https://doi.org/10.48048/tis.2025.9042

Photocatalytic Activity of ZnO Nanoparticles from Pineapple Skin for Degradation of Congo Red Dye

Woro Setyarsih[1], Lydia Rohmawati[1,*], Fadhil Figo Ardiansyah[1], M. Samsul Maarif[1] and Darminto Darminto[2]

[1]*Department of Physics, Faculty of Mathematics and Natural Science, Universitas Negeri Surabaya, Surabaya 60231, Indonesia*
[2]*Department of Physics, Faculty of Science and Data Analytics, Institut Teknologi Sepuluh Nopember, Surabaya 60111, Indonesia*

([*]Corresponding author's e-mail: lydiarohmawati@unesa.ac.id)

Received: 18 September 2024, Revised: 19 October 2024, Accepted: 26 October 2024, Published: 10 December 2024

Abstract

The development of the cloth industry can trigger a large amount of liquid waste to be produced, which, of course, can pollute the environment without proper and effective processing. This fluid waste comes from the dyeing process and usually uses dyes made from azo compounds such as Congo Red (CR), where these compounds cannot be degraded naturally in the environment. For this reason, appropriate waste processing methods are needed that are capable of degrading dye waste produced by the industry, namely with photocatalysis. ZnO nanoparticles are semiconductor materials with the potential to be catalysts because of their high electron mobility, cheapness, and non-toxicity. These nanoparticles can be extracted using the green synthesis method with pineapple peel extract as a bio-reduction. The effectiveness of the photodegradation of the synthesized ZnO nanoparticles is altered by the mass of the catalyst and the duration of UV light irradiation. Catalyst masses of 5, 8, 10, 12, 20, and 30 mg were able to degrade CR dye with a concentration of 30 ppm, respectively 93.51, 93.87, 95.15, 96.15, 97.72, and 97.08 % after irradiation for 210 min. With the large percentage of dye photodegradation, the ZnO nanoparticles resulting from the research showed good photocatalytic activity, which could later be used to process liquid waste from the textile industry.
Keywords: Photocatalytic, Congo Red, ZnO nanoparticles, Pineapple peel

Introduction

Pineapple peel is an organic waste often found in traditional markets and fruit traders. Its existence has so far been considered to have no economic value, so it has been neglected. If studied further, pineapple skin contains bioactive commixtures such as saponins, flavonoids, tannins, anthocyanins, vitamin C, carotenoids, and the enzyme bromelain [1]. The presence of bioactive compounds from pineapple peel can be used to reduce zinc ions into ZnO nanoparticles via the green synthesis method [2]. Apart from acting as a bio-reduction, pineapple peel is also a capping agent that can help the stability of metal precursors to form nanostructures that are biological, biocompatible, and environmentally friendly [3].

ZnO nanoparticles are one of the most practical catalyst materials because they are cheap and have high thermodynamic stability [4]. When compared with other oxides, ZnO has a nanostructure with a standard band gap of 3.37 eV [5] and has been used in wastewater treatment due to its high redox potential, good electron mobility, and effective catalytic activity [6] and high efficiency in degrading CR dye pollutants [7]. Rao *et al.* [8] reported that, among other semiconductors, ZnO nanoparticles showed better efficiency in the photodegradation of a few natural colors than TiO_2. Because of their ability, ZnO nanoparticles can be utilized more widely as catalysts in degrading dye liquid wastage, especially those produced from textile waste. Dye waste is usually made from azo compounds, namely aromatic hydrocarbons such as benzene, toluene, naphthalene, phenol, and aniline [9]. CR is an azo dye that cannot be degraded naturally in the environment [10]. It can create water and environmental pollution problems because these compounds will be complex to decompose and potentially cause disease if they persist in the surroundings for ages [11]. The reasoning is that these organic dyes are synthetic materials that cannot undergo a natural degradation process by the environment, so these compounds will accumulate in nature.

Photocatalysis is a method that makes it possible to degrade organic dyes because its operation is easy, straightforward, and effective in scouring natural and chemical pollutants [12]. The photocatalytic degradation reaction works based on exposure to sunlight or UV light [13]. The photocatalytic process occurs when the photocatalyst absorbs energy from light, which produces electron and electron-hole pairs that can reduce and oxidize O_2 molecules and H_2O to produce hydroxyl radicals ($•OH^-$) and superoxide anion ($•O_2^-$) on the photocatalyst surface [14]. Hydroxyl radicals play an active role in degrading dye molecules adsorbed on the catalyst surface [7]. In this research, Nwaiwu *et al*. [15] revealed that ZnO nanoparticle results from the calcination method could degrade CR dye by 70 % under UV irradiation for 120 min. Likewise, what was done by Arul and Senthilnathan [16], where ZnO nanoparticles through the soft chemical method could degrade CR by 55 % under 180 min of UV irradiation. Consequently, in this study, the method of making ZnO nanoparticles through green synthesis refers to the research of Rohmawati *et al*. [17]. However, it differs from previous studies where the ZnO nanoparticles produced were only for the photodegradation of MB dyes. In contrast, it has never been reported for CR dyes, so in this study, ZnO nanoparticles obtained from the green synthesis method were used as photocatalysts in degrading CR dyes. Natural materials from pineapple skin waste are abundant and must be optimally utilized. Thus, this study was conducted to determine the effect of the mass of ZnO nanoparticle catalysts from pineapple skin extract on the ability of its photocatalytic activity in degrading CR dyes under UV irradiation for 120 min.

Materials and methods

Material

In this research, the materials that need to be prepared include pineapple skin (*Ananas comosus* L.), distilled water, Sodium Hydroxide (NaOH) (Sigma Aldrich 99 %), aluminum foil, filter paper, zinc acetate dihydrate (Zn $(CH_3COOH)_2.6H_2O$) (Merck), and CR (Merck). Apart from materials, the equipment used in the research included: UV-C lamp (Germicidal, 15 W 45 cm), 200 mesh sieve, beaker, measuring cup, beaker, magnetic stirrer, hot plate, dry oven, petri dish, digital scales, mortar and pestle, pH paper, glass vials, sonicators, and centrifuges.

Methods

Green synthesis of ZnO nanoparticles

The 1st stage in synthesizing ZnO nanoparticles is that the pericarp of the pineapple skin is first washed until clean, then ground using a mortar and pestle until it becomes mush. Next, distilled water was added and shaken for 1 h, heated at 80 °C, and then cooled to room temperature. The solution is strained and gains a yellow limpid solution. After that, 4 g of zinc acetate and 100 mL of distilled water were added and sonicated at 40 °C until 1 h. In the next stage, the solution was appended 100 mL of NaOH and stirred at 350 rpm for 5 min until a solution with a white precipitate was obtained. Next, the solution was centrifuged at a fleetness of 3000 rpm, and the resulting white was warmed at 120 °C until 12 h. The procedure for making ZnO nanoparticles using the green synthesis method refers to research by Dewi and Rohmawati [18], and the stages can be illustrated in more detail in **Figure 1**.

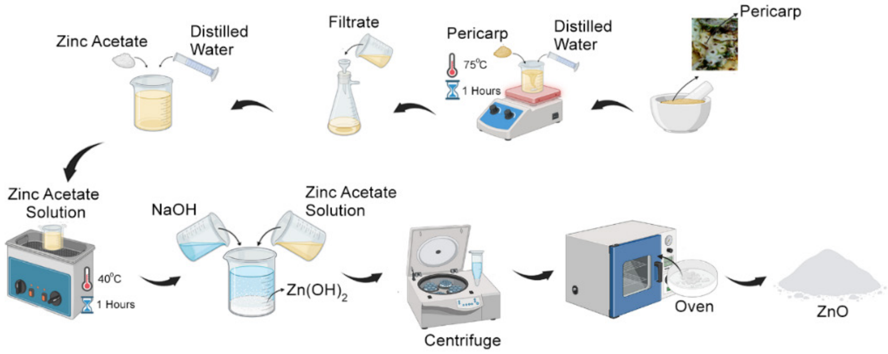


Figure 1 Stages of ZnO nanoparticle synthesis with bio-reduction from pineapple peel extract through the green synthesis method.

Preparation of photocatalytic test

Before photodegradation of the dye, it is necessary to prepare a CR dye solution at a 30 ppm dose. Each sample of synthesized ZnO with varying masses of 5, 8, and 12 mg was appended to 100 mL of CR solution in a glass beaker. After that, the solution was mixed for 60 min in dark conditions and irradiated with UV light at 30, 60, 90, 120, 150, 180, and 210-minute intervals. At each interval, 7 mL of solution was taken and centrifuged at 2500 rpm for 5 min. After that, the solution was tested using a UV-vis tool to determine the level of absorbance and degradation of the CR dye. More details in **Figure 2** can be presented to the photodegradation test preparation.

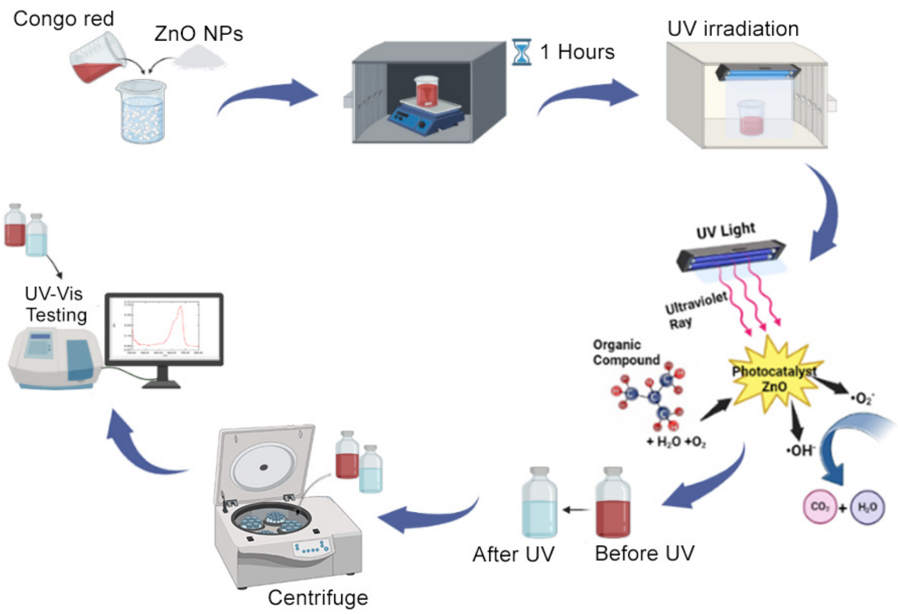


Figure 2 Preparation of photocatalytic degradation.

Characterization of ZnO nanoparticles

The synthesized ZnO nanoparticle powder was analyzed for each diffraction peak using Smartlab Rigaku type X-ray Diffraction (XRD) characterization with a double angle of 20 - 80 °, a CuKα wavelength of 1.54056 Å, and using a Bragg-Brentano optical beam. Results of the characterization XRD were investigated by applying the software Match! to determine the test sample's phase by matching its diffraction peaks with the data in the software database. The structural shape of the ZnO particles can be seen from the results of the Hitachi H7700 brand Transmission Electron Microscopy (TEM) characterization. ImageJ software further analyzed data from this characterization distribution. This research used Brunauer-Emmett-Teller (BET) characterization of the Quantachrome Quadrasorb-Evo brand to specify the pore dimension and surface area of the ZnO sample. The characterization results are an adsorption-desorption isotherm curve investigated using the Barret-Joyner-Halenda (BJH) method. The absorbance level of the sample can be determined from the UV-vis characterization of the Shimadzu 1800 brand Spectrophotometer, where testing is carried out in the wavelength range of 200 - 800 nm. The data in the form of absorbance was then analyzed for bandgap energy using the Tauc Plot method. The ability of the sample to have photocatalytic activity against CR dye can be determined from the absorbance data by calculating the percentage of photocatalytic degradation efficiency (η%) according to Eq. (1) with A_0 and A_t being the absorbance before and after being exposed to UV light at t minutes [17] as follows:

$$\eta\% = \frac{A_0 - A_t}{A_0} \times 100\ \% \quad (1)$$

Results and discussion

Phase analysis

According to **Figure 3**, the XRD data, each diffraction peak of the sample has had its phase identified using Match! Software, namely hexagonal wurtzite phase. This phase has been matched with the database in the software and is based on the data of the Joint Committee on Powder Diffraction Standards (96-900-4118, zincite phase). The highest diffraction peak was observed at a 2θ angle of 36.21 °, which indicates the crystal plane orientation (101). This phase is also by JCPDS data (01-075-0576, wurtzite phase), where the maximum intensity of the wurtzite phase is formed at 2θ = 36.3 ° with a crystal plane orientation (101) [19]. Other diffraction peaks are also indicated by the wurtzite phase, which is observed at angles with the crystal plane orientation as follows: 31.72 (100), 34.38 (002), 47.48 (102), 56.52 (110), 62.81 (103), 66.25 (200), 67.88 (112), 69.27 (201), 72.50 (004), and 76.96 ° (202). In **Figure 3**, no other diffraction of peaks indicates impurities; it is proven that all peaks are 100 % identified as the wurtzite phase.

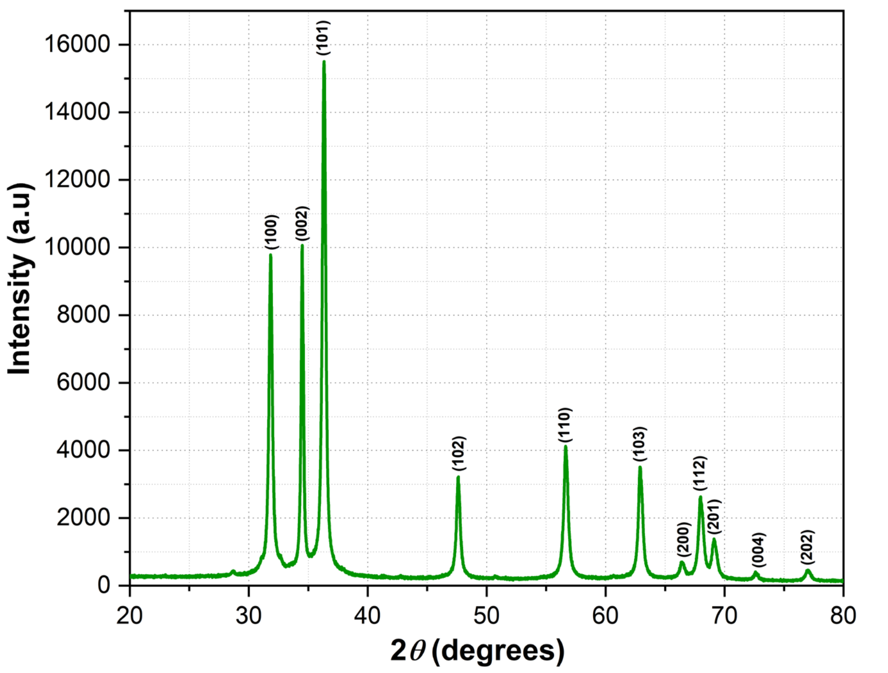
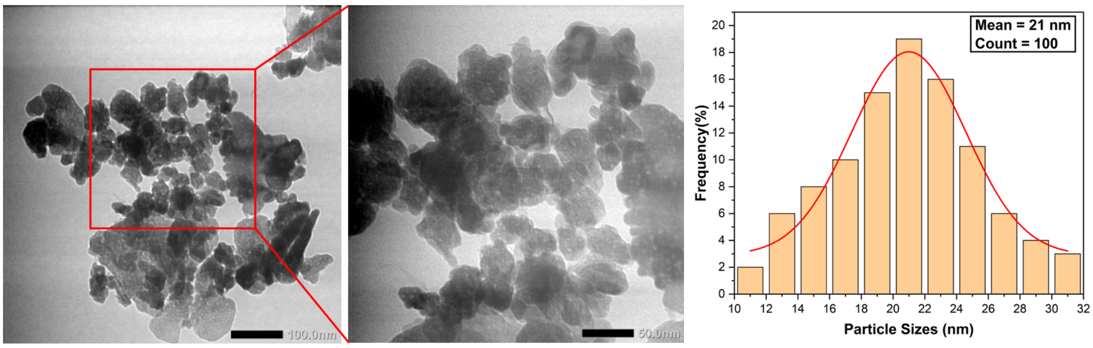


Figure 3 X-ray diffractrogram of ZnO sample.

Morphological analysis

The results of TEM characterization can provide information related to the sample's grain size, shape, and structure. **Figure 4(a)** shows that the sample has a uniform polyhedral shape and little agglomeration. Piling between particles is found in the dark black part, while the gray part shows a single particle. The distribution of grain size in the sample from the TEM characterization results can be further analyzed using ImageJ software, namely by considering 100 data grains, which is known that the sample has a grain size of 21 nm, as shown in **Figure 4(b)**. The synthesized sample's uniform polyhedral shape and structure can affect its effectiveness in photocatalytic activity against liquid dye pollutants [20], so in this study, SAED characterization was not carried out. In this study, only the morphology and particle size distribution are needed. At the same time, the diffraction pattern and crystal orientation can be sufficiently known from the results of the XRD analysis.

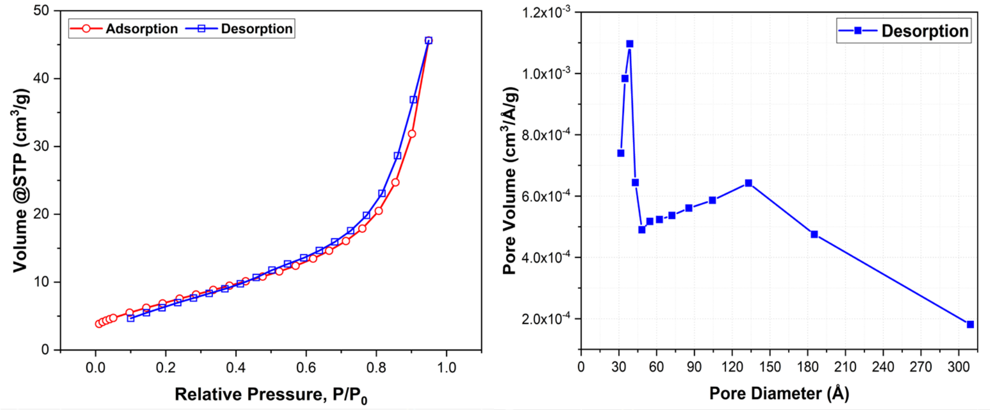


(a) (b)

Figure 4 TEM characterization results, (a) morphological structure and (b) particle size distribution of ZnO samples.

Pore size analysis

The specific surface area and pore size distribution of the synthesized ZnO nanoparticles can be determined from the BET characterization results. **Figure 5(a)** points to the isotherm curve of ZnO nanoparticles classified as type IV because the pore width is smaller than 4 nm [21], which is analogous to the IUPAC (International Union of Pure and Applied Chemical) arrangement, which means that ZnO nanoparticles are mesoporous [22]. Nanoparticles are mesoporous because they have a pore size ranging from 2 - 50 nm [23]. From the isotherm curve, a hysteresis loop is formed, which is type H3, which shows a narrow loop and is at a nitrogen gas pressure (N_2) ranging from 0.45 to 0.94937 P/P_0 temperature of 77.3 K [24-26].



(a) (b)

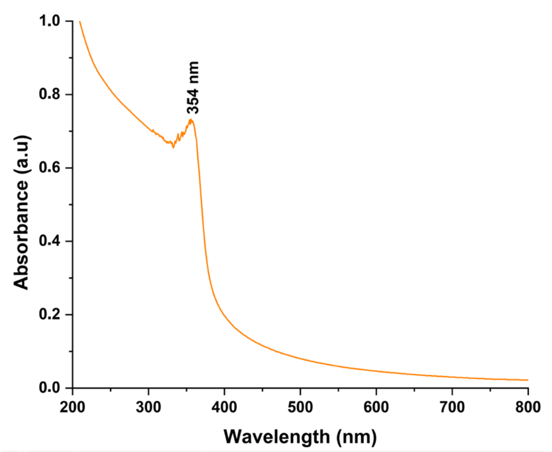
Figure 5 BET characterization results of ZnO samples, (a) isotherm curves, and (b) distribution of pore diameter on the desorption curve

Based on the BJH analysis in **Figure 5(b)** of the desorption curve of the ZnO sample, it is known that the pore diameter distribution is 3.86 nm. This site is included in the mesoporous category (2 nm < d < 50 nm) [22]. BET analysis shows that the ZnO nanoparticle sample has a surface area of 26,754 m²/g. This value is greater than the results of several researchers, including 13.56 m²/g [27], 6.032 m²/g [28], and 1.44 m²/g

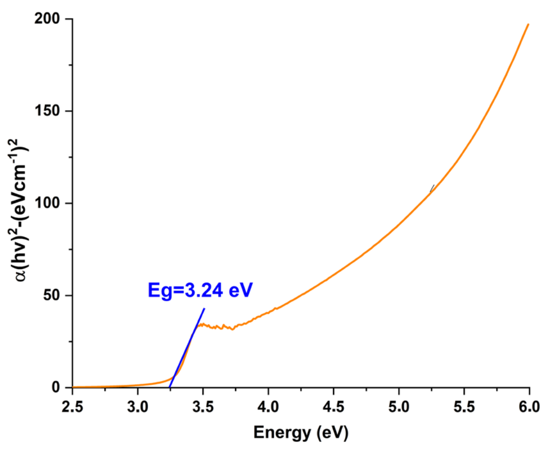
[29]. The surface area and pore size distribution will influence the performance of the photocatalytic process in degrading dyes, where the more significant the surface area and the smaller the pore size will increase the photocatalytic activity [30]. It happens because the more significant the surface area and the smaller the pore size, the more active surfaces are exposed to light so that more photon energy is received, which can increase the occurrence of electron excitation and more free radical compounds are produced. This event can trigger an increasingly rapid degradation process in the photocatalysis process [31,32].

UV-vis analysis and bandgap energy

The absorbance peak of the ZnO sample can be determined from the UV-vis characterization results, as shown in **Figure 6(a)**. The absorbance of the ZnO sample was detected at a wavelength of 354 nm, indicating that the particles were in the ultraviolet region [33]. Electrons that experience excitation always require band gap energy so that the electrons can move from the valence band to the conduction band [34]. **Figure 6(b)** shows that the band gap energy value of the synthesized ZnO nanoparticles is 3.24 eV, smaller than the standard ZnO value, namely 3.37 eV [7]. It shows that these nanoparticles are more effective in the photocatalytic process. The smaller the bandgap energy, the easier it is for a material to excite electrons from the valence band to the conduction band, making it more significant to the productivity of free radicals in the photocatalytic process. It causes more dyes to be degraded in the photocatalytic process [17]



(a)



(b)

Figure 6 UV-vis characterization results (a) absorbance spectrum of ZnO samples, (b) bandgap energy of ZnO samples using Tauc Plot method.

Photocatalytic activity analysis

The photocatalytic activity of ZnO nanoparticles against CR dye was carried out under UV irradiation for 210 min, with variations in catalyst mass of 5, 8, 12, 20, and 30 mg. **Figure 7** shows that the change in the absorbance value of CR dye on the photocatalytic activity of ZnO nanoparticles occurs at a wavelength of 498 nm, where the CR dye can be degraded by ZnO nanoparticles as evidenced by the gradual fading of the dye along with increasing catalyst mass and the duration of exposure. Continuous UV light illumination treatment during the photocatalysis process can cause the absorption of photon energy by the surface of the ZnO nanoparticle catalyst to be greater, thereby enabling the photodegradation of CR dye to be more efficient [7].

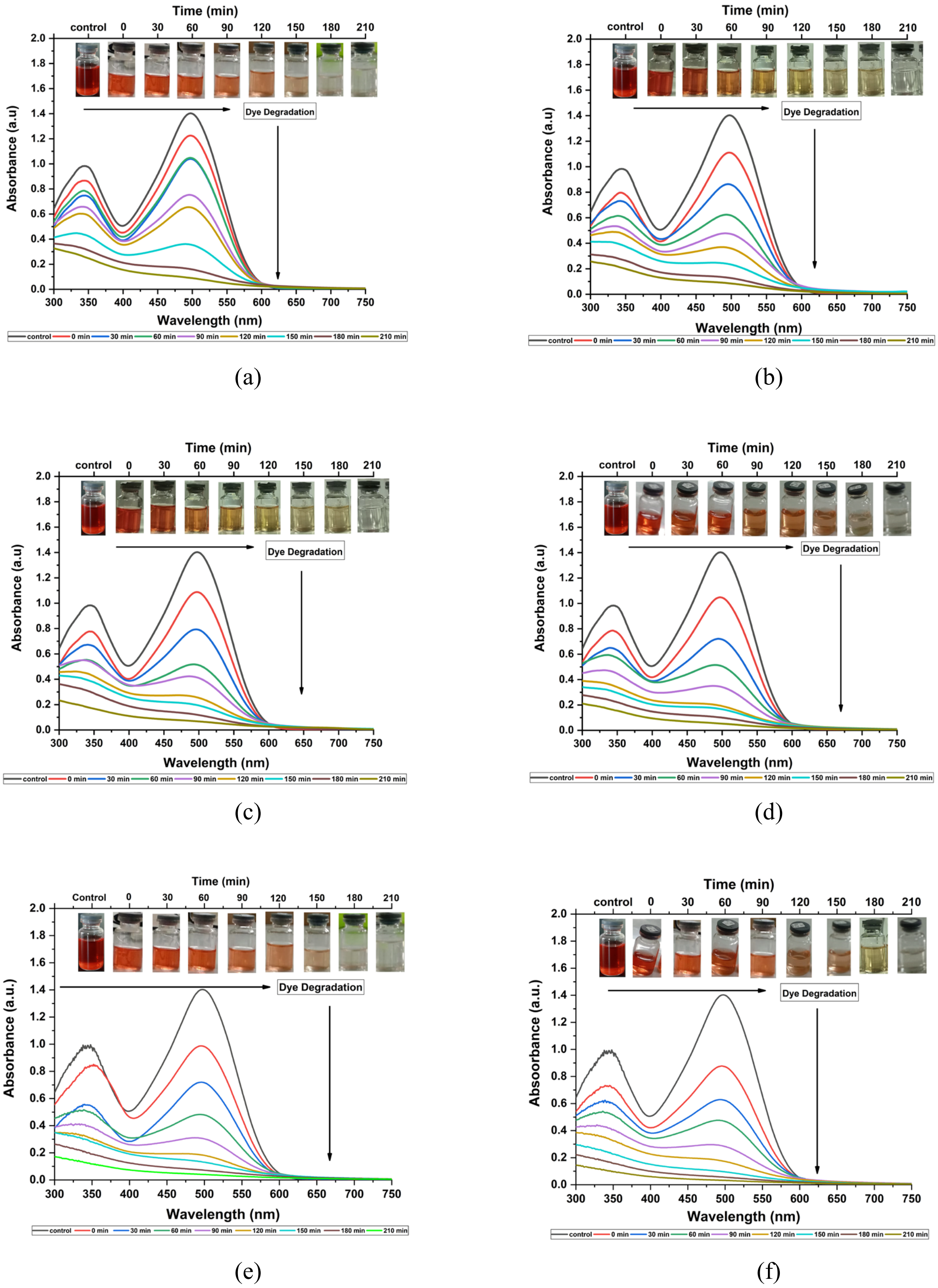


Figure 7 UV-vis absorption spectrum of CR dye under UV irradiation with variation of catalyst mass of ZnO sample (a) 5 mg, (b) 8 mg, (c) 10 mg, (d) 12 mg, (e) 20 mg, and (f**)** 30 mg.

From the research carried out, it can be seen that variations in catalyst mass of 5, 8, 10, 12, 20, and 30 mg in **Figure 8** show the level of degradation efficiency of CR during 210 min of UV irradiation of 93.51, 93.87, 95.15, 96.15, 97.72, and 97.08 %, respectively. It proves that the more catalyst mass provided, the rate of photocatalytic activity will increase because there will be more active sites on the surface of ZnO nanoparticles to capture photon energy so that more free radicals will be produced, which will decompose and degrade dyes more quickly, increasing photodegradation of dyes [35].

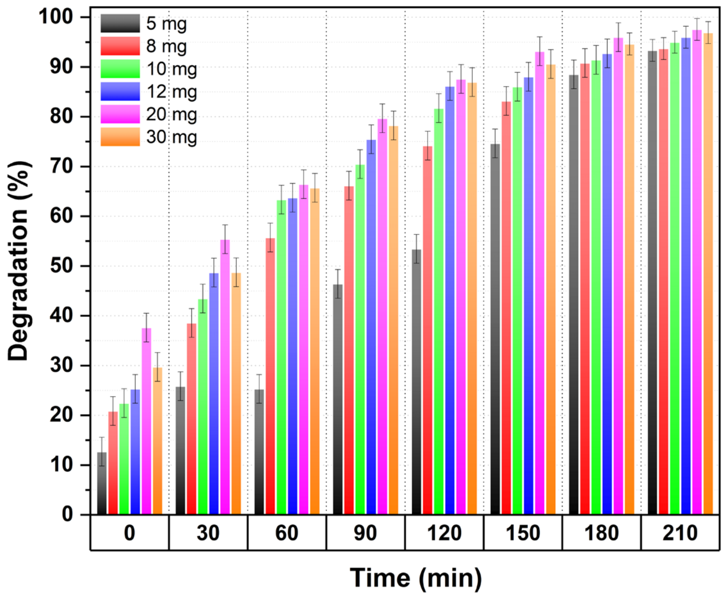


Figure 8 The effect of irradiation time and catalyst mass on the percentage of CR dye degradation.

Rajesh *et al*. [36] reported that photodegradation activity generally depends on H^+ and OH^- formation. Increasing the amount of catalyst will increase the surface area, which can increase the amount of H^+ and OH^- produced. It causes the photodegradation rate to increase. In this research, the optimum degradation percentage for a ZnO catalyst mass of 20 mg was 97.72 %. The use of a catalyst mass of 30 mg has a lower percent degradation value when compared to the use of a 20 mg catalyst, which can be seen before and after UV irradiation for 210 min. It is due to the catalyst dose exceeding the optimum, where the suspended ZnO particles aggregate together, thereby reducing the amount of UV light that reaches the active sites of the catalyst, which causes the reaction rate to decrease [15,37]. Excessive catalyst dosage can reduce light penetration, resulting in increased light scattering [36] because there is overlapping adsorption due to the density of the adsorbent so that collisions occur between active catalysts, especially at the ground level, and this causes the catalyst particles to be deactivated [38]. The results of CR photodegradation with a concentration of 30 ppm in this study showed a higher efficiency of 79.69 % after UV irradiation for 90 min. Even during 210 min of irradiation, the CR dye was degraded by 97.72 %. The figure is much better than that of Brishti *et al*. [39] in their previous research, which only achieved a degradation efficiency of 41.78 % after 100 min of UV irradiation.

Although the ZnO nanoparticles used in the study were also produced using the green synthesis method, the type of bio-reduction in that study was different. Previous research used *Epipremnum aureum* leaf extract [39]; this study was from pineapple peel extract. The difference in bio-reduction in the ZnO nanoparticle production process can affect the efficiency of its photocatalytic activity, especially in the degradation of CR dyes. In this study, ZnO nanoparticles have good photocatalytic activity in degrading CR dyes optimally at a catalyst dose of 20 mg with UV irradiation for 210 min. However, at a catalyst mass of 20 to 30 mg, further research has yet to be carried out regarding its ability to degrade dyes, so it is unknown how much the degradation percentage is, which is a limitation in this work.

Conclusions

ZnO nanoparticles obtained through the green synthesis method using bio-reduction from pineapple peels have been proven to have effective photocatalytic activity in degrading CR dye. The effect of catalyst mass is very significant on the ability to degrade CR. The results showed that catalyst masses of 5, 8, 10, 12, 20, and 30 mg each had degradation efficiencies of 93.51, 93.87, 95.15, 96.15, 97.72, and 97.08 % after UV irradiation for 210 min. However, excessive catalyst doses can reduce light penetration, increasing light scattering. In this study, a catalyst mass of 20 mg showed optimal photocatalytic degradation, even more effective than catalyst masses of 5 to 12 mg and 30 mg. Thus, the resulting ZnO nanoparticles can be used as catalysts in the photocatalytic degradation process of organic dye liquid waste.

Acknowledgements

The author thanks the Materials Laboratory, Faculty of Mathematics and Natural Sciences, Universitas Negeri Surabaya, for providing facilities for making samples and testing photocatalytic activity. The author also thanks the Institute of Biological Sciences and Engineering, Universitas Airlangga, and the ILRC Laboratory (Integrated Laboratory and Research Center), Universitas Indonesia, for providing complete technical support for using characterization tools during this research.

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