Chemical oxygen demand (COD) degradation of herbal, tofu and fertilizer wastewater using UV/Ozone oxidation methods

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Abstract. The herbal, tofu and fertilizer industries contribute considerable waste. Unprocessed waste disposal can cause environmental pollution. The waste contains chemical oxygen demands (COD), and organic substances can be degraded by Advanced Oxidation Processes (AOPs) degradation method. The process of AOPs in this study used a combination of UV rays and ozone to produce hydroxyl radicals. This study was aimed to investigate the effect of UV, Ozone and UV-Ozone methods on COD degradation of herbal waste, tofu, and fertilizer. The result showed that the optimum degradation was obtained at experiment by using UV/ozone method. The COD degradation at tofu wastewater was from 1308 to 942 ppm, herbal wastewater was from 1011 to 414 ppm, and fertilizer wastewater was from 510 to 89 ppm by the use of 4 hours UV-Ozone method.

1. Introduction
Waste is any substance which is discarded after primary use or is worthless, defective and of no use. The main pollutant in wastewater is chemical oxygen demand (COD) which is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. COD needs to be anticipated when the wastewater is dumped into a body of water continuously; it will give the negative effects that will be adverse for human, incurred a foul smell and became a source of disease, also COD can make environmental pollution [1].

Advanced oxidation process (AOP) of wastewater utilizes UV photons to enable the ozone molecules to form hydroxyl radical and use the ozone method in the presence of activated carbon can accelerate the decomposition of ozone being hydroxyl radical, UV-Ozone method very potential to oxidize organic compounds contained in the wastewater [2]. Through this method, it is expected that liquid waste produced by industrial wastewater that contains COD levels can be processed and meet the requirement of wastewater quality standards. The AOP system works using hydroxyl radical (·OH) which results from the reaction between the combination of Ozone- UV-H2O2 in water. The strong oxidizing agent can use an ozone mixture with hydrogen peroxide (O3 + H2O2), ozone with ultraviolet (O3 + UV), and a mixture of hydrogen peroxide with ultraviolet light (H2O2 + UV). The active radicals released by the above compounds will quickly oxidize dye pollutants in wastewater [3].

This study focused on the implementation of these advanced oxidation process (AOP) methods to degrade the COD content in wastewater. The wastewater from tofu, herbal and fertilizer industries are considerably containing high COD content and give high pollution impacts to the environments.

Herbal wastewater contains high COD content of 200-2000 ppm [4,5]. Tofu wastewater generated
from the process from washing, boiling, pressing and molding [6], which contains COD up to 7000-10000 ppm [7]. The fertilizer wastewater mostly contains relatively high ammonia and urea contents and has COD contents up to 2000 ppm [8]. This study was aimed to investigate the effect of UV, Ozone and UV-Ozone methods on COD degradation of herbal waste, tofu waste, and fertilizer waste.

2. Materials and methods
2.1. Material
Tofu, herbal and fertilizer wastewater from local industries in Semarang city were used in this study. Distilled water was used for dilution of wastewater and COD kits reagent was used to analyze the COD contents in the sample.

2.2. Equipment
The advanced oxidation process (AOP) equipment consists of UV and ozone generators and waste tank and controller (Fig 1). The wastewater was fed to the generator unit where the resident time of wastewater was set by adjusting the flow rate.

![Figure 1. UV-Ozone oxidation instruments](image)

2.3. Variables
The controlled variables in this study were a resident time 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 the methods; there are UV, Ozone, and UV/Ozone methods.

2.4. COD degradation and analysis
The experiment was divided into two steps; the first step was waste pre-treatment using UV, Ozone, and UV/Ozone, then the second step was COD analysis. The first stage aims to determine which method has more influence on COD degradation. Waste samples (in triple experiments) are diluted 20x, and 1.5 L of the sample was processed into the device according to various UV, Ozone and UV/Ozone tools. The experiment was carried out for 4 hours, and the sample was taken every 1 hour as much as 50 mL. The COD analysis was carried out by using Hanna COD MR reagent.

3. Result and discussion
Figure 2 shows the degradation rate of COD in three different waste water. The degradation rate during 4 hours oxidation of wastewater shows different trends. Almost three of oxidation shows
significant reduction of COD by using a combination of UV/Ozone methods. The rate of degradation was also higher by using UV/ozone methods. Long exposure of oxidation process leads to a reduction of COD in wastewater, because the longer exposure intensity, an increase in temperature causes a decrease in the levels of dissolved oxygen and bacterial decomposition so that the impact to the decline of COD [9].

![Graphs showing COD degradation](a) tofu wastewater, (b) herbal wastewater and (c) fertilizer wastewater

Among three wastewaters, herbal wastewater shows a low rate of degradation as compared to fertilizer and tofu wastewater and oxidation only by using ozone give a low rate of degradation. However, by combining UV with ozone has shown strong oxidizing properties and can degrade organic compounds [1]. Ozone oxidizes compounds through two ways, direct and indirect reaction. Direct reaction, the oxidation is carried out by ozone itself that dissolved in water. Than indirect reaction, the oxidation occurs by producing OH radicals that would oxidize other compounds. Longer time of ozone contacts in wastewater will generate more ozone and therefore oxidize the compounds and change to the simpler compounds [10]. But the strength of degradation by ozone alone is not that high and can be optimized by combining ozone with UV to change hydroxyl ion to superoxide as shown by the reaction below [11].

\[
\begin{align*}
O_3 + UV & \rightarrow O_2 + O(^1D) \\
O(^1D) + H_2O & \rightarrow 2 \cdot OH
\end{align*}
\]

(1) (2)

With O(^1D) is excited oxygen atom, also known as singlet oxygen [12]. Where a free radical which has a very high oxidation potential, so instrumental in overhauling 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 wastewater [9].

| Wastewater | COD (ppm) Before treatment | COD after treatment (ppm) | UV | Ozone | UV/ozone |
|------------|---------------------------|--------------------------|----|-------|---------|
| Tofu       | 800                       | 900                      | 1000 | 1100  | 1200    |
| Herbal     | 1300                      | 1400                     | 1500 | 1600  | 1700    |
| Fertilizer | 50                        | 150                      | 250  | 350   | 450     |

**Figure 2.** Degradation of COD in (a) tofu wastewater, (b) herbal wastewater and (c) fertilizer wastewater
Table 1 shows the final reduction after 4 hrs oxidation. The significant degradation has been shown by fertilizer wastewater at the level of 51-82% reduction, while the hardest degradation was shown by tofu wastewater (25-27% reduction). This may be due to the nutrients contents in the wastewater which affect the oxidation reaction. Moreover, the initial concentration will also affect the degradation of COD in wastewater.

4. Conclusion
UV/ozone radiation method has been studied in this study and showed the significant reduction as compared to UV and ozone as a single oxidation method. The reduction of COD in fertilizer wastewater was 51-82%, herbal wastewater was 25-59%, and tofu wastewater was 25-27%. The oxidation of herbal wastewater showed slow degradation rate as compared to fertilizer and tofu wastewater.

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