EFFECT OF OZONIZATION ON COD AND BOD₅ VALUES OF WASTEWATER FROM DETERGENT MANUFACTURER

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ABSTRACT

The aim of this experiments were to examine the effect of ozonization on COD and BOD₅ value of wastewater from a detergent manufacturer and to put forward the efficiency of COD and BOD₅ removal as a function of the ozonization. It has been known that the detergent industry produces wastewater with high concentration of both COD and BOD₅. The observation showed that the ozonization alone was not a practical approach for COD and BOD₅ removal. However, the role of ozonization as a preliminary process before the biological one seems to be significant.

INTRODUCTION

A common property of all wastewaters containing organic matter is their pronounce affinity for oxygen. This condition varies according to the nature and quantity of oxidizable materials. Therefore, to assess their strength the oxygen consuming characteristics of wastewater are usually used such as COD and BOD₅. The COD is the amount of oxygen utilized in the oxidation of organic matters by potassium dichromate under standard conditions of time and temperature (Nicoll, 1988). The BOD₅, organic carbon, and organic matters from a specific sample source can be related to each other (APHA, AWWA, WEF, 1992).

Livke et al. (1972, cited in Rice and Browning, 1980) ozonized the wastewaters from the caprolactam synthesis at two different Russian chemical plants. Ozonization was conducted after biological treatment. Following the ozonization, the ozonized effluents were sent to the biological ponds prior to reuse as cooling water. The result of ozonization (ozone dosage 15 to 25 ppm) indicated that the BOD₅ values increased as the COD values decreased, and the ratios of BOD₅: COD changed from 0.1 to 0.5. This phenomena showed that the increasing of BOD₅ value is a result of oxidative degradation of the resins to simpler compounds.

Davis et al. (1976, cited in Rice and Browning, 1980) investigated an ozonization of wastewaters from the production of several alkyl amines employing a submerged turbine contactor. The result showed that during the first two hours of ozonization, the residual COD of isobutyl amine wastewater increased. However, after an additional two hours ozonization, the COD then dropped to about 33% of the original content. The concentration of ozone applied was 39 mg/l-min.

Ozonization of wastewater generated from a synthetic organic chemicals plant manufacturing chelating agents was conducted by the same authors. The result identified that ozonization had little effect on the COD of the wastewater before biological treatment, but the COD decreased significantly after biological treatment. However, ozonization of dissolved organic compounds can improve their biodegradability (van Leeuwen, 1987; Harrington and Di Giano, 1989; Krithof, 1989; and DeWaters and DiGiano, 1990). Another ozonization was performed on used metal-containing dyes. The result indicated that the colour removal was 37

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approximately 80-90% for a COD removal limited to approximately 10% (Le Tareau and Rovel, 1982).

Wastewater from detergent industries or from synthetic tenside manufacturer is known to contain high concentration of organic pollutants which reflected their components in their products. Generally, this kind of wastewater contains organic materials like fat and oil components, tenside substances, stabilizing agents (phosphate, nitroloacetate, EDTA) and other substances (Poppinghaus et al., 1994).

The aims of this experiments were to examine the effect of ozonization on COD and BOD\textsubscript{5} values of wastewater from a detergent manufacturer and to evaluate the efficiency of COD and BOD\textsubscript{5} removal as a function of the ozonization.

**MATERIALS AND METHODS**

1. **Sampling**

Samples were provided by a detergent manufacturer and consisted of soap lyes (S sample) and untreated wastewater (W sample). These samples were stored in a cold room for three days prior to ozonization and analysis of the COD and BOD\textsubscript{5}.

2. **Ozonization**

Figure 1. illustrates a schematic design of the laboratory study plant. Ozone (O\textsubscript{3}) was generated from pressurized dry air by a laboratory corona discharge ozonator. The details of the ozonization was described elsewhere (Mulyanto, 1995).

The ozone dosages was the function of the ozonization time with a constant gas flow rate of 1.36 l/min.

![Figure 1. Schematic design of the laboratory study plant](image)

3. **COD Analysis**

The analysis of COD was carried out using prepared reagent vials obtained from Hach. Two kinds of reagent were used, namely low range (0-150 mg COD/L for W type sample) and high range (0-1500 mg COD/L for S type sample) reagent. The reagent vials contained a prepared mixture of sulfuric acid, mercuric sulfate, chromic acid, silver sulfate, and water. Two millilitres of diluted samples (100 times for raw and 50 times for ozonized W type, 200 times for raw and ozonized S type samples) were pipetted into the vials. The vials were then heated on the heating block (Hach COD Reactor, USA) for 2 hours at 150 °C. Following digestion, the vials were allowed to cool to room temperature and the COD was measured using a spectrophotometer (Hach DR/ 2000). The COD value was displayed on the screen of the spectrophotometer in mg/l (ppm).

The principle of the reaction can be illustrated as follows (Nicoll, 1988):

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Cr_{2}O_{7}^{2-} + 8H^{+} \rightarrow 2Cr^{3+} + 4H_{2}O + 30
\]

4. **BOD\textsubscript{5} Analysis**

The analysis of BOD\textsubscript{5} was conducted for the wastewater sample before and after ozonization. Both types of sample (W and S) were expected to have a high BOD\textsubscript{5} value. Therefore, dilution of 500 and 13,333 times were applied respectively.

The BOD\textsubscript{5} test requires the measurement of dissolved oxygen of sample before and after incubation for 5 days at 20 °C and is calculated from the difference between the two measurements. The test was conducted in an overflowing airtight BOD bottle of the specified size, with the flared mouth for overflow of sample. This provided a water-seal in order to prevent drawing air into the dilution bottle during incubation. The BOD incubation was carried out in the dark to prevent possibility of photosynthetic production of DO (APHA, AWWA, WEF, 1992).

The dilution water was prepared by the aeration of potable water with pressurized air for 2 days in order to realase the chlorine content and to achieve the DO saturation. The dilution water contained of phosphate buffer (potassium dihydrogen phosphate, di-potassium hydrogen phosphate, di-sodium hydrogen phosphate), ammonium chloride, magnesium sulfate, calcium chloride, and ferric chloride solution. The quality of dilution water was checked in order to know the DO uptake in 5 days at 20 °C.

The analysis of DO was done by using the azide modification method. Before titrating with sodium thiosulfate and adding starch as an indicator, manganous sulfate solution was added to the sample followed by alkali-iodide-azide reagent. The alkali-iodide-azide reagent consisted of sodium hydroxide, potassium iodide, and sodium azide. To dissolve the floc which might develop concentrated sulfuric acid was added. For the titration of a 200 ml sample, 1 ml 0.025 M sodium thiosulfate = 1 mg DO/l.

**RESULTS AND DISCUSSION**

Figures 2. and 3. illustrate the effect of ozonization on COD and BOD\textsubscript{5}, values of Soap Lyes (S samples). The initial
concentration of COD and BOD, values were considerably high, namely 155,000 ppm and 85,200 ppm respectively. It was obtained that the concentration of COD become slightly higher than the initial sample after ozonatization using ozone dosage of 1 g/l. This was the result of oxidative degradation of the organic matter to simpler compounds. Using more than 3 g/l ozone dosage, the COD-concentration of S-wastewater decreased significantly from 154 g/l to 144 g/l. In general, the influence of ozone dosage on the concentration of COD was significantly decreased.

The change in concentration of BOD, showed different trend than that of the COD. It decreased from 85.2 g/l to 64.2 g/l using ozone-concentration less than 1 g/l, and then tend slightly to increase on higher ozone dosages.

The maximum COD removal was 7.5 % by using ozone dosage of 7 g/l (Figure 4). The low efficiency of COD removal may be due to incomplete oxidation of the detergent contained wastewater sample into carbon dioxide by ozone.

In some cases it was discovered that the BOD, level of the ozonized S-wastewater tend to increase slightly with increasing the ozone dosages. This phenomenon is attributed to the fact that ozone can oxidise non-biodegradable material to biodegradable material which then exerts additional oxygen demand. The maximum BOD, removal was 25.3% by using ozone dosage of 0.671 g/l (Figure 5). Figure 6 showed that the ratios of BOD, to COD tend to increase with increasing the ozone dosage.
Untreated Wastewater (W samples) can be seen in Figures 7 and 8. The result of original COD and BOD$_5$ values were 6.3 g/l and 2.9 g/l respectively. Ozonization caused the COD-concentration to decrease to 5.9 g/l in average. On the contrary the BOD, tend to increase than the initial BOD$_5$-concentration by using ozone dosage of more than 0.3 g/l.

The maximum removal of COD in W-wastewater was 7.9 % by 0.5 g/l ozone dosage (Figure 9). In average the ozonization caused 7 % COD-removal. Whereas, the maximum efficiency of BOD$_5$ removal was 21% by using ozone dosage less than 0.1 g/l, but the BOD$_5$ removal decreased drastically to values of lower than 0 % at higher ozone dosage (Figure 10). This phenomenon could be caused by the formation of biodegradable organic materials contained in the W-type wastewater. Through ozonization at ozone dosage of more than 0.1 g/l, the non-biodegradable COD-content in wastewater was oxidized to biodegradable materials and increased the BOD$_5$-concentration. Figure 11 showed those tendencies on the BOD$_5$/COD-ratios.

On ozonization at the highest ozone dosage level (9.636 g/l and 0.616 g/l), the residual ozone trapped in the Drexel bottle was 3.7 ppm and 21.3 ppm for S and W samples respectively. This investigation gives evidence of the existence of an ozone refractory compounds in wastewater. Performance of organic material removal between S and W wastewater was different. It was shown that more components in W samples were easier to be degraded rather than those contained in the S samples.
CONCLUSION

The effect of ozonization on COD values was insignificant for treating wastewater from detergent industries. It was obtained that highest COD removal was only 8% even when high ozone dosage (7.29 g/l) was applied. With certain ozone dosages, the ozonized S- and W-wastewater had lower COD value than the un-ozonized one. In the same manner, ozonization caused a decrease in BOD value by ozonization of the S-wastewater. However, the BOD trend to remain constant as the initial concentration or slightly higher by ozonization on the W-wastewater.

In summary, ozonization of the wastewater alone from a detergent manufacturer was not a practical approach for COD and BOD removal. However, the application of ozone before the biological process is necessary to be taken into consideration in view of the phenomenon that ozone has capability to oxidize non-biodegradable material to become biodegradable one. Therefore, continuation of research and a feasibility study are recommended before the manufacturer begin applying the treatment process.

REFERENCES


