained at time t.

Chemical Oxygen Demand tests were performed by oxidation with dichromate according to Standard Methods of Examination of Water and Wastewater [**Erreur ! Signet non défini.**] with a subsequent colorimetric determination using Hach DR 2000 photometer. The percentage of dye mineralization was evaluated from the measurement of COD removal.

$$COD(\%) = \frac{CODi - CODt}{CODi} \times 100 \qquad (9)$$

Where COD_i corresponds to the initial value and COD_t is the value obtained at time t.

III. RESULTS AND DISCUSSIONS

A. Effect of $[H_2O_2]/[FeSO_4]$ molar ratio

Although the Fenton reaction has been widely studied, there is still not an agreement on the ratio $[H_2O_2]/[FeSO_4]$ that gives the best results [**Erreur ! Signet non défini.**,9]. Many researchers have reported the use of different ratios of the two reactants [8, 13, 14]. Excess of H_2O_2 or $FeSO_4$ might be detrimental, since these species can react with some of the intermediates like $OH^{\bullet}$, responsible for the direct oxidation of the organic load. Such reaction can lead to a decrease in process efficiency by consumption of the $OH^{\bullet}$. Some other side reactions can occur causing destabilization on pH values during experiments or the formation of iron II or III hydroxyl sludge's [15].

Figures 1 and 2 contain data concerning experiments with several initial $[H_2O_2]/[FeSO_4]$ ratios. Experiments were carried out for duration of 1 h at 40°C and pH 3 for both real and

International Journal of Scientific Research & Engineering Technology (IJSET)
ISSN: 2356-5608, Vol.3, issue 2
Copyright IPCO-2015-pp.102-106

stimulated wastewaters. In this case it is clear that for both tested wastewaters increasing the $[H_2O_2]/[FeSO_4]$ ration leads to larger color removal, with no detrimental effects detected for the highest ratio. Nevertheless, the small difference between the color removal attained with 50 and 100 ratios indicates that improvements of reaction rate may not compensate the large amounts of oxidant consumed.

Figures 1 and 2 show also that during the first 10 minutes the reaction proceeds at a faster rate. With high ratios of $[H_2O_2]/[FeSO_4]$ (50 or 100) the decolorization decay was slightly minor than the decolorization rate obtained with lower ratios. This behavior is no longer maintained for higher durations. This can be explained by taking into account that Fenton reaction, which is completed after few seconds, benefits from larger $[H_2O_2]/[FeSO_4]$ ratios. While for lower ratios, Fenton process needs more time to manifest, and its oxidation effect appears only for longer reaction times.

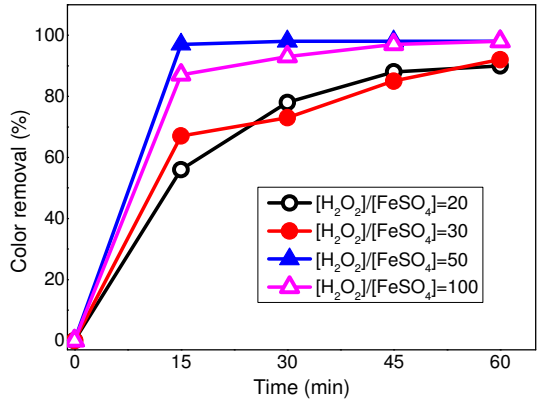

Fig. 1. Effect of $[H_2O_2]/[FeSO_4]$ ratio on decolorization of Real Wastewater (Temperature 40°C, pH 3)

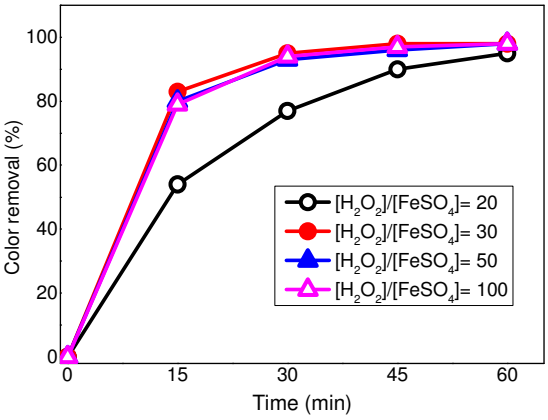

Fig. 2. Effect of $[H_2O_2]/[FeSO_4]$ ratio on decolorization of Synthetic Wastewater (Temperature 40°C, pH 3)

The synthetic wastewater treated with Fenton process with varying $[H_2O_2]/[FeSO_4]$ molar ratio showed similar behavior of color removal in function of time. Figure 2 shows that the evolution of color removal take place in regular way, clearly more systematic than results obtained with real wastewater. Such wastewater is characterized by non-stable composition or concentration of pollutants. Here, it should be pointed that organic dyes used in this study have vinylsulfonic and polyaromatic structures with –N=N– and –C=C– type double bonds in their chromophoric groupings. These dyes will readily react with $OH^{\bullet}$ that is the major oxidizing agent at acidic pH. Considering the presence of $OH^{\bullet}$ scavengers/competitors (anionic surfactant, antifoam, acetic acid, equalizer, dispersing agent…) in the real wastewater formulation, significant difference and variability should be expected between the reaction rates throughout all studied ratios. Consequently, hydroxyl radicals will react more selectively with the dye than with the other auxiliary chemicals that contributed also to the total COD load [**Erreur ! Signet non défini.**, 16, 17].

B. Effect of pH

The real dye wastewater has a wide range of initial pH values that can reach 11 or even 12. The solution pH is an important operating parameter affecting removal efficiency in AOP. It affects directly the mechanism of oxidation dye, because a change in pH of the solution, involves a variation of the concentration of Fe^{2+}, and therefore the rate of production of $OH^{\bullet}$ radicals responsible for oxidation dyes, will be restricted [9, 18, 19]. Thus, the decomposition reaction of H_2O_2 was fined to be catalyzed most efficiently by Fe^{2+} ions in water solutions with pH value between 2 and 3. In order to determine the optimum pH, color and COD removal were investigated in a large range of pH values.

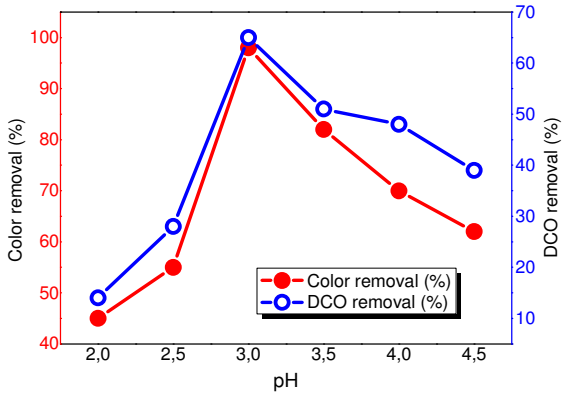

Fig. 3. Effect of pH on color and COD removal of real wastewater (reaction time 30 min, temperature 40°C, pH 3, $[H_2O_2]/[FeSO_4]$= 50)

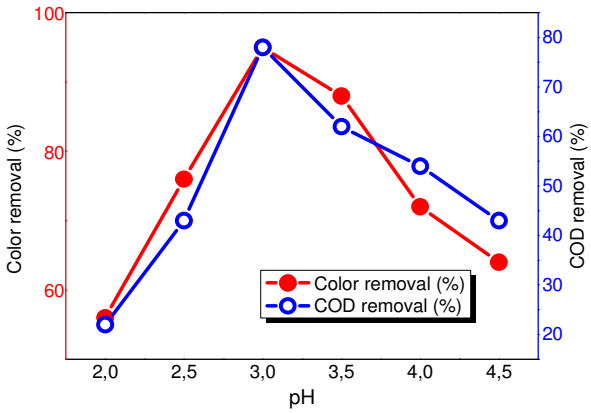

Fig. 4. Effect of pH on color and COD removal of synthetic wastewater (reaction time 30 min, temperature 40°C, pH 3, $[H_2O_2]/[FeSO_4]$= 30)

International Journal of Scientific Research & Engineering Technology (IJSET)
ISSN: 2356-5608, Vol.3, issue 2
Copyright IPCO-2015-pp.102-106

As illustrated in Figures 3 and 4 the optimum pH varies in a small scale between 3.0 and 3.5 for both tested wastewaters. Figures shows also that the discoloration with Fenton's reagent for the examined dye bath solutions proceeded the fastest with pH value equal to 3 which is in accordance with the literature. Kuo [**Erreur ! Signet non défini.**] observed 93% of decolorization of dye in 30 min. Meric et al. [**Erreur ! Signet non défini.**], showed that more than 99% of color removal was possible in the pH range of 3-3.5. In our case, the color removal of the real wastewater was about 98% and 95% for the synthetic wastewater. The COD removal was 78% and 65% for synthetic and real wastewater respectively.

C. Effect of temperature

In any case, temperature is a key parameter that has to be taken into account, especially for those applications where color and COD removal rate can be increased by varying temperature. It is important to remark that in comparison to most industrial wastewaters, the temperature of textile effluents has big fluctuations [**Erreur ! Signet non défini.**]. During the dyeing process, dye bath and rinse waters temperatures up to 90°C are normally encountered. For the finishing process, lower temperature are used (about 40°C). Fenton process was tested in optimal conditions of pH and $[H_2O_2]/[FeSO_4]$ molar ratio at three temperature levels: 40° C when finishing effluent is alone, (60°C) and when it is mixed with dyeing wastewater and 90°C when dyeing effluent is alone.

As seen from Figures described elsewhere optimum temperature for a Fenton process is 40°C at which 78% COD and 95% color removal were obtained for the synthetic wastewater. For the real wastewater, the maximum COD removal (64%) was also obtained at 40°C. in the case of higher temperatures up to 60°C and higher $[H_2O_2]/[FeSO_4]$ molar ratios the COD removal was affected negatively at both tested wastewaters. This was explained by the destabilization of flocks resulting in increased ferrous ions that scavenged OH radicals during Fenton's reactions [**Erreur ! Signet non défini.**, **Erreur ! Signet non défini.**, 20]. Higher temperatures were also tested and results confirmed the hypothesis of flocks destabilization and the disturbance of the sedimentation process [**Erreur ! Signet non défini.**]. An example of this phenomenon is well illustrated in Figure 5.

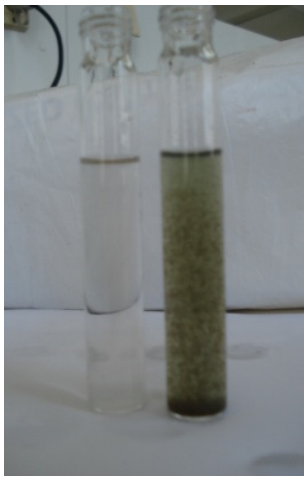

Fig. 5. Decolorization by Fenton process of the real wastewater in pH 3, $[H_2O_2]/[FeSO_4]$= 50 at 40°C (at left) and in pH 5, $[H_2O_2]/[FeSO_4]$= 100 at 90°C (at right)

As shown in Figure 5, the application of the Fenton's reagent in the destruction of organic compounds at different experimental conditions generated a dark brown slurry phase. The formed sludge is mainly constituted by heavy metals-Fe(III)/Fe(II)-iron, with a formation of high level of suspended solids [**Erreur ! Signet non défini.**]. Thus, the overall result of the waste chemicals treatment by Fenton´s reagent is the production of an aqueous solution with a substantially lower total carbonaceous load. However, the treated liquor still presented levels of heavy metals and sulfate that were too high to meet discharge standards. Thus, the Fenton's reagent cannot be applied as a standalone treatment option, but it can be used in combination with other treatment techniques [21]. In our case, the oxidized wastewater was supported by a flocculation/sedimentation for all experimental conditions. Table 2 gives the evolution of pollution level of tested wastewaters before Fenton process application, after oxidation and finally after sedimentation.

TABLE II. CHARACTERISTICS OF TESTED WASTEWATERS BEFORE TREATMENT, AFTER FENTON PROCESS OXIDATION AND AFTER SEDIMENTATION

Parameter	Synthetic wastewater			Real wastewater		
	Before	***End of the oxidation stage***	***End of the sedimentation stage***	***Before***	***End of the oxidation stage***	***End of the sedimentation stage***
Color (at λmax)	3.55 (diluted 10 times)	0.09	0.07	4.01 (diluted 10 times)	0.11	0.05
COD (mg O_2/L)	1785	402	386	19900	7010	6580
BOD (mg O_2/L)	820	430	402	1100	500	480
MES (g/L)	200	86	57	672	398	180
Trubidity (NTU)	78	40	35	138	60	42
Conductivity (mS/cm)	18.07	23.45	22.32	24.24	26.99	25.17

Characteristics of wastewater after flocculation/sedimentation treatment shows that there is a significant decrease of all pollution parameters of the supernatant. The presented investigations are preliminary, and their aim was to establish whether the application flocculation/sedimentation could patch-up the sludge production problem after a Fenton process.

IV. CONCLUSION

In this study a synthetic and real wastewaters were subjected to Fenton process. On the basis of obtained results it is hypothesized that the performance of pollutants degradation on both tested samples is different with regard to intermediates of oxidation. During oxidation of synthetic wastewater one pollutant is easier decomposed to smaller molecules which are difficult to oxidize further. While during oxidation of real wastewater with such complex composition, other unknown and chaotic reactions between pollutants can take place. Thus, the decomposition process became slower and more difficult. Optimum conditions were found to be pH equal to 3, temperature equal to 40°C and$[H_2O_2]/[FeSO_4]$ about 30 for the synthetic wastewater and $[H_2O_2]/[FeSO_4]$ about 50 for the real

wastewater respectively. In these conditions, the decreasing in COD was about 65% in real wastewater case, comparing to 78% COD removal in synthetic wastewater which is higher than expected. For both tested solutions, the percentage removal of color was found to be higher than 95%. This indicated that the decolorization process took place completely by the breakage of the chromophore's groups. The results obtained in laboratory scale experiments indicate that Fenton process assisted by flocculation/sedimentation treatment guarantee a better final quality of the effluent with characteristics that fulfil the requirements of Tunisian Standards for discharge wastewaters.

REFERENCES

[1] Carmen, Zaharia, and Suteu Daniela. "Textile organic dyes–characteristics, polluting effects and separation/elimination procedures from industrial effluents–a critical overview." Organic Pollutants Ten Years After the Stockholm Convention-Environmental and Analytical Update. InTech: Croatia, 2012.

[2] Allegre, C., Maisseu, M., Charbit, F., & Moulin, P. (2004). Coagulation–flocculation–decantation of dye house effluents: concentrated effluents. Journal of hazardous materials, 116(1), 57-64.

[3] Banat, Ibrahim M., et al. "Microbial decolorization of textile-dyecontaining effluents: a review." Bioresource technology 58.3 (1996): 217-227.

[4] Miled, Wafa, A. Haj Said, and S. Roudesli. "Decolorization of high polluted textile wastewater by indirect electrochemical oxidation process." Journal of Textile and Apparel, Technology and Management 6.3 (2010).

[5] Ganesan, R., and K. Thanasekaran. "Decolourisation of textile dyeing Wastewater by modified solar Photo-Fenton Oxidation." International Journal of Environmental Sciences 1.6 (2011).

[6] Ledakowicz, Stanislaw, Monika Solecka, and Renata Zylla. "Biodegradation, decolourisation and detoxification of textile wastewater enhanced by advanced oxidation processes." Journal of Biotechnology 89.2 (2001): 175-184.

[7] Martins, A. F. "Advanced oxidation processes applied to effluent streams from an agrochemical industry." Pure and applied chemistry 70.12 (1998): 2271-2279.

[8] Al-Kdasi, Adel, et al. "Treatment of textile wastewater by advanced oxidation processes—a review." Global Nest Int J 6.3 (2004): 222-30.

[9] Palaniandy, Puganeshwary, Hamidi Bin Abdul Aziz, and Shaik Feroz. "A review on the Fenton process for wastewater treatment." Journal of Innovative Engineering 2.3 (2014): 4.

[10] Zaharia, Carmen, et al. "Textile wastewater treatment by homogeneous oxidation with hydrogen peroxide." Environmental Engineering and Management Journal 8.6 (2009): 1359-1369.

[11] Perkowski, Jan, and Lech Kos. "Treatment of textile dyeing wastewater by hydrogen peroxide and ferrous ions." Fibres and Textiles in Eastern Europe10.3 (2002): 78-81.

[12] APHA,2002, Standard methods for the examination of water and wastewater, 20 thedn., "American Public Health Association", Washington, DC.

[13] Meriç, Süreyya, Deniz Kaptan, and Tuğba Ölmez. "Color and COD removal from wastewater containing Reactive Black 5 using Fenton's oxidation process." Chemosphere 54.3 (2004): 435-441.

[14] Wang, Shaobin. "A comparative study of Fenton and Fenton-like reaction kinetics in decolourisation of wastewater." Dyes and Pigments 76.3 (2008): 714-720.

[15] Benatti, Cláudia Telles, and Célia Regina Granhen Tavares. "Fentons Process for the Treatment of Mixed Waste Chemicals." Faculdade Ingá–UNINGÁ, Universidade Estadual de Maringá–UEM, Brazil unpublished (2012).

[16] Kuo, W. G. "Decolorizing dye wastewater with Fenton's reagent." Water Research 26.7 (1992): 881-886.

[17] Benitez, F. J., et al. "The role of hydroxyl radicals for the decomposition of p-hydroxy phenylacetic acid in aqueous solutions." Water Research 35.5 (2001): 1338-1343.

[18] Ertugay, Nese, and Filiz Nuran Acar. "Removal of COD and color from Direct Blue 71 azo dye wastewater by Fenton's oxidation: Kinetic study." Arabian Journal of Chemistry (2013).

[19] Sun, Jian-Hui, et al. "Fenton oxidative decolorization of the azo dye Direct Blue 15 in aqueous solution." Chemical Engineering Journal 155.3 (2009): 680-683.

[20] Peralta-Hernández, J. M., et al. "Comparison of hydrogen peroxide-based processes for treating dye -containing wastewater: decolorization and destruction of Orange II azo dye in dilute solution." Dyes and Pigments 76.3 (2008): 656-662.

[21] Mansoorian, Hossein Jafari, et al. "Removal of Azo Dyes From Aqueous Solution Using Fenton and Modified Fenton Processes." (2014).