Ozonation of Yarn dyed Wastewater in a Continous Stirred Tank Reactor : Kinetic Study and Performance Optimisation

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Abstract. This paper describes the ozonation process in yarn dyed wastewater using continuous stirred tank reactor with the objective to study the kinetic of COD degradation at various volumetric flow rate (30, 50, 70 ml/min) and ozone concentration (2.70 %, 4.25%, 5.86 % mol/mol). The wastewater which was collected from a yarn dying process located in Surabaya area was pretreated by electrocoagulation prior to ozonation process. The electrocoagulation process was carried out to reduce the color intensity and total suspended solid. The pretreated wastewater was then processed using ozonation for 2.5 hours. The result showed that at various concentration of ozone, maximum COD removal was 90.78% which was achieved at 5.86 %mol/mol of Ozon and volumetric flow rate 50 ml/min. It was found that the degradation process followed the pseudo-first order kinetic model. The obtained pseudo-first order rate constants for volumetric rate of 50 mil/min were 0.0307 min^{-1}, 0.0419 min^{-1} and 0.053 min^{-1} for ozon concentration of 2.70 %, 4.25%, 5.86 % mol/mol respectively. The residence time were 41 minutes, 31 minutes and 23 minutes for ozone concentration of 2.70 %, 4.25%, 5.86 % mol/mol respectively. These findings offers an alternative treatment for wastewater containing dyes.

1 Introduction

Yarn dyeing industry generates large amount wastewater with high color intensity, high chemical oxygen demand (COD), suspended solids and some heavy metals. The dyes may be carcinogenic and mutagenic which are harmful for human beings. The dyes have a complex aromatic molecular structure which is difficult to biodegrade [1,2]. Physical methods which are known to be used in the treatment usually used as primary treatment such as precipitation,adsorption, and chemical coagulation. Since the COD content is quite high enough after the primary treatment, it is further treated by other treatment such as chemical degradation or biodegradation. Biological process is slower, requires large area especially in the process of color removal. The electrochemical technique has been used which removed color but not the COD content [3].

Chemical processes are generally more simple in application and need oxidizing agents such as hydrogen peroxide, ozone and hydroxyl radicals. The process is known as Advanced Oxidation Process. Ozone is a strong oxidation agent (E°= 2.07 V) which has been used to oxidize wastewater contained phenols and cyanides [4]. Due to its dipolar nature, ozone can either react as an electrophilic and nucleophilic agent or cause dipolar cycloaddition with most of the compounds with double bonds [5]. As a powerful oxidizing agent, ozone can

breakdown the double bonds of dye chromophores and also other functional groups such as complex aromatic rings of dyes [6]. The wastewater used in this study was collected from yarn dyeing industry located in southern part area of Surabaya.

The mechanism of ozonation, follow two main paths: a direct path corresponding to the action of molecular ozone, and an indirect path is a result from the decomposition of ozone to radicals, in which the reaction is initiated by hydroxyl ions (OH$^-$) [7].The wastewater has a lot of azo dyes which is an aromatic double bonds as can be seen in Figure 1. The wastewater was treated using electrocoagulation in batch system prior ozonation.

The characteristic of wastewater prior and after electrocoagulation is shown in Table 1. The allowable concentration of COD in wastewater to be discharged is 150 ppm as stated in East Java regional government regulation (SK Gub 72/2013). The objectives of this work are to study the effect of ozone concentration, flow rate of wastewater in COD removal efficiency. The pH and conductivity profiles of wastewater during ozonation were also observed. This work also studied kinetic model for COD removal in a Continuous Stirred Tank Reactor (CSTR) mode.

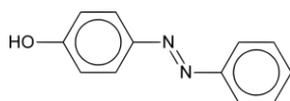* Corresponding author: lieke@staff.ubaya.ac.id

Fig.1. chemical structure of azo dye.

Table 1. Characteristic of wastewater

Parameter	Prior electrocoagulation	After electrocoagulation
Color OD$_{498}$	1.3117	0.0053
TSS [mg/L]	18,780	2,913
COD [ppm]	745	334
pH	12	8.5
Conductivity [mS/cm]	19.35	13.50

2 Materials and Methods

2.1. Materials

2.1.1 Wastewater

Wastewater used in this study was collected form yarn dyeing industry located in southern part area of Surabaya. Since the fluctuation of wastewater characteristic, we have two types of wastewater with different COD.The wastewater used to study effect of flow rate had a COD content about 1300 ppm prior electrocoagulation and 780 ppm after electrocoagulation. Other experiments for parameter of ozone concentration and pH used wastewater with characteristic as shown in Table 1.

2.1.2. Ozone and oxygen gases

Ozone was generated from oxygen by Ozone generator (Viresco, Singapore). The ozone output was adjusted from 0-50 g/h. The oxygen ouput at 5-15 L/min. The exit port of ozone generator is connected with deep tube and the ozone gas was delivered to the reactor through tube sparger at the bottom of the reactor. The residual ozone was decomposed by trapping excess ozone at the reactor outlet which is connected to 2% potassium iodide (KI) solution trap.

2.2. Combined Electrocoagulation and Continuous Stirred Tank Reactor (CSTR)

An electrocoagulation (EC) reactor with 1.5 L volume was used. The real wastewater was taken form yarn industry located in Surabaya, East Java province, Indonesia. Anode and Cathode Al/Al was used with a

distance between two electrodes was 2 cm. The electrodes were connected to DC power supply. The size of Alumunium plate was 8 cm x 8 cm, with a thickness of 2 mm.

The EC process was run for 10 minutes and used a method as described by Riadi *et al.* [8]. The effluent from EC process was then collected and used as influent for ozonation process. A CSTR with 1250 mL volume was developed using a glass vessel connected to collection tank of effluent from electrocoagulation process. Ozone fed to CSTR from ozone generator and diffused through a diffuser in a bottom of reactor.The system used in the experiment can be seen in Figure 2.

2.3. Analysis of wastewater

COD was measured using closed reflux, colorimetric method based on Standard Methods for the Examination of Water and Wastewater [9]. Total Suspended solid was measured using dried method, color measurement was conducted using UV-Vis spectrophotometer at 498 nm wavelength based on Standard Methods for the Examination of Water and Wastewater [9].

The wastewater was also analysed using GC-MS to find out the components of dye in the wastewater. The GC serie is Agilent 7890 and the MS is agilent 5975, the column used was HP5MS, 30 m length and the diameter is 0.2 μm. Ozone concentration trapped in KI solution was measured using sodium thiosulfate tritation procedure. Ozone consumed was calculated as: Ozone produced – Ozone trapped in KI trapper, with an assumption there is no ozone left to the environment.
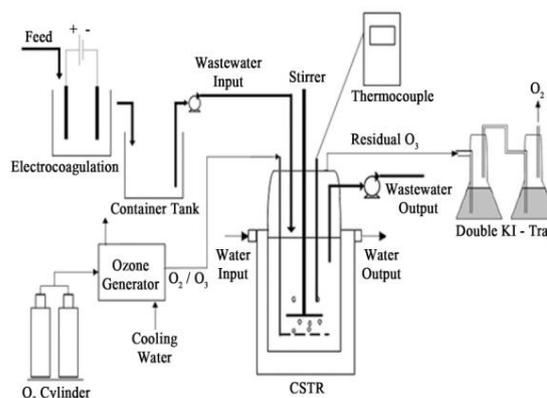

Fig. 2. Scheme of ozonation in CSTR

2.4. Ozonation process

Ozonation process was carried out to evaluate the performance of COD degradation in a CSTR with working volume of 800 mL, and agitation of 200 rpm at 30°C. The parameters used in the experiment were volumetric flowrate of wastewater (30, 50, 70 ml/minutes) with ozone concentration of 4,25 % mol/mol; the effect of ozone concentration (2,70, 4,25, 5,86 %mol/mol) was studied with wastewater flow rate of 50 mL/min. Samples were taken periodically for 2.5

hours. pH and conductivity were measured using pH meter and counductivity-meter from METTLER.

3 Results and Discussions

3.1. Effect of ozone concentration

Experiments were carried out at 2.7 % mol/mol , 4.25 % mol/mol and 5.86 % mol/mol of ozone concentration with the wastewater flow rate (v) of 50 mL/minute. Ozone was assumed dissolved perfectly in wastewater, so the reaction can be considered as homogenous reaction. Since ozone was fed in excess then the reaction (1), is a pseudo first order reaction with z = stochiometri coefficient.

$$O_3 + z\ COD\ \text{--->}\ \text{degraded pollutant} \qquad (1)$$

In a CSTR model [10] , we get :

$$\tau = \frac{V}{v_0} = \frac{Ca_0\ X}{k\ Ca} \qquad (2)$$

By rearranging equation (2), we get :

$$k = \frac{Ca_0 - Ca_f}{\tau\ Ca_f} \qquad (3)$$

Ca_o = initial COD concentration, Ca_f = final COD concentration, τ = space time, k= first order kinetic constant.

The pseudo first order model fit with the data at the first 10 minutes of ozonation (Fig.3), hence based on the equation (3), we can calculate the pseudo first order kinetic constant at different ozone concentration as can be seen in Table 2.

Table 2. Pseudo-first order kinetic constant at different $[O_3]$

Ozone [% mol/mol]	C_{AO} [ppm]	C_{AS} [ppm]	k' [minute^{-1}]
2.70	337.967	225.91	0.031
4.25	345.523	206.65	0.042
5.86	332.930	180.15	0,053

Ca_o = initial COD concentration, Ca_s = COD concentration at steady state, k'= pseudo first order kinetic constant which is = k x C_{O3}.

The value of k' using 5.86% mol/mol ozone was similar to k' from batch experiment which was 0.0521 min^{-1}. The pseudo first order kinetic constant in batch experiment was also obtained at the first 10 minutes of ozonation and also used 5.86 %mol/mol ozone [11]. Result from the experiment showed that higher concentration of ozone will result in higher COD removal efficiency as can be seen in Fig.3. If we used 150 minutes timeline from the experiments, the percentage removal of COD were 33.17%; 49.57% and 90.78% for 2.7% , 4.25 %, 5.86% mol/mol ozone respectively.

Since the allowable COD concentration to be discharged is 150 ppm (East Java province regulation), then we can recalculate the space time and reactor volume needed using the value of k' as stated in Table 2.

To get 150 ppm of COD concentration in the wastewater at 50 mL/min flowrate (v), we need bigger reactor volume (V) and longer space time (τ) for lower ozone concentration (Table 3).
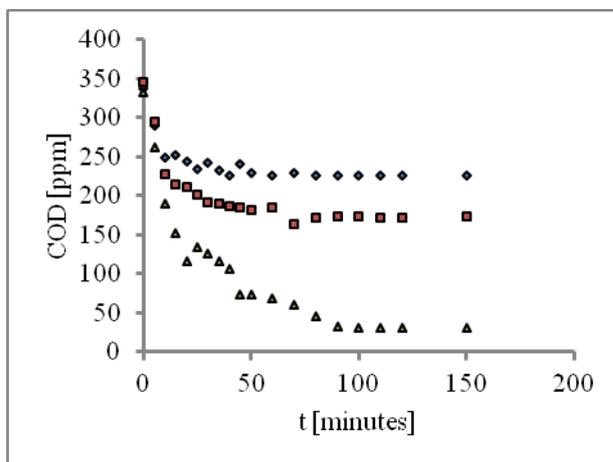

Fig.3. COD profile at different ozone concentration,(♦) 2.7% Ozone , (■) 4.25%, Ozone (▲) 5.86% Ozone.

Table 3. Value of pseudo first order kinetic constant at different ozone concentration

Ozone % mol/mol	C_{AO} (ppm)	C_{AS} (ppm)	k' min^1	τ (min)	V (ml)
2.70	337.96	150	0.031	41	2.021
4.25	345.52	150	0.042	31	1.552
5.86	332.93	150	0,053	23	1.151

3.2. Effect of wastewater volumetric flow rate.

The ozone concentration used in the experiment was 4.25% mol/mol, the flow rate variable were 30,50,70 mL/minute. Result from this study showed that higher flow rate of wastewater will result in lower removal of COD as can be seen at Table 4. The experiment result of COD profile was similar to that in simulated model as written in equation (3) as presented in Fig.4. The best removal of COD was at flow rate of 30 mL/min. By working with smaller flow rate at constant volume ,we have bigger space time and we will have higher conversion in a single CSTR.

However, implementation in the field with smaller flow rate may consider the size of reactor which is not favorable from economic point of view. Hence, performance optimization as written in Table 3 gave us an insight that working with high concentration of Ozone is favorable than lower volumetric flowrate. Therefore, a volumetric flow rate of 50 mL/min and 5.86% mol/mol ozone was a suitable parameter for a CSTR with 1150 mL volume to reduce the COD up to an allowable level to be discharged by the regulation (150 ppm). The optimum performance of the reactor to maintain COD level at 150 ppm, was in 1150 L volume of CSTR, 200 rpm of agitation, 50 mL/min volumetric flow rate, 23 minutes of space time and 5.86 % mol/mol of ozone.

Table 4. Removal of COD (%) at different flow rate using 4.25 % mol/mol Ozone

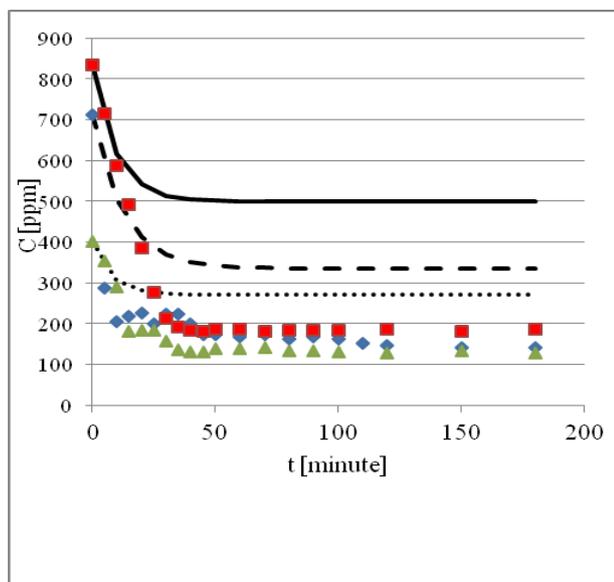| flow rate (v), mL/min	% removal of COD
30	80.09
50	77.6
70	67.84

Fig.4. Removal of COD in ozonation process.(♦) 30mL/min experiment,(■)50mL/minexperiment,(▲)70mL/min experiment. (---)30mL/min,model, (−)50mL/min,model, (....)70mL/min,model

3.3 Profile of pH and conductivity during ozonation process

There is no significant change of pH and conductivity during ozonation process, pH and conductivity practically remained constant, it can be seen that pH after ozonation decreased in only 0.4 units (Fig.5).
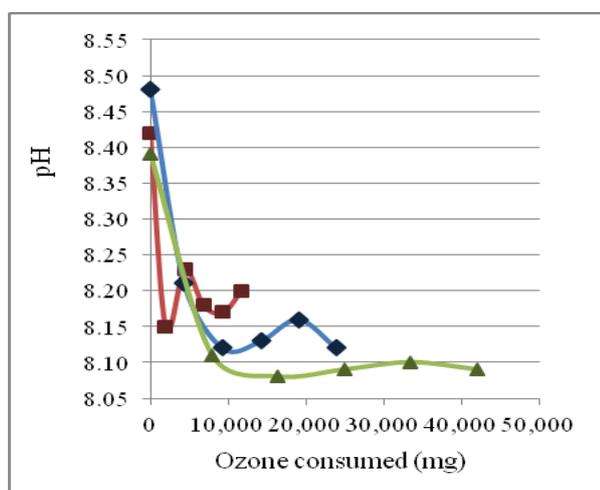

Fig. 5. pH profile during ozonation (■) 2.7% ozone,(♦) 4.25% ozone, (▲) 5.86% ozone

Conductivity after treatment is slightly reduced (Fig.6). It implied that the Total Dissolved Solid (TDS) in the wastewater was stable. Both parameters were determined along the ozonation reaction as a function of mg of ozone/L consumed. This result is similar with the previous work done by Sarasa et.al [12]. Ozonation doesn't have any effect in pH and conductivity, so the treatment doesn't give additional cost to adjust the pH after the treatment. Moreover, ozonation works better in alkaline medium, since the oxidation capacity of ozone may increase due to the formation of highly reactive hydroxyl radicals (HO●) with E^o = 2.8eV, which can attack the double bonds of dye chemical effectively.
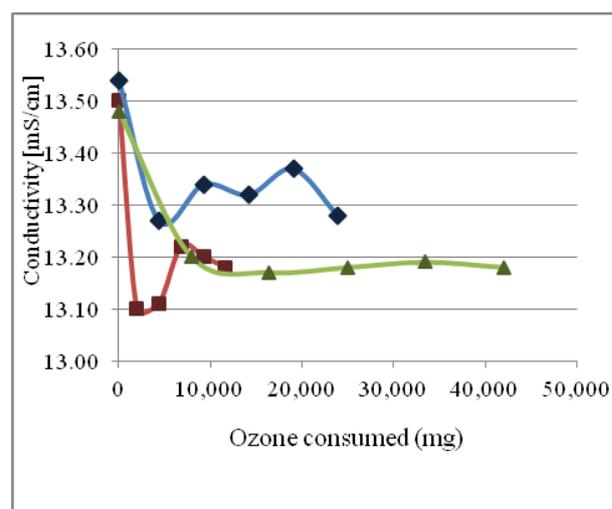

Fig.6. Conductivity profile during ozonation (■) 2.7% ozone, (♦) 4.2% ozone, (▲) 5.86% ozone.

4 Conclusion

Ozone treatment is very effective in removing compounds derived from yarn dyeing manufacture, The optimum performance of ozonation was 23 minutes of space time with 1150 mL reactor volume, 50 mL/min volumetric flow rate and 5.86 % mol/mol of ozone. The pseudo first order kinetic constant was 0.053 min^{-1}.There is no significant change of pH and conductivity during the ozonation process.

References

1. N. Azbar, T. Yonar, K. Kestioglu, Chemosphere **55**,35-43 (2004)
2. R. G. Saratale. G. D. Saratale, J. S Chang, S. P. Govindwar, J. Taiwan Inst. Chem. Eng., **42**,138-157 (2011)
3. G. R. P. Malpass, D. W. Miwa, D. A. Mortari, S. A. S. Macado, A. J. Motheo, Water Res., **41**, 2969-2977 (2007)
4. J. C. Cardoso, G. G. Bessegato, M. V. B. Zanoni, Water Res., **98**, 39-46 (2016)

5. P. R. Gogate, A. B. Pandit, Adv. Environ. Res., **8**, 501-551 (2004)

6. Q. Ruijuan, X. Bingzhe, M. Lingjun, W. Liansheng, W. Zunyao, Water Res., **68**, 316-327 (2015)

7. A. M. Dore, N. Merlet, B. Legube, J. P. Croue , Ozone Sci. Eng., **10**, 153-172(1988)

8. L. Riadi, W. Ferydhiawati, L. D. S. Loeman, Reaktor, **15**, 73-78 (2014).

9. APHA, *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association, 1998)

10. H. S. Fogler, *Essentials of Chemical Reaction Engineering* (Prentice Hall, 2011)

11. L. Riadi, A. Altway, S. M. Vania, A. Widyasayogo, Journal WPT, **12**, 690-697(2017)

12. J. Sarasa, M. P. Roche, M. P. Ormad, E. Gimeno, A. Puig, J. L. Ovelleiro, Water Res., **32**, 2721-2727 (1998)