

Enhancing BOD₅/COD ratio co-substrate tofu wastewater and cow dung during ozone pretreatment

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Abstract. Ozonation pretreatment was applied to enhancing BOD/COD ratio co-substrate tofu wastewater and cow dung. Ozonation pretreatment were conducted at pH of 5.2, 8.0, and 10.0, with contact times of 20, 40, and 60 minutes. The results showed that the best condition for enhancing biodegradability is pH of 10 and contact time of 60 minutes with increasing BOD/COD ratio from 0.06 to 0.49, indicating an easy biodegradable substrate category.

1 Introduction

The ineffective tofu industry wastewater (TW) treatment can decrease surface water quality due to its containing protein, carbohydrate, and fat respectively 40-60%, 25-50%, and 10% [1, 2]. However, the low of soluble chemical oxygen demand (sCOD) concentration of the wastewater to be used in the study (3305 mg/L) makes anaerobic processing inefficient, where at least sCOD is required more than 4000 mg/L [3]. Therefore, to increase the value of sCOD, in this study the addition of cow dung (CD), which has a dissolved COD of 10,770 mg/L. However, cow dung is difficult to biodegrade because it contains cellulose, hemicellulose, and lignin respectively 25.2%, 18.6%, and 20.2% [1, 4].

The biodegradability of wastewater can be known through the BOD₅/COD ratio and wastewater characteristics test showed that the BOD₅/COD ratio of the mixture of tofu and cow dung wastewater was 0.063 and the BOD₅/COD ratio was <0.1 which indicated that the waste contained organic matter that was difficult to be biodegradable, could be toxic and non-biodegradable [5-8]. The minimum BOD₅/COD ratio in order to wastewater easily biodegradable is 0.4 [9], and the optimal ratio is more than 0.5 [10]. Therefore, it is necessary to pretreatment the waste so that the complex structure of decomposed organic compounds becomes simpler and easily broken down by bacteria. One of the pretreatment methods is the advanced oxidation processes using ozone which will oxidize complex organic compounds into simpler compounds so that the biodegradability of the waste will increase [11].

Some researchers have proven that the pH and contact time of ozonation can increase biodegradability level of waste from 0.05 to 0.32 [12] for kraft pulp wastewater; 0.06 to 0.32 for pulp and paper wastewater [13, 14]; 0.1 to 0.40 for hardwood kraft bleaching [15].

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Meanwhile, based on our best literature study the effect of pH and contact time of ozonation on the BOD₅/COD ratio of a mixture of tofu and cow dung liquid waste is unknown, so it needs to be studied. The study aimed to investigate the effect of pH of 5.2, 8.0, and 10.0 and contact time of 20, 40, and 60 minutes to determine the optimal pH and contact time for increasing BOD₅/COD ratio from co-substrate tofu wastewater and cow dung.

2 Materials and methods

2.1 Collection tofu wastewater and cow dung

The both of fresh tofu wastewater and cow dung was collected at tofu industry in Tampan Sub District of Pekanbaru City, Indonesia. Cow dung diluted using aquades at a ratio 1:2 (% , gr/gr) and the best ratio co-substrate tofu wastewater and cow dung for biogas formation of 50:50 (% , v/v) [16]. The characteristics of this substrate after mixing are shown in Table 1.

Tabel 1 Characteristics of substrate

Parameters	Co-substrates CD + TW
Soluble COD (mg/L)	16,845.51
Total COD (mg/L)	26,564.08
BOD (mg/L)	1681
pH	5.22
BOD/COD ratio	0.063

2.2 Operational reactor

Batch experiments were conducted in 500 mL Erlenmeyer with working volume 250 mL and operated at pH 5.2 (natural pH after CD and TW mixed), 8.0, and 10.0, and ozonization contact time of 20, 40, and 60 minutes. Reactor pH adjusted by 2 M HCl or 2 M NaOH. Ozone generator using ozonizer WS8801i and its productivity of 1.24×10^{-6} mg/min. The schematic experiment was shown in Fig 1.

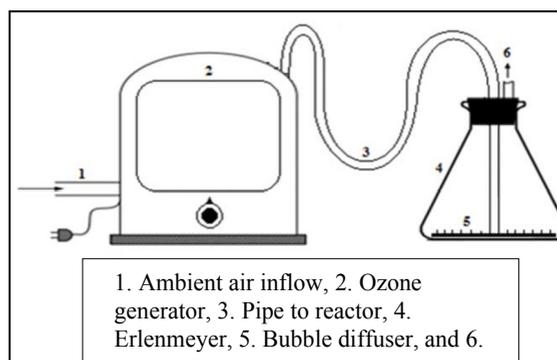


Fig. 1. Configuration of ozonisation CD and TW.

2.3 Analytical method

Ozone generation measurement by iodometry method [17] and COD and BOD analytics by SM 5520 and SM 5210 [18] respectively.

3. Results and discussion

3.1. pH vs contact time

Fig. 2 show of effect pH and contact time to total COD (Fig. 2a) and soluble COD (Fig. 2B) removal. Both total and soluble COD removal efficiency increased gradually in the following increasing pH and contacted time, and this results in-line with previous findings of [13, 14]. The longer the ozonation process, more O₃ will formed and amount of OH[°] and O₃ ions which oxidize organic substances in waste will be higher. The half-life of OH[°] is very fast, and prolongs ozonation contact time will maintain its existence so that the degradation process of organic compounds is more optimal [19, 21] or complex compounds will be more oxidized and will change in molecular weight to smaller one [21, 22].

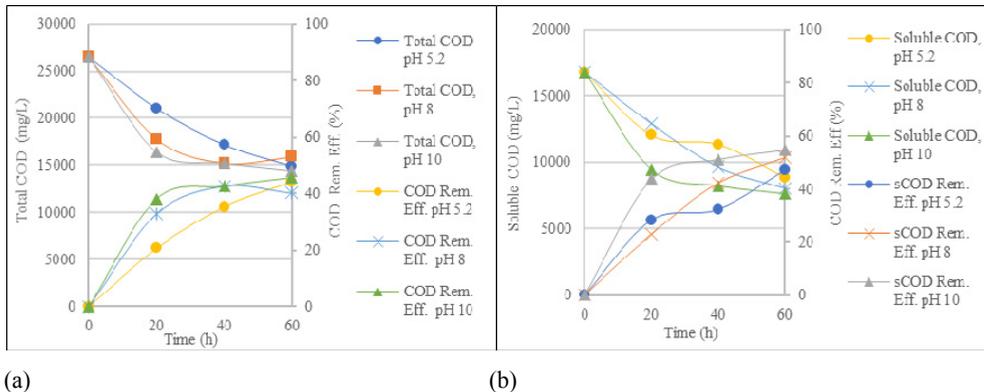


Fig. 2. Effect of pH and contact time to removal of total COD (a) and COD (b), and efficiency.

In this study, the highest percentage removal of total and dissolved COD occurred at pH 10. At alkaline pH (pH >8) the presence of OH⁻ acts as an initiator in the decomposition process of ozone to OH[°], in other words, the ozone solubility decreases with increasing pH [22]. When O₃ reacts with OH⁻, it will produce OH[°], O₂, and HO₂[°] in the waste. OH radicals are one of the strong oxidizing agents with the oxidation potential of 2.8 V and non-selective, so any compounds that are not oxidized by ozone will be oxidized by OH radicals. OH radicals react with dissolved components and produce a series of oxidation processes until components are minimized completely.

COD parameter decreased as the effect of the presence of OH radicals. COD which consists of organic and inorganic substances will be oxidized to CO₂ and H₂O. Oxidation process causes mineralization of organic components in the wastewater [8]. OH radical in this process was able to reduce COD with the highest values reaching 45.7% and 54.8%. At acidic pH the presence of OH⁻ is very low so that the formation of OH radicals is limited. The reaction occurs directly at acidic pH, where ozone reacts directly with organic compounds in the wastewater, but not all organic components can be completely oxidized by ozone because of its selectivity. Under acidic conditions, O₃ reacts with H⁺ to form HO³; then dissociates to form OH[°] and O² at a slow rate. For solutions with pH > 4 and < 10, both reactions occur directly and indirectly [24]. In this study ozonation at pH 5.22 and 8, the process occurs is directly and indirectly through the role of O³ and OH radical, therefore

difference in efficiency of COD reduction at that pH when compared to pH 10 does not look so significant. Percentage of dissolved COD removal at pH 5.22, 8, and 10 respectively were 47.4, 47.3, and 54.8%.

3.2. Effect pH and contact time to BOD₅/COD ratio

BOD is a characteristic that shows the amount of dissolved oxygen needed by microorganisms to decompose organic compounds in aerobic conditions. Boyd (1990) emphasized that organic matter decomposed in BOD is readily decomposable organic matter, even though it states the amount of oxygen used, but it can also be interpreted that BOD is an illustration of the amount of organic matter that is easily decomposed. Fig. 3 shows the relationship between pH and contact time in the ozonation process against waste BOD.

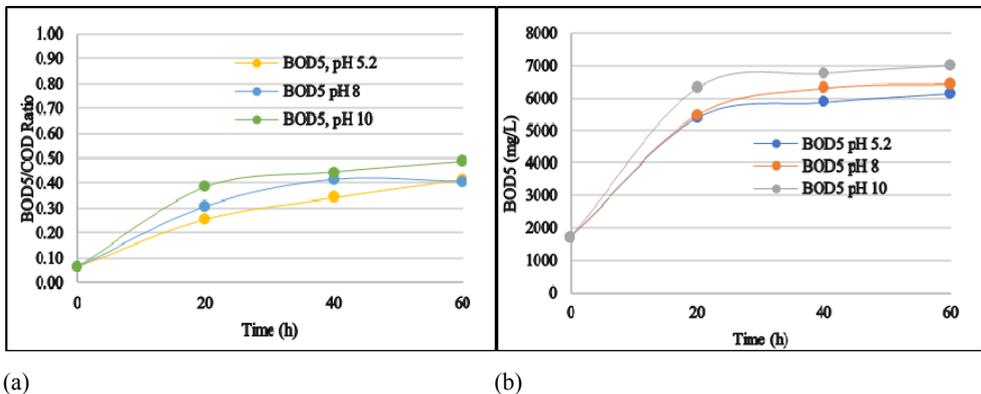


Fig. 3. Effect of pH and contact time to BOD concentration (a) and BOD/COD total ratio (b).

Fig. 3 shows that BOD percentage increases with increasing pH and ozonation contact time. That is because the longer time of ozone contact, more O₃ is formed and more organic compounds oxidized by ozone. The highest increase in BOD occurred in 60 minutes at pH 10 with reaching 76.02%. However, there was no significant increase in BOD at each pH. At 60 minute, pH 5.22 and 8, the increase in percentage BOD were 72.72 and 72.91% respectively. Increase in BOD caused by oxidation by O³ and OH radicals on compounds with long molecular chains (hard to decompose) which will be converted into compounds with shorter molecular chains (easily decomposed). Oxidation process at pH 10 is occurred by use of OH radicals, so that all organic compounds present in the waste are oxidized to simple compounds, at pH 5.22 and 8, oxidation process that occurs in both, namely by using O³ and OH radical, so the amount of organic compounds which decomposes into simple is also high. In this study, recalcitrant lignin to the biological degradation process is very easy to oxidize by ozone and OH radical. Lignin is composed of 3 types of phenylpropanoid compounds, namely coumaryl alcohol, coniferyl alcohol, and synapyl alcohol which are linked to carbon bonds (C-C) and ether bonds (COC) and have high molecular weight. All three were arranged randomly to form irregular lignin polymers.

Ozonation of lignin will change double bond in the conjugate chain to a single bond. Ozonation causes morphological changes to lignin layer so that the polymer chain broke to a hydroxyl group and induced by decreasing the bond number of the hydrogen chain [25]. According to [12], oxidation of lignin causes organic acid compounds such as muconic, maleic and oxalic acids will increase. Ozonation of protein compounds will increase the number of amino acid compounds such as cysteine, methionine, tryptophan, tyrosine, histidine, and phenylalanine [26]. Ozonation of carbohydrate compounds indirectly degrades carbohydrate compounds at a slow rate. However, decomposition products of

ozone OH radicals react quickly with carbohydrates, cellulose, and hemicellulose to increase the amount of glucose in the wastewater [27].

Oxidation process causes the formation of more biodegradable compounds, so BOD becomes higher than the initial BOD of the waste. According to Mtui (2001) decrease in COD accompanied by an increase in BOD will increase the ratio of BOD₅/COD waste. Based on Fig. 3b increase in BOD₅/COD ratio during ozonation is directly proportional to the increase in waste pH and time of ozone contact given. BOD₅/COD ratio before ozonation was 0.06, and increase to 0.49 during the ozonation process at pH 10 for 60 minutes. Decreasing COD and increasing BOD during the ozonation process indicate that the formation of biodegradable products [28]. Changes in biodegradability of these wastes are due to ozonation being able to change the structure of complex molecules from waste into simpler molecules [2]. Comparison effect ozonation to BOD₅/COD ratio showed in Table 2.

Table 2. Comparison ozonation process to increase BOD₅/COD ratio

Wastewater	Optimum condition	BOD ₅ /COD ratio	Ref.
Kraft pulp	pH = 12, t = 10 h	0.05 to 0.41	[12]
Pulp dan paper	pH = 7.5, t = 60 min	0.1 to 0.32	[14]
Pulp dan paper	pH = 9, t = 60 min	0.06 to 0.11	[13]
Hardwood kraft bleaching	pH = 11.7, t = 30 min	0.1 to 0.40	[15]
Tofu wastewater + cow dung	pH = 10, t = 60 min	0.06 to 0.49	This research

4 Conclusions

Based from the study above, it can be concluded that Ozonation process of co-substrate tofu wastewater and cow dung to increasing biodegability significantly influenced by pH process. Observation results showed increasing biodegradability were pH 10 > pH 8 > pH 5.2 with BOD/COD ratio respectively 0.49; 0.41; and 0.42 and all of it categorized as easily biodegradable for biological wastewater treatment process.

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