

Treatment of Pulp and Paper Industry Wastewater by using Fenton Method

Salsabilla A. Yani^{1*}, Tuty Emilia Agustina¹, M. Fitri Hadiah¹

¹Chemical Engineering Master Program, Faculty of Engineering, Universitas Sriwijaya, Jalan Srijaya Negara, Bukit Besar, Palembang, South Sumatera

*Corresponding Author: salsabillaDAP@gmail.com

Abstract

The pulp and paper industry wastewater has not met the environmental quality standards set by the government so it may causes pollution to the environment; therefore, it is necessary to find a better wastewater treatment. The problem of this study is how to find the wastewater treatment alternative in order to get a more effective and efficient treatment. Fenton reagents are H₂O₂ compounds (hydrogen peroxide) with iron catalysts and is one of the Advance Oxidations Process (AOPs) methods, which can be used as an alternative to process wastewater from the pulp and paper industry. In this study, the ratio of Fenton reagent molar concentration, temperature, and stirring time were varied, with stirring speed of 300 rpm, Fenton reagent volume of 25 mL, and pH set at 3. The visible parameters in this study were COD and TSS degradation. From this study, the best ratio of Fenton reagent is 1:2000, where this ratio can reduce the COD from 1002 mg/L to 176.05 mg/L and the TSS from 125 mg/L to 49.3 mg/L. This value has met the environmental quality standards for the pulp and paper industry set by the Indonesian government.

Keywords: Pulp and Paper Industry, Wastewater, Fenton, COD, TSS

Abstrak (Indonesian)

Limbah cair industri pulp dan kertas sejauh ini belum memenuhi standar baku mutu lingkungan yang di tetapkan oleh pemerintah sehingga masih memerlukan pengolahan yang baik agar tidak mencemari lingkungan. Permasalahan dari penelitian ini adalah bagaimana menemukan alternatif pengolahan limbah agar mendapatkan metode yang lebih sederhana dengan waktu pengolahan yang lebih singkat. Reagen Fenton yang merupakan senyawa H₂O₂ (hidrogen peroksida) dengan katalis besi adalah salah satu metode Advance Oxidations Processes (AOPs) yang dapat dijadikan alternatif pengolahan limbah cair industri pulp dan kertas. Penelitian ini menggunakan perbandingan konsentrasi molar reagen Fenton, temperatur, dan lama pengadukan, dengan kecepatan pengadukan 300 rpm, volume reagen Fenton 25 mL, dan pH yang diatur 3. Parameter yang dapat dilihat pada penelitian ini adalah degradasi COD dan TSS. Dari penelitian ini, rasio reagen Fenton yang terbaik adalah 1 : 2000, dimana rasio ini mampu menurunkan COD dari 1002 mgr/L menjadi 176,05 mgr/L dan TSS dari 125 mgr/L menjadi 49,3 mgr/L. Nilai tersebut telah memenuhi baku mutu lingkungan untuk industri pulp dan kertas yang ditetapkan oleh pemerintah Indonesia.

Kata Kunci: Industri *Pulp* dan Kertas, Limbah Cair, Fenton, COD, TSS

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INTRODUCTION

Paper industry is one of the largest industries in the world, producing 178 million tons of pulp, 278 million tons of paper and cardboard and spending 670 million

tons of wood. In the next decade, its growth is estimated between 2% to 3.5% per year, which produced from one to two million hectares forest area every year [1]. The paper industry produces several

types of waste including sludge, bio sludge, and pith. The solid waste comes from the reject process of stock supplies, fiber recovery units, and wastewater in the form of sludge coming out of the belt press as the result [2]. These wastes, along with the industry growth, affect the environmental problems caused by B3 pollution (hazardous and toxic materials). Generally, the pollution caused by pulp and paper industry causes the death of fish, shellfish and other aquatic invertebrates. It also causes the entry of carcinogens and other substances that interfere with hormone activity, the depletion of millions liters of fresh water, and the risk to exposed to hazardous chemical waste that pollutes the environment [3].

In most cases, the pulp and paper industry wastewater contains very potential pollutants, especially suspended solids, BOD, and COD which are colloidal stable and difficult to separate [4]. Wastewater from pulp and paper industry are classified into six categories: 1) suspended solids containing wood particles, fibers and pigments, 2) dissolved colloidal organic compounds such as hemicellulose, sugar, alcohol, lignin, fiber decomposers, starch adhesives and synthetic substances that produce high BOD, 3) solid liquid waste originating from lignin and paper coloring, 4) inorganic materials such as NaOH, Na₂SO₄ and chlorine, 5) wastewater with high temperature, and 6) microbes such as coliform bacteria. These wastes are very dangerous to human health since many diseases can be transmitted through it. Other than that, wastewater also contain toxic materials, irritants, odors, and has high temperatures and other flammable materials [5]. Wastewater physical quality is seen based on the suspended floating solid materials and precipitated [6]. The precipitating material consists of coarse, sand and mud, fine mud, and colloidal mud [7].

The paper and pulp industry wastewater has not met the environmental quality standards set by the government therefore; it must be processed properly in order to save the environment from the pollution. In order to meet the environmental quality standards set by the government, it is necessary to process the waste through several stages that require a considerable amount of time, while the pulp and paper industry operations run every day. Wastewater treatment technology is the key in maintaining environmental sustainability. It is needed to find an alternative in treating the wastewater in more effective and efficient way. Fenton Reagent, H₂O₂ (hydrogen peroxide) compounds with iron catalyst is one of the Advance

Oxidations Processes (AOPs) methods that can be used as an alternative to process pulp and paper industry wastewater to reduce environmental pollution. The Fenton process can have a dual function, known as oxidation and coagulation in the treatment process [9]. Hence, the purpose of this study was to conduct analyses on the variable such as Fenton molar reagent (FeSO₄ and H₂O₂), stirring time and temperature used. It also conducted to get the optimum condition of wastewater treatment of pulp and paper industry. With the implementation of this study, it was expected to help the community, especially the industry, to reduce the dangers of wastewater so it will not pollute the environment.

MATERIALS AND METHODS

Materials

The materials used in this study are pulp and paper industry wastewater, H₂O₂ 30 % (v/v), FeSO₄.7H₂O, Aquadest, NaOH 0.1 M, HCl 0.1 M and Na₂S₂O₃.5H₂O 1 N.

Methods

There were three stages in this study: 1) taking samples the wastewater from pulp and paper factory, 2) making Fenton reagents, and 3) to determine the optimum conditions for processing pulp and paper industry wastewater. Fenton reagent was made using FeSO₄.7H₂O and H₂O₂ with molar ratio of 1:1000, 1:2000, and 1:3000 which keep the constant Fe concentration of 4 mM.

The temperature used in this study were 35, 45, 55, and 65°C, while the stirring time set at 2, 4 and 6 hours. In each molar comparison, the Fenton reagents volume was 25 mL, stirring rotation speed was 300 rpm, and pH set at 3. To obtain the optimum conditions for processing Pulp and Paper wastewater using Fenton reagents, 250 mL Pulp and Paper wastewater was added with 25 mL FeSO₄.7H₂O catalyst with a concentration of 4 mM then, stirred using magnetic stir at a speed of 300 rpm at a predetermined temperature, and pH was adjusted to 3 by adding NaOH or HCl. Then, H₂O₂ was added as much as 25 mL with the predetermined concentration. After the specified stirring time, add 0.5 mL Na₂S₂O₃.5H₂O 1 N to stop the reaction.

RESULTS AND DISCUSSION

According to the regulation of the Minister of Environment of the Republic of Indonesia No. 5 Year 2014 [8], the characteristics of wastewater from pulp

and paper industry should meet the requirements as follows as Table 1.

Table 1. Wastewater characteristic of pulp and paper

Parameter	Analysis Result	Quality Standard
COD (mg/L)	1002	350
pH	10	6-9
TSS (mg/L)	125	100

The Effects of Fenton Molar Ratio in COD and TSS Degradation

The molar ratio of Fenton reagent ($\text{Fe}^{2+}/\text{H}_2\text{O}_2$) greatly influences the degradation rate in wastewater in the pulp and paper industry. The best Fenton reagent ratio for reducing COD and TSS was 1:2000 molar ratio since it was being able to reduce COD from 1002 mg/L to 176.05 mg/L as shown in figure 1, and TSS from 125 mg/L to 49.3 mg/L, as shown in figure 2. This value meets environmental quality standards for the pulp and paper industry.

Wastewater decreased at 1:1000 and 1:2000 molar comparisons. While at the ratio of 1:3000, there were no more decrease in COD because the pollutants remaining in the waste could no longer be degraded by Fenton reagent.

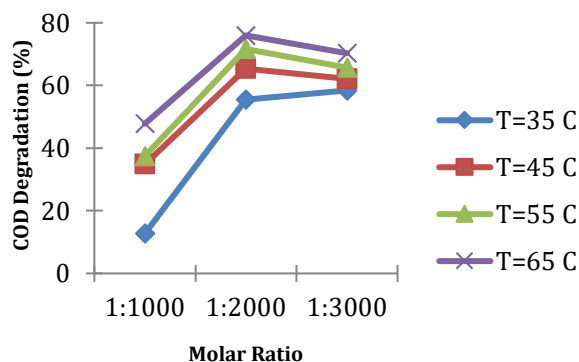


Figure 1. The effects of Fenton molar ratio on COD degradation

Scavenger reaction may occur on hydroxyl radicals, which reacts with other compounds that have weaker oxidation power compared to hydroxyl radicals and can reduce the amount of hydroxyl radicals to break down organic compounds in waste. Possible reactions to hydroxyl radicals are as follows:

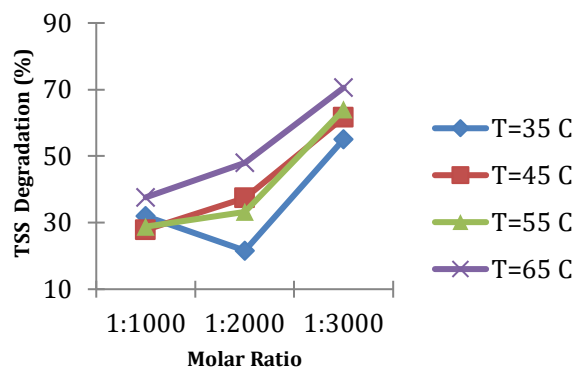
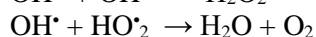
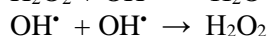
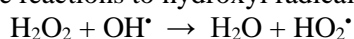


Figure 2. The effects of Fenton molar ratio on TSS degradation

Therefore, the optimum molar ratio between Hydrogen Peroxide and iron ions were varied depending on the parameters, such as the type of waste, pollutants and the level of pollution in the waste.

The Effects of Temperature in COD Degradation

Higher temperatures helped to break down the reactions formed in the process. The higher the temperature, the faster the reaction. Therefore, at the same time period (6 hours), a higher temperature will cause more degradation in COD, as shown in figure 3.

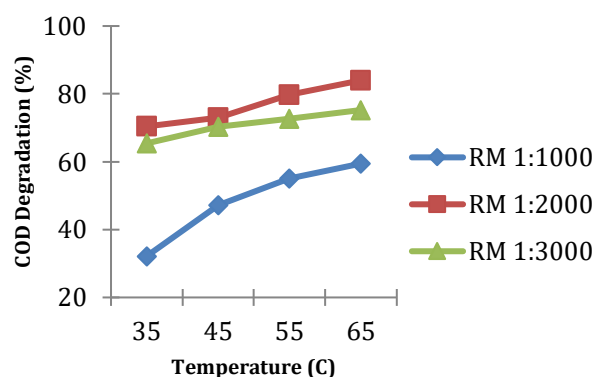


Figure 3. The effects of temperature on COD degradation

As can be seen in the figure, by using Fenton reagent molar ratio of 1:2000, the highest COD degradation of 82% was achieved by using the higher temperature of 65°C. High efficiency of this technique can be explained by the formation of strong hydroxyl radicals (OH^\bullet) and oxidation of Fe^{2+} to Fe^{3+} .

The Effects of Stirring Time in COD and TSS Degradation

There were significant difference along with increasing stirring time. The most optimal stirring time was 6 hours with a decrease of 40% - 80%. The stirring time would greatly affect the process because the longer the processing time, the more collisions occur [10]. This could happen because the length of stirring time is proportional to the decrease in contaminants in the wastewater, as shown in figure 4 and figure 5.

Oxidation and reduction reactivity are produced at the $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ system initiation reaction. Fenton reactions in waters are influenced by several factors namely HO^* radicals, iron (II), organic radicals and reaction conditions. The maximum effectiveness of the degradation process depends on the stoichiometric relationship between Fe^{2+} , RH and Fe^{3+} . Decomposition of H_2O_2 will take place faster in the ratio of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ to " ≥ 2 " [11].

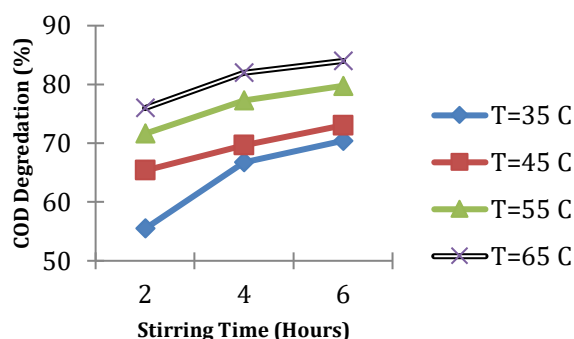


Figure 4. The effects of stirring time on COD degradation

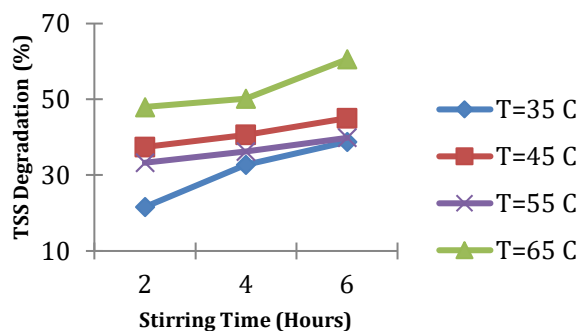


Figure 5. The effects of stirring time on TSS degradation

Addition of H_2O_2 and Fe^{2+} to the optimum condition will cause a decrease in the cleaning effect.

This is due to the reaction between H_2O_2 and Fe^{2+} and OH^\bullet production. In this case, H_2O_2 and Fe^{2+} will act as radical sweepers, so the produced OH^\bullet radicals will drop.

CONCLUSION

Considering the results of this study, found out that the best condition of COD decrease was achieved at Fenton reagent molar ratio of 1:2000, by using 65°C of temperature, within 6 hours of stirring time, which caused decreases in COD of 82% with a value that meets the environmental quality standards for pulp and paper industry. Besides, the higher the temperature, the faster the reaction, therefore, the same stirring time with higher temperature will cause a higher decrease in COD. The stirring time also has an influence on COD and TSS.

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