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A Comparative Study of Yarn Dyed Wastewater Using Fenton's Reagent and Ozonation : Removal Efficiency and Economic Analysis

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Abstract

This study makes a comparison between Fenton and Ozonation processes treatment methods to examine the removal of COD in yarn dyed wastewater with initial concentration of 525 ppm. Results indicated that the COD degradation efficiency was in order of Fenton > Ozone. In Fenton method, the ratio of Fe^{2+}/H_2O_2 used was 1:10, the concentration of H_2O_2 was 10.2 gram/L. In ozonation, the ozone concentration used in the study was 5.8% mol, and the agitation was 400 rpm. The effect of operational parameters including, initial pH and time were studied in both processes. The results indicated that it was 86.2% COD were removed, when the pH was about 3 using Fenton's reagent and 83.06% COD removal in ozonation for one hour experiment. To achieve the standard requirement for allowable parameters in wastewater to be discharged, there is only 15 minutes needed for Fenton process to remove COD by 84.8%, while the ozonation needs 30 minutes for 81% removal. Fenton process is more economic feasible compare to ozonation which is almost one-tenth of the operation cost for 1 liter of wastewater being process. Though both processes can demonstrate the high removal efficiency to achieve the allowable COD concentration in the wastewater to be discharged, Fenton process is favor to ozonation.

Keywords: *fenton; ozonation; removal of COD; yarn dyed wastewater*

Abstrak

STUDI PERBANDINGAN AIR LIMBAH PEWARNA BENANG MENGGUNAKAN REAGEN FENTON DAN OZONASI: EFFISIENSI PENGHILANGAN WARNA DAN ANALISA EKONOMI. *Studi perbandingan pengolahan limbah dengan menggunakan metode fenton dan ozonasi ini dilakukan untuk mengkaji penghilangan COD di limbah pewarnaan benang dengan konsentrasi COD mula mula 525 ppm. Hasil penelitian menunjukkan bahwa efisiensi degradasi COD berada pada urutan metode Fenton lebih baik dari pada Ozonasi.Pada metode Fenton, perbandingan Fe^{2+}/H_2O_2 yang digunakan adalah 1:10, dan konsentrasi H_2O_2 sebesar 10,2 gram/L. Pada ozonasi, konsentrasi ozon yang digunakan adalah 5,8% mol dengan agitasi 400 rpm. Efek parameter operasional yaitu pH dan waktu dipelajari dalam penelitian ini.Hasil penelitian menunjukkan bahwa 86,2% COD berhasil dihilangkan ketika digunakan pH=3.0 untuk metode Fenton, dan 83,06% COD dapat dihilangkan dengan ozonasi selama 1 jam. Untuk memenuhi standar baku mutu pembuangan air limbah, waktu yang dibutuhkan hanya 15 menit untuk menghilangkan 84,8% COD dengan metode*

Fenton, sedangkan ozonasi membutuhkan 30 menit untuk mencapai 81% penghilangan COD. Proses Fenton lebih ekonomis dibandingkan ozonasi dengan biaya operasi hampir 1/10 dari biaya ozonasi untuk 1 liter limbah. Proses Fenton lebih disukai daripada ozonasi karena aspek ekonomi, walaupun kedua metode ini mamapu menurunkan kadar COD sampai batas ambang yang diijinkan.

Kata kunci: *fenton; ozonasi; penghilangan COD; limbah pewarnaan benang*

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INTRODUCTION

Yarn dyed wastewater is one of recalcitrant wastewater and it is one of highly toxic wastewater. The wastewater is characterized by the parameters of biological oxygen demand (BOD), chemical oxygen demand (COD), pH, suspended solids and color. Some of these parameters are removed by coagulation but failed to be treated biologically since the ratio of COD to BOD is more than 6.0. Advanced oxidation processes including UV/H_2O_2, TiO_2/UV, photo-fenton, fenton's reagent and ozonation have been tried to treat such wastewater (Modirshahla *et al.*, 2007; Khataee *et al.*, 2009; Baban *et al.*, 2003; Gunten, 2003; Georgiou *et al.*, 2003).

Dyes present in wastewater are of particular environmental concern since the presence of color in water and also the harmful compounds in the dyes are carcinogen and mutagenic which can cause severe dysfunctional of brain and nerve systems (Kadirelu *et al.*, 2003). Advanced oxidation processes are based on the generation of hydroxyl radicals (•OH) which degrade organic pollutants quickly (Khataee *et al.*, 2009). The organic matter (OM) in the solution are oxidized by hydroxyl radical as soon as •OH is generated, as described in the following equation:

$$\bullet OH + OM \rightarrow \text{intermediates} \rightarrow \text{harmless species such as } CO_2, H_2O, \text{etc.} \quad (1)$$

We have conducted two AOPs in this study which were using Fenton'reagent and ozonation. Fenton's reagent is a mixture of ferrous ion (Fe^{2+}) and hydrogen peroxide (H_2O_2) generating hydroxyl radical (•OH) according to the following equation:

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

Fe(III) which was being produced, can catalyze the decomposition of H_2O_2. The reaction of H_2O_2 with Fe(III) (so called the Fenton's-like reagent) goes through the formation of hydroperoxyl radical $HO_2\bullet$ (Ensing *et al.*, 2003):

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

As peroxide is available in the system, the cycle of Fe^{2+} and Fe^{3+} is continue. Ozonation is another AOP that we also used in this study. Ozone is able to react with organic matter due to its reactivity. The free radicals come from reaction mechanisms of ozone decomposition in water due to hydroxyl ion as shown as follows:

$$O_3 + OH^- \xrightarrow{k=70\ M^{-1}s^{-1}} HO_2^- + O_2 \quad (4)$$

$$O_3 + HO_2 \xrightarrow{k=2\ x\ 10^6 M^{-1}s^{-1}} HO_2 + O_2^{\ -} \quad (5)$$

Reactions (4) and (5) are important because these are the initiating steps of the radical mechanism leading to the formation of hydroxyl radicals when ozone decomposes (Tarr, 2003).

The wastewater used in this study was previously treated using electrocoagulation to remove suspendend solid and color. The wastewater then treated using AOPs namely fenton's reagent and ozonation separately. The aim of this study is to compare the efficiency of COD removal using both methods and also to analyse the economic feasibility. The effect of initial pH and time were also studied. The Fenton's method has been implemented in the real yarn dyed wastewater with capacity of 15 m^3 wastewater/day.The economic analysis was used as a decision to choose fenton's method rather than ozonation.

MATERIALS AND METHODS

The Characteristic of Wastewater

The wastewater was collected from a yarn dye manufacturing located in South of Surabaya city, East Java Province, Indonesia. The wastewater has characteristic of COD 850 ppm, TSS (Total Suspended Solid) 4200 ppm, BOD 100 ppm, color 1.66 cm^{-1} and pH 10.6. After electrocoagulation, the characteristic of wastewater can be seen in Table 1.

Table 1. Characteristic of wastewater prior AOP

Parameters	Unit	After coagulation
COD	ppm	525.28
BOD	ppm	80
TSS	ppm	2100
pH	-	7.5
color	cm^{-1}	0.124

Fenton Process

The wastewater after treated by electrocoagulation was then treated in a 1.5 L glass reactor equipped with stirrer and cooling jacket to maintain the experiment at room temperature. The chemicals used in the process were hydrogen peroxide and $FeSO_4.7H_2O$. The operating conditions were set at the best condition as follows: ratio of Fe^{2+}/H_2O_2 1:10, initial pH 3.0 and dosage of H_2O_2 was 10.2 gram/L (Riadi *et al.*, 2016). Samples were withdrawn periodically up to 90 minutes of experiment. All samples from fenton oxidation process were measured for COD content. The equipment used can be seen in Figure 1.

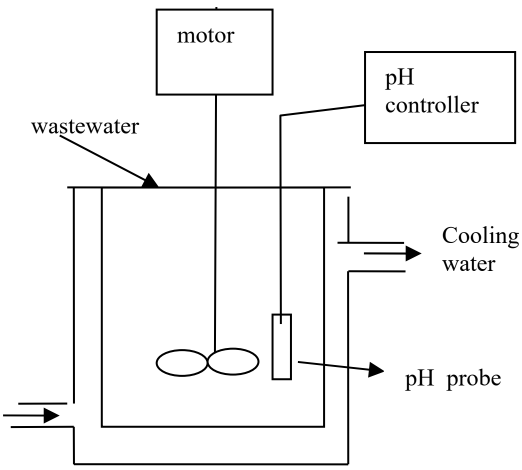

Figure1. Fenton process in batch system

Ozonation

The wastewater was fed to a 1.5 L stainless steel reactor equipped with stirrer, sparger, thermocouple and cooling jacket which was used for the experiment. The cooling jacket was used to maintain the experiment at 25°C. The equipment used in the experiment can be seen in Figure 2. Ozone was generated from oxygen by ozone generator. The exit port of ozone generator is connected with deep tube and the ozone gas is delivered to the reactor through tube sparger at the bottom. The agitation was done at 400 rpm with the ozone concentration of 5.8% mol. Samples were withdrawn periodically up to 60 minutes of experiment, and aerated for 5 minutes to remove residual ozone (Selcuk, 2005). The ozone trapped in a KI in container to prevent the loss of ozone to the environment.

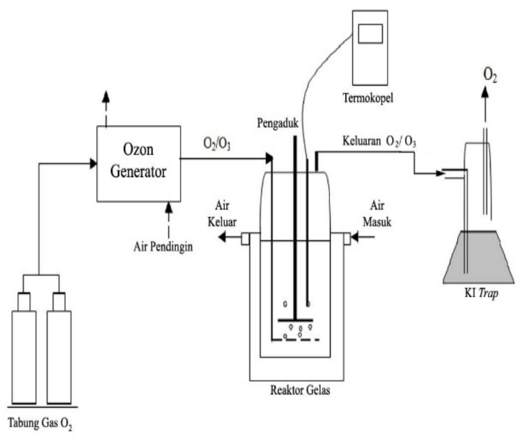

Figure 2. Ozonation process

Assay

Chemical oxygen demand was measured using closed reflux, colorimetric method (APHA, 1998). Total Suspended solid was measured using dried method based on a method from APHA, color measurement was conducted using UV-Vis spectrophotometer at 498 nm wavelength (APHA, 1998). The BOD (biological oxygen demand) was measured by respirometer using BOD system BD600, Lovibond. The percentage of COD removal was calculated as {(initial COD concentration-final COD concentration)/(initial COD concentration)}x 100%.

RESULTS AND DISCUSSION

Effect of pH

Effect of initial pH in wastewater was studied both in fenton process and ozonation. Initial pH of wastewater usually has a big influence on dye degradation (Zaied *et al.*, 2011). Fenton process perform better at lower pH since the production of hydroxyl radicals is influenced by pH (Qiao *et al.*, 2005). Result from the experiment is similar to a review reported by Wang *et al.* (2016). Figure 3 illustrates the effect of pH in fenton process and ozonation. In higher pH (pH > 3.0) the hydrolysis and precipitation of Fe^{3+} in the liquid phase can reduce the capacity of the the catalyst itself (Fassi *et al.*, 2014). There is not much different in COD removal at different pH in ozonation. Lower pH (pH < 7) can give a better result for COD removal since at higher pH (pH >7.0), ozone can be decomposed (Peleg, 1976). However, we found that the reduction of COD is not much different at pH=5.0 compare to that at pH=7.0 in ozonation process. So, the experiment at pH=3.0 was not carried out.

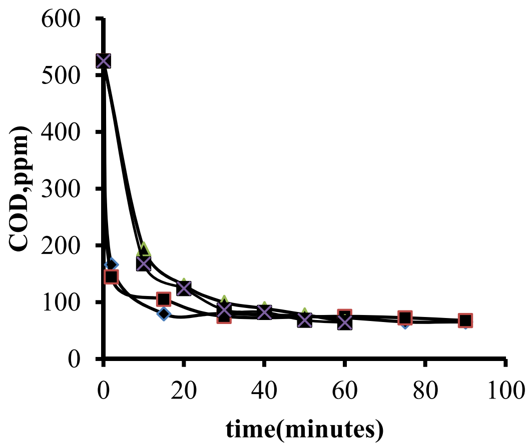

Figure 3. COD profile at different initial pH in fenton process (♦=pH3.0; ■=pH5.0) and ozonation (▲=pH=7.0; X=pH=5.0).

The experiments for the fenton were conducted at pH=3.0 and pH=5.0 as described above. However, there will be a strong scavenging effect of hydroxyl radical by H^+, if the pH is too low (< 2.50) which decribes by reaction below :

$$HO^- + H^+ + e^- \rightarrow H_2O \quad (6)$$

Hence, we don't work in higher pH for Fenton process (pH=7.0) and also at low pH (pH=2.5). So, for Fenton process, we favor to work at pH=3.0, whereas in ozonation we favor to work at neutral pH.

Effect of Time in Removal of COD

The removal of COD in both processes were obvious. Fenton process resulted in a better of COD removal efficiency as can be seen in Table 2. The better percentage of COD removal in Fenton process is due to the standard redox potential of hydroxyl radical is 2.80 V, which is higher than ozone (2.07 V).

Table 2. Removal overall efficiency at different initial pH for one hour experiment

	pH=3.0	pH=5.0	pH=7.0
Fenton process	86.2%	85.7%	n/a
Ozonation	n/a	84.9%	83.06 %

Though the reduction potential of hydroxyl ions is higher than ozone, the value for overall removal efficiency of both processes were not big different (see Table 2 at pH=5.0). The significant different in percentage removal of COD is at the first 10 minutes of reaction, Fenton process gave a spontaneous reaction to degrade COD content, while ozonation gave a fast reaction. The removal of COD at the first 2 minutes experiment in Fenton process was 68.3%, meanwhile the removal of COD at the first 10 minutes experiment of ozonation was 63.07%. This phenomena indicates that redox potential of hydroxyl ion in fenton process is stronger than that in ozone which may degrade the COD faster. There is only 15 minutes needed to remove COD by 84.8% in Fenton process in order to achieve the standard requirement of COD in wastewater to be discharged (150 ppm COD). On the other hand, there is 30 minutes needed in timelength for ozonation to remove COD for the same purpose which is 81% removal. To have an objective comparison of both system performance, we need to also analyse both processes from economic point of view.

Economic Analysis

Economic analysis for both processes will be focused on operation cost and examined using one hour experiment time and removal of COD. By neglecting the electricity used for both reactors, the operation cost for fenton will include the cost for chemicals such as $FeSO_4.7H_2O$, hydrogen peroxide and hydrocloric acid. The operation cost for ozone is the electricity used for ozone generator. In 1 liter of wastewater, the operation cost for Fenton process is IDR. 256, whereas for ozonation, the operation cost is based on the electricity used for ozone production, which are 2 kwh, using middle industrial cluster, the tariff for electricity is IDR 1110/kwh. Hence the operation cost is IDR 2220. Looking at the province regulation in the country (SK Gub. no 72 year 2013), which put the maximum of COD in wastewater can be disharged is 150 ppm, then we want to use both technology in 30 minutes time, which can result in remaining COD of 80 ppm and 100 ppm for Fenton and ozonation respectively. The operation cost for 30 minutes operation of 1 L wastewater will be IDR 128 and IDR 1110 for Fenton and ozonation consecutively. Consider the timelength used for experiment, Fenton process just need 15 minutes to degrade COD in wastewater at level below stated in the regulation, while ozonation needs 30 minutes to achieve the requirement level of COD in wastewater by the same regulation. Hence, it is obvious that the operation cost of Fenton's reagent is cheaper than that in ozonation.

CONCLUSION

This study investigated the COD removal in yarn dyed wastewater using Advanced Oxidation Procesess, Fenton's reagent and ozonation. It is apparent that Fenton process is more favor to ozonation, both in the ability on removal efficiency and economic feasibility. The overall removal efficiency using Fenton's reagent and ozonation were 86.2% and 83.06% respectively. The initial pH of wastewater was favor for pH 3.0 and 7.0 in Fenton process and ozonation respectively. The first two minutes of Fenton process was spontaneous since the removal efficiency was 68.3% and the first 10 minutes of ozonation give 63.07% removal. There is only 15 and 30 minutes needed for Fenton process and ozonation to achieve the allowable of COD in wastewater to be discharged, the COD removal for 15minutes in Fenton process and 30 minutes in ozonation were 84.8% and 81% respectively. The operation cost of Fenton process was almost one-tenth compare to ozonation.

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