Color removal by ozonation process in biological wastewater treatment from the breweries

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Abstract. Colors from the final stage of processing of brewery biological wastewater treatment by Upflow Anaerobic Sludge Blanket (UASB) reactors have caused extremity problems. The aim of this research was to investigate the ozone dosage required to remove the color from brewery industrial wastewater effluent. The dosage of ozone is varied between 50 to 300 mg/L for 18 minutes, flow rate 45 L/hr., pH 8.4. As the result, the increasing depolarization efficiency is obtained with the increase in an ozone dose. Maximum depolarization of 90% is achieved at an ozone measurement of 300 mg/L. Moreover, the kinetic of depolarization is fitted by the first order equation. The constant of the reaction (k) was 0.120 1/minute. Electrical energy required to move color was 6 kW-h/m³.

1. Introduction
Organic compounds are one of the most significant components from wastewater products of brewery operations [1] which are a result of the fermentation process of malt (usually barley malt), hops, fermented proteins and waste yeas lead to the water discharged being found with highly organic waste, especially lignin. Biological wastewater treatments in the brewing industry have two (2) continuous systems. 1. Upflow anaerobic sludge blanket (UASB) reactor systems have the efficiency to reduce organic pollutant concentration up to 75-85% [1, 2] and 2. Activated Sludge (AS) system gave a maximum removal efficiency of Chemical Oxygen Demand (COD) range from 50 to 100 mg/l being under value according to Thai Industrial Effluent Standards (COD not exceeding 120 mg/l) [3]. However, although the wastewater effluents were passed both UASB and AS systems had COD less than 120 mg/l, color due to a last stage process of brewery biological wastewater treatment was still more than 500 ADMI color index (The ADMI color index is American Dye Manufacturer’s Institute) making it over the limit according to Thai Industrial Effluent Standards (Color not exceeding 300 ADMI color index) [3]. The purpose of this research is to reduce the colour of the effluent to obtain a standard and unobjectionable effluent from the surrounding communities by using the ozonation method as an oxidation process. Ozone is one of the most powerful and commercially available oxidants and is proven to be one of the most efficient methods of treatment of coloured aqueous effluent [4]. Furthermore, the ozone affects removal of true color and destroys the structure of organic compounds in the same time.
2. Materials and Methods

2.1. The materials
The wastewater samples used in this study were collected from the wastewater effluent after passing both the Upflow Anaerobic Sludge Blanket (UASB) and Activated Sludge (AS) systems from industrial breweries in the Pathum Thani province, one of the central provinces of Thailand. The wastewater samples characteristics were pH 8.4, COD and ranged from 56.96 to 68.35 mg/l where the true color was 500 ADMI.

2.2. The methods
The experimental setup was used the ozonation process on color reduction and studied factors influencing ozone dosages of 50, 60, 75, 100, 150, and 300 mg/l where the true color was 500 ADMI. The production of ozone was created by using an ozone reactor as seen in Figure 1. By pumping water into the system. Then opened an Ozone generator. The reactor would drain the water through water inlet and vacuum the air through the air duct. Both water and air were pumped into an Ozone generator for producing ozone. After that the water was sprayed out a sprinkler at the tip of the water tube. The system would circulate the water back into contact with the ozone again, repeating the cycle until it reaches the equilibrium condition.

![Figure 1. Experimental Setup for Ozonation of waste water treatment.](image)

2.3. kinetics of degradation of color with ozonation process experiment
The study was conducted in the three models as follows 1.Zero-order reaction 2.First-order reaction and 3.Second-order reaction. The wastewater samples used in this study were controlled the pH at 8.4 ± 0.1. and 5 ml. were collected at 2, 4, 6, 8, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, and 60 minutes, respectively. The obtained data was analyzed for ozone degradation kinetics based on color (ADMI) and COD, respectively. The reaction tanks used in this study were 30 cm in diameter, 45 cm in height, 38 liters in total, and 5-30 liters in capacity as depicted in Figure 1. EE/O (that is the electrical energy required to remove a pollutant by one order of magnitude in one m³ of Waste water) used in the degradation of colour by using ozone has been calculated by applying the following empirical formula equation (1) [5].

\[
EE/O \left( \frac{kWh}{m^3} \right) = \frac{P \times t \times 1000}{V \times 60 \times \log \left( \frac{C_i}{C_e} \right)}
\]

When \( P \) (kW) is the power input, \( t \) is the oxidation time (in min), \( V \) is the volume of the effluent sample (in litter) and \( C_i \) and \( C_e \) are the initial and final concentrations of the contaminant.
3. Results and Discussion

3.1 Efficiency of Color and COD removals

The results in Figure 2 and Figure 3 show that Color and COD removals efficiency were increased with the increase of the ozone dosages [6]. The effect of ozonation on color removal were grew from 50 to 300 mg/l during the 18th minute of ozone contact time and on Color and COD removals were increased from 57% to 80% and 28% to 50% (Figure 4) respectively.

![Figure 2](image1.png)

**Figure 2.** Effect of ozone dosage on the efficiency of ozonation for color removal of wastewater.

![Figure 3](image2.png)

**Figure 3.** Effect of ozone dosage on the efficiency of ozonation for COD removal of wastewater.
3.2 The kinetics of degradation of color with ozonation process

Degradation kinetics describe the rate of color degradation in the ozonation process in three models as follows 1. Zero-order reaction 2. First-order reaction and 3. Second-order reaction are shown in Equations (2) - (4), respectively.

\[
\begin{align*}
\frac{dc}{dt} &= k 
\Rightarrow [C] = [C]_0 - k_0 t 
\tag{2} \\
\frac{dc}{dt} &= k [C] 
\Rightarrow \ln[C] = \ln[C]_0 - k_1 t 
\tag{3} \\
\frac{dc}{dt} &= k [C]^2 
\Rightarrow \frac{1}{[C]} = \frac{1}{[C]_0} + k_2 t 
\tag{4}
\end{align*}
\]

When \(-\frac{dc}{dt}\) = rate of degradation (ADMI/min), \(k_0\), \(k_1\) and \(k_2\) = constants of reactions of a zero order, first order and second order respectively, \([C]\) and \([C]_0\) = concentration of Color in effluent and influent (ADMI) and \(t\) = time (minutes).

The regression analysis Multiple (R^2) of the plotted data by Equations (2) - (4) shown in Figure 5 and Table 1, which found that wastewater being oxidized by OH • with the ozonation process was fitting the first reaction in all ozone concentrations and the initial wastewater pH was 8.4.

![Figure 5. 1st order reaction](image-url)
Table 1. The values of constant K, and R² of the kinetics of ozonation process.

| Ozone concentration (mg/L) | 0th Order Reaction | 1st Order Reaction | 2nd Order Reaction |
|---------------------------|--------------------|--------------------|--------------------|
|                           | K₀ (mg/L.min)      | K₁ (1/min)         | K₂ (L/mg.min)      |
|                           | R²                 | R²                 | R²                 |
| 300                       | -3.7136            | -0.12              | -0.0042            |
|                           | 0.837              | 0.9841             | 0.7971             |
| 150                       | -4.1682            | -0.1023            | -0.0034            |
|                           | 0.9439             | 0.9674             | 0.751              |
| 100                       | -2.8999            | -0.0832            | -0.0034            |
|                           | 0.8921             | 0.9864             | 0.92               |
| 75                        | -2.6663            | -0.0639            | -0.0025            |
|                           | 0.9133             | 0.9809             | 0.9349             |
| 60                        | -1.7752            | -0.0479            | -0.0018            |
|                           | 0.8984             | 0.9933             | 0.9208             |
| 50                        | -1.5837            | -0.0424            | -0.0016            |
|                           | 0.9025             | 0.9894             | 0.9176             |

In this study, it seems that k rate was the first order reaction and was consistent with [7] research. k rate was increased with an increase in the graph of ozone concentration. In the other hand, the k rate in color removal was higher than the k rate in COD removal almost 10 times due to the wastewater having a very high initial color while the COD is very low because the wastewater had the characteristics of effluent discharging similar to Industrial Effluent Standards already [8]. The EE /O was used in the degradation of color was 3-6 kW-h/m³. As the amount of water increased, the EE /O was reduced. The amount of ozone was lower and the cause of the efficiency of color and COD removal were decreased. The use of electrical energy is not very high compared to the performance that can be treated which was consistent with Yasar’s research [5] that used ozone removal of color and COD showing energy requirements for using pre ozonation at 20.8 and 20.4 kWh/m³, respectively and energy requirements for using post ozonation were 1.3 and 7 kWh/m³, respectively.

4. Conclusion
The ozonation process has been used for the successful removal of color from brewery wastewater. The concentration of ozone that can affect the performance impact of wastewater treatment was 300 mg/L which can increase the efficiency of the treatment up to 90%. In addition, mathematical equations can be calculated for evaluating the effectiveness of the ozonation process which had the multiple regression coefficient (R²) being 0.9841.

5. References
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