Fenton Degradation of Lignin Wastewater in a Batch Process for Pulp and Paper Industry : Kinetic and Economic Aspect

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***Abstract* — Lignin wastewater from pulp and paper industry is a hazardous and toxic waste which has to be treated prior to disposal due to high content of recalcitrant organics which lead to high concentration of COD. The wastewater can be treated with Advanced Oxidation Technology (AOT) by using Fenton's reagent (H_2O_2 and Fe^{2+}) in batch and isothermal (30°C) condition. The experiments were carried out to evaluate the kinetic and economic aspects for the application of Fenton's reagent in lignin wastewater degradation. The parameters used in this study were 1) concentration of H_2O_2, 2) molar ratio of Fe^{2+}/H_2O_2, and 3) the value of initial wastewater pH. The Fenton process is effective at H_2O_2 concentration of 0,084 mol/L, Fe^{2+}/H_2O_2 ratio of 1:20, and pH of 3.0. The results show that the removal of lignin, COD and colour are 100%, 67% and 99% respectively after 120 minutes reaction. The COD degradation kinetic is pseudo first order with the kinetic constant is 0.0113 min^{-1} and chemical cost for this treatment is estimated to be IDR 350.433/L wastewater.**

Keyword - kinetic model, Fenton, lignin wastewater, pulp and paper, COD

I. INTRODUCTION

Pulp and paper industries produce a large amount of lignin wastewater that must be treated due to its complex aromatic heteropolymer (oxyphenylpropanoid) and high molecular weight [1]. Lignin which is not treated in 200 days will form toxic by-products due to its decomposition to phenols, aldehydes, ketones, methanol, and carboxylic acids which is harmful for aquatic life. Biological treatment of lignin wastewater needs 54 days to remove 45% lignin contents [2]. Non-biological or chemical treatment has less period of treatment time and must be used to increase the efficiency of COD removal and lignin degradation. In recent years, Advanced Oxidation Technology has been studied as one of powerful treatment method to oxidize the organic compounds with hydroxyl radicals ($OH^\bullet$). Hydroxyl radicals can oxidize the organic molecules into environmentally safe molecules like carbon dioxide (CO_2) and water (H_2O) [3,4]. Recently, Advanced Oxidation Technology has been applied to wastewater treatment such as Fe(II)/H_2O_2/UV [5-8], TiO_2/UV [9], synergistic catalytic action (Fe^0, Fe^{2+}, Fe^{3+}) [10], and Fe)II)/H_2O_2 [11,12]. Fenton oxidation is a simple and efficient oxidation method which uses Fenton's reagent, like hydrogen peroxide which has been known as a strong oxidation agent. The reagent produces hydroxyl radicals with the presence of ferrous ions as catalyst to foster the reaction. Fenton oxidation of lignin wastewater has not been studied over the last few years. This method has many advantages such as it is operated under ambient conditions, non-toxic, the ability to reduce the toxicity of wastewater, environmentally benign, less cost, easy to control, easy-to-handle reagents, need less energy input to activate oxidation agents, and effective in treating various industrial wastewater components, such as aromatic amines [13-14]. AOT method using Fenton's reagent can be operated effectively if the wastewater contains less of suspended solid [15].

Hydroxyl radicals ($OH^\bullet$) are formed by the reaction of Fenton's reagent [16]:

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

Hydroxyl radicals ($OH^\bullet$) attack organic molecules (RH) rapidly in lignin wastewater producing carbon dioxide and water:

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

$$R\bullet + RH \rightarrow CO_2 + H_2O \qquad (3)$$

Ferrous ions can be regenerated from the reaction of hydrogen peroxide and ferric ions:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2 \bullet \quad (4)$$

$$Fe^{3+} + HO_2 \bullet \rightarrow Fe^{2+} + H^+ + O_2 \quad (5)$$

The aims of this study are 1) to determine the percentage removal of lignin, COD, and colour in lignin wastewater, 2) to study kinetic degradation of COD, and 3) to estimate the operational cost of the method in batch system.

II. EXPERIMENTAL

A. Materials

Lignin wastewater for this study was taken from a pulp and paper production which located in Surabaya, Indonesia. Hydrogen peroxide 30% w/w (H_2O_2) and ferrous sulfate heptahydrate ($FeSO_4.7H_2O$), hydrochloric acid 37% w/w (HCl), and sodium hydroxide (NaOH) were all obtained from Merck, Germany. All chemicals quantities were analytical grade and used without any further purification. COD reagents such as potassium hydrogen phtalat, silver sulfate ($AgSO_4$), sulfuric acid 96% w/w, mercurous sulfate (Hg_2SO_4), and potassium dichromate ($K_2Cr_2O_4$) were all obtained from Merck, Germany.

B. Methods

Fenton oxidation was carried out in a 1 L batch reactor (UFO Labglass Singapore) with the mixing speed of 350 rpm at 30°C and stirred for 120 minutes (Figure 1). The pH of each solution was adjusted to the appropriate value (2.0, 3.0, 4.0) by adding HCl 3 M. The reaction was initiated by adding $FeSO_4.7H_2O$ and H_2O_2 with different amounts ratio of $[Fe^{2+}]/[H_2O_2]$ (1:10, 1:15, 1:20) and H_2O_2 concentration (0.042; 0.084; 0.168 mol/L). Upon the solution of H_2O_2 was added to reactor, the start time was recorded in order to measure the reaction period. Sample was taken from the reactor every 20 minutes by using a syringe and neutralized the pH solution using NaOH, to stop the peroxide reaction. Each sample was analysed for COD, while the TSS, lignin, and colour measurements were carried out before and after treatment.

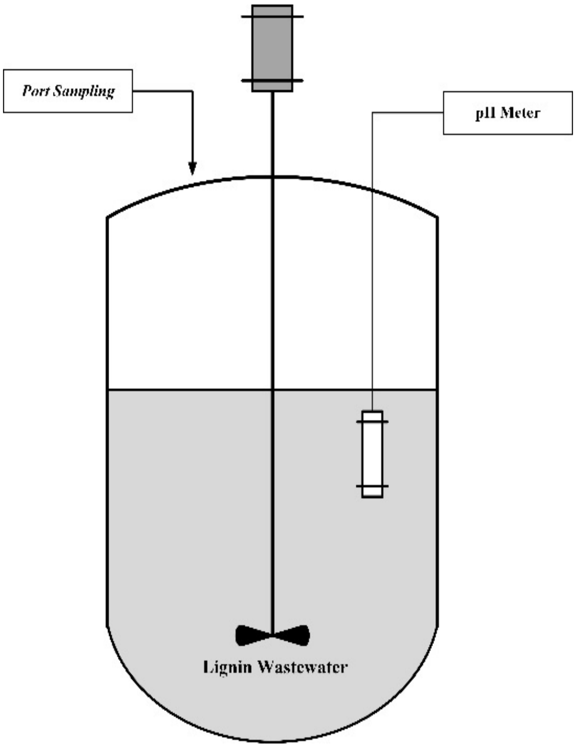

Figure 1. Experimental set-up

C. Assay

COD was measured using closed reflux spectrophotometry method, TSS measurement was carried out by using gravimetric method (SNI 06-0989.3-2004) [17], lignin was measured using Klakson method (SNI 0492:2008) [18], and colour measurement was recorded from 200 to 800 nm wavelengths using a UV/Vis spectrophotometry with the absorbance values at 629 nm as optical density [19].

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III. RESULTS AND DISCUSSION

A. *Effect of H_2O_2 Concentration*

The characteristics of lignin wastewater before and after treatment are presented in Table 1.

TABLE 1. The characteristics of lignin wastewater before and after Fenton oxidation

Parameters	Before	After
Lignin	20,250 ppm	0
COD	666.457 ppm	218.546 ppm
TSS	8,570 ppm	4,900 ppm
Color (Optical Density)	1.4335	0.018865
pH	11-12	7

Hydrogen peroxide has a higher value of standard potential redox than other oxidation agents such as ozone (O_3). Standard potential redox value of hydrogen peroxide is 2.8 V while ozone is 1.77 V [20]. As shown in Table 1, the lignin contents of this wastewater is reduced from 20,250 ppm to 0 ppm while the COD removal is 67%. It shows that this treatment can remove lignin compounds (cell wall polymer) significantly although some organic compounds may not be removed completely during 120 minutes of experiment which is indicated by the amount of COD content after the experiment. High initial concentration of TSS in the wastewater may hinder the degradation of COD. Higher concentration of hydrogen peroxide will lead in higher hydroxyl radicals ($OH^\bullet$) formed which will oxidize organic pollutant and lignin in the wastewater. However, results which are presented in Table 2 show that the best concentration of H_2O_2 used in the oxidation is 0.084 mol/L. Higher concentration of hydrogen peroxide (0.168 mol/L) will not give a better result for COD removal due to a scavenging reaction of hydroxyl radicals as the presence of Fenton's reagents excess which is indicated in Equation 6 and 7 [21].

TABLE 2. Experimental data at Fe^{2+}/H_2O_2 molar ratio = 1:20 and initial wastewater pH = 3.0

H_2O_2 concentrations	COD removal	TSS removal	Colour removal
0.042 mol/L	60% w/v	40% w/v	97%
0.084 mol/L	67% w/v	43% w/v	99%
0.168 mol/L	60% w/v	33% w/v	98%

$$\mathrm{OH}\bullet + \mathrm{H_2O_2} \rightarrow \mathrm{HO_2}\bullet + \mathrm{H_2O} \quad (6)$$

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

The scavenging reaction generates perhydroxyl radicals ($HO_2^\bullet$) that can reduce the effectiveness of Fenton oxidation because it has a lower value of standard potential redox (1.77 V) than hydrogen peroxide. The perhydroxyl radicals then reacts with hydroxyl radicals to produce oxygen and water as indicated in Equation 8. Moreover, when the concentration of hydrogen peroxide is higher than the optimum concentration, there will be a recombinant reaction between hydroxyl radicals that can generate hydrogen peroxide by Equation 9.

$$\mathrm{HO_2}\bullet + \mathrm{OH}\bullet \rightarrow \mathrm{O_2} + \mathrm{H_2O} \quad (8)$$

$$OH^\bullet + OH^\bullet \rightarrow H_2O_2 \quad (9)$$

Based on the reaction written above, high concentration of H_2O_2 won't lead to effective oxidation.

B. *Effect of Fe^{2+}/H_2O_2 Molar Ratio*

The dosage of Ferrous ions is another important parameter in Fenton oxidation which serves as catalyst to decomposes hydrogen peroxide to generate hydroxyl radicals. The molar ratio of Fe^{2+}/H_2O_2 was varied to get the best ratio of Fe^{2+}/H_2O_2. The results are shown in Table 3.

TABLE 3. The COD removal at H_2O_2 concentration = 0.168 mol/L and initial wastewater pH = 3.0

Fe^{2+}/H_2O_2 molar ratio	COD removal	TSS removal	Colour removal
1:10	61% w/v	32% w/v	95%
1:15	64% w/v	30% w/v	94%
1:20	67% w/v	43% w/v	98%

Table 3 shows that the highest COD, TSS, and colour removals were reached at 1:20 Fe^{2+}/H_2O_2 molar ratio, which explains that Fe^{2+}/H_2O_2 molar ratio directly affect the production of hydroxyl radicals in Fenton oxidation. However, the increase of Ferrous ions relate to the amount of Ferrous hydroxide sludge ($Fe(OH)_3$) which was generated from Fenton oxidation process and increased a brown turbidity in wastewater and hinder the oxidation process [21,22].

C. Effect of initial wastewater pH

pH is the most important parameters in Fenton oxidation because the generation of hydroxyl radicals is pH dependent. pH will affect the effectiveness of Fenton oxidations. The optimum pH that has been studied was at pH 3.0 [23]. To investigate the effect of initial pH, experiments were conducted in range of pH 2.0, 3.0, and 4.0.

TABLE 4. Experimental data at H_2O_2 concentration = 0.168 mol/L and Fe^{2+}/H_2O_2 molar ratio = 1:20

pH	COD removal	TSS removal	Color removal
2.0	32% w/v	13% w/v	97%
3.0	67% w/v	43% w/v	99%
4.0	66% w/v	15% w/v	99%

Table 4 shows that the best result for COD, TSS and colour removals is at initial wastewater pH of 3.0. If the pH is too low (pH < 3.0), there will be strong scavenging effect from hydroxyl radicals by H^+ ions that decrease the oxidation process as indicated in Equation 10. The lower value of initial pH will reduce the reactivity of the reaction between hydrogen peroxide and ferrous ions to generate hydroxyl radicals because hydrogen peroxide can capture a proton to form a hydroxyoxidanium ions ($H_3O_2^+$) as indicated in Equation 11. Moreover, for pH below 3.0, complex species $(Fe(H_2O)_6)^{2+}$ will be formed which react slowly and inhibit the oxidation process of hydrogen peroxide and ferrous ions [21,22].

$$\mathrm{OH}\bullet + \mathrm{H}^+ + e^- \rightarrow \mathrm{H_2O} \tag{10}$$

$$\mathrm{H_2O_2} + \mathrm{H}^+ \rightarrow \mathrm{H_3O_2^+} \tag{11}$$

If the wastewater initial pH is greater than 3.0, ferric hydroxide ($Fe(OH)_3$) is formed which will decompose hydrogen peroxide into oxygen and water molecules. Ferrous and ferric ions dissolve under high alkaline conditions that will affect the regeneration of hydroxyl radicals. Standard potential redox value of hydroxyl radicals is lower with the increase of pH (E° at pH 0.0 = 2.8 V and E° at pH 14.0 = 1.94 V)

D. Kinetic Study

The kinetic study of lignin wastewater in this research is different from previous study. Riadi, *et al.*[24] observed that the kinetic follows an instantaneous reaction in the first two minutes of the reaction. The instantaneous reaction doesn't happen in the lignin degradation. The oxidation reaction works when the Fenton's reagent was added to lignin wastewater. There is an intermediate compound in lignin like carboxylic acid which is not reactive to hydroxyl radicals [25]. All organic compounds in lignin wastewater is represented by COD parameter. The COD removal profile is shown in Figure 2.

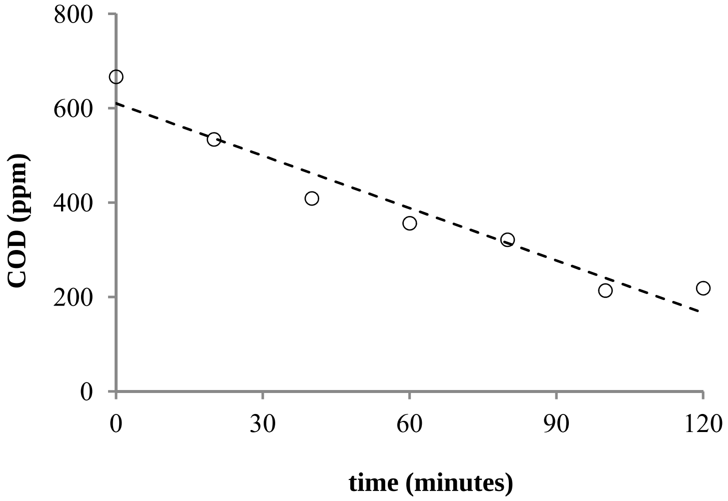

Figure 2. COD profile at Fe^{2+}/H_2O_2= 1:20, initial pH 3.0 ,$[H_2O_2]$ = 0.168 mol/L,(o) experiment; (---)model

Figure 2 shows COD reduction was not instantaneous because the generation of ferric ions (Equation 1) from ferrous ions is slower than the generation of ferrous ions from ferric ions (Equation 4 and 5), since the standard potential value of perhydroxyl radicals (1.77 V) is lower than hydroxyl radicals (2.8 V). The kinetic COD removal was studied using parameters based on the best results from the experiment. Since hydrogen peroxide is in excess, the kinetic COD removal of lignin wastewater in batch and isothermal (30°C) conditions followed the pseudo first order which can be written as follows:

$$-r_{COD} = \frac{-dCOD}{dt} = k'[COD] \tag{12}$$

k' is kinetic constant in pseudo first order ($k' = k. C_{OH\bullet}$), Eq. 12 is solved to get Eq. 13:

$$ln\frac{[COD]initial}{[COD]} = k't \qquad (13)$$

Based on Eq. 13, we can plot the values of $ln\frac{[COD]initial}{[COD]}$ and reaction time which is depicted in Figure 3.

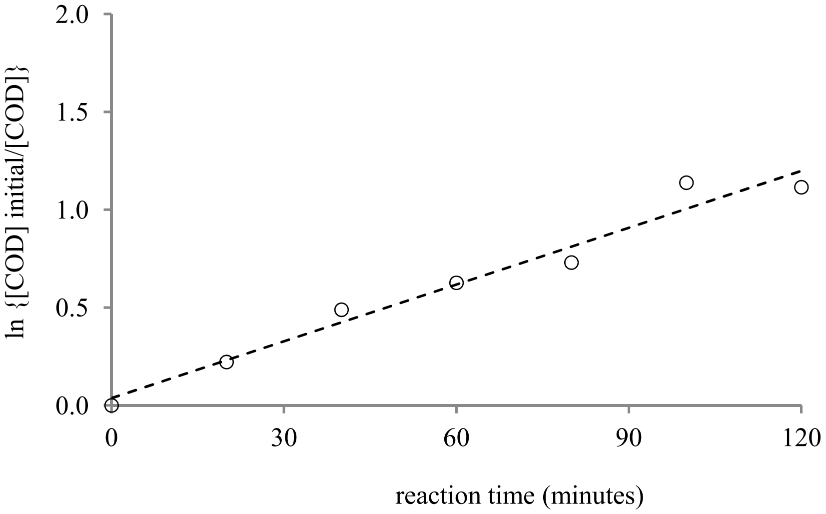

Figure 3. Plot $ln\frac{[COD]initial}{[COD]}$ vstime, $[H_2O_2]$= 0.168 mol/liter, Fe^{2+}/H_2O_2 molar ratio = 1:20, initial pH = 3.0, (o)experiment; (---) model

As shown in Figure 3, the kinetic constant is 0.0113 min^{-1} and the rate of COD degradation is written as:

$$-r_{COD} = 0.0113[COD][\frac{mg}{L\,min}] \qquad (14)$$

The kinetic constant in lignin degradation is lower than kinetic constant for yarn dyed wastewater degradation (0.07046 min^{-1}) [26], which shows that the rate of COD degradation in lignin wastewater is slower than that in yarn dyed wastewater.

E. *Cost Analysis*

The operation cost for Fenton process is estimated based on two hours batch mode at optimum conditions. The chemicals used in this Fenton process are hydrochloric acid to adjust initial wastewater pH, sodium hydroxide to neutralize wastewater after treatment, hydrogen peroxide as source of hydroxyl radicals and oxidizing agents, and ferrous sulphate heptahydrate as catalyst. Total chemical cost for Fenton oxidation is shown in Table V.

TABLE V. The chemical cost of Fenton oxidation process for 1 L lignin wastewater

Items	Quantity	Cost/unit (IDR/unit)	Cost (IDR)
HCl 37% w/w	3.823 mL	3.9 / mL	14.910
NaOH	0.432 gram	6.5 / gram	2.808
H_2O_2 96% w/w	8.5 mL	39 / L	331.500
$FeSO_4.7H_2O$	1.168 gram	1.04 / gram	1.215
TOTAL			350.433

IV. CONCLUSION

Results from the study showed that Fenton oxidation process can remove 100% lignin, 67% COD, and 99% colour from lignin wastewater of pulp and paper industry in a batch mode and isothermal (30°C) condition for 2 hours. The optimum parameters used in this study are: H_2O_2 concentration = 0,168 mol/L, Fe^{2+}/H_2O_2 molar ratio = 1:20, and initial wastewater pH of 3.0. The Fenton oxidation process follow pseudo first order model with kinetic constant is 0.0113 min^{-1}. The chemical cost used in batch system is IDR 350.433/L lignin wastewater.

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