

DECOLORIZATION KINETICS FROM COFFEE EFFLUENT WITH PHOTO-FENTON REACTION

KINETIKA PENGHILANGAN WARNA PADA LIMBAH KOPI DENGAN METODE FOTO-FENTON

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Abstract

Coffee effluent contains a high amount of dark brown pigments. When this waste is released in the river, it will block the sun ray and disturb the photosynthesis process. The decolorization of coffee effluent using photo-Fenton and Fenton processes is presented in this paper. On the photo-Fenton reaction, UV light, ion Fe(II) and H₂O₂ will produce •OH. This will react with organic contaminant, so the color of the effluent will be changed from brown to yellow, and finally became a clear solution. On the Fenton process, reaction occurred without the existence of UV light. The rate of this decolorization is slower than photo-Fenton reaction. The reaction consists of three phases, the first phase happen when H₂O₂ is added to the reactor and the color changes rapidly, the color of the solution start to be removed fast (second phase) and then it became faster and there were no more changes in its color (third phase). The color removal rate for second phase at the coffee effluent concentration of 250 ppm, 300 ppm, 400 ppm were : $r = -0,0322 \text{ (Abs)}^2$; $r = -0,0271 \text{ (Abs)}^2$; $r = -0,0196 \text{ (Abs)}^2$, whereas the color removal rate for third phase at the coffee effluent concentration of 250 ppm, 300 ppm, 400 ppm were : $r = -0,0049 \text{ (Abs)}$; $r = -0,0211 \text{ (Abs)}$; $r = -0,005 \text{ (Abs)}$.

Keywords: coffee effluent, photo-Fenton decolorization, color removal rate

Abstrak

Limbah cair dari industri kopi mengandung sejumlah besar pigmen yang berwarna coklat. Ketika limbah cair ini dibuang ke perairan, warna coklat ini akan menghalangi sinar matahari masuk ke perairan dan mengganggu proses fotosintesis. Makalah ini akan mempresentasikan proses penghilangan warna dan kinetika penghilangan warna pada limbah cair dengan metoda Fenton dan Foto-Fenton. Pada metode Foto-Fenton, limbah direaksikan dengan ion besi (II) dan hidrogen peroksida dengan bantuan sinar ultra-violet. Radikal OH yang dihasilkan dari metoda ini akan bereaksi dengan limbah cair sehingga menurunkan kandungan bahan organik total dan warnanya. Pada proses Fenton, reaksi penghilangan warna yang terjadi tanpa bantuan sinar ultra-violet. Selama proses penghilangan warna tersebut, limbah cair yang berwarna coklat akan berubah menjadi kuning dan akhirnya jernih. Kecepatan penghilangan warna pada metoda Foto Fenton lebih cepat dibandingkan metoda Fenton. Reaksi terdiri dari 3 fase, fase pertama terjadi ketika H₂O₂ ditambahkan, perubahan warna terjadi sangat cepat, warna larutan berubah sangat cepat (fase kedua) yang kemudian menjadi lebih cepat, sampai tidak terjadi perubahan warna lagi (fase ketiga). Laju penghilangan warna untuk fase kedua pada konsentrasi efluen kopi 250 ppm, 300 ppm, 400 ppm adalah : $r = -0,0322 \text{ (Abs)}^2$; $r = -0,0271 \text{ (Abs)}^2$; $r = -0,0196 \text{ (Abs)}^2$, sedangkan laju penghilangan warna untuk fase ketiga pada konsentrasi efluen kopi 250 ppm, 300 ppm, 400 ppm adalah : $r = -0,0049 \text{ (Abs)}$; $r = -0,0211 \text{ (Abs)}$; $r = -0,005 \text{ (Abs)}$.

Kata kunci: limbah kopi, penghilangan warna, Foto Fenton, laju penghilangan warna

1. INTRODUCTION

Coffee effluent has a dark color and contains a big amount of dark pigment. The pigment contains melanoidins, which are considered as final product of Maillard reaction (Andriot, 2004) and contribute to high concentration of COD. The effluent doesn't have high concentration of BOD, hence it's difficult to be treated biologically. The dark color will be danger for aquatic life due to sun ray blocking, moreover it also creates toxicity on the environment. It shows the importance of toxic component removal in coffee effluent. The main composition of the coffee effluent is melanoidin.

Melanoidin consists of several ligand group, such as tannin, polysaccharides, peptide, and its combinations. Melanoidin is antioxidant, and toxic for many organisms in the waste treatment. Melanoidin can bind Fe^{2+} , so the usage of photo-fenton and fenton reactions could be effective to degrade the melanoidin and also remove the color of coffee effluent. The photo-Fenton method has successfully treated waste water from textile and dying process (Modirshahla, 2007). Therefore, in this experiment, a coffee effluent was treated. The colored wastewater which was treated with photo-fenton reaction still contained high Fe^{3+} concentration. This problem was not solved in the experiment of Tokumura et al. (2006). In this experiment, the Fe^{3+} degradation was also examined to comply with the wastewater quality standards of the Indonesian Government.

2. METHODS

Coffee effluent was made by diluting instant coffee powder, Nescafe black (Nestle Group) in aqueous solution with the addition of sulfuric acid to make an initial pH of 3. The concentrations of coffee effluent were 250, 300 and 400 mg/L. According to Tokumura et al. (2006), pH 3 was the optimum pH for Fenton and photo-Fenton processes. The reagents were hydrogen peroxide (30%

solution), iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$), sulfuric acid (0,1 M), and sodium hydroxide (0,1 M). The Fenton reactions were initiated by the addition of H_2O_2 to a mixture solution of coffee effluent and Fe^{2+} , and the solution was mixed completely by using a magnetic stirrer.

Experiments were done in a cylindrical glass reactor. The working volume was 1 L. All experiment was done in a batch mode, and neglecting temperature and pH changes. All experiment were carried out triplicate. The UV sources were two near-UV fluorescent lamps (352 nm wavelength), having light intensity at light source 10 W/unit. These lamps were vertically located oppositely, and externally irradiated the solution. The samples were withdrawn every 30 minutes, using a 15 mL syringe. Fine solids were removed from the sample by treating it in the centrifuge before measuring the color absorbance and TOC.

Assay: Coffee effluent decolorization was measured as the decrease in color density at 400 nm, using a direct reading spectrophotometer DR/2000 HACH. The TOC was measured using a TOC analyzer V-CN. The concentration of total Fe ion and Fe^{2+} ion in the sample solution were measured by the 1,10-phenantroline method (Clesceri, 1998) periodically, using UV-Vis spectrophotometer. The concentration of Fe^{3+} ion was determined as the difference between total Fe ion concentration and the Fe^{2+} ion concentration.

3. RESULT AND DISCUSSION

The initial coffee effluent color was light brown. During the photochemical decolorization process, the color was changed from light brown to yellow and finally clear. At the end of the process, the pH was around 3-4. The characteristic of the decolorization is shown by the absorbance measured on wavelength 400nm using UV-Vis spectrophotometer. Figure 1 shows the

relationship between relative color absorbance

to the initial absorbance during reaction time.

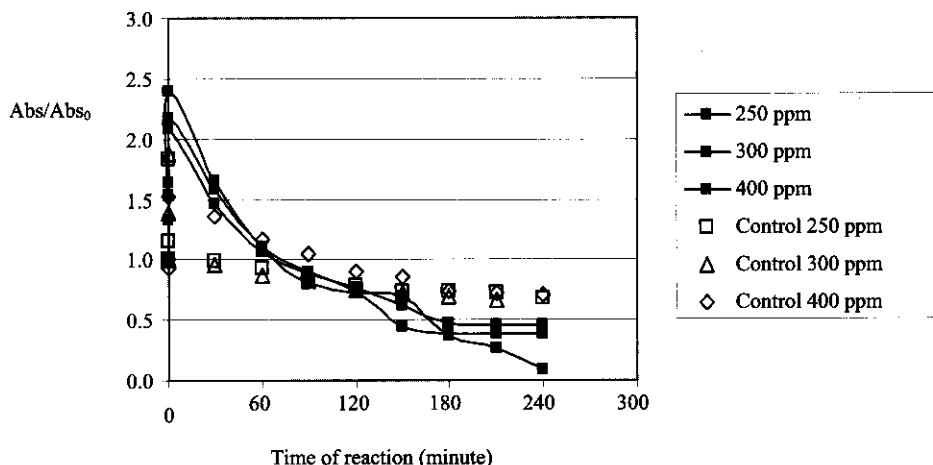
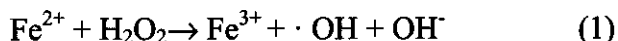


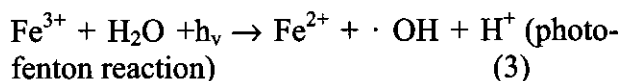
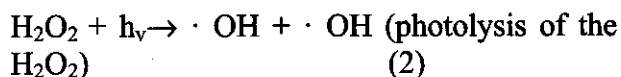
Figure 1. Coffee effluent decolorization with various coffee concentration, at initial concentration of ferrous ion = 15 mg/L, hydrogen peroxide = 700 mg/L with 2 UV lamps

The initial color absorbance of the coffee effluent was 1. The addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2O_2 increased the color absorbance. On the photo-fenton reaction, UV light and H_2O_2 produced radical OH that reacted with organic contaminants, so the color of waste water was changed from light brown to yellow, and finally became clear. The UV light influenced the results of the experiment. In fenton process, the color removal is a slower, and the color removed is lower without the UV light, compared to the treatment with UV light. The relative absorbance of coffee effluent was plotted as a function of time under various conditions, as shown in Figure 2. The 'control' in this figure referred the decolorization with Fenton method.

Some reactions between Fe ion of the $\text{Fe}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$ with H_2O_2 and UV occurred during the color removal process. The processes included Fenton, photolysis of H_2O_2 , and photo-fenton reactions. These reactions worked continuously and produced radical OH which bonded the melanoidin. The fenton reaction is shown below.



The photo-fenton reaction combined UV, Fe^{3+} , and H_2O_2 , resulting radical OH as followed.



In the beginning of the process, the Fe^{2+} decreased because of the fenton reaction, meanwhile, the Fe^{3+} increased (reaction 1). After that, the radical OH produced from the fenton and photolysis reaction (reaction 2) reacted with the Fe^{3+} , so the Fe^{3+} concentration decreased, and the Fe^{2+} concentration increased (reaction 3).

During the experiment, total Fe in the solution was hard to measure. A model was applied to the data, by assuming the total Fe characteristic during the color removal follow 3rd order polynomial. Fe concentrations at different states are shown in Figure 3.

Figures 2 to 5 show the total Fe, Fe²⁺, and Fe³⁺ in the sample. During the beginning of the process, the Fe²⁺ started to decrease because of the fenton reaction producing Fe³⁺.

photo-fenton reaction, Fe³⁺ started to react and produced Fe²⁺ and radical OH. On the minutes of 240, the color absorbance from the sample tended to be constant, and the color of sample was clear. At the end of the experiment,

Fe concentration in the sample was still quite high. This problem was solved by the addition

Quality Standards according to the Indonesian Government, which is below 15 ppm for the 3rd river (Dinas Perindustrian, 2001).

For 250 mg/L and 300 mg/L concentrations of coffee, the Fe²⁺ decreased within 0-150 minutes, while in 400 mg/L of coffee, the decrease occurred on 0-90 minutes. After the

of NaOH in order to adjust pH to 8, for precipitating Fe³⁺ to Fe(OH)₃. The precipitate could be removed using centrifuge. The addition of NaOH was continued up to pH of 10 for precipitating Fe²⁺ into Fe(OH)₂. After this process was conducted, Fe concentration in the sample was analyzed. It was found that Fe had been reduced to the Wastewater

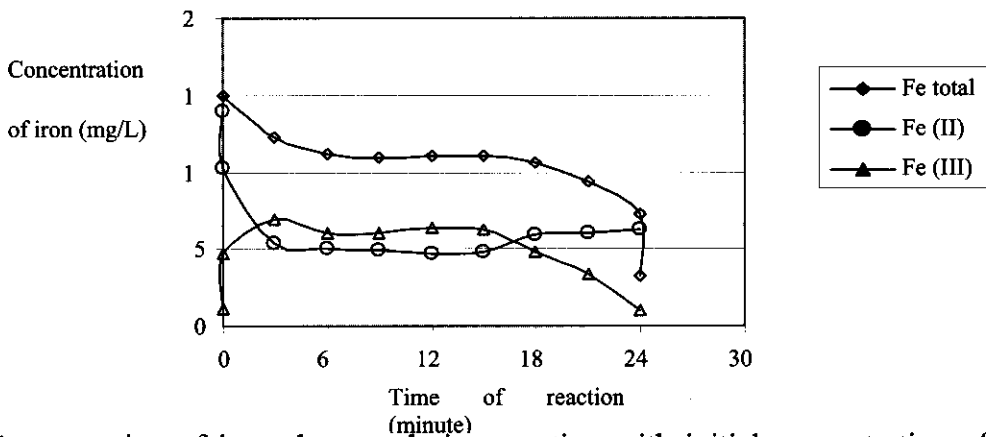


Figure 2. Concentration of iron changes during reaction with initial concentration of coffee =250 mg/L, ferrous ion =15 mg/L, hydrogen peroxide =700 mg/L, and 2 units of UV lamp.

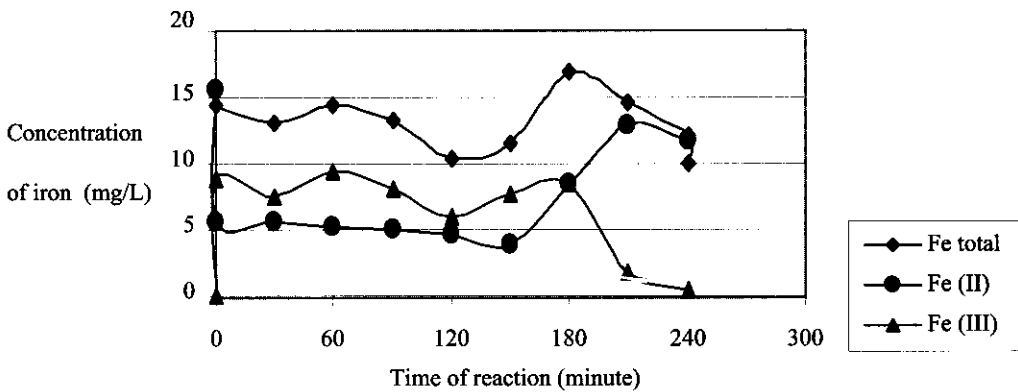


Figure 3. Concentrations of iron changes during reaction with initial concentration of coffee =300 mg/L, ferrous ion =15 mg/L, hydrogen peroxide =700 mg/L, and 2 units of UV lamps.

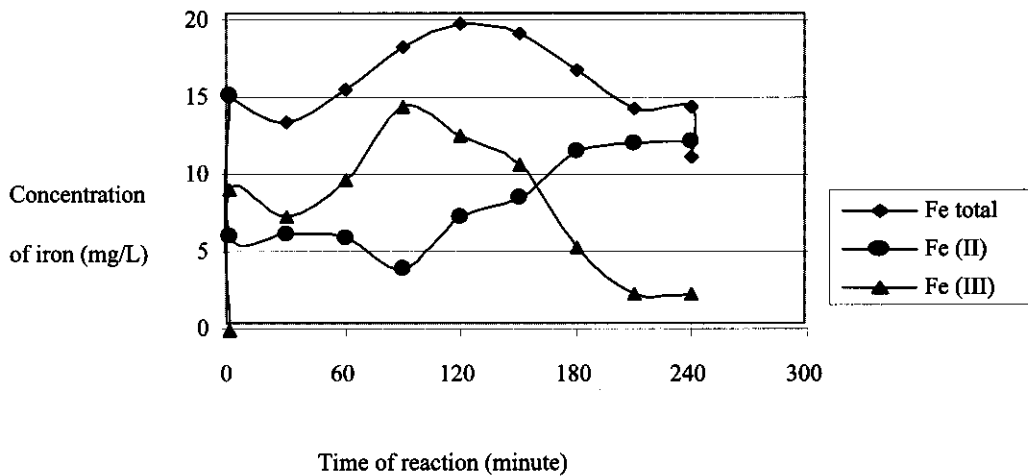


Figure 4. Concentration of iron changes during reaction with initial concentration of coffee =400 mg/L, ferrous ion =15 mg/L, hydrogen peroxide =700 mg/L, and 2 units of UV lamp

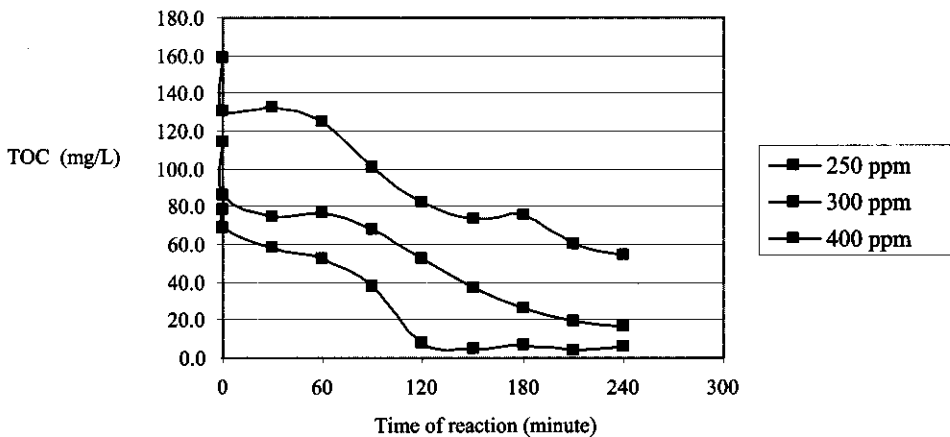


Figure 5. TOC changes during reaction with various concentrations, $CF_0=15$ mg/L, $CH_0=700$ mg/L, 2UV lamps.

The addition of $FeSO_4 \cdot 7H_2O$ to coffee effluent increased the TOC (Total Organic Carbon), while the addition of H_2O_2 decreased the TOC. However, the photo-fenton treatment showed the Total Organic Carbon (TOC) on the coffee effluent decreased during the reaction time, so the wastewater was safe for the environment.

The color removal process on coffee effluent can be separated to three phases. The first phase happened when H_2O_2 was added to the reactor and the color changed rapidly. After that, the color of the solution started to be removed fast (second phase) and then it became faster and there was no more change in its color (third phase).

By following the reaction model from Tokumura et al., the reaction rate for second phase can be explained by second order reaction kinetics below.

$$r = -d(Abs) / dt = k_2 (Abs)^2 \quad (4)$$

where k_2 is the second order reaction rate constant. Plot between

versus time on second phase will give a linear line (Figure 6), where its slope is the rate constant for second phase.

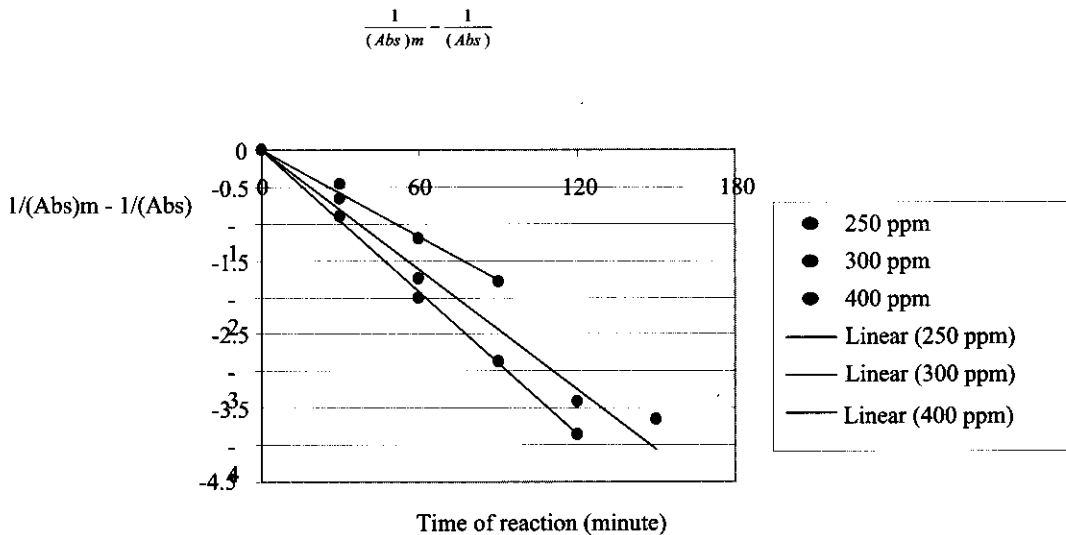


Figure 6. Kinetics for color removal in second phase.

The reaction rate of the third phase can be explained by first order reaction kinetics below.

$$r = -d(Abs) / dt = k_1 (Abs) \quad (5)$$

where k_1 is the first order reaction rate constant.

Plot between $\ln \frac{(Abs)}{(Abs)_m}$ versus time on second phase will give a linear line (Figure 7), where its slope is the rate constant for third phase. As has been discussed before, the H_2O_2 addition will give a significant change on the absorbance, so as the initial value, this absorbance is used, and showed as $(Abs)_m$.

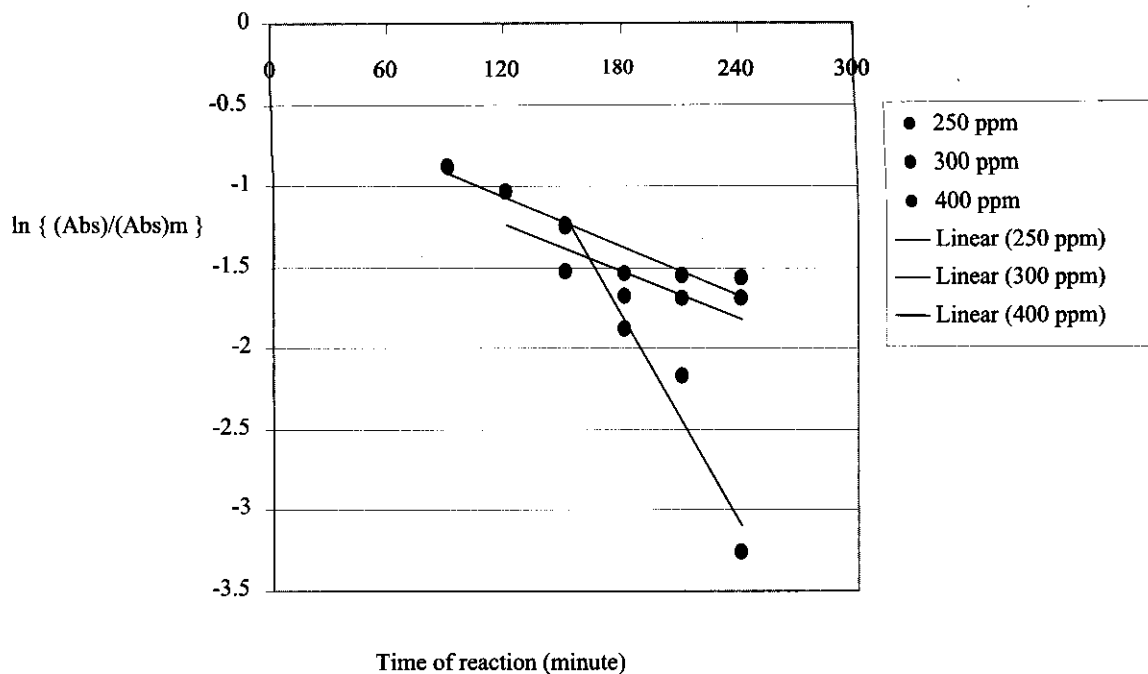


Figure 8. Kinetics for color removal in third phase

The color removal rate for several concentration is shown on Table 1. The constant for concentration 250 mg/L and 300 mg/L can be used, but the 400 mg/L needs to be reexamined. For a higher concentration, a longer time is needed to remove the color of the solution. Decolorization rate in second phase decreases with the increasing of initial

coffee concentration. The dark brown color will prevent UV light irradiation into the solution. According to Tokumura et al. (2006), this is one of the factors responsible for the significant decrease in decolorization rate constant in second phase.

Table 1. The decolorization rate of coffee effluent in 2nd phase and 3rd phase

Coffee effluent concentration (mg/L)	Color removal rate (min ⁻¹)	
	2 nd phase	3 rd phase
250	$r = -0,0322 (Abs)^2$	$r = -0,0049 (Abs)$
300	$r = -0,0271 (Abs)^2$	$r = -0,0211 (Abs)$
400	$r = -0,0196 (Abs)^2$	$r = -0,005 (Abs)$

4. CONCLUSIONS

The results suggested that the photo-fenton reaction was very efficient for decolorization of coffee effluent. The process could be separated in three phases. The sudden increase of color absorbance was the first phase. The significant decolorization was controlled by Fenton reaction in the second phase, and the decolorization controlled by photo-Fenton reaction was the third phase.

The increase of coffee concentration resulted in a decrease of second order rate constant, while the result for the third phase needed more examination. The residual iron in the process was reduced by adding sodium hydroxide and resulted in $\text{Fe}(\text{OH})_3$ and $\text{Fe}(\text{OH})_2$ precipitates.

Nomenclature:

Abs	Absorbance of coffee effluent
(Abs) _m	Maximum absorbance observed at the initial reaction stage
C _c	Concentration of coffee effluent (mg/L)
CF ₀	Concentration of iron in solution (mg/L)
C _h	Concentration of hydrogen peroxide in solution (mg/L)
Abs ₀	Initial absorbance, after the addition of hydrogen peroxide.
k ₁	Rate constant of first order kinetics with respect to absorbance (min ⁻¹)
k ₂	Rate constant of second order kinetics with respect to absorbance (min ⁻¹)
T	Time (minute)
r	Decolorization rate (min ⁻¹)
-d(Abs)/dt	Decrease of color absorbance during time
S _L	Light intensity at light source per unit length (W/m)

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