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TOFU INDUSTRIAL WASTEWATER TREATMENT WITH OZONATION AND THE ADSORPTION METHOD USING NATURAL ZEOLITE

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ABSTRACT

Tofu industrial wastewater is usually disposed of directly without undergoing waste treatment, a process that endangers the environment. The amounts of chemical oxygen demand (COD) and total suspended solids (TSS) in the wastewater exceed the maximum levels determined by the government of Indonesia. Ozonation and adsorption are well-known methods that can effectively degrade organic and inorganic compounds in wastewater. In this research, the removal of COD and TSS from tofu industrial wastewater was examined through the use of the ozonation method, the adsorption method using natural zeolite, and both methods combined. The sample was passed into a packed-bed column containing natural zeolite and ozone used for about 60 minutes. The effectiveness of the method was evaluated by COD and TSS degradation, with varying dosages of ozone and amounts of natural zeolite (50 g, 75 g, and 100 g). The best result was achieved by using a combination of ozonation and adsorption, with 100 g of zeolite and an ozone dosage of 155.1 mg/h, which achieved 219.4 mg/L and 25 mg/L removal COD and TSS, respectively.

Keywords: Adsorption; COD; Ozonation; Tofu; TSS

1. INTRODUCTION

Tofu is a popular traditional food in Indonesia. This has led many Indonesians to run home-based tofu businesses with traditional technology, resulting in a relatively high amount of waste. There are two types of tofu waste: solid and liquid. The solid waste is usually reprocessed into animal food, while the liquid waste is disposed of directly into the environment without undergoing a waste treatment process, which can pollute the ecosystem. The amount of liquid waste from the tofu industry is quite high compared to solid waste because almost every process involved uses water; one kilogram of tofu raw material requires 45 liters of processing water, resulting in 43.5 liters of tofu wastewater. *Dinas Lingkungan Hidup* DKI Jakarta reported that the average amounts of chemical oxygen demand (COD) and total suspended solids (TSS) in tofu industrial wastewater are high, at 8,640 and 2,350 mg/L, respectively. These amounts exceed the maximum levels determined by the government, which is 100 mg/L for COD and 200 mg/L for TSS.

Tofu industrial wastewater can be treated using the Advanced Oxidation Processes (AOPs) technique, which combines the ozonation and adsorption methods using natural zeolite. Ozonation is a well-known method that can degrade and reduce the toxicity of organic and inorganic compounds. Ozone can easily decompose to hydroxyl radicals, which can eliminate pollutants in wastewater (Derco et al., 2015; Desmiarti et al., 2019). The addition of adsorbent to this process can also increase hydroxyl radical production, resulting in more effective and faster oxidation of organic compounds (Fujita et al., 2004; Zhang et al., 2016; Ghuge & Saroha, 2018).

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Zeolites have been widely used as an adsorbent or catalyst because of their non-flammability and thermal stability (Zaitan et al., 2016; Hidayat et al., 2018). Zeolites can function as adsorbents and catalysts because they are safe to use in catalytic oxidation processes operating at high temperatures. Ikhlaq and Kasprzyk-Hordern (2017) studied the removal of volatile organic compounds (VOC) by catalytic ozonation process using γ-alumina and ZSM-5 zeolite. They found that zeolites promoted the decomposition of VOCs. The presence of hydroxyl radical scavengers had no significant effect on the removal rates of VOCs and the generation of chlorides in the presence of zeolites. Ikhlaq and Kasprzyk-Hordern suggested that catalytic ozonation of organic VOCs on zeolites proceeds via a non-radical mechanism that involves reactions of molecular ozone with pollutants adsorbed on the surface of zeolites (Iklaq & Kasprzyk-Hordern, 2017).

In the present study, the effectiveness of COD and TSS removal from tofu wastewater was analyzed by the ozonation method, the adsorption method using natural zeolite, and both combined. To find the optimum conditions for these methods, ozone dosages and amounts of zeolite were varied. The parameters evaluated were COD and TSS content before and after treatment and the formation of hydroxyl radicals.

2. METHODS

2.1. Ozone Production Rate

To know the dosage of ozone from the ozonator, the ozone production rate was needed. This rate was calculated using the iodometry titration method. 200 mL of potassium iodide (KI) 0.1 M were inserted into an ozone bubbler already connected to the outlet of the commercial ozonator for 60 minute at 20 minute intervals. Subsequently, 25 mL of KI that had been reacted with ozone was titrated with sodium thiosulfate ($Na_2S_2O_3$) 0.01 M until it became colorless. The production rate of ozone can be calculated using the equation below:

$$O_3\ Production\ \left(\frac{mg}{hour}\right) = \frac{1}{2}x\frac{V_{Na_2S_2O_3}\ x\ M_{Na_2S_2O_3}\ x\ Mr_{O_3}}{2\ x\ t(minutes)}x\frac{60\ minutes}{1\ hours}x\frac{200\ mL}{25\ mL} \tag{1}$$

2.2. Preparation of Natural Zeolite

The natural zeolite was activated thermally using heat from the oven. It was crushed and sieved to obtain a uniform size (1.7–3 mm in diameter), washed with demineralized water, rewashed with boiled demineralized water for 30 minutes, then filtered to remove any inorganic impurities. The zeolite was then dried at 200°C for four hours. Its surface area and pore volume before and after activation can be evaluated using the Brunauer-Emmett-Teller (BET) Autosorb.

2.3. Calculation of Hydroxyl Radical Production

Calculation of the hydroxyl radicals was carried out to establish how many were formed by the various process configurations used, employing the permanganometry titration method. Aquades with a pH similar to tofu wastewater (pH = 3.7) were used as samples; pH 3.8 is the pH of tofu wastewater. 5 L of aquades were poured into the packed-bed column, which contained natural zeolite. Ozone was then injected into the system for 60 minutes. 10 mL of the sample were titrated with potassium permanganate ($KMnO_4$) 0.0001 M until it changed color from clear to slightly pink. The hydroxyl radicals formed were calculated at 15, 30, 45, and 60 minutes, using the equation below:

$$OH\ Radicals\ \left(\frac{mg}{L}\right) = \frac{3\ x\ V_{KMnO_4}\ x\ M_{KMnO_4}\ x\ Mr_{OH}}{V_{sample}\ (mL)}x\frac{1000\ mL}{1\ L} \tag{2}$$

2.4. Tofu Wastewater Treatment

The treatment of tofu wastewater was conducted by the ozonation method, the adsorption method using natural zeolite, and a combination of both methods. For the ozonation method, the dosage of ozone varied (62.21 mg/h, 110.88 mg/h, and 155.1 mg/h), whereas in the adsorption method the mass of natural zeolite varied (50 g, 75 g, and 100 g) to achieve the best COD and TSS removal results. A combination of the ozonation and adsorption methods was also employed, using the best results obtained from the single methods to lower COD and TSS levels.

Before treatment, five liters of tofu wastewater were filtered using a 400-mesh filter to remove large particles. In the ozonation method, filtered wastewater flowed from the reservoir tank into the column at a flow rate of 1.5 L/minute for 60 minutes, allowing the COD and TSS removal to be examined. This procedure was repeated for the different ozone dosages.

In the adsorption method, five liters of wastewater flowed from the reservoir tank into the packed-bed column, which already contained natural zeolite, at a flow rate of 1.5 L/minute for 60 minutes. 10 mL samples were then taken at 15, 30, 45, and 60 minutes to establish the level of COD and TSS removal. This procedure was repeated for different amounts of zeolite.

In the combined ozonation and adsorption method, the procedure was a combination of the two single methods. COD content was examined using Ultraviolet-Visible Spectrophotometry (UV-Vis) at a wavelength of 600 nm, while the TSS content was examined using a HACH Colorimeter. The instrumentation used to experiment is shown in Figure 1.

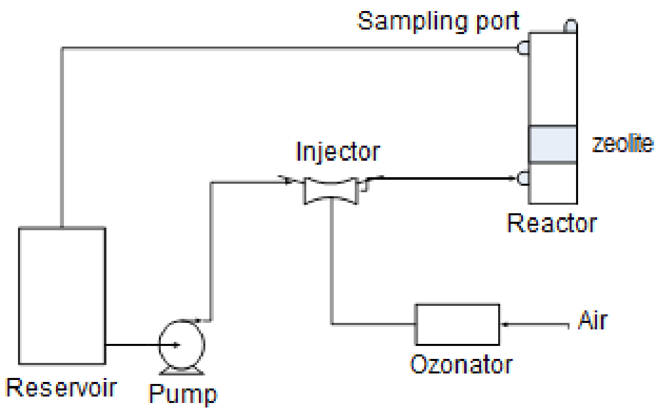

Figure 1 Experimental instrumentation

3. RESULTS AND DISCUSSION

3.1. Ozonator Production Rate

The results of the average ozone production were 62.21 mg/h for one ozonator, 110.88 mg/h for two ozonators, and 155.1 mg/h for three ozonators. It can be observed that the configuration with three ozonators had the highest ozone production, followed by two ozonators and one ozonator. In the configuration with three ozonators, the electric voltage received by the ozonator was greater than the other configurations, resulting in a higher level of conversion of air into ozone. Therefore, the results indicate that merging two or three commercial ozonators can produce a higher ozone dosage.

3.2. Analysis of Hydroxyl Radicals Production

Figure 2 shows the results and correlations between the processing time and hydroxyl radical production in each configuration process. Based on these figures, it can be seen that all the configurations produced the same result, which was an increase in hydroxyl (OH) radicals concentration in line with the processing time. This was due to the accumulation of ozone injection, resulting in a higher level of ozone in the system, which produced more OH radicals. It can also be observed that the configuration with the 155.1 mg/h ozone dosage and 100 g zeolite achieved higher hydroxyl radical production than the other configurations: 2.75 mg/L, compared to 0.96, 1.3, 1.78, 2.39, and 2.6 mg/L. This was because the higher ozone dosage and amount of zeolite in the system resulted in more OH radicals being formed because the adsorption capacity of ozone on zeolite increased. This increase in turn accelerated and multiplied the decomposition of ozone to form OH radicals. Moreover, these results show that the presence of zeolite in ozonation can decompose ozone to OH radicals and can speed up the reaction by cracking and maintaining ozone stability in water (Fujita et al., 2004; Nawrocki & Kasprzyk-Hordern, 2010).

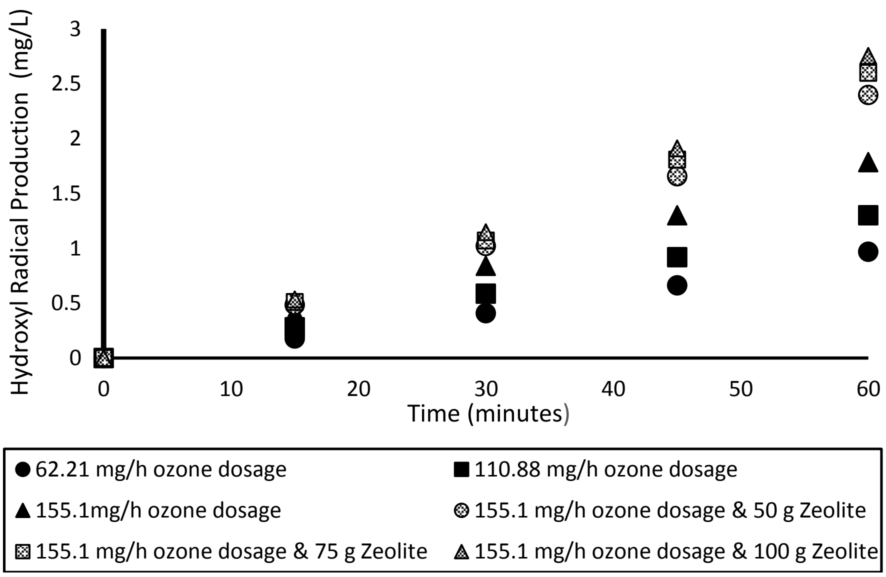

Figure 2 Production of hydroxyl radicals in each configuration process (pH 3.8, flow rate 1.5 LPM)

3.3. Effect of the Ozonation Method on COD and TSS Content

Figures 3 and 4 show the results of COD and TSS removal in each ozone dosage variation. Based on the figures, it can be seen that all the configurations produced the same result, which was a decrease in COD and TSS content, in line with the processing time.

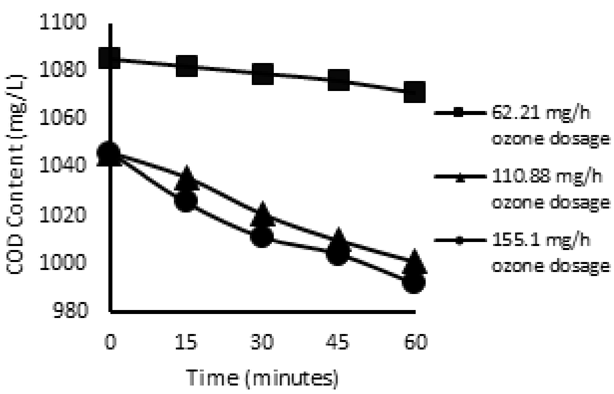

Figure 3 COD removal in the ozonation method process (pH 4.6, flow rate 1.5 LPM)

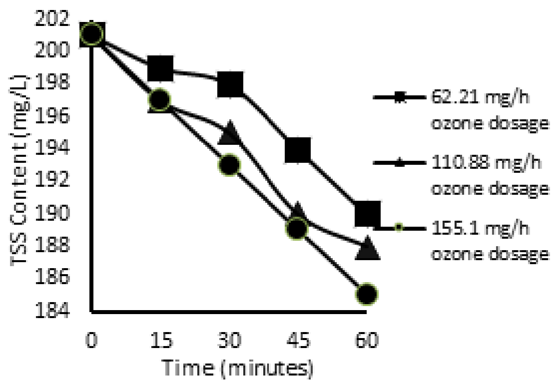

Figure 4 TSS removal in the ozonation method process (pH 4.6, flow rate 1.5 LPM)

The decrease in COD content is because ozone reacts very selectively through electrophilic, nucleophilic, or cyclo formation by its diplo and easily decomposes to form hydroxyl radicals (Gomes et al., 2017). Therefore, during the process of COD removal, the organic and inorganic contaminants preferred by ozone will be oxidized into simpler compounds, thus reducing the need for dissolved oxygen in wastewater. Moreover, ozone also decreases TSS content. It acts as a coagulant agent, which helps to agglomerate suspended solids, resulting in lower TSS content (Gomes et al., 2017). The configuration with an ozone dosage of 155.1 mg/h produced the best COD and TSS removal result, with 54.36 mg/L for COD and 16 mg/L for TSS, while the ozone dosages of 62.21 mg/h and 110.88 mg/h achieved 14.11 mg/L and 45 mg/L, respectively, for COD removal and 11 mg/L and 13 mg/L, respectively, for TSS removal in 60 minutes. This was because the configuration with 155.1 mg/h had higher ozone production, leading to more ozone reacting with the contaminants.

3.4. Effect of the Adsorption Method on COD and TSS Content

Figures 5 and 6 show the results of COD and TSS removal with the adsorption method. Based on the figures, it can be seen that all the configurations produced the same result, which was a decrease in COD and TSS content in line with the processing time for each variation of the zeolite level. The decrease in COD content is caused by zeolite's large number of pores and surface area, which can absorb organic and inorganic compounds in wastewater (Yousef et al., 2011; Ikhlaq et al., 2014). It can be observed that adsorption with 100 g of zeolite produced better COD and TSS removal results than 50 and 75 g of zeolite. After 60 minutes, the amounts of COD and TSS removal with 100 g of zeolite were 99.62 mg/L and 23 mg/L. On the other hand, COD removal with 50 g and 75 g of zeolite was 51.4 mg/L and 86.58 mg/L, respectively, while TSS removal with 50 g and 75 g of zeolite was 8 mg/L and 19 mg/L, respectively. These results show that increasing the amount of zeolite leads to a larger adsorption surface area, thus lowering the level of COD in wastewater.

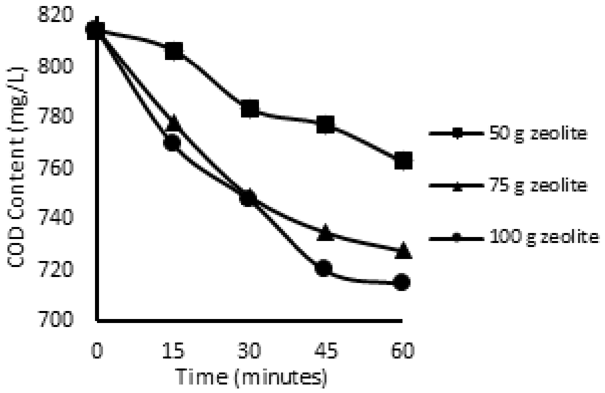

Figure 5 COD removal in the adsorption method process (pH 5.1, flow rate 1.5 LPM)

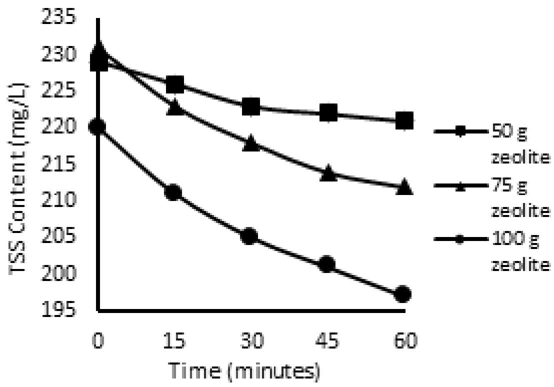

Figure 6 TSS removal in the adsorption method process (pH 5.1, flow rate 1.5 LPM)

3.5. Effect of the Combined Ozonation and Adsorption Method on COD and TSS Content

Figures 7 and 8 show the results of COD and TSS removal with a combination of ozonation, with an ozone dosage of 155.1 mg/h, and adsorption, with 100 g of zeolite. Based on the figures, it can be seen that the combined method lowered COD and TSS content in line with the processing time. COD and TSS removal with this method were 219.4 mg/L and 25 mg/L, respectively, in 60 minutes. The decrease in COD results from the presence of zeolite, which not only absorbs the organic and inorganic pollutants in wastewater but also optimizes COD removal by accelerating the decomposition of ozone into hydroxyl radicals (Ikhlaq et al., 2012; Ikhlaq & Kasprzyk-Hordern, 2017). Zeolite will adsorb and dissolve ozone. Ozone on the surface of the zeolite then forms O (oxygen) and OH radicals, which oxidize the organic and inorganic pollutants in wastewater (Valdés et al., 2009; Ikhlaq & Kasprzyk-Hordern, 2017;). Also, the combination of ozonation and adsorption can immediately agglomerate and adsorb suspended solids, so TSS content decreases. Therefore, the results indicate that combining ozone, hydroxyl radicals, and zeolite can degrade the pollutants in wastewater, lowering COD content.

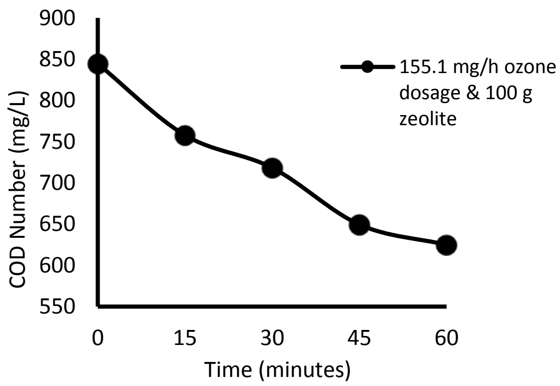

Figure 7 COD removal in the ozonation and adsorption method (pH 5.6, flow rate 1.5 LPM)

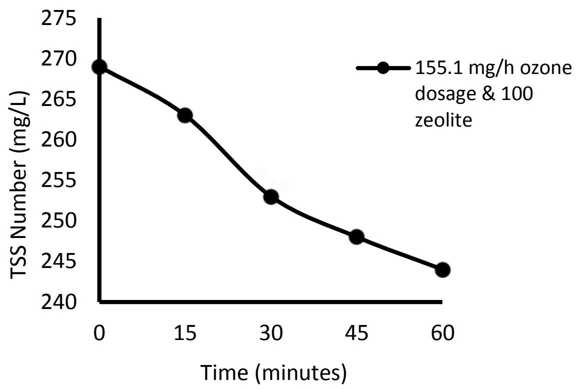

Figure 8 TSS removal in the ozonation and adsorption method (pH 5.6, flow rate 1.5 LPM)

3.6. Zeolite Characterization

In zeolite treatment, the process of washing and heating natural zeolite can increase the BET surface from 39.22 m^2/g to 47.85 m^2/g and the BET pore volume from 0.0822 cm^3/g to 0.0938 cm^3/g. It can be observed that the process of washing and heating at 200^{o}C can increase the surface area of zeolite by 8.63 m^2/g and its pore volume by 0.0116 cm^3/g. These results show that the zeolite activation process removed the impurities that covered the pore surface of the zeolite, increasing its adsorption capacity and ability to reduce pollutants, and helping to increase the formation of hydroxyl radicals. After the process, the BET surface area fell from 47.85 m^2/g to 43.82 m^2/g, and BET pore volume also decreased from 0.0938 cm^3/g to 0.0892 cm^3/g. These results indicate that zeolite adsorbed the organic and inorganic compounds in the wastewater, which decreased the size of the surface area and the pore volume. This result was in line with Ikhlaq and Kasprzyk-Hordern's research (2017), which shows that catalytic ozonation on zeolite can take place through a non-radical mechanism that involves reactions of molecular ozone with pollutants adsorbed on the surface of zeolites.

4. CONCLUSION

The removal of COD and TSS from tofu wastewater is influenced by ozone dosage and the amount of zeolite. A combination of the ozonation and adsorption methods using natural zeolite is very effective in removing COD and TSS compared to the single ozonation and adsorption methods. It was found that the best condition for decreasing COD and TSS levels was achieved using an ozone dosage of 155.1 mg/h and 100 g of zeolite, which resulted in COD and TSS removal of 219.4 mg/L and 25 mg/L, respectively, after 60 minutes. This indicates that combining ozone and zeolite can improve organic and inorganic compounds removal in tofu wastewater.

5. ACKNOWLEDGEMENT

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