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Effectiveness of Ozonation Process on Treating Tofu Industrial Liquid Waste: Effect of pH Conditions

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Abstract. The tofu industries in Indonesia produce a considerable amount of liquid waste. Most of these tofu industries do not treat waste properly. Liquid waste is channeled directly to the nearest water stream, and thus the values of COD, BOD and TSS are considerably high, which can damage the aquatic ecosystems. According to the Indonesian government rule (Permen LH no.5/2014), the maximum levels of COD, BOD and TSS are 300 mg/L, 150 mg/L, and 200 mg/L. One of alternative methods to reduce these three parameters is the ozonation method. Ozone is able to break down organic components well because of its strong oxidative properties (2.07 mV) and it can decompose into OH radicals which have stronger oxidative properties (2.80 mV). The objectives of this study are to reduce the levels of COD, BOD and TSS of tofu liquid waste into below of the maximum level set by the Indonesian government rule and to study the effect of pH conditions on the effectiveness of ozonation process. Ozonation is carried out under conditions at acidic pH, alkaline pH, and neutral pH, and with a waste concentration of 10%. Ozonation is done by flowing ozone directly into the waste for 120 minutes with an interval of 30 minutes. The levels of BOD, COD, and TSS before ozonation were 1,200 mg/L, 880 mg/L and 600 mg/L. After ozonation, it was found that the levels of COD, BOD and TSS of the waste without any pre-treatment (or acidic condition) was able to be reduced by 46.6%, 44.5% and 41.6%, respectively. Whereas, in neutral conditions the decreases of COD, BOD, and TSS were about 64.3%, 67.0%, and 62.4%, respectively. Optimum ozonation was found in alkaline conditions with the decreases in COD, BOD, and TSS values were about 85.4%, 84%, and 100%, respectively.

Introduction

Tofu industries have been widely established in many regions in Indonesia. This is due to the high consumption of tofu in Indonesia which reaches 7.4 kg / person / year [1]. The tofu production process requires a lot of water, and thus there are a lot of liquid wastes produced. Tofu waste is one of the wastes that highly pollutes the environment. Several parameters that can describe the magnitude of the waste pollution are COD (*Chemical Oxygen Demand*), BOD *(Biological Oxygen Demand*), and TSS (*Total Suspended Solid*). In general, high COD and BOD indicate that organic components in waste are high. While, TSS level indicates that in addition to high organic components, there are also high suspended components such as dust or sand which can cause siltation in the waters. Organic components in tofu waste include carbohydrates, ammonia and phosphates [2]. High organic components can cause eutrophication in waters. A high BOD value will cause a decrease in oxygen dissolved in water, making it dangerous for aquatic ecosystems [3]. One of alternative methods for processing liquid waste is ozonation which is currently developing rapidly.

Ozone is a fairly strong oxidizer (E = 2.07 mV) compared to Hydrogen Peroxide (E = 1.78 mV), and under certain conditions ozone decomposes into OH radical with the highest oxidation potential compared to other compounds (E = 2.80 mV) [4]. Ozonation can take place in three conditions. First is direct ozonation which takes place under acidic conditions with ozone as oxidizer, secondly is ozonation with oxidizing ozone and OH radical which occurs under neutral conditions, and the third is ozonation with OH radical as oxidizer which takes place under alkaline pH conditions [5]. Ozone and OH radicals can reduce organic components in waste because they react with organic pollutants, degrade pollutants by breaking down molecules [6].

In the previous study, the reduction of BOD, COD, and TSS levels of tofu liquid waste has been carried out with a pool of biofilms with fish jar and bio-ball bio-filter media, but the efficiency of BOD reduction was below 50% [7]. Besides, it was also found that the parameters of COD, BOD, and TSS from processing tofu liquid waste with microorganisms still did not meet the levels set by the government law according to Minister of Environment Regulation No. 5 of 2014 (Permen LH no.5/2014) about Wastewater for Soybean Processing Business. This law explains that the maximum levels of COD, BOD, and TSS are 300 mg/L, 150 mg/L, and 100 mg /L, respectively [8, 9]. Previous ozonation tests on tofu waste have been done to reduce the levels of BOD, COD and TSS until they can be used as microalgae [10] growth media. In this study, the ozonation process was carried out using untreated tofu sewage under different pH conditions and duration time of 120 minutes to achieve a minimum level so that microalgae can survive.

In addition to being used for waste treatment, ozone has also been used for various purposes, including disinfection of Vibrio Vulnificus [5], and for the removal of *Escherichia Coli* bacteria by combining ozone and ultraviolet radiation as disinfectant in drinking water [11]. With the indication that there is a more effective treatment method in tofu waste treatment, the purpose of this study is to determine the optimum pH conditions of ozonation to reduce pollution levels in tofu waste including BOD, COD, and TSS to comply with the maximum level set by the Indonesian government law.

Experimental

Materials. Tofu liquid waste was obtained from the "UD Sumurrejo" tofu industry in Sumurrejo Sub-District, Gunungpati District, Semarang City, Central Java. The liquid waste is the result of final processing of tofu production. About 4.5 liters of liquid waste was taken. The liquid waste samples (at 10% waste concentration) were analyzed first to determine the levels of BOD (*Biological Oxygen Demand*), COD (*Chemical Oxygen Demand*), and TSS (*Total Suspended Soil*) before ozonation. The analysis of BOD, COD and TSS was carried out according to the Indonesian National Standard for testing these three parameters [12-14]. Table 1 shows the analysis results of BOD, COD, and TSS of the tofu liquid waste (at concentration of 10%) prior to the ozonation process. The table showed that the levels of BOD, COD and TSS were still above the maximum level set by the government.

Table 1 Pre-Ozonation Waste Test Results

Parameter	Standard of Government[9]	Content
COD	275 mg/L	560 mg/L
BOD	150 mg/L	400 mg/L
TSS	100 mg/L	250 mg/L

Ozonation process. Fig. 1 shows the schematic design of the ozonation reactor. Tofu liquid waste was put into 1 L beaker glass. The bubbling ball was used so that ozone is spread evenly throughout the beaker glass surface. The agitator stirring speed was set about 200 rpm. The ozonation process was carried out using Hanaco ozonator tsh-278 with an ozone concentration of 0.0325 g/h out for 120 minutes. The ozonation process was carried out under acid condition

(i.e. pH = 4), neutral (i.e. pH = 7), and alkaline (pH = 9). The pH of the tofu liquid waste during the ozonation process was controlled by adding NaOH 0.1 M. A little amount of each sample was taken every 30 minutes for analysis of BOD, COD and TSS.

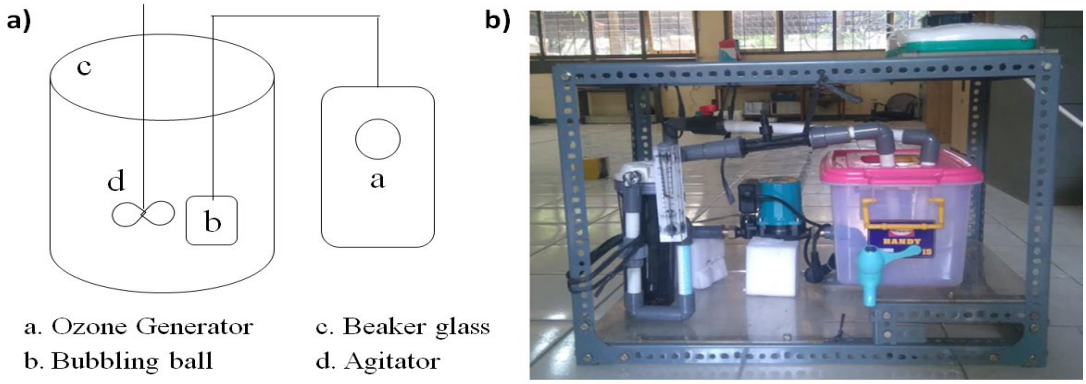

Fig. 1 a) Schematic design of ozonation reactor, and b) Appearance of ozonation reactor

Results and Discussion

Effect of pH on the ozonation process. Table 2, 3, and 4 shows the effect of pH during the ozonation process of tofu liquid waste on the values of COD, BOD, and TSS. Table 2 shows that ozonation process in alkali condition decreased COD, BOD and TSS about 85.4%, 84% and 100% respectively. Whereas in neutral pH condition (i.e. pH = 7) the decrease of COD, BOD and TSS was about 64.3%, 67.0% and 62.4% (see Table 3). Whereas, in acidic condition (i.e. pH = 4) or untreated waste the decrease of COD, BOD and TSS was about 46.6%, 44.5% and 41.6% (see Table 4). Based on those three tables, the most effective ozonation process occured in the alkaline condition. Under alkaline condition the degradation of organic components takes place most rapidly. It is because, in the alkaline condition, ozone will decompose into OH radical which has a greater reduction potential than other compounds (refer Equation (1) and (2):

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \quad (1)$$

$$O_3 + HO_2^- \rightarrow OH^* + O_2^{*-} + O_2 \quad (2)$$

Table 2 Ozonation Test Results on Acid pH

Time (minute)	COD (mg/L)	BOD (mg/L)	TSS (mg/L)
0	560	400	250
30	480	290	243
60	400	265	211
90	465	314	187
120	345	222	146

Table 3 Ozonation Tests on Neutral pH

Time (minute)	COD (mg/L)	BOD (mg/L)	TSS (mg/L)
0	560	400	250
30	280	209	170
60	360	281	134
90	247	186	116
120	200	13ta2	94

Table 4 Ozonation Test Results at Alkaline pH

Time (minute)	COD (mg/L)	BOD (mg/L)	TSS (mg/L)
0	560	400	250
30	683	448	102
60	213	103	63
90	123	78	21
120	82	64	0

In neutral pH conditions, the ozonation process was slightly better than the liquid waste condition without acid treatment (or pH conditioning) because under neutral conditions, OH radical also acts as an oxidizer together with the ozone. While at acidic pH only ozone is oxidizing, which has a smaller oxidation potential than OH radical (see Table 5).

Table 5 Compound Oxidation Potential Data[4]

Compound	Potential Oxidation (mV)
Florin	+3,06
OH Radicals	+2,80
Ozone	+2,07
Hydrogen Peroxide	+1,77
Permanganate	+1,67
Chlorine dioxide	+1,50
Hypochlorous Acid	+1,49
Chlorine Gas	+1,36

In acidic conditions, after OH radicals are formed, it reacts with carbonate and bicarbonate causing a chain reaction of ozone decomposition to be inhibited [15], so the amount of OH radicals decreases resulting in degradation of organic components under acidic conditions not as fast as alkaline or neutral conditions, the reaction is as follows:

$$OH^{*} + CO_3^{2-} \rightarrow CO_3^{*-} + OH^{-} \quad (3)$$

$$CO_3^{*-} + O_3^{*-} \rightarrow CO_3^{2-} + O_3 \quad (4)$$

Based on Tables 2, 3, and 4, the levels of BOD and COD experienced fluctuations at different times. In acidic conditions an increase in BOD and COD values in the 90 minutes, at a neutral pH at 60 minutes and alkaline at 30 minutes, but after that the BOD and COD levels again dropped until 120 minute. This fluctuation is due to unstable ozone certain ozone will decompose to hydrogen superoxide. After decomposing into hydrogen superoxide, this compound will react with ozone again and hydroxyl radicals or OH ozone radicals will form which will oxidize organic compounds quickly. In an ozone base atmosphere decomposes rapidly to form OH radicals because there are many hydroxide ions which act as initiators in ozone decomposition while acidic conditions occur at the latest due to the absence of hydroxide ions, but there are carbonate (CO_3^{2-}) and bicarbonate (HCO^{3-}) ions such as on the reaction equation (3) and (4) due to high alkalinity under acidic conditions [15]. Whereas in neutral conditions the hydroxide ions contained in the sample are not as much as those in alkaline waste conditions.

Ozone is not only able to oxidize dissolved organic compounds as mentioned above, but is able to oxidize suspended organic compounds. Suspended organic compounds in tofu waste come from

the screening process after the milling and cooking process of soybeans. This is proven by research that has shown that ozone can reduce total dissolved solids (TSS). TSS levels drop because during the ozonation process, small solids will form ozone-triggered floc because ozone has the effect of being flocculant [16]. Floc can be separated from waste by filtering, then drying until it gets a constant weight to find out the total suspended solids in the waste sample. From the research that has been done, it is proven that ozone can degrade organic components well, pH conditions greatly affect the ozonation process itself. The longer the ozonation time, the better the ozonation process due to continuous ozone supply makes component degradation faster.

Conclusion

The levels of COD, BOD and TSS of tofu waste before ozonation are still above the maximum level set by the Indonesian government rule (i.e. Permen LH no.5/2014) concerning Waste Water for Soybean Processing Enterprises. The optimum ozonation of tofu industry wastewater occurs at alkaline pH conditions within 120 minutes, followed by neutral pH and acid pH within 120 minutes. Ozonation process in alkali condition decreased COD, BOD and TSS about 85.4%, 84% and 100% respectively Ozone is unstable, at certain times ozone will decompose into OH radical. During the decomposition process, before OH is formed radicals will form superoxide hydrogen which causes fluctuating levels of BOD and COD. Ozone has an effect as flocculant so that it can degrade suspended organic compounds by forming floc, so that suspended solids can be separated from waste water.

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