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Decolorization and degradation of sunset yellow in aqueous solutions by advanced Fenton oxidation

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Abstract

Decolorization of sunset yellow dye (SY) in an aqueous solution was investigated by Fenton reaction using H_2O_2/Fe^{2+} system. Different parameters controlling the degradation efficiency as pH and H_2O_2 and Fe^{2+} concentrations were evaluated. The optimal operational conditions were found to be $[Fe^{2+}] = 2.55 \times 10^{-3}$ mmol, $[H_2O_2] = 0.2425$ mmol at pH 2.7. The study of the Kinetics of decolorization indicated that the degradation kinetics of SY followed the second-order kinetics with ($K_2 = 4.9 \times 10^{-4}$ mgL^{-1}min^{-1}). The results of this study showed high efficiency for removal of SY by Fenton process which is a cheap, versatile and efficient method for removal of this kind of pollutants.

Keywords: Sunset yellow; degradation; Fenton; removal.

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1. Introduction

Dyes are an important class of pollutants that show notable structural variety and could be classified in several ways. Among the different types, azo dyes are the largest category of synthetic dyes which are characterized by the presence of azo group (-N=N-) with one or more aromatic systems, which may also have sulfonic acid groups [1]. These dyes are widely used in a variety of industries like textile, plastic, rubber, leather, food and cosmetics industries. A massive amount of azo dyes from these sources is discharged into natural water supplies [2] causing the water to be colored and toxic and making it unfit for any use.

Various conventional and non-conventional methods are used for removing color from polluted water. The development of process on these areas is the most important challenge faced by chemical scientists due to their complex structure and synthetic origin [3]. Dyestuffs wastewater can be removed by different chemical and physical methods including adsorption [4], photocatalytic oxidation [5], coagulation-flocculation [6] and electrochemical methods [7].

Different chemical oxidation processes have developed in the last decades. These methods can be divided into two categories: (a) classical chemical treatments; where an oxidizing agent (chlorine, potassium permanganate, hydrogen peroxide, oxygen and ozone) is usually added to the water containing the pollutant [8] (b) advanced oxidation processes (AOPs); as hydrogen peroxide/ozone (H_2O_2/O_3), ozone/ultraviolet irradiation (O_3/UV), hydrogen peroxide/ ultraviolet irradiation (H_2O_2/UV), emerging technologies, high energy electron beam irradiation (E-beam), cavitation (sonication & hydrodynamic), TiO_2-catalyzed UV oxidation and Fenton's reaction.

The term advanced oxidation process refers specifically to processes in which oxidation of organic contaminants occurs primarily through reactions with hydroxyl radicals produced from H_2O_2 [9]. The AOPs methods are based on the generation of hydroxyl radicals (•OH) which are very reactive species, non-selective and powerful oxidizing agent having a strong oxidative potential (E^0 =2.80 V) [10]. Hydroxyl radicals (•OH) can destruct organic compounds via hydroxylation of the non-saturated bonds in the molecule of the organic pollutant or by dehydrogenation with the loss of hydrogen atoms producing stable inorganic compounds or, at least, causing their change into biodegradable or harmless products [11].

Fenton's reagent is one of the most important AOPs that used for water treatment from organic pollutants. Fenton reagent is a homogenous catalytic oxidation process using a mixture of ferrous ions (Fe^{2+}) and hydrogen peroxide (H_2O_2) and in an acidic environment which generates hydroxyl radical (•OH) [12] according to the following reactions:

Fe(II) is oxidized to Fe(III) in the presence of higher amounts of hydrogen peroxide.

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

Hydrogen peroxide decomposes by Fe (III) and generates again hydroxyl radicals according to the following reactions [13]:

$$Fe^{3+} + H_2O_2 \rightarrow H^+ + Fe\text{-}OOH^{2+} \quad (2)$$

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

The resulting ferrous ions react with hydrogen peroxide again as shown in eq. (1).

The main advantages of Fenton's reaction [14] are that this process requires very little energy compared to other oxidation technologies that utilize O_3 or UV and produces no vapor emissions and, therefore, requires no off-gas treatment.

The main objective of this study is to evaluate the feasibility of using Fenton reagent for the removal of sunset yellow from polluted water. Sunset yellow (E110) is one of a number of dyes which used as a synthetic colorants in food, cosmetics, and drugs [15,16].

Food coloring dyes are a class of food additives without nutritional value which are added to foods for providing color thus making the product more attractive and increasing its consumer acceptability. It is widely used as an additive in many kinds of foods as orange squash, orange jelly, Swiss roll, apricot jam, citrus marmalade, lemon curd, sweets, packet soups, breadcrumbs, cheese sauce, ice cream, canned fish, and many medications. It is widely used in candy, desserts, snacks, sauces, and preserved fruits. It is controversial in relation to its toxic activity and attract the interest of toxicologists and allergists. It is seen as responsible for various immunological reactions causing urticaria or even asthma [17]. It is also responsible for rhinitis, nasal congestion and hyperactivity in children.

In the last few years, various adsorbents were applied for SY dye removal from aqueous solutions. In these studies, mainly, single component systems have been investigated including adsorption on different adsorbents [18,19], chemical reduction [20] or chemical oxidation [21]. Few AOPs studied were applied to remove SY from its aqueous solutions as electro-Fenton [22], photoelectron-Fenton [23] and ctlytic oxidation with hydrogen peroxide in the presence of copper loaded bentonite [24] or chloroperoxidase [25].

To find the optimum conditions to maximize dye removal efficiency with applying Fenton reaction, a number of variables were examined through minimum number of experiments.

2. Experimental

2.1. Chemicals and apparatus

Sunset yellow (SY) dye removal was performed in batch mode by adding ferrous ammonium sulfate hexahydrate $Fe(NH_4)_2.(SO_4)_2.6H_2O$ as a source of Fe^{2+} and the hydrogen peroxide (H_2O_2) (30%) as an oxidant to the dye solution. Sodium hydroxide (NaOH), sulfuric acid (H_2SO_4) and sodium chloride (NaCl) were all of analytical grade and purchased from Merck (Germany). All chemicals were utilized as received without further purification. Distilled water was used in the preparation of all solutions.

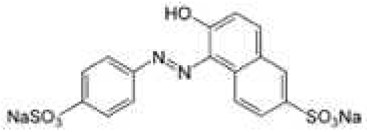


Fig (1): Chemical structure of Sunset Yellow (SY).

2.2. Analytical method

The pH of 100 mL dye sample (20 mg/L) was adjusted to the desired value by adding either NaOH or H_2SO_4 and then Fenton reagents (H_2O_2 and Fe^{2+}) were added to the stirred dye solution. Sampling was done by withdrawing the sample (about 1 ml) after 15 min of mixing. The absorbance of remaining dye was measured by UV–Vis Spectrophotometer (Unico-1200 spectrophotometer, U.S.A.) at 430 nm.

A calibration curve was achieved using the standard solutions of SY with different concentrations in the range of 0.5–50 mg/L. Liner curve ($R^2 = 0.9997$) was obtained in the range 1.0-30 mg/L. The efficiency of the proposed process was evaluated by monitoring SY removal after measuring absorbance. The dye removal efficiency of SY was calculated as follows:

$$Dye\ Removal\ Effeciency\ \% = \frac{C_0 - C_t}{C_0} \times 100$$

where C_0 (mg/L) is the initial concentration of SY, and C_t (mg/L) is its concentration at reaction time t (min).

3. Results and discussion

3.1. Effect of pH

To study the effect of pH on degradation efficiency of SY by Fenton oxidation and to find the optimal pH of reaction mixture, a series of experiments were conducted at different pH values 2.7, 4.7, 7.2, 9.0 and 10.4. In all experiments the $[SY]_0$, $[H_2O_2]_0$ and $[Fe^{2+}]_0$ were maintained at 20 mg/L, 0.485 mmol, $2.55x10^{-3}$ mmol, respectively. The results (Fig. 2) given indicated that the degradation of SY was significantly influenced by the pH of the solution. The optimal solution pH was observed at 2.7 which correspond to maximum removal (48.5%) after 120 min of continuous reaction. As shown in Fig. 2, an increase of pH over 2.7 causes decrease in the degradation efficiency. The pH value of degradation solution is an important parameter for Fenton's reaction as can be shown in the following equations:

$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + \bullet OH + H_2O$ (1)

$Fe^{3+} + H_2O_2 \rightarrow Fe–O_2H^{2+} + H^+$ (2)

$Fe–O_2H^{2+} \rightarrow Fe^{2+} + \bullet OOH$ (3)

$SY + \bullet OH \rightarrow$ oxidized products (4)

$Fe^{3+} + \bullet OOH \rightarrow Fe^{2+} + O_2 + H^+$ (5)

$Fe^{3+} + \bullet R \rightarrow Fe^{2+} + R^+$ (6)

Eq. (1) confirms the importance of the presence of H^+ ions in the production of •OH radicals. So, the drop in removal efficiency at high pH values may be due to the reduction of hydroxyl radicals produced and also the precipitation of $Fe(OH)_3$ which catalyzes the decomposition of H_2O_2 into oxygen and water [26], and consequently the degradation rate decreases because less hydroxyl radicals are available.

Similar results were reported indicating that optimum pH is about 3.0 for the degradation of a number of azo dyes by Fenton reaction as Malachite Green [27], Orange G [28], Peach Red [29] and Reactive Blue 4 [30].

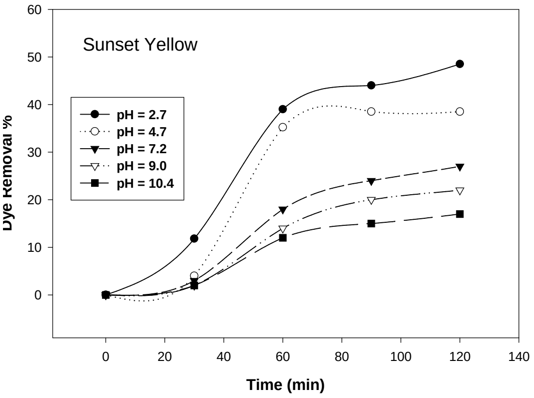


Fig (2): Effect of solution pH on the decolorization of SY by Fenton oxidation.

Experimental conditions: [SY] = 20 mg/L; $[H_2O_2]$ = 0.485 mmol; $[Fe^{2+}] = 2.55x10^{-3}$; temperature = 25 °C.

3.2. Effect of initial Fe^{2+} concentration

Ferrous ions concentration is another important parameter which affects Fenton reaction efficiency by catalyzing the decomposition of H_2O_2 to generate •OH radicals. To study the role of initial concentration of Fe^{2+} on the degradation of SY by Fenton oxidation, different doses of Fe^{2+} ($1.275x10^{-3} – 5.1x10^{-3}$ mmol) were used for the degradation of 20 mg/L of SY keeping H_2O_2 concentration constant at 0.0485 mmol. As shown in Fig. 3, the lowest degradation efficiency (40.5%) was recorded at $[Fe^{2+}]_0$ value of $1.275x10^{-3}$ mmol after 120 min reaction time, while the highest degradation efficiency (51.52%) was recorded at $[Fe^{2+}]_0$ value of $3.82x10^{-3}$ mmol after the same reaction time.

Many researchers have reported [27, 31-33] that the use of a much higher concentration of Fe^{2+} could lead to the self-scavenging of •OH radical by converting it to hydroxyl ions during oxidation of Fe^{2+} according to the eq. (7):

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

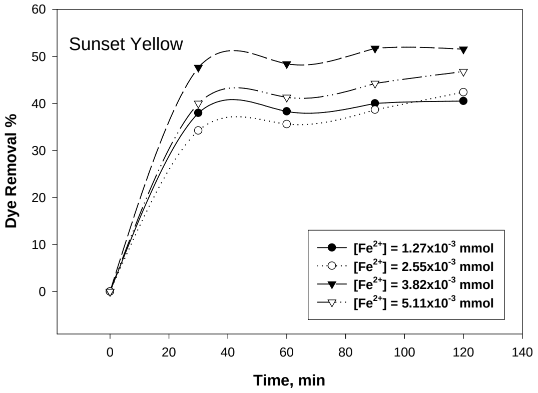


Fig (3): Effect of Fe^{2+} concentration on SY decolorization [[SY] = 20 mg/L; $[H_2O_2]$ = 48.5 mmol; pH = 2.7; temperature = 25 °C].

3.3. Effect of H_2O_2 concentration

H_2O_2 plays an important role as an oxidizing agent in the Fenton process. So, the selection of an optimal H_2O_2 concentration for the decolorization of SY is of great importance from practical point of view due to the cost of H_2O_2. The effect of H_2O_2 dosage on the decolorization of SY was examined by varying initial concentration of H_2O_2 from 4.85 to 29.10 mmol keeping both Fe^{2+} concentration and SY concentration constant at $2.55x10^{-3}$ mmol and 20 mg/L, respectively. The results are shown in Fig. 4. As it can be seen, the effect of increasing H_2O_2 initial concentration from 0.0485 to 24.25 mmol increased the rate of decolorization of the dye, while further increase to 29.10 mmol didn't affect the removal efficiency. This is expected due to the oxidation power of Fenton process which was improved with increasing amount of •OH radicals obtained from the decomposition of increasing H_2O_2. It is important to control the initial concentration of H_2O_2 since the high concentration my reduce the decolorization of dye and also increase the cost of the wastewater treatment process [34].

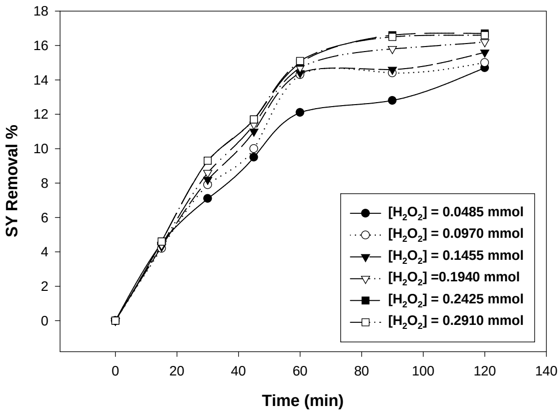


Fig (4): Effect of H_2O_2 concentration on SY decolorization [SY] = 20 mg/L; $[Fe^{2+}] = 2.55x10^{-3}$ mmol; pH = 2.7; temperature = 25 °C].

3.4. Effect of initial SY concentration

The effect of variation of initial concentration of SY on the rate of degradation has been examined in the range from 5 to 75 mg/L. It has been observed that the degradation efficiency decreases with increasing concentration of dye up to 75 mg/L. The influence of the initial dye concentration is shown in Fig. 5. With increasing the initial dye concentration, a decrease in the decolorization rate is observed in the beginning of reaction till 60 min. At higher dye concentrations, the generation of •OH radicals on the surface catalyst is reduced since the active sites may be occupied by more dye molecules and because the number of dye molecules is increased but not the •OH radical number [35]. After 160 min of reaction time, the decolorization efficiency increased to 51.8% for 5 mg/L and to 36.8% for 75 mg/L.

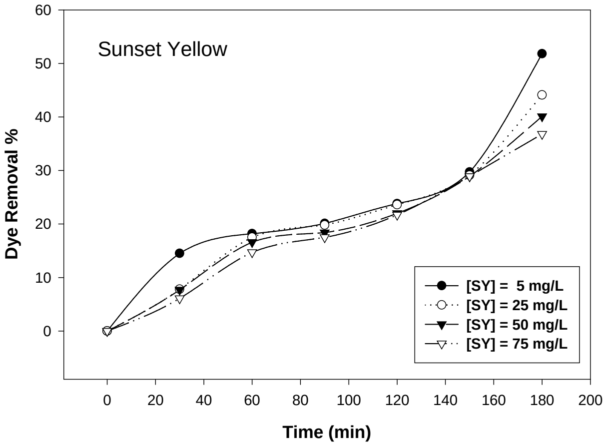


Fig (4): Effect of initial SY concentration on dye decolorization [H_2O_2] = 0.485 mmol; [Fe^{2+}] = $2.55x10^{-3}$ mmol; pH = 2.7; temperature = 25 ^oC].

3.5. Kinetic studies

The decolorization kinetics of SY by Fenton process was studied for various contact times varying from 30 to 180 min at 25 ^oC. Zero-, first- and second-order reaction kinetics were used to study the decolorization kinetics of SY by Fenton oxidation process. The individual expression was presented as:

Zero-order reaction kinetics:

$$\frac{dc}{dt} = -K_0 \qquad (8)$$

First-order reaction kinetics:

$$\frac{dc}{dt} = -K_1 C \qquad (9)$$

Second-order reaction kinetics:

$$\frac{dc}{dt} = -K_2 C^2 \qquad (10)$$

where C is the concentration of SY; k_0, k_1 and k_2 represent the apparent kinetic rate constants of zero-, first- and second-order reaction kinetics, respectively; t represents the reaction time.

The integrated forms of Eqs. (8) - (10) could be presented as:

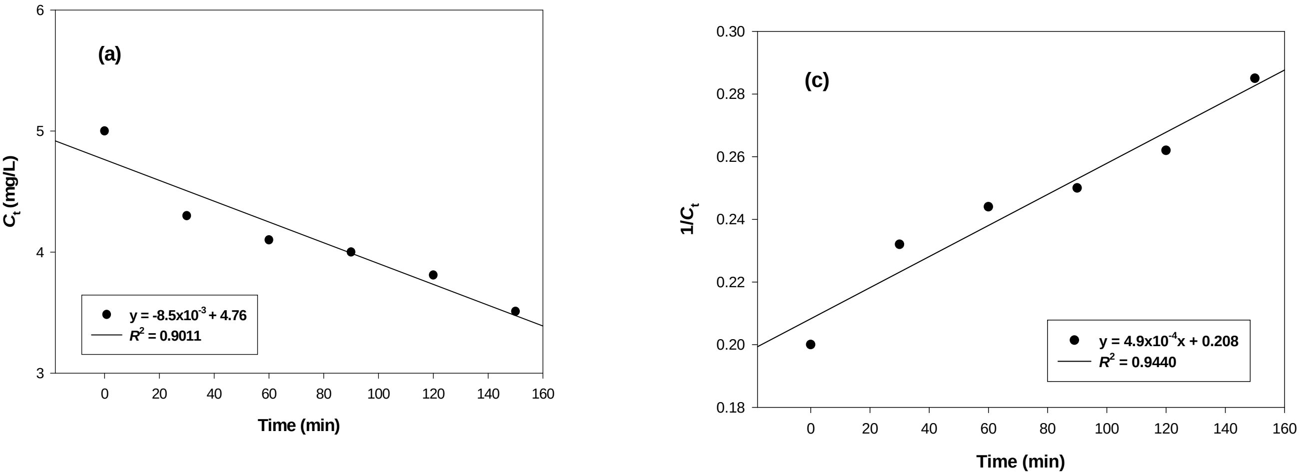
$$C_t = C_0 - K_0 t \qquad (11)$$

$$C_t = C_0 e^{-K_1 t} \qquad (12)$$

$$\frac{1}{C_t} = \frac{1}{K_0} + K_2 t \qquad (13)$$

where C_t is the concentration of SY at reaction time t.

The regression analyses based on the three kinetic models were conducted and the results are shown in Fig. 5 (a, b, c). By comparing the regression coefficients (R^2) evaluated from Fig. 5(a)–(c), it can be seen that R^2 based on the second-order reaction kinetics (Fig. 5(c)) was 0.9440, which is higher than those based on the zero-order (R^2 = 0.9011) and the first-order (R^2 = 0.9251) reaction kinetics. These results indicated that the decolorization kinetics of SY followed the second-order kinetics model. Based on the above analysis, the second-order kinetic rate constant (K_2) for the decolorization of SY at reaction conditions: [SY] = 5 mg/L; [H_2O_2] = 0.485 mmol; [Fe^{2+}] = $2.55x10^{-3}$ mmol; pH = 2.7, at 25 ^oC, was obtained to be K_2 = $4.9x10^{-4}$ $mgL^{-1}min^{-1}$. The theoretical C_0 of SY was 4.8 mg/L.



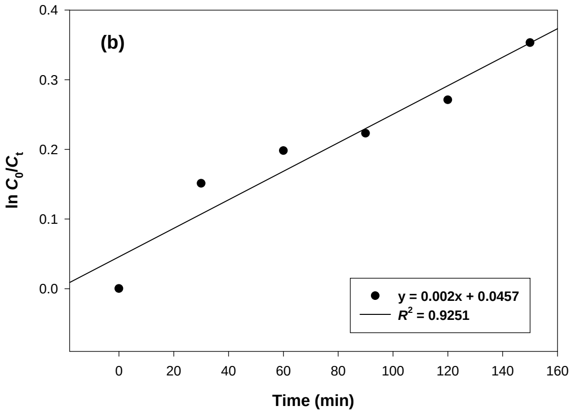


Fig (5): Application of (a) zero-order, (b) first-order and (c) second-order kinetic models for the decororization of SY by Fenton process.

4. Conclusion

In this work, the decolorization of SY in aqueous solution by Fenton oxidation process has been studied at different experimental conditions, including pH value of solution, initial concentration of H_2O_2 and Fe^{2+} dose, as well as the initial dye concentration. The examined Fenton's reaction was found to be more effective at pH 2.7. The best removal efficiency was achieved at $[H_2O_2]$ = 0.2425 mmol/L and $[Fe^{2+}]$ = 2.55x10^{-3} mmol/L at 25^{o}C. At the given conditions, more than 51.5% of decolorization efficiency was achieved within 90 min of reaction foe initial SY solution of 20 mg/L. The Kinetic study indicated that the degradation kinetics of SY followed the second-order kinetics.

References

[1] V.K. Gupta, Susah, Application of low cost adsorbents for dye removal. J. Environ. Manage. 90 (2009) 2313–2342.

[2] C. Su, M. Pukdee-Asa, C. Ratanatamskul, M.-C. Lu, Effect of operating parameters on decolorization and COD removal of three reactive dyes by Fenton's reagent using fluidized-bed reactor. Desalin. 278 (2011) 211–218.

[3] H. Xu, M. Li, H. Wang, J. Miao, L. Zou, Fenton reagent oxidation and decolorizing reaction kinetics of reactive red SBE, Energy Procedia 16 (2012) 58 – 64.

[4] G. O. El-Sayed, Removal of methylene blue and crystal violet from aqueous solutions by palm kernel fiber, Desalin. 272 (2011) 225–232.

[5] L. Karimi, S. Zohoori, M.E. Yazdanshenas, Photocatalytic degradation of azo dyes in aqueous solutions under UV irradiation using nano-strontium titanate as the nanophotocatalyst, J. Saudi Chem. Soc. 18 (2014) 581–588.

[6] G. Han, C.-Z. Liang, T.-S. Chung, M. Weber, C. Staudt, C. Maletzko, Combination of forward osmosis (FO) process with coagulation/flocculation (CF) for potential treatment of textile wastewater, Water Res. 91 (2016) 361-370.

[7] D.C. de Moura, M.A. Quiroz, D.R. da Silva, R. Salazar, C.A. Martínez-Huitle, Electrochemical degradation of Acid Blue 113 dye using TiO_2-nanotubes decorated with PbO_2 as anode, Environ. Nanotechnol. Monit. Manage. 5 (2016) 13-20.

[8] A. Asghar, A.A.A. Raman, W.M.A.W. Daud, Advanced oxidation processes for in-situ production of hydrogen peroxide/hydroxyl radical for textile wastewater treatment: a review, J. Clean. Product. 87 (2015) 826-838.

[9] Glaze W.H., Kang J.W., and Chapin D.H. "The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide, and Ultraviolet Radiation." Ozone Sci. Eng. 9 (1987) 335-352.

[10] M.F. Hou, L. Liao, W.D. Zhang, X.Y. Tang, H.F. Wan, G.C. Yin, Degradation of rhodamine B by Fe(0)-based Fenton process with H2O2. Chemosphere, 83 (2011) 1279–1283.

[11] M. Trapido, 2007. Ozone based advanced oxidation process. In: Munter, R., Cockfield, A.J. (Eds.), Ozone Science and Technology. E-Publishing Inc., Eolss..

[12] M. Pera-Titus, V. García-Molina, M.A. Banos, J. Giménez, S. Espulgas, Degradation of chlorophenols by means of advanced oxidation process. Appl. Catal. B Environ. 47 (2004) 219–256.

[13] R. Munter, Advanced oxidation process- current status and prospects. Proc. Estonian Acad. Sci. Chem. 50 (2001) 59–80.

[14] H.J.H. Fenton, Oxidation of Tartaric Acid in Presence of Iron, J. Chem. Soc. 165 (1894) 899-910.

[15] Wood, M. Roger (2004). Analytical methods for food additives. Boca Raton: CRC Press.

[16] Committee on Food Chemicals Codex (2003). Food chemicals codex (5th ed.). Washington, DC: National Academy Press.

[17] K.M.S. Gomes, M.V.G.A. de Oliveira, Citotoxicity of food dyes Sunset Yellow (E-110), Bordeaux Red (E-123), and Tatrazine Yellow (E-102) on *Allium cepa* L. root meristematic cells, Food Sci. Technol, Campinas, 33: 218-223, 2013.

[18] M. Ghaedi, N. Mosallanejad, Study of competitive adsorption of malachite green and sunset yellow dyes on cadmium hydroxide nanowires loaded on activated carbon, J. Indust. Eng. Chem. 20 (2014) 1085-2096.

[19] M. Ghaedi, D. Elhamifar, M. Roosta, R. Moshkelgosha, Ionic liquid based periodic mesoporous organosilica: An efficient support for removal of sunset yellow from aqueous solutions under ultrasonic conditions, J. Indust. Eng. Chem. 20 (2014) 1703-1712.

[20] A.H. Gemeay, Kinetics and mechanism of the reduction of some azo-dyes by inorganic oxysulfur compounds, Dyes Pigm. 54 (2002) 201–212.

[21] A.H. Gemeay, A.-F.M. Habib, M.A.B. El-Din, Kinetics and mechanism of the uncatalyzed and Ag(I)-catalyzed oxidative decolorization of Sunset Yellow and Ponceau 4R with peroxydisulphate, Dyes Pigm. 74 (2007) 458-463.

[22] M.M. Ghoneim, H.S. El-Desoky, N.M. Zidan, Electro-Fenton oxidation of Sunset Yellow FCF azo-dye in aqueous solutions, Desalin. 274 (2011) 22-30.

[23] F.C. Moreira, S. Garcia-Segura, V.J.P. Vilar, R.A.R. Boaventura, E. Brillas, Decolorization and mineralization of Sunset Yellow FCF azo dye by anodic oxidation, electro-Fenton, UVA photoelectro-Fenton and solar photoelectro-Fenton processes, Appl. Catal. B: Environ. 142–143 (2013) 877-890.

[24] K. Chanderia, S. Kumar, J. Sharma, R. Ameta, P.B. Punjabi, Degradation of Sunset Yellow FCF using copper loaded bentonite and H_2O_2 as photo-Fenton like reagent, Arab. J. Chem. (2012) In Press.

[25] J. Zhang, M. Feng, Y. Jiang, M. Hu, S. Li, Q. Zhai,, Efficient decolorization/degradation of aqueous azo dyes using buffered H_2O_2 oxidation catalyzed by a dosage below ppm level of chloroperoxidase, Chem. Eng. J. 191 (2012) 236– 242.

[26] L. Szpyrkowicz, C. Juzzolino, S.N. Kaul, A comparative study on oxidation of disperse dyes by electrochemical process, ozone, hypochlorite and Fenton reagent, Water Res. 35 (2001) 2129–2136.

[27] B.H. Hameed, T.W. Lee, Degradation of malachite green in aqueous solution by Fenton process, J. Hazard. Mater. 164 (2009) 468–472.

[28] S.-P. Sun, C.-J. Li, J.-H. Sun, S.-H. Shi, M.-H. Fan, Q. Zhou, Decolorization of an azo dye Orange G in aqueous solution by Fenton oxidation process: Effect of system parameters and kinetic study, J. Hazard. Mater. 161 (2009) 1052–1057.

[29] M.-W. Chang, Jia-Ming Chern, Decolorization of peach red azo dye, HF6 by Fenton reaction: Initial rate analysis, J. Taiwan Instit. Chem. Eng. 41 (2010) 221–228.

[30] H. Hassan, B.H. Hameed, Fe–clay as effective heterogeneous Fenton catalyst for the decolorization of Reactive Blue 4, Chem. Eng. J. 171 (2011) 912– 918.

[31] M. R. Sohrabi, A. Khavaran, S. Shariati, S. Shariati, Removal of Carmoisine edible dye by Fenton and photo Fenton processes using Taguchi orthogonal array design, Arab. J. Chem. (2014) In Press.

[32] S. I. Abou-Elela, M. E. M. Ali, H. S. Ibrahim, Combined treatment of retting flax wastewater using Fenton oxidation and granular activated carbon, Arab. J. Chem. (2014) In Press.

[33] P. Vaishnave, A. Kumar, R. Ameta, P.B. Punjabi , S. C. Ameta, Photo oxidative degradation of azure-B by sono-photo-Fenton and photo-Fenton reagents, Arab. J. Chem. 7 (2014) 981–985.

[34] N. Kang, D.S. Lee, and J. Yoon, Kinetic modeling of Fenton oxidation of phenol and monochlorophenol, Chemosphere, 47 (2002) 915-924.

[35] R. Idel-aouad, M.l Valiente, A. Yaacoubi, B. Tanouti, M. Lopez-Mesas, Rapid decolourization and mineralization of the azo dye C.I. Acid Red 14 by heterogeneous Fenton reaction, J. Hazard. Mater. 186 (2011) 745–750.