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Oxidation Process of $\text{H}_2\text{O}_2$/UV for COD Reduction of Wastewater from Soybean Tofu Production

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Abstract

Chemical Oxygen Demand (COD) reduction of wastewater from soybean tofu production was studied by conducting advanced oxidation process (AOP) using hydrogen peroxide with UV radiation catalysts in a closed cylindrical glass reactor. The hydroxyl radical (*OH) concentration from $\text{H}_2\text{O}_2$ decomposition was modeled, and exponential trends were found for the *OH concentration over radiation time and operation temperature. As a result, it was found that the maximal *OH concentration was 0.209 mol L$^{-1}$ at 240 minutes and 50 °C. The *OH concentration exponentially increased following rise in operation temperature. The $\text{H}_2\text{O}_2$/UV AOP application reduced COD concentration to approximately 42.41% from 10,545 to 6,073.2 mol L$^{-1}$ at 240 minutes and 50 °C. In addition, the pseudo second order kinetics is a reliable model to present the COD reduction kinetics with the correlation coefficient $R^2$ in the range of 95.9 to 99.4%. The kinetics constant increased with rise in operation temperature, and it was approximately 2.30E-07, 2.590E-07, and 3.03E-07 L mg$^{-1}$min$^{-1}$ for 30, 40, and 50 °C, respectively. The activation energy of COD reduction obtained was approximately 0.0138 J mol$^{-1}$.

Keywords: COD reduction, hydroxyl radical, oxidation, radiation, kinetics, modeling

1. Introduction

Among others, soybean tofu is the most preferred tofu by the majority of Indonesians. To meet the demands for tofu in Indonesia, there were approximately 84,000 tofu factories, ranging from home-scale to big-scale factories in Indonesia. The factories are generally located in residential areas, and unfortunately there is no wastewater treatment scheme available. The wastewater, called whey, discharged to the open channel in urban areas with high population density. Meanwhile, the total consumption of soybean for tofu has been predicted to be 2.5 million ton per year. This soybean consumption resulted in approximately 20 million m$^3$ per year of untreated wastewater [1]. Another study showed that 1 ton of soybean used for
 tofu production is equal to about 1,400 m³ per year untreated wastewater. Chemical Oxygen Demand (COD), which is one of the contamination parameters of the untreated wastewater, was varied in the range of 8,556-21,889 mg/L [2]. The COD values are absolutely much far from and exceeding the WHO standard [3]. Because most of the tofu factories dispose their wastewater directly into the environment, the tofu industry in Indonesia is still doing environmentally damaging production practices, and chemical process would be needed to deal with this problem.

There are many chemical processes that can be used for the treatment of wastewater. One of the chemical processes is known as advanced oxidation processes (AOPs) [4-6]. AOPs are well known as the oxidation processes based on the generation of hydroxyl radicals. Hydroxyl radical is one of the most reactive free radical and has a high electrochemical oxidant potential. It is the main reactive species, and it reacts with organic pollutants and governs the degradation of the pollutants by attacking and breaking the molecules down [7,8]. Most AOPs methods are coupled with the strong oxidants of hydrogen peroxide, oxygen, or ozone with the catalysts of UV radiation, irons, transition metals, semiconductor powders, or ultrasound. The methods can be written as H₂O₂/UV, TiO₂/UV, TiO₂/H₂O₂/UV, H₂O₂/Fe(II), O₃/UV, and O₃/H₂O₂/UV [7,9,10]. Controlling various contaminants, both organic and inorganic chemicals in industrial wastewater had been investigated, and ultraviolet light coupled with hydrogen peroxide (UV/ H₂O₂) had been applied among other AOPs [11-13].

Even if the application of advanced oxidation processes for the treatment of wastewater is not new, there is a limited number of studies on the AOPs application on the treatment of wastewater from soybean tofu production, especially using the strong oxidant of hydrogen peroxide with UV radiation catalysts. Therefore, this study aims to investigate the reduction of COD from soybean tofu production wastewater by conducting advanced oxidation process using hydrogen peroxide with UV radiation catalysts. The effects of manipulated variables, such as the time and temperature of UV radiation and oxidation on the transformation of hydrogen peroxide into hydroxyl radical and COD reduction, were investigated in a bath reactor. In addition, oxidation reaction kinetics was studied using the experiment data, and kinetics model and activation energy of COD reduction were obtained.

2. Methods

Material. A sample of fresh soybean tofu production wastewater (whey) was collected from a tofu factory in Banda Aceh, Indonesia. To minimize the decomposition of whey substrate during collecting and travelling from the factory to the Kinetics and Catalysis Laboratory in Chemical Engineering Department Syiah Kuala University, it was put in sample bottles with lead. Then, the sample bottles were kept in an icebox. Centrifuge was used to separate solid and liquid of the wastewater.

Advance oxidation process of H₂O₂/UV. Batch experiment of H₂O₂/UV advance oxidation process took place in a closed cylindrical glass reactor (Ace Glass Incorporated, Vineland NJ USA) with internal diameter of 8 cm, height of 30 cm, and a total liquid volume of 1.5 L. The reactor was filled with 1 liter working volume of liquid (wastewater and hydrogen peroxide). Twenty milliliters of hydrogen peroxide (30% w) was dropped at a closeable hole on the reactor lead. The reactor was placed on a hot plate magnetic stirrer (Barnstead International, Mode: No.S131120-33) at 50 rpm and 30 °C operation temperature. A 15 W UV lamp (Sen Light Corporation, UVL15D model, λ=254 nm, a straight tube type LP Hg lamp) was vertically put in the center of the reactor to supply UV light. Using a variable volume pipette, 5 and 2 ml samples for H₂O₂ and COD analysis respectively were taken before dropping hydrogen peroxide (radiation time equal to 0 minute), and at the radiation time of 5, 15, 30, 45, 60, 120, 180, and 240 minutes. The experiment was repeated for the operation temperature of 40 and 50 °C.

H₂O₂ and COD analysis. Determination of the concentration hydrogen peroxide was done using titrimetric analysis method. The concentration of hydrogen peroxide was immediately determined after sampling at the total radiation time of 0, 5, 15, 30, 45, 60, 120, 180, and 240 minutes The fresh pipette 5 ml sample was put into a 250 ml Erlenmeyer. The sample was added with 1 drop of Ferro indicator. Then, the sample was titrated with a CeSO₄ solution of 0.1 N to achieve the endpoint of the titration which was indicated by a color change of the sample from the solution from orange to light blue. When light blue was reaching steady state condition, the titration was stopped, and the CeSO₄ solution volume used was noted. The concentration of hydrogen peroxide was obtained based on the CeSO₄ solution volume used.

3. Results and Discussion

The effect of radiation time on H₂O₂ decomposition. In advance oxidation process of H₂O₂/UV, it is critical to know the hydrogen peroxide concentration since hydroxyl radical (·OH) is the hydrogen peroxide transformation product from direct photolysis of H₂O₂ under UV radiation as the catalyst. The decomposition of hydrogen peroxide is presented in Equation (1) [14]:

$$H_2O_2 \xrightarrow{UV} 2*OH$$  \hspace{1cm} (1)

As a result of direct photolysis of H₂O₂ with UV catalyst, hydrogen peroxide decomposes by which the concentration of hydrogen peroxide decreases with the increase in radiation time, as seen in Figure 1.
It is important to note that hydrogen peroxide transformed very fast from approximately 0.176 mol/L to 0.068 mol/L in the first 5 minutes of radiation time with operation temperature of 30 °C. It was about 0.057 and 0.054 mol/L with operation temperature of 40 and 50 °C respectively at 5 minutes radiation time. Then, the concentration of hydrogen peroxide gradually decreased over radiation time after 5 minutes. Overall, the concentration of hydrogen peroxide decreased exponentially over radiation time.

**Effect of temperature on H$_2$O$_2$ conversion.** As stated in the previous literatures, hydroxyl radical is the product of hydrogen peroxide UV radiation [11-14]. The conversion of hydrogen peroxide to hydroxyl radical can be worked out both from the increase of hydroxyl radical concentration and the decrease of hydrogen peroxide concentration in the liquid. However, hydrogen peroxide concentration was obtained using titrimetric analysis method in this study, and hydroxyl radical was not analyzed. The conversion of hydrogen peroxide into hydroxyl radical was calculated in % M (mol/L) and plotted in Figure 2.

As illustrated in Figure 2, the hydrogen peroxide conversion moderately increased from about 61.3 to 67.6% for the increase in operation temperature from 30 to 40 °C at 15 minutes of radiation time. Then it slowly increased to approximately 69.3% at 50 °C of operation temperature. The same trends also took place for 15 to 240 minutes of radiation time as shown in Figure 2. For example, it was approximately 64.7, 71.0, and approximately 72.1% for operation temperature of 30, 40, and 50 °C respectively at 45 minutes of radiation time; and it was approximately 68.7, 76.1, and 77.2 respectively at 240 minutes of radiation time. Overall, the conversion of peroxide exponentially increased following higher operation temperature.

**Modeling concentration of hydroxyl radical.** Because hydroxyl radical is the product of hydrogen peroxide transformation, the concentration of hydroxyl radical can be modeled and predicted using the conversion value and the total value of H$_2$O$_2$ decomposition at a steady state condition wherein the concentration of hydrogen peroxide in the liquid is unchanged with time. Even if a steady state condition was reached in the H$_2$O$_2$ decomposition presented in Figure 1, the change in hydrogen peroxide concentration was very small in the last 120 minutes leading to a steady state condition.

An assumption of total decreased H$_2$O$_2$ concentration as steady state value was made, generation of the hydroxyl radical followed Equation (1), and the concentration of hydroxyl radical formed could be predicted using the conversion. The predicted hydroxyl radical concentration is shown in Figure 3. As expected, the $^•$OH concentration sharply increased from 0 to 0.148, 0.181, and 0.188 mol/L at 5 minutes radiation time for the operation temperature being 30, 40, and 50 °C respectively. Following this radiation time, the $^•$OH concentration slowly increased leading to exponential trend.

The effect of operation temperature is also clearly shown in Figure 3. The $^•$OH concentration at 5, 15, 30, 45, 60, 120, 180, and 240 minutes radiation time was approximately 0.148, 0.151, 0.154, 0.157, 0.158, 0.162, 0.164, and 0.166 mol/L respectively for the operation temperature of 30 °C; it was approximately 0.181, 0.184, 0.187, 0.19, 0.192, 0.195, 0.199, and 0.204 mol/L respectively for operation temperature of 40 °C; and it was approximately 0.188, 0.191, 0.193, 0.196, 0.198, 0.202, 0.207, and 0.21 mol/L respectively for the operation temperature of 50 °C. Calculated based on $^•$OH concentration, increasing operation temperature from 30 to 40 °C resulted in approximately 21.63% increase of $^•$OH concentration on average. In addition, it was 25.89% when the operation temperature changed from 30 to 50 °C, meaning
that it was only 4.26% increase in \(^*\)OH concentration for 10 °C increase in operation temperature from 40 °C. It seemed that the increase in \(^*\)OH concentration would be smaller and smaller for the next 10 °C increases in operation temperature. Hence, further research would be needed to clearly see the increase trend.

**Effect of Reaction time on COD Reduction.** The formation of hydroxyl radical highlighted in the previous discussion was reasonable because it was found that COD reduced over reaction time in the reactor wherein \(\text{H}_2\text{O}_2/\text{UV} \) advance oxidation process took place. As can be seen in Figure 4, the COD concentration increases moderately over reaction time, which was approximately 10478.3, 10345.2, 10156.2, 9967.2, 9636.5, 8313.6, 7534.1 and 6754.4 mg/L at the reaction time of 5, 15, 30, 45, 60, 120, 180, and 240 minutes respectively for 30 °C of operation temperature. Meanwhile the decrease in COD concentration for 40 and 50 °C operation temperatures was a bit sharp compared to the one for 30 °C in the beginning 45 minutes of reaction time. It was approximately 10390.2, 10080.2, 9533.2 and 8986.2 mg/L at the reaction time of 5, 15, 30 and 45 minutes respectively for 50 °C, and it was approximately 10388.9, 10076.5, 9418.4 and 8759.5 mg/L respectively. The COD reduction at 60 to 240 minutes of reaction time for 40 and 50 °C of the operation temperature was typically the same as the one for 50 °C.

**Effect of Temperature on COD Reduction.** As stated in the previous literatures, hydroxyl radical as a result of hydrogen peroxide conversion can attack organic pollutant such as COD leading to the pollutant degradation [7,8]. Therefore, the effect of operation temperature on COD reduction could be the same as the effect of operation temperature on hydrogen peroxide conversion, seen when Figure 2 and 5 are in comparison. The effect of operation temperature on COD reduction is clearly shown in Figure 5 in which increasing operation temperature mostly results in the higher COD reduction.

**The COD reduction insignificantly increased from approximately 0.63 to 1.47 and 1.48% for the operation temperature of 30, 40, and 50 °C respectively at 5 minutes of reaction time as shown in Figure 5.** Meanwhile, it increased moderately with higher operation temperature at 10 minutes of reaction time, and it increased significantly with reaction time higher than 10 minutes, as can be seen in Figure 5. For examples, the COD reduction was approximately 8.62, 17.57, and 20.52% for the operation temperature of 30, 40 and 50 °C respectively at 60 minutes of reaction time, and it was approximately 35.95, 39.63, and 42.41% for the operation temperature of 30, 40 and 50 °C respectively at 240 minutes of reaction time. It is interesting to note that the COD reduction seemed to follow exponential trend at the reaction time being the same and less than 60 minutes as seen in Figure 5. Even if it was a typically linear increase in the COD reduction for the operation temperature from 30 to 50 °C at the reaction time being the same and higher than 120 minutes, the exponential trend should be obtained when the operation temperature increased to higher than

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50 °C. As the result, it is obviously possible to get higher COD reduction by increasing the operation temperature to higher than 50 °C especially at the reaction time being the same and higher than 120 minutes.

**COD reduction kinetics.** The COD reduction can be expressed by pseudo second order kinetics as follows:

\[
-r_{\text{COD}} = -\frac{dC_{\text{COD}}}{dt} = kC_{\text{COD}}^2
\]  

(2)

where \( r_{\text{COD}} \) is the COD reduction rate; \( C_{\text{COD}} \) represents as the COD concentration; and \( k \) denotes as the kinetics constant of COD reduction. Equation (2) can be rearranged to Equation (3). Equation (3) is then integrated between \( C_{\text{COD}} \) at the initial concentration and \( C_{\text{COD}} \) at the reaction time \( t \) for the left hand side, and it is also integrated between at the reaction time \( t = 0 \) (zero) and \( t \) as shown in Equation (4). The solved equation of COD reduction rate is finally expressed as Equation (5). As a result of Equation (5), using a linear plot of \( 1/C_{\text{COD}} \) versus time \( t \), the kinetics constant \( k \) of COD reduction can be obtained which equals to the linear plot slope.

\[
\frac{dC_{\text{COD}}}{C_{\text{COD}}^2} = -kdt
\]

(3)

\[
\int_{C_{\text{COD0}}}^{C_{\text{COD}}(t)} \frac{dC_{\text{COD}}}{C_{\text{COD}}^2} = k \int_0^t dt
\]

(4)

\[
\frac{1}{C_{\text{COD}}(t)} = kt + \frac{1}{C_{\text{COD0}}}
\]

(5)

Figures 6(a), 6(b) and 6(c) show the linear plots of \( 1/C_{\text{COD}} \) versus time \( t \) at the different operation temperature being 30, 40, and 50 °C.

As obtained from Excel linear trend line shown in Figures 6 (a), (b) and (c), pseudo second order kinetics taken is reliable to model the COD reduction kinetics as shown by the correlation coefficient \( R^2 \) from 95.9 to 99.4%. As obtained from the slope of linear trend line, the kinetics constant of COD reduction increased with the increase in operation temperature. It was approximately 2.30E-07, 2.59E-07, and 3.03E-07 L mg\(^{-1}\) min\(^{-1}\).

**Activation energy of COD reduction.** From the previous discussion, it is obvious that operation temperature affects the COD reduction rate whereas the higher operation temperature causes the faster COD reduction. Hence, it is also important to identify temperature dependency on the COD reduction as the COD determination is based on the reaction between hydroxyl radical and organic substances. Temperature dependency on the COD reduction can be obtained based on Arrhenius’ law\(^{[15]}\) as follows:

\[
k = k_0 e^{-E/RT}
\]

(6)

Where \( k_0 \) represents a magnitude of the COD reduction; \( E \) is activation energy of the reaction between hydroxyl radical and organic substance (J/mol); \( R \) denotes as a constant (8.314 J mol\(^{-1}\)); and \( T \) is absolute operation temperature (K). Equation (6) is solved by taking the natural logarithm of the left and right hand sides of Equation (6) as expressed in Equation (7). Using a

\[
\ln k = \ln k_0 - \frac{E}{RT}
\]

(7)

**Figure 6. Pseudo Second Order Kinetics of COD Reduction and the Linear Trend Line at Different Temperature**
linear plot of $\ln k$ versus time $1/T$, activation energy of the reaction between hydroxyl radical and organic substance, $E$ can be obtained which equals to the linear plot slope.

$$\ln k = \ln k_0 - \frac{E}{R} \left(\frac{1}{T}\right)$$  \hspace{1cm} (7)

Figure 7 shows the plot of $\ln k$ versus time $1/T$ and the linear trend line with the correlation coefficient $R^2$ being approximately 99.4% presenting very good agreement between the experiment-based data and the linear trend line fitting. As a result, the activation energy of COD reduction due to the reaction between hydroxyl radical and organic substance was approximately 0.0138 J mol$^{-1}$.

4. Conclusions

The reduction of COD from soybean tofu production wastewater was studied by conducting advanced oxidation process using hydrogen peroxide with UV radiation catalysts in a closed cylindrical glass reactor. The effect of UV radiation time or resident time in the range of 0-240 minutes and operation temperature in the range of 30-50 °C were investigated. A result showed that the concentration of hydrogen peroxide exponentially decreased with the increase in radiation time. In contrast, the conversion of hydrogen peroxide exponentially increased with higher radiation temperature. Meanwhile, modeling the concentration of hydroxyl radical showed that it could be predicted using the conversion value and the total value of $H_2O_2$ decomposition at a steady state condition. The predicted concentration of hydroxyl radical sharply increased in the beginning 5 minutes, and then slowly increased following exponential trend. Exponential trends were also found for the hydroxyl radical concentration over operation temperature. As a result, the maximal concentration of hydroxyl radical was predicted to be 0.209 mol L$^{-1}$ at 240 minutes of radiation time and 50 °C of operation temperature. As the result of attacking organic pollutant by hydroxyl radical, the COD concentration exponentially decreased with the increase in resident time. Meanwhile, the COD reduction exponentially increased with higher operation temperature. Overall, the $H_2O_2$/UV advance oxidation process reduced COD concentration to approximately $42.41\%$ from approximately 10,545 to 6,073.2 mol L$^{-1}$ at 240 minutes of radiation time and 50 °C of operation temperature. The kinetics study of COD reduction showed that COD reduction could be expressed in pseudo second order kinetics with the correlation coefficient $R^2$ in the range of 95.9 to 99.4%. As a result of COD reduction kinetics, the kinetics constant increased with the increase in operation temperature, and it was 2.30E-07, 2.590E-07 and 3.03E-07 L mg$^{-1}$ min$^{-1}$ for the operation temperature being 30, 40 and 50 °C. Moreover, the activation energy of COD reduction was approximately 0.0138 J mol$^{-1}$ of many kinds of carbon clusters to develop new engineering materials.

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