Decomposition Behavior of Curcumin during Solar Irradiation when Contact with Inorganic Particles

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Abstract. Curcumin is one of materials which have been widely used in medicine, Asian cuisine, and traditional cosmetic. Therefore, understanding the stability of curcumin has been widely studied. The purpose of this study was to investigate the stability of curcumin solution against solar irradiation when making contact with inorganic material. As a model for the inorganic material, titanium dioxide (TiO2) was used. In the experimental method, the curcumin solution was irradiated using a solar irradiation. To confirm the stability of curcumin when contact with inorganic material, we added TiO2 micro particles with different concentrations. The results showed that the concentration of curcumin decreased during solar irradiation. The less concentration of curcumin affected the more decomposition rate obtained. The decomposition rate was increased greatly when TiO2 was added, in which the more TiO2 concentration added allowed the faster decomposition rate. Based on the result, we conclude that the curcumin is relatively stable as long as using higher concentration of curcumin and is no inorganic material existed. Then, the decomposition can be minimized by avoiding contact with inorganic material.

1. Introduction
Curcumin is one of the organic compounds that has a natural yellow pigment and is commonly used as natural coloring agent in industries [1,2]. Curcumin can be obtained naturally from the turmeric extracted using ethanol [3,4]. From the extraction process, several compounds of curcumin can be obtained, such as diferuloyymethane/curcumin (curcumin I), demethoxycurcumin (curcumin II), and bisdemethoxycurcumin (curcumin III) [1,2]. Curcumin has been widely used because of its excellent properties, such as slightly soluble in water [1,2], sensitive to metal ions, oxygen, light, enzymes, bases, ascorbic acid, and temperature [5,6]. Although curcumin has been less stability, it can be improved by forming complex compound with surfactants [1,2].

Since curcumin is a fragile chemical, many papers have investigated several factors involving the curcumin decomposition process. For example, curcumin can decompose into vanillin and ferullic acid when exposed to light [3]. Although many reports studied the stability of curcumin, their reports are limited to the specific light radiation wavelength. Since curcumin has a maximum absorption at a wavelength 408-430 nm [3], it is required to investigate the effect of solar irradiation on the curcumin photodecomposition profile, while until now there is no detailed information for this topic available.
Here, the purpose of this study was to investigate the stability of curcumin solution against solar irradiation, specifically when contact with inorganic material. As a model for the inorganic material, titanium dioxide (TiO$_2$) was used. In the experimental method, the curcumin solution was irradiated using a solar irradiation. To confirm the stability of curcumin when contact with inorganic material, we added TiO$_2$ microparticles with different concentrations. The results showed that the concentration of curcumin decreased during solar irradiation. The less concentration of curcumin affected the more decomposition rate obtained. The decomposition rate was increased greatly when TiO$_2$ was added, in which the more TiO$_2$ concentration added allowed the faster decomposition rate. Since the decreases in the concentration of curcumin without additional TiO$_2$ were less than 10%, we conclude that the curcumin is relatively stable as long as there is no inorganic material existed.

2. Hypotetical of Photodecomposition

2.1. Photodecomposition of organic component using TiO$_2$ photocatalyst

Figure 1 shows the illustration of the photodecomposition of curcumin using a photocatalyst in the common process [7]. In the common process, the solar light emits the photon, which influenced the photocatalytic activity. The photon produces the amount of energy, in which this energy will be absorbed by the catalyst (Route R1)[8]. Then, this photon produced electron (e-) in the conduction band (CB) and holes (h+) in valence bonding (Route 2). This electron and holes interact with oxygen and water, in which their radical forms can attack and organic material into smaller structures such as carbon dioxide and water (Route 3) [9]. Therefore, if the system contained curcumin, curcumin would be decomposed, shown by the decreases in the concentration in the system [10,11].

![Figure 1](image)

Figure 1. The proposal mechanism of photodecomposition of organic material in the inorganic material system under the solar light irradiation. Figure was adopted from reference [7]

3. Experimental Methode

The stability of curcumin against solar radiation was investigated in Universitas Pendidikan Indonesia (6,86340 SL, 107.59430 EL), Bandung, Indonesia at 8 March 2016. Curcumin was obtained by extraction process of turmeric. In short of the process, turmeric was washed, sliced into small pieces (sizes of about 1 mm), then dried at 130°C to remove water. The dried turmeric was then grounded to become tumeric powder. Next, tumeric powder was dissolved in ethanol 95% and heated at 50°C in water bath for 1 hour. The solution then filtered. Then, the filtrate was put in rotary evaporator (at 90°C) to remove excess ethanol in the filtrate. For the photodecomposition process, the concentration of curcumin was set at 10 and 25 ppm. For some cases, we also added titanium dioxide (TiO$_2$; Bratachem Co. Ltd., Indonesia). The concentrations of TiO$_2$ were 3 and 6 ppm.
For checking the stability of curcumin against solar radiation, we used home-made photocatalytic reactor. The photocatalytic reactor consisted of a batch-glass reactor (500 mL), a magnetic stirrer (800 rpm), a bubbler, several sensors (i.e. a lux meter as light intensity sensor, a voltage measurement analysis, a thermocouple, conductivity meter and pH meter). The mixed material (containing curcumin and TiO$_2$ in the aqueous solution) then irradiated by the sunlight naturally. During the photodecomposition process, the air (2.50 L/min) was bubbled into the reactor to keep the oxygen concentration constant. To identify the concentration of curcumin during the photodecomposition process, we used a turbidity analysis based on the light exposed into the mixed solution (containing curcumin and TiO$_2$), in which the data analysis was obtained from the sensors. To make sure that the process is in a real time, the sensors were connected to computer system. To compare the concentration result from real time analysis using turbidity sensors, a spectrophotometer (UV-VIS mini 1240, Shimadzu Corp., Japan) was used.

4. Results and Discussion

Figure 2 shows photodecomposition profile of curcumin with various catalyst amounts. We took 3 hours of reaction in the morning time (from 06:00 to 09:00 am). We believe this processing time is sufficient time for analyzing the effect of sunlight irradiation on the stability of curcumin.

Figures 2a and 2b are the samples used 25 and 10 ppm of curcumin, respectively. Based on these figures, we found that the curcumin concentration decreased concomitant with the photodecomposition time from 06:00 to 09:00 am, and the rate of the photodecomposition process increases as the amount of TiO$_2$. In addition, the higher concentration of curcumin has a correlation to the stability of curcumin. Thus, the lower concentration of curcumin relatively decomposed easier than the higher concentration of curcumin. This is because of the possibility of sunlight to penetrate the deepest position in the solution. Indeed, the more sunlight penetrate the solution the more interaction between sunlight and curcumin to be done. We also found that the additional inorganic material, such as TiO$_2$, can provide higher decomposition rate.

![Figure 2](a-b). Effect of TiO$_2$ amount on the photodecomposition of curcumin. Figures (a) is the samples using 25 ppm of curcumin, whereas Figures (b) is using 10 ppm of curcumin. Figures (a) and (b) are the process conducted in the sunny day. LT is local time. Figure was adopted from reference [11].
To confirm the photodecomposition of curcumin, the photodecomposition rate was calculated based on the solid–solute photochemical reactions. Typically, to get this calculation, the Langmuir–Hinshelwood kinetic model was used, and the photodecomposition rate can be written as

\[ -\frac{dC}{dt} = \frac{k_1 k_2 C}{1 + k_2 C} \]

where \( C \) and \( t \) are the concentration and the photoreaction time, respectively. \( k_1 \) and \( k_2 \) are the apparent reaction rate constant and the apparent equilibrium constant for adsorption of the chemical on the catalyst surface, respectively. Since the concentration of curcumin used in this study was very low (less than 100 ppm), the equation (1) can be re-expressed as a first-order rate constant, as follows:

\[ -\frac{dC}{dt} = k_i C \]

where \( k_i \) is the reaction rate constant at time \( t \). Then, solving the differential problem in the equation (2) results

\[ k_i = \frac{\ln(C_i/C_0)}{t} \]

where \( C_0 \) is the initial concentration of curcumin \((t = 0)\) and \( C_t \) is the concentration of curcumin at time \( t \). Finally, since the \( k_i \) value depends on the specific time \( t \), the photodecomposition rate \((k)\) can be approximated as the average of \( k_i \) values. Or, we can write

\[ k = \frac{\sum_{i=0}^{n} \ln(C_i/C_0)}{n} \]

where \( n \) is the total number of calculated sample \( i \). \( C_i \) is the concentration of curcumin at time \( i \).
Figure 3 presents the effect of initial concentration of curcumin on the photodecomposition rate. Figures 3a and b are the profile of photodecomposition of curcumin with concentration of TiO$_2$ of 6 and 3 ppm, respectively. The photodecomposition rates were verified by the value of “$\ln (C/Co)$” against the photodecomposition time. The result showed that the decomposed curcumin increased along with the photodecomposition time from sunrise to morning for all variations. Then, changes in concentration of organic material allowed to the attainment of different photodecomposition rates.

At the constant TiO$_2$ amount, the photodecomposition rate depended on the initial curcumin concentration. The use of curcumin with concentration of 25 and 10 ppm allowed to the photodecomposition process with $k$ value of 4.46 $10^{-2}$ and 5.53 $10^{-2}$ min$^{-1}$. This concluded that the lower concentration of curcumin leads to the attainment of faster photodecomposition process.

In addition, if we compare Figures 3a and b, the photodecomposition using 6 ppm of TiO$_2$ was faster than that using 3 ppm of TiO$_2$, while when there is no catalyst, the rate is near to zero. This result confirmed that the effect of inorganic component on the photodecomposition process is very high. Therefore, we can conclude that decomposition of curcumin can be minimized by avoiding contact with inorganic material.

5. Conclusion

This study investigated the decomposition behavior of curcumin during solar irradiation when contact with inorganic particles. In the experiments, curcumin were diluted in water, mixed with TiO$_2$ as a model of inorganic material, and illuminated with solar radiation naturally. We found that the concentration of curcumin and inorganic material changes the stability of curcumin. The higher concentration of curcumin caused the slower decomposition rate, and the higher amount of inorganic material resulted in the faster decomposition rate. Based on the results, we can conclude that decomposition of curcumin can be minimized by avoiding contact with inorganic material.

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