Effect of ozonation on COD fractionation of wastewater from poultry processing industry

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Abstract. The objectives of this study were to evaluate the effect of ozonation on the solubility and biodegradability of wastewater from poultry processing industry. In addition, the wastewater also characterized based on the COD fractionation. The wastewater sample used was collected from Advance Chicken Processing (M) Sdn. Bhd., Perlis, Malaysia. Ozonation process was carried out in a semi-batch glass reactor which has a 2 L volume. The COD fractionation of poultry wastewater indicated that non-biodegradable COD is predominant compare to other fractions. However, the wastewater is containing higher percentage biodegradable COD comprehensively. It is expected that ozonation treatment would transform both particulate and soluble non-biodegradable COD towards biodegradable constituent that easily remove by biodegradation. The removal of COD was significant at ozonation duration up to 5 min. However, COD removal efficiency was only increased slightly with the increased of the ozonation duration after 5 min. This may be due to the fact that ozonation for long time would possibly producing constituent that inhibit ozone dissociation.

1. Introduction

In Malaysia, poultry is an important human food source as it is easy to access at low price. To supply sufficient demand of this food to consumers, the raw materials should be treated in poultry processing industry, which eventually produces wastewater from the slaughtering of animals. The wastewater from this industry may containing a huge amount of biodegradable organic matter and colloidal matter such as fats, proteins and cellulose [1]. Consequently, the wastewater should be treated properly to ensure the safety and sustainability of the water prior release to the environment. However, non-biodegradable materials and the ammonia nitrogen of the poultry processing wastewater cannot be removed completely by the conventional biological water treatment process. This may cause the decrease in the biodegradability and solubility of the ultimate effluent. The effluent’s organic contents will be above those standard limits and have a risk to flow into water bodies such as river, lake and sea. This may lead to serious environmental issues [2,3].

Ozonation is an emerging technology in water treatment that could be used to oxidize non-biodegradable materials in wastewater due to its high oxidation potential [4]. In the water environment, ozone will destroy microorganism and degrades organic pollutants through direct reaction of ozone dissociation or the formation of highly reactive hydroxyl radicals, •OH [5]. In particular, ozonation has showed satisfactory effectiveness for the degradation of a wide variety of organic pollutants, including pesticides, pharmaceuticals and surfactants [6]. Consequently, low degradable organic materials will be transformed by ozone into by-product with smaller molecular
size as well as convert the ammonia to nitrate which is more biodegradable \[3\]. However, previous research work on ozonation of poultry wastewater not clearly evaluate and characterize the transformation of Chemical Oxygen Demand (COD) fractions of wastewater in term of solubility and biodegradability. Hence, in this study the effect of ozonation on COD fractionation of wastewater from poultry processing industry will be evaluated. The fractionation of COD will be based on biodegradability and solubility.

2. Materials and methods

2.1. Collection of poultry processing industry wastewater
The wastewater sample used in this study was poultry processing industry wastewater at Advance Chicken Processing (M) Sdn. Bhd., Perlis, Malaysia. The samples were collected from influent of conventional activated sludge process. The wastewater pH was adjusted using 1 M NaOH or 1 M HCl solutions to a required experimental setting.

2.2. Ozonation treatment
The ozonation process was carried out in a semi–batch glass reactor which has a 2 L volume. The oxygen tank was used to supply 99.8% purified O\textsubscript{2} gas to the ozone generator. Ozone was generated in A2Z ozone generator with the flow rate of 300 mL/min and flow into bottom of glass reactor through the glass diffuser, in which O\textsubscript{3} gas contacted with constituents in the wastewater. The residual O\textsubscript{3} gas was decomposed in KI trap solution.

2.3. COD fractionation with physiochemical method
Four water samples (I – IV) will be created by different pre-treatments including sedimentation, filtration and alum treatment. The four water samples and their descriptions are shows in the Table 1.

| Sample I, “wastewater” | The primary effluent from Advance Chicken Processing (M) Sdn. Bhd. |
| Sample II, “settled wastewater” | The supernatant of wastewater that been settled for 90 min. |
| Sample III, “settled and filtrated wastewater” | Supernatant from the “settled wastewater” is filtering with a 0.45 µm filter paper. |
| Sample IV, “flocculated and filtrated wastewater” | The wastewater from Advance Chicken Processing (M) Sdn. Bhd. flocculates with 150 mg/L of alum and the pH is neutral. The sample after that is mixing with a jar test apparatus for 1 min at a high speed of 300 rpm and 5 min slow mixing at 30 rpm, then follows with 1 hour of sedimentation. The supernatant is withdrawn and filter by a 0.45 µm filter paper to produce the “flocculated and filtrated wastewater”. |

The differences in COD concentration between those water samples help in calculate the settable solids (C\textsubscript{SS}), non-settable solids (C\textsubscript{NS}), soluble COD (C\textsubscript{S}) and colloidal COD (C\textsubscript{C}). The equations to calculate those fractions show in the Table 2 according to Wu et al. \[7\]. Next, a conversion matrix was used. Through the conversion matrix, the fractions mentioned above (C\textsubscript{SS}, C\textsubscript{NS}, C\textsubscript{S} and C\textsubscript{C}) were converted to the COD fractionation which were soluble biodegradable COD (SS), particulate biodegradable COD (XS), soluble non-biodegradable COD (SI) and particulate non-biodegradable COD (XI). The conversion matrix is used as shown below to calculate the fractions of interest.

\[
SS = 0.11 \, C_{SS} + 0.21 \, C_{NS} + 0.23 \, C_{S} + 0.92 \, C_{C} + 20
\]
\[ \text{XS} = 0.17 \, C_{\text{SS}} + 0.37 \, C_{\text{NS}} + 0.59 \, C_{\text{C}} + 0 \, C_{\text{S}} \pm 10 \]  
(2)
\[ \text{SI} = 0 \, C_{\text{SS}} + 0 \, C_{\text{NS}} + 0 \, C_{\text{C}} + 0.08 \, C_{\text{S}} \pm 4 \]  
(3)
\[ \text{XI} = 0.72 \, C_{\text{SS}} + 0.42 \, C_{\text{NS}} + 0.18 \, C_{\text{C}} + 0 \, C_{\text{S}} \pm 44 \]  
(4)

| COD Differences | Fraction |
|-----------------|----------|
| Sample I “wastewater” – Sample II “settled wastewater” | \( C_{\text{SS}} \) |
| Sample II “settled wastewater” – Sample III “settled and filtrate wastewater” | \( C_{\text{NS}} \) |
| COD in Sample IV “flocculated and filtrated wastewater” | \( C_{\text{S}} \) |
| COD in Sample I “wastewater” – \((C_{\text{SS}} + C_{\text{NS}} + C_{\text{S}})\) | \( C_{\text{C}} \) |

**Table 2. COD Differences.**

2.4. **Analytical methods**

Chemical oxygen demand (COD) analysis was carried out according to the Standard Method 5220 D: Closed-reflux, calorimetric method [8].

3. **Results and discussion**

3.1. **COD fractionation**

Figure 1 shows the initial COD percentage of wastewater from poultry processing industry. It is clear that in the wastewater sample from Advance Chicken Processing (M) Sdn. Bhd. particulate non-biodegradable COD is predominant (40%). It is followed by soluble biodegradable COD (33%) and particulate biodegradable COD (25%). On the other hand, initial percentage of soluble non-biodegradable COD is negligible (2%). This results indicate that the wastewater is containing higher percentage biodegradable COD (58%). Since it was in solid state and separable from the wastewater, the particulate non-biodegradable COD might be removed from the wastewater effluent through filtration, coagulation or flocculation technique. However, it is also possible to be removed through biodegradation when the biodegradability of this fraction is increasing. The soluble non-biodegradable COD had the lowest COD fraction, but it was able to bring enormous consequences to the environment as it will flow to the river as well as sea together with the treated wastewater. It is expected that ozonation treatment would transform both particulate and soluble non-biodegradable COD towards biodegradable constituent that can be easily removed by biodegradation.

![Figure 1. Initial COD fractionation of wastewater sample.](image-url)
3.2. Variation of solubility and biodegradability of wastewater after ozonation

Figure 2 depicts the transformation of COD fractions of poultry industrial wastewater after ozonation. At 5 min ozonation, the total COD was significantly decrease down from 1400 to approximately 1000 mg/L. It is observed that COD removal may contribute by the decrease in SS, XS and XI. In addition, the total COD removal efficiency was only increased slightly with the increased of the ozonation duration after 5 min. There was 30.37 % of total COD removal at the first 5 min of ozonation; however, only 39.85 % of COD removed after a 25 min of ozonation. This may be due to the fact that ozonation for long time would possibly producing constituent that inhibit ozone dissociation. Although the removal efficiency of COD was achieved the highest at the 25 min ozonation time, the trend of removal tend to be continue in longer ozonation time. However, the efficiency and cost of ozonation technique need to be considered.

Among the four COD fractionation, the SI had the highest removal efficiency which was 52.56 % when compared to SS, XS and XI with 47.39 %, 44.26 % and 30.43 % respectively. This result was satisfying as the SI will flow to the water surface with the ultimate effluent. The reduction of the soluble biodegradable COD fraction was able to prevent it to pollute our environment.

Through ozonation technique, the large molecular, non-biodegradable organic materials were able to break down into small molecular [9]. The ozonation technique was also able to improve treatability of refractory nature of the non-biodegradable organic pollutants as well as transformed non-biodegradable COD components to the biodegradable COD. According to Khan [10], ozonation was effective in improving the biodegradability of quaternary ammonium compound.

The reduction of XI after ozonation may be due to the fact that some of the XI components were transformed to particulate biodegradable. Theoretically, as some of the XI was transformed to XS, the XS amount should be increased. However, the experiment result showed that there was a decline in XS amount, this was due to that the ozonation able to mineralize the biodegradable matter in the wastewater. Ozonation was proved to mineralize the simple organic pollutants into the carbon dioxide gas (CO₂) and water (H₂O) and inorganic salts [11]. Besides, the oxidation of biodegradable COD will form the oxygenated organic products as well as low molecular weight organic acid. These organic acids were relatively contributed to the COD and it was easily biodegradable [6].

Similarly, the SI which consist of refractory materials may potentially break down and transformed to biodegradable components. Hence, there was a decrease in value of SI after ozonation. Ozonation was able to improve the bio-treatability of wastewaters containing non-biodegradable organics, which are toxic to common microorganism and yet it will not form hazardous by-product [12]. Due to this
reason, the ozonation reduce water pollution by transforming non-biodegradable pollutants toward biodegradable substances.

Next, the soluble biodegradable COD component was able to remove; hence, there was a decline in the SS when ozonation carried out. This proved that the ozonation technique able to mineralize the simple organic, biodegradable COD as well as degrade the colloidal and complex organic matter into the simpler organic biodegradable COD. In conclusion, the biodegradability of the wastewater is increased after the ozonation treatment.

Solubility was the ability of a substance to mix with the liquid. In COD fractionation, XS and XI had a low solubility. The removal efficiency of the XS and XI were 36.26 and 27.57% respectively after a 5 min ozonation. The reason of COD removal happened due to that the non-biodegradable COD was transformed to the biodegradable COD as well as the biodegradable COD was mineralized or broke into the small substances. The next possible reason was the particulate COD such as colloidal and suspended solid may oxidized and degraded to the smaller organic particles which were soluble in the wastewater. In conclusion, the solubility of the wastewater can be increased by the ozonation treatment.

Ozonation was believed to able to degrade the particulate COD to soluble COD as well as non-biodegradable COD. The processes were carried out simultaneously; hence, the reason was predicted. However, the particulate non-biodegradable COD was not a main issue for the wastewater treatment as they can be removed with the flocculation and coagulation process as well as the conventional biological treatment such as waste activated sludge process [13].

4. Conclusion

This research was carried out to investigate the effect of ozonation to the COD fractionation of wastewater from poultry processing industry. The conclusions that can be derived from this study are as follows:

- COD fractionation of poultry wastewater indicated that non-biodegradable COD is predominant compare to other fractions. However, the wastewater is containing higher percentage biodegradable COD comprehensively. It is expected that ozonation treatment would transform both particulate and soluble non-biodegradable COD towards biodegradable constituent that easily remove by biodegradation.
- The removal of COD was significant at ozonation duration up to 5 min. However, COD removal efficiency was only increased slightly with the increased of the ozonation duration after 5 min. This may be due to the fact that ozonation for long time would possibly producing constituent that inhibit ozone dissociation.

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