

**FENTON DEGRADATION OF FAST GREEN DYE**

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<sup>a</sup> Dept. of Chemistry, Faculty of Science, University of Zakho, Zakho, Kurdistan Region, Iraq - haydar.kovly@gmail.com**Received: Dec. 2016 / Accepted: Mar. 2017 / Published: Mar. 2017**<https://doi.org/10.25271/2017.5.1.305>**ABSTRACT:**

The degradation of commercial textile dye named fast green (FG) was investigated by Fenton reagent under different operating conditions in an aqueous solution. The operating conditions were amount of hydrogen peroxide (0.05, 0.1 and 0.15 mL), pH (2-12) and concentration of ferrous ion (10, 20 and 30 mg). The initial rate of degradation was affected by the concentration of Fenton reagents [Fe(II) and H<sub>2</sub>O<sub>2</sub> solution]. The rate of degradation enhanced as the concentration of ferrous ion increased. As the ferrous ion concentration increased from 10 to 30 mg, the removal percent was increased from 73% to 89%, respectively, at 25 min of reaction time. Also, the removal percent of FG increased from 74% to 81% as the amount of H<sub>2</sub>O<sub>2</sub> increased from 0.05 to 0.15 mL, respectively, at 25 min of reaction time. It was also found that at pH 3 removal percent reach maximum value with 91.8%. The kinetic study of FG degradation was also studied in this work and the results indicated that the degradation kinetics of FG followed the first-order kinetic.

**KEYWORDS:** Fenton's Reagent, Dye, Water Pollution, Fast Green, Kinetic.**1. INTRODUCTION**

The dyestuffs lost in the textile dyeing, paper printing, cosmetics, food and other industries poses a major problem to wastewater sources (Shah & Madamwar, 2013; Sleiman, Vildoza, Ferronato, & Chovelon, 2007). Every year, it is estimated that about five thousand tons of dyeing materials are discharged into the environment (Pirkarami & Olya, 2014). These materials are considering poisonous and absorb the oxygen of the water (Mahmoodi & Arami, 2009; Pirkarami, Olya, & Yousefi Limaee, 2013). The dyes removal from industrial effluents is an area of research receiving increasing attention. Common ways of wastewater treatment include chemicoagulation, sedimentation, biological methods, advanced oxidation processes and adsorption (S. A. M. S. Haydar A. Mohammad Salim, Reving A. Rashid, 2016; S. M. S. Haydar A. Mohammad Salim, 2015; Mohammad Salim & Mohammad Salih, 2015; Salim, 2014a, 2014b; Tizaoui, Mohammad-Salim, & Suhartono, 2015).

Biological treatment of wastewater containing dyes is considered unsatisfactory due to the low reaction rate and low efficiency of the treatment (Xu, Li, Wang, & Gu, 2004). Consequently, dye-containing wastewater is usually treated using chemical and physical methods (Chang, Chen, Chen, & Lin, 2003). Activated carbon adsorption and flocculation have been used to treat wastewater containing dyes, but adsorption regeneration and sludge generation are the main weakness of these processes (Slokar & Majcen Le Marechal, 1998). The Fenton process, one of the advanced oxidation processes (AOPs), that uses iron (II) ion to react with hydrogen peroxide to generate hydroxyl radical (OH<sup>•</sup>) with powerful oxidizing ability, has been proposed for the degradation of organic pollutants including some dye pollutants (Chen & Pignatello, 1997; Feng, Hu, Yue, Zhu, & Lu, 2003; Kang, Liao, & Chen, 2002). In this research, degradation of fast green (FG) dye in aqueous solution by the

Fenton process was performed at different operating conditions.

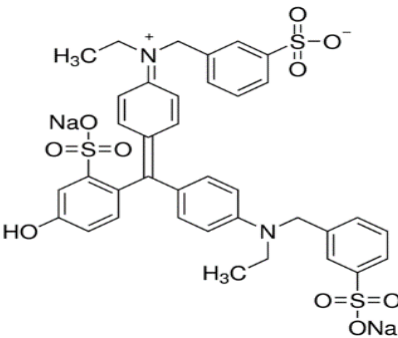
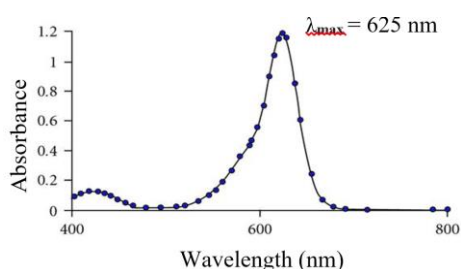
**2. MATERIALS AND METHODS****2.1 Materials**

Fast green FCF (FG) was purchased from Hopkin and Williams LTD, UK and used as received without further purification. Table 1 shows the characteristics of FG dye. A stock solution of FG (1000 mg/L) was prepared in distilled water. The prepared stock solution was covered by aluminum foil and kept in dark. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) with 30% concentration, nitric acid and sodium hydroxide were purchased from Fisher-Scientific, UK. Ferrous sulfate was purchased from Alpha Chemika, India. Various concentrations of NaOH and HNO<sub>3</sub> were used to adjust the pH value of solutions between 2 and 12. The pH of the solution was determined using pH meter (EUTECH, Malaysia). Visible spectrophotometer (Jenway 6700) was used to analyse the collected sample.

Table 1. Characteristics of FG dye

C.I. index	C.I. 42053
Molecular Formula	C <sub>37</sub> H <sub>34</sub> N <sub>2</sub> Na <sub>2</sub> O <sub>10</sub> S <sub>3</sub>
IUPAC Name	Disodium 2-[[4-[ethyl-[(3-sulfonatophenyl)methyl]amino]phenyl]-[4-[ethyl-[(3-sulfonatophenyl)methyl]azanumylidene]cyclohexa-2,5-dien-1-ylidene]methyl]-5-hydroxybenzenesulfonate
Molar Mass	808.86 g/mole
Colour	Blue
λ <sub>max</sub>	625 nm

\* Corresponding author

pKa	3.53
Solubility	Soluble in water (20 g/100 mL)
Structure Formula	
Absorption Spectrum	

## 2.2 Methods

The UV–VIS spectra of the dyes were recorded from 200–800 nm using a UV–VIS spectrophotometer (PerkinElmer Lambda 25). The maximum absorbance wavelength ( $\lambda_{max}$ ) of FG dye is 625 nm from the spectra.

All experiments were carried out at room temperature,  $25 \pm 1$  °C. The aqueous dye solutions (200 mL) were placed in a container with 250 mL volume under magnetic stirring. The required amount of  $Fe^{2+}$  and  $H_2O_2$  were added into the dye solution simultaneously. The concentration of dye, every 5 minutes, was determined spectrophotometrically using Jenway 6700 at 625 nm.

## 3. RESULTS AND DISCUSSION

### 3.1 Effecting of $Fe^{+2}$ Concentration

Catalyst loading is an important factor that can significantly influence the Fenton reaction. In general, a higher catalyst loading leads to a faster degradation of the organic compounds until a saturated catalyst loading is achieved (Hsueh, Huang, Wang, & Chen, 2005).

Figure 1 depicts a plot of the removal percent of FG dye as a function of the time when different loadings of the  $Fe^{+2}$  catalyst were employed. It can be seen that when the catalyst loading increases from 10 to 20 mg of  $Fe^{+2}$  catalyst, the degradation of FG is enhanced markedly. However, the degradation of FG does not change significantly when the catalyst loading is larger than 30 mg of  $Fe^{+2}$ . Hence, the saturated catalyst loading is about 30 mg of  $Fe^{+2}$  catalyst. Same results have been found for Orange II, methylene blue and Ponceau S (El-Desoky, Ghoneim, & Zidan, 2010; Feng et al., 2003; Lv et al., 2015).

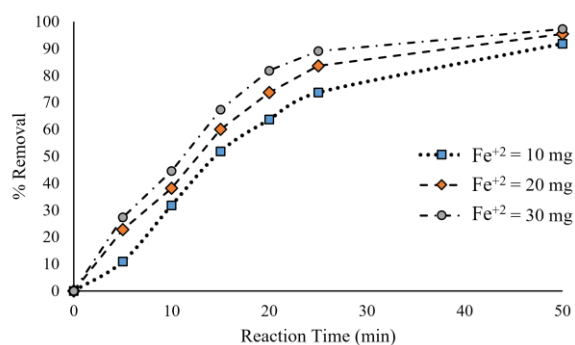


Figure 1. Effect of  $Fe^{+2}$  Concentration ( $[FG]_0 = 10$  mg/L, Volume = 200 mL, pH = 3,  $H_2O_2 = 0.05$  mL)

### 3.2 Effect of $H_2O_2$ concentration on removal percent

In a Fenton reaction, it has been found that  $H_2O_2$  amount is a key factor that can significantly influence the degradation of aromatic organic compounds (Feng et al., 2003). This is because the  $H_2O_2$  concentration is directly related to the number of  $\bullet OH$  radicals generated in the Fenton reaction (Pesakhov et al., 2007).

Figure 2 shows the removal percent of FG as a function of the reaction time when different  $H_2O_2$  molar concentrations were used. Apparently, as the amount of  $H_2O_2$  increases from 0.05 to 0.1 mL, the degradation of FG was enhanced because more  $\bullet OH$  radicals are formed at higher amount of  $H_2O_2$  in solution. However, when the  $H_2O_2$  amount increased to 0.15 mL, the degradation rate of FG slightly increased. This can be explained by the so-called scavenging effect when using a higher  $H_2O_2$  molar concentration on the further generation of  $\bullet OH$  radicals in aqueous solution as expressed by the following equation:



Generally, the degradation rate of organic compounds increases as the  $H_2O_2$  concentration increases until a critical  $H_2O_2$  concentration is achieved. When a concentration higher than the critical concentration is used, the degradation rate of organic compounds will decrease as a result of the so-called scavenging effect. Several groups have observed this phenomenon (Dhananjeyan, Kiwi, Albers, & Enea, 2001; Fernandez, Bandara, Lopez, Buffat, & Kiwi, 1999; Fernandez, Dhananjeyan, Kiwi, Senuma, & Hilborn, 2000).

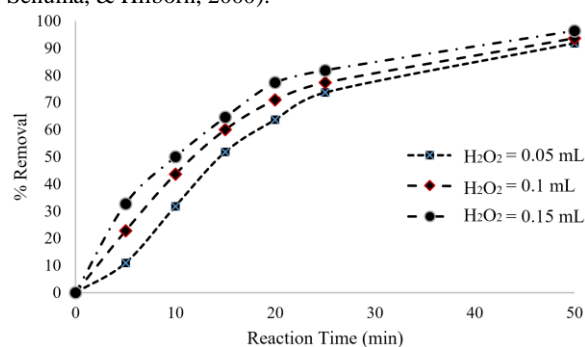


Figure 2. Effect of  $H_2O_2$  amount ( $[FG]_0 = 10$  mg/L, Volume = 200 mL, pH = 3,  $Fe^{+2} = 10$  mg)

### 3.3 Effect of Dye Concentration

The effect of FG concentration on the removal percent was studied by keeping all other parameters constant. The studied FG concentration were 10, 20 and 30 mg/L. It was observed that removal percent decreases with increasing the concentration of dye as shown in Figure 3. As shown in Figure 3, when FG concentration increased from 10 to 20 and 30 mg/L, the removal

percentage of FG at 50 min of reaction time decreased from 91.8 % to 79.9 % and 62.4 %, respectively.

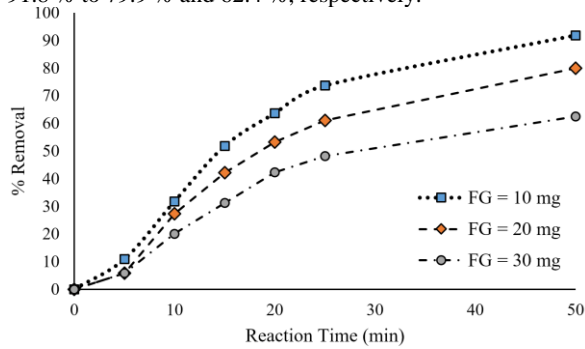


Figure 3. Effect of FG concentration ( $Fe^{+2}= 10$  mg, Volume = 200 mL, pH = 3,  $H_2O_2= 0.05$  mL)

### 3.4 Effect of pH

The effect of pH (2 to 12) on degradation of FG dye was investigated. As shown in Figure 4, the degradation rate increases when pH changed from 2 to 3 and then it decreases with increasing pH from 3 to 12. It was indicated to be the optimum pH for this study. As shown from the figure, the initial pH of solution plays an important role in controlling the removal of FG dye using Fenton reaction. The removal percent reached maximum value in high acidic medium with a value of 91.8 %; however, removal percent reached minimum value at pH 10 with a value of 81%.

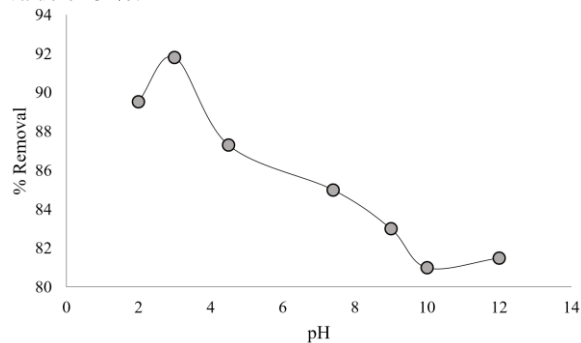


Figure 4. Effect of pH ( $[FG]_0= 10$  mg/L, Volume = 200 mL, pH = 3,  $Fe^{+2}= 10$  mg,  $H_2O_2= 0.05$  mL)

### 3.5 The Kinetic Study of Dye Decolourisation

The kinetics of decolorization for the FG dye were summarized and presented in Figure 5. First-order reaction kinetics were used to study the degradation kinetics of FG by Fenton oxidation process using the following equation:

$$\left(\frac{dc}{dt}\right) = -k_1 C \quad (2)$$

where C is the concentration of FG  $k_1$  the apparent kinetic rate constants of first-order reaction kinetic and t is the reaction time. Regression analysis based on the first-order reaction kinetic for the degradation of FG in Fenton oxidation process was conducted and the results are shown in Figure 5. Since the value of  $R^2$  is very close to 1, therefore; the results indicating that the degradation kinetics of FG followed the first-order kinetic well.

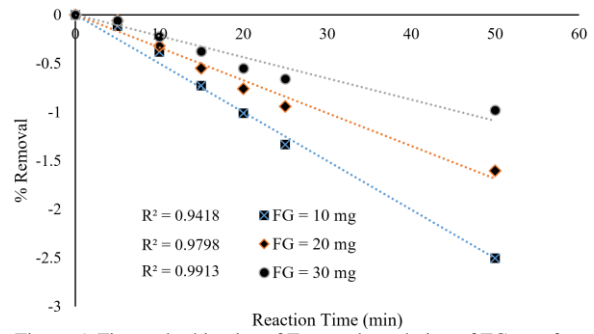


Figure 5. First order kinetics of Fenton degradation of FG as a function of initial FG concentration ( $[FG]_0= 10$  mg/L, Volume = 200 mL, pH = 3,  $Fe^{+2}= 10$  mg,  $H_2O_2= 0.05$  mL)

## 4. CONCLUSION

The degradation of FG in aqueous solution by Fenton reaction was studied at different experimental conditions including dosages of  $H_2O_2$  and  $Fe^{+2}$ , FG dye concentration and pH of the solution. The rate of degradation of FG dye enhanced as the concentration of  $Fe^{+2}$  and  $H_2O_2$  increased. A suitable operating condition were selected as:  $[FG] = 10$  mg/L,  $[Fe^{+2}] = 30$  mg and  $H_2O_2 = 0.15$  mL. It was found that the optimum pH for this study is pH 3. The Kinetic study indicated that the degradation kinetics of FG followed the first-order kinetics.

## REFERENCES

- Chang, D.-J., Chen, I. P., Chen, M.-T., & Lin, S.-S. (2003). Wet air oxidation of a reactive dye solution using CoAlPO4-5 and CeO2 catalysts. *Chemosphere*, 52(6), 943-949.
- Chen, R., & Pignatello, J. J. (1997). Role of Quinone Intermediates as Electron Shuttles in Fenton and Photoassisted Fenton Oxidations of Aromatic Compounds. *Environmental Science & Technology*, 31(8), 2399-2406.
- Dhananjeyan, M. R., Kiwi, J., Albers, P., & Enea, O. (2001). Photo-Assisted Immobilized Fenton Degradation up to pH 8 of Azo Dye Orange II Mediated by Fe3+/Nafion/Glass Fibers. *Helvetica Chimica Acta*, 84(11), 3433-3445.
- El-Desoky, H. S., Ghoneim, M. M., & Zidan, N. M. (2010). Decolorization and degradation of Ponceau S azo-dye in aqueous solutions by the electrochemical advanced Fenton oxidation. *Desalination*, 264(1-2), 143-150.
- Feng, J., Hu, X., Yue, P. L., Zhu, H. Y., & Lu, G. Q. (2003). Degradation of Azo-dye Orange II by a Photoassisted Fenton Reaction Using a Novel Composite of Iron Oxide and Silicate Nanoparticles as a Catalyst. *Industrial & Engineering Chemistry Research*, 42(10), 2058-2066.
- Fernandez, J., Bandara, J., Lopez, A., Buffat, P., & Kiwi, J. (1999). Photoassisted Fenton Degradation of Nonbiodegradable Azo Dye (Orange II) in Fe-Free Solutions Mediated by Cation Transfer Membranes. *Langmuir*, 15(1), 185-192.
- Fernandez, J., Dhananjeyan, M. R., Kiwi, J., Senuma, Y., & Hilborn, J. (2000). Evidence for Fenton Photoassisted Processes Mediated by Encapsulated Fe ions at Biocompatible pH Values. *The Journal of Physical Chemistry B*, 104(22), 5298-5301.
- Haydar A. Mohammad Salim, S. A. M. S., Reving A. Rashid. (2016). Removal of Acid Alizarin Black Dye from Aqueous Solution by Adsorption Using Zinc Oxide. *International Research Journal of Pure & Applied Chemistry*, 11(2), 1-8.
- Haydar A. Mohammad Salim, S. M. S. (2015). A comparison study of two different types of clay for heterogeneous photo degradation of dye. *International Journal of Advanced and Applied Sciences*, 2(2), 6-10.
- Hsueh, C. L., Huang, Y. H., Wang, C. C., & Chen, C. Y. (2005). Degradation of azo dyes using low iron concentration of Fenton and Fenton-like system. *Chemosphere*, 58(10), 1409-1414.
- Kang, S.-F., Liao, C.-H., & Chen, M.-C. (2002). Pre-oxidation and coagulation of textile wastewater by the Fenton process. *Chemosphere*, 46(6), 923-928.

- Ly, H., Zhao, H., Cao, T., Qian, L., Wang, Y., & Zhao, G. (2015). Efficient degradation of high concentration azo-dye wastewater by heterogeneous Fenton process with iron-based metal-organic framework. *Journal of Molecular Catalysis A: Chemical*, 400, 81-89.
- Mahmoodi, N. M., & Arami, M. (2009). Numerical finite volume modeling of dye decolorization using immobilized titania nanophotocatalysis. *Chemical Engineering Journal*, 146(2), 189-193.
- Mohammad Salim, H. A., & Mohammad Salih, S. A. (2015). Photodegradation Study of Toluidine Blue Dye in Aqueous Solution using Magnesium Oxide as a Photocatalyst. 2015, 7(2).
- Pesakhov, S., Benisty, R., Sikron, N., Cohen, Z., Gomelsky, P., Khozin-Goldberg, I., . . . Porat, N. (2007). Effect of hydrogen peroxide production and the Fenton reaction on membrane composition of *Streptococcus pneumoniae*. *Biochimica et Biophysica Acta (BBA) - Biomembranes*, 1768(3), 590-597.
- Pirkarami, A., & Olya, M. E. Removal of dye from industrial wastewater with an emphasis on improving economic efficiency and degradation mechanism. *Journal of Saudi Chemical Society*.
- Pirkarami, A., Olya, M. E., & Yousefi Limaee, N. (2013). Decolorization of azo dyes by photo electro adsorption process using polyaniline coated electrode. *Progress in Organic Coatings*, 76(4), 682-688.
- Salim, H. A. M. (2014a). HOMOGENEOUS PHOTOCATALYTIC DEGRADATION OF ACID ALIZARIN BLACK USING HYDROGEN PEROXIDE. *Journal of University of Zakho*, 2(2), 110-116.
- Salim, H. A. M. (2014b). PHOTOCATALYTIC DEGRADATION OF ACID ALIZARIN BLACK USING POWDER AND NANOPARTICLES OF TITANIUM DIOXIDE. *Journal of University of Zakho*, 2(2), 117-122.
- Shah, V., & Madamwar, D. (2013). Community genomics: Isolation, characterization and expression of gene coding for azoreductase. *International Biodeterioration & Biodegradation*, 79, 1-8.
- Sleiman, M., Vildoza, D., Ferronato, C., & Chovelon, J.-M. (2007). Photocatalytic degradation of azo dye Metanil Yellow: Optimization and kinetic modeling using a chemometric approach. *Applied Catalysis B: Environmental*, 77(1-2), 1-11.
- Slokar, Y. M., & Majcen Le Marechal, A. (1998). Methods of decoloration of textile wastewaters. *Dyes and Pigments*, 37(4), 335-356.
- Tizaoui, C., Mohammad-Salim, H., & Suhartono, J. (2015). Multiwalled Carbon Nanotubes for Heterogeneous Nanocatalytic Ozonation. *Ozone: Science & Engineering*, 37(3), 269-278.
- Xu, X.-R., Li, H.-B., Wang, W.-H., & Gu, J.-D. (2004). Degradation of dyes in aqueous solutions by the Fenton process. *Chemosphere*, 57(7), 595-600.

### كورتيا لئكوليني:

ژبو وردبيني يا شكاندنا بويغا بازرگاني يا جلکان ئەوا ناھن وئ کەسکا ب لە ز (FG) دەست ب ڤن ڤه کۆليني ھاھه کرن ، ب رڤکا ديارکەرئ ڤنتون ل بن سيبهرا وان کاودائين ژڤک جودا ئەوڤين مه تيدا کارکري دناڤ شیکهروههين شلي يين ناھن دا. کارکرن مه دناڤ ڤان کاودانان دا و ب ڤي رهنگي بو هايديروجين پيروکسايڤ (0.05، 0.1، 0.15 مل) و نمراترشياتي يئ (2-12) و خه ستي يا ڤايونين ناسني (10 و 20 و 10 مل) سهره تاي يا خيري اي شکاندنا FG ھاھه کارتيکرن ب رڤکا خه ستي يا ديارکەرئ ڤنتوني ( $Fe^{+2}$ ) و شیکهروههين ( $H_2O_2$ ) زيده بيئا تيکرتي يا شکاندن ب بها کەفت ل دەمئ خه ستي يا ڤايونين ناسني هه روهکي زيده بيئا ڤايونين ناسني ژ 10-30 مل زيده بيئا ڤاڤيرنا سهدي ژ 73% بو 89% دهه مئ 25 خوله کين ل دويڤ ئيکين دهه مئ 25 خوله کين دويڤ ئيکين دهه مئ 91.8% . ديسان زيده بو رڤزه ي يا سهدي يا ژ ناڤچووي يا FG ژ 74% بو 81% هه روه سان ب زيده کرنا رڤزه يا  $H_2O_2$  ژ 0.05 بو 0.15 مل دهه مئ 25 خوله کين دويڤ ئيکين دهه مئ 91.8% . ژ خاندنا مه دياربو ، خاندنا لڤينا FG ڤاڤيرنا ، ديسان دهئ کاريدا نه نجام ڤامازئ دهه ته وئ چهندي کولفاندنا شکاندن دويڤچووا خيري اي يا ئيکي به .

### خلاصة البحث:

وقد تم التحقيق تدهور صبغ النسيج التجاري اسمه أخضر سريع (FG) بواسطة كاشف فنتون في ظل ظروف تشغيل مختلفة في محلول مائي. كانت ظروف التشغيل كمية بيروكسيد الهيدروجين (0.05، 0.1، 0.15 مل)، ودرجة الحموضة (2-12) وتركيز أيون حديدية (10 و 20 و 30 مل). تأثر معدل الأولي من التدهور عن طريق تركيز الكواشف فنتون [الحديد (I)] وحل  $H_2O_2$ . ارتفع معدل تدهور المعزز، حيث تركيز أيون الحديدية. كما زاد تركيز أيون الحديدية 10-30 مل، زادت إزالة في المئة من 73 إلى 89%، على التوالي، في 25 دقيقة من وقت رد الفعل. أيضا، زادت في المئة إزالة FG من 74% إلى 81% عندما زادت كمية  $H_2O_2$  من 0.05 مل إلى 1.5 مل، على التوالي، في 25 دقيقة من وقت رد الفعل. وتبين أيضا أنه في درجة الحموضة 3 إزالة بالمية تصل القيمة القصوى مع 91.8%. وقد درس دراسة الحركية للتدهور FG أيضا في هذا العمل، وأشارت النتائج إلى أن حركية تدهور FG اتبعت الحركية من الدرجة الأولى.