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Abstract. The herbal, tofu and fertilizer industries contribute considerable waste to the environment. The waste contains COD and organic substances which should be reduced before it is discharged to the environmental body. One of methods is by using Advanced Oxidation Processes (AOPs) degradation method. The process of AOPs in this study used a combination of UV irradiation and ozone to produce hydroxyl radicals. This study was aimed to investigate the degradation of Chemical Oxygen Demand (COD) by using AOP techniques and to evaluate the treated waste for microalgae growth. This research consists of two steps: (1) the initial COD degradation using UV-Ozon. (2) utilization of the treated waste for microalgae cultivation by combining a mixed nutrient of waste and 10 mg/L TSP, 10 mg/L Urea, 80mg/L NaHCO3. The results showed that the COD degraded by UV/Ozone follows the first order equation by k value of 0.082/ day, 0.223/ day and 0.436/ day for tofu, herbal and fertilizer waste respectively. The growth rate of *Spirulina* cultivated in waste medium was in comparable with the one cultivated in control medium.

Keywords: Degradation, COD, UV-Ozon, Spirulina sp, cultivation

1. Introduction

Currently, the industrial waste is the major problem for environment especially the waste containing high chemical oxygen demand (COD). COD values of waste need to be reduced when the wastewater is discharded into a body of water, since it will give the negative effects to human, incurred a foul smell and become a source of disease, and it can make an environmental pollution.

Degradation of COD using advanced oxidation process (AOP) i.e UV-Ozone is one of efficient method to treat the waste. The UV photons are enable the ozone molecules to form hydroxyl radical and by addition of activated carbon can accelerate the decomposition of ozone being hydroxyl radical [1]. Through this method, it is expected that liquid waste that contain high COD levels can be processed to meet the liquid waste quality standards. The AOP system works using hydroxyl radical (·OH) which results from the reaction between the combination of Ozone-UV-H_2O_2 in water. The strong oxidizing agent can be an ozone mixture with hydrogen peroxide (O_3 + H_2O_2), ozone with ultraviolet (O_3 + UV),

and a mixture of hydrogen peroxide with ultraviolet light (H_2O_2 + UV). The active radicals released by the above compounds will quickly oxidize COD pollutants in wastewater [2].

The study focused on the use of UV/ozone for degradation of waste (tofu, herbal and fertilizer), and application of treated wastewater for microalgae *Spirulina sp*. Microalgae is microorganism that capable to use nutrient of nitrogen and phosphorous for photosynthesis in order to produce biomass [3].

2. Materials and methods

2.1 Materials

Tofu waste, herbal waste and fertilizer wastewater were used in this study and they were obtained from local industries in Semarang. Distilled water was used for dilution of waste and to make the solution of blank reagent. While COD medium range reagent set was used to analyse degradation of COD.

2.2 Experimental Procedure

The controlled variables in this study were oxidation period of 240 minutes (4 hours) with observation time for every 60 minutes (1 hour). The response variable in this study was the degradation of COD. Independent variables in this study were UV, Ozone, and UV-Ozone methods. The equipment and set are shown by Fig 1,2 and 3.

Figure 1. Scheme of Wastewater Treatment and Its Utilization for *Spirulina sp.* Cultivation

Figure 2. UV-Ozone Wastewater Intrument

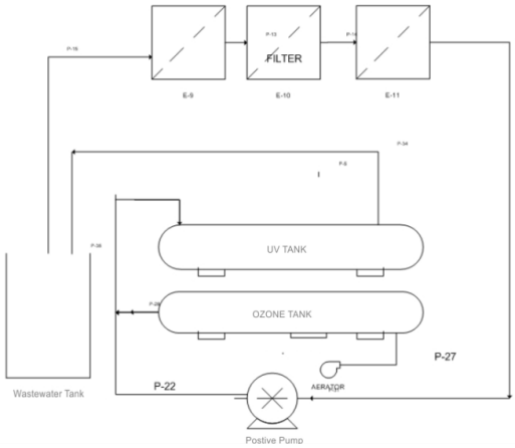

Figure 3. Sceme of UV-Ozone Wastewater

2.3 Wastewater pre-treatment and COD analysis

The experiment was divided into 2 steps (Fig 1), the first step was waste pretreatment using UV Ozone, then the second step was COD tes and implement the treated waste for microalgae. The first stage aims to find out which method has more influence on COD degradation. Waste samples are diluted 20x and 1.5 L of the sample was processed into the device according to various UV, Ozone and UV-Ozone tools (Fig 2). The experiment was carried out for 4 hours and the sample was taken every 1 hour as much as 50 mL.

After degradation of COD, the treated wastewater was applied for *Spirullina sp*. cultivation for 10 days. The cultivation of *Spirullina sp.* used 500ml erlenmeyer glass, aeration and lighting for 24 hours and TL lamp as light sources. *Spirullina sp* was provided nutrients for control variable as much as 50

mg / L TSP, 50 mg / L Urea and 400 mg / $NaHCO_3$ every two days, and used waste of 10, 25, 50% v/v as a cultivation medium and the remaining *Spirullina sp*. on 500 ml and with variations in the composition of nutrient addition as much as 10 mg / L TSP, 10 mg / L Urea and 80 mg / $NaHCO_3$. The optical density was monitored by spectrophotometer at wavelength of 680nm.

2.4. Degradation rate

The degradation of COD was evaluated according to the first order model (Eq 1)

$$-r_A = -\frac{dCOD}{dt} = kC_{COD}^{1} \quad (1)$$

And Eq 1 can be derived in logarithmic function as shown by Eq 2

$$\ln\frac{COD}{COD0} = k.t \quad (2)$$

where k: degradation rate constant (1/h), C_{COD0} : wastewater before treatment and C_{COD} : wastewater after treatment

3. Result and discussion

3.1. COD degradation

Figure 4 shows the degradation of COD of three wastes and the rate constants are depicted in Table 1. The degradation rate using UV-Ozone oxidation process shows faster than ozone or UV alone. , The decrease in COD degradations of tofu, herbal and fertilizer waste using the UV-Ozone method are 28%, 59%, and 83%, respectively. In this study, combination of UV radiation and ozone was significant for reducing COD because the combination of ozone and ultraviolet is able to produce strong oxidation agent of hydroxyl radicals (×OH) [4], as shown by the following reactions:

$$O_3 + UV \rightarrow O_2 + O(^1D) \quad (3)$$
$$O(^1D) + H_2O \rightarrow 2\ \cdot OH \quad (4)\ [5]$$

With $O(^1D)$ is excited oxygen atom, also known as singlet oxygen [6]. Where a free radical which has a very high oxidation potential, so instrumental in over hauling the bonds from chemical compounds, both organic as well as inorganic contained in the waste, so that microorganisms will experience shortages of materials or nutrients that will be parsed, thus reducing the amount of oxygen contained in the waste [7]. The degradation of tofu wastewater from 1308 ppm to 942 ppm, herbal wastewater from 1011 ppm to 414 ppm and fertilizer wastewater from 510 ppm to 89 ppm.

Table 1. First-Order Kinetics UV-Ozone for COD degradation

Wastewater types	**Reaction Kinetics (k)**		
	Uv-Ozon	**UV**	**Ozone**
Tofu	0.0820	0.0783	0.0744
Herbal	0.2232	0.1060	0.0723
Fertilizer	0.4364	0.3745	0.1782

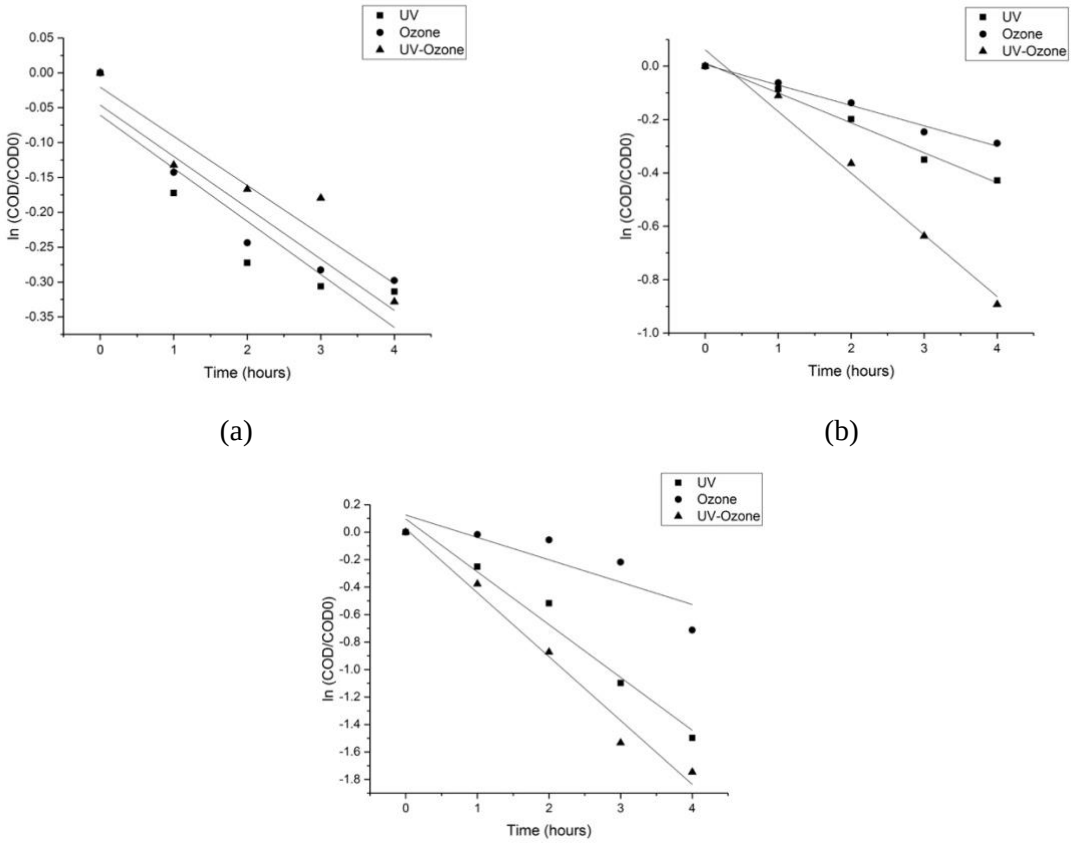

Figure 4. First-Order Kinetic of Degradation of COD (a) Tofu, (b) Herbal and (c) Fertilizer Wastewater

3.2 Utilization of Tofu, Herbal and Fertilizer Wastewater for Cultivation of Spirullina sp.

The best results were obtained at the addition of 10% v / v because it had the highest OD value and growth rate. This causes the ratio of nutrient composition is right for the growth of *Spirulina sp.*[8]. It contained simple organic compounds such as acetic acid contained in tofu liquid waste are directly utilized as a source of organic nutrition [9]. But in the cultivation of *Spirulina sp.* with the addition of 50% v/v of herbal nutrients increased on first day and then second day to tenth day decreased, this was due to the higher addition of herbal wastewater, the growth of Spirulina sp. increasingly inhibited. Addition of high COD concentration causes dark colour and high turbidity in the cultivation culture. This causes the penetration of light into the media is very small so that photosynthetic activity is disrupted. *Spirulina sp* can not grow well (Table 2 and Fig 5) on media containing high organic substances because it can affect the dark colour and turbidity so that it affects the rate of microalgae photosynthesis [10].

Table 2. Growth Rate of *Spirulina sp*

Wastewater	Nutrients (ppm)	Growth Rate μ / hari	Maximum Optical Density
Control	50	0,283	0,671
Tofu	10	0,078	0,436
	20	0,261	0,755
	50	0,181	0,912
Herbal	10	0,358	1,018
	20	0,183	0,850
	50	0,71	0,209
Fertilizer	10	0,467	0,843
	20	0,258	0,666
	50	0,231	0,698

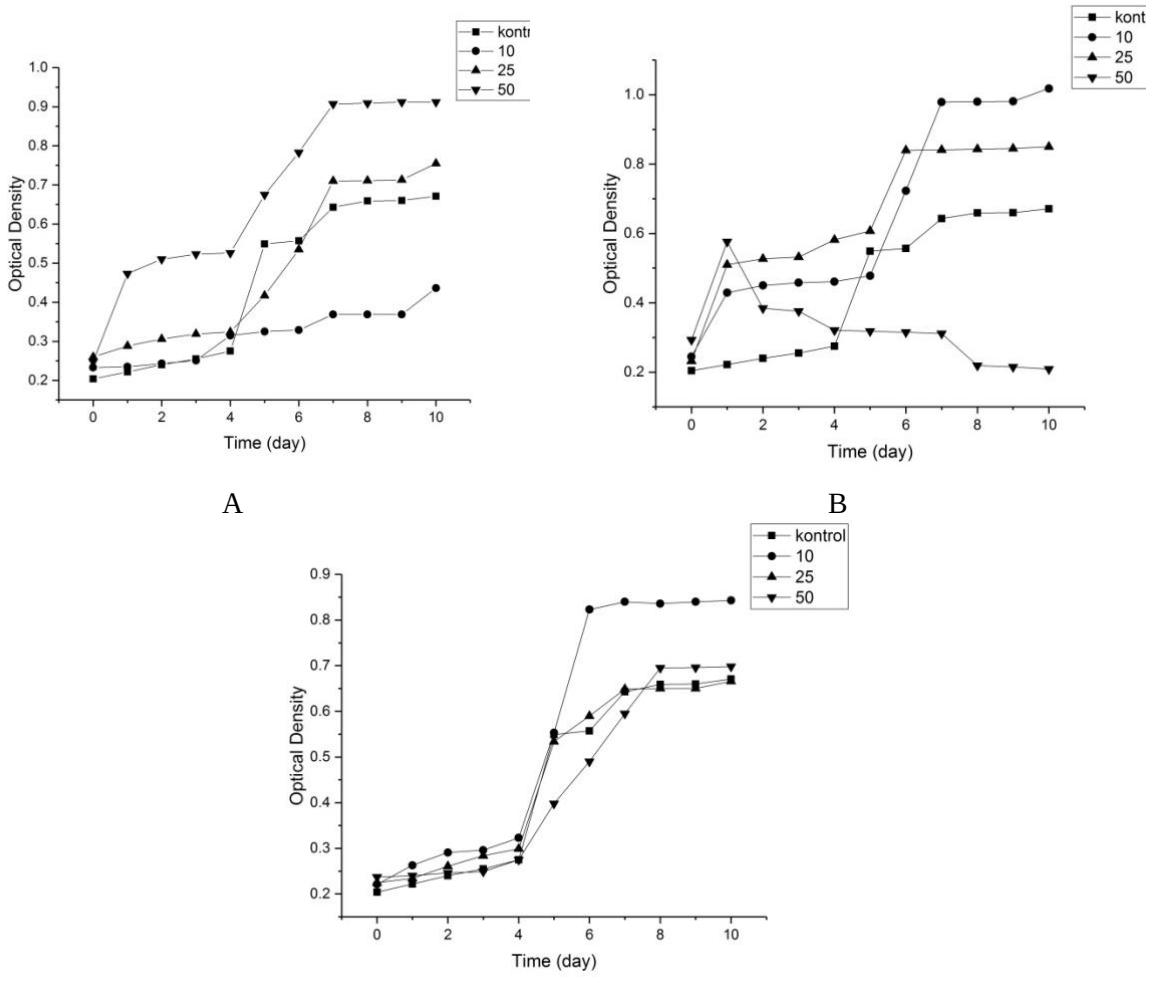

Figure 5. Cultivation of *Spirulina sp.* with (a) Tofu, (b) Herbal and (c) Fertilizer culture media

4. Conclusion

UV radiation + Ozone method is possible to eliminate the smell of wastewater and reduced the COD. So, it can be proven that the method of UV + AOP is suitable to be applied to treatment tofu, herbal, and fertilizers wastewater. In the variation of waste and tool methods on the waste, the optimum decrease was obtained using UV-Ozone method, where the COD decrease in tofu from 1308 ppm to 942 ppm, herbal wastewater from 1011 ppm to 414 ppm, and fertilizer wastewater from 510 ppm to 89 ppm on the use of 4 hour UV-Ozone method the decrease in COD is appropriate using order 1. The decrease in COD based on the UV-Ozone method for tofu waste, herbal waste, and fertilizer waste respectively are 0.0820 $hours^{-1}$, 0.2232 $hours^{-1}$, and 0.4364 $hours^{-1}$. The best results were obtained at the addition of 10% v / v because the ratio of nutrient composition is right for the growth of *Spirulina sp.* But in the cultivation of *Spirulina sp*. with the addition of 50% v/v *Spirulina sp* can not grow well on media containing high organic substances because it can affect the dark colour and turbidity so that it affects the rate of microalgae photosynthesis.

5. References

[1] Huang C, Dong C, Tang Z. 1993 *Waste Management* **13(5)** 361–77.
[2] Rice R G 1996 *Ozone: Sci. Eng*. **18(6)** 477-515
[3] Wen Z, Gross M, Ninno M D and Michael C 2015 *Bioresource Technology* **170**, 473-482
[4] Zhou, H and DW Smith 2002 *Journal of Environmental Engineering Science* **1** 247-264
[5] Mohajerani M, Mehrvar M and Ein-Mozaffari F 2009 *Int. J. Eng.(IJE)*. **3 (2)** 120 – 46
[6] Gottschalk C, Libra JA, Saupe A. Ozonation of water and waste water: a practical guide to understanding ozone and its applications. John Wiley & Sons; 2009.
[7] Tchobanoglous G, Kreith F. Handbook of solid waste management. New York: McGraw-Hill; 2002.
[8] Nur MMA and Hadiyanto H 2015 *J. Eng. Technol. Sci., **47** 487-497*
[9] Hadiyanto H and Nur MMA 2014 *World Applied Sciences Journal* **31** 959-967
[10] Cheunbam S and Peerapornpisal Y 2010 *International Journal of Agricultural & Biology 12 586-590*

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