

Application of Nanoparticles as Nanoadsorbents for Methylene Blue 2 Waste Using Zinc Oxide and Titanium Dioxide

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Abstract: Nanoparticles are particles that have a size of ± 1 to 100 nm. There are various applications of nanoparticles, one of which is nanoadsorbent as used in wastewater treatment. One of the nanotechnology material products is zinc oxide (ZnO) nanoparticles which have the ability as a dye sensitized solar cell, catalytic converter, and catalytic activity so that it can be used as an adsorbent in environmental pollution treatment systems such as dichlorophenol-indophenol color degradation of heavy metal Pb (II) removal and methylene blue dye degradation. In the method used preparation, synthesis and test on methylene blue by means of photocatalyst and photodegradation, then on characterization using XRD, FTIR, SEM and DSC methods.

Keywords: nanoparticles, nanoadsorbent, zno, tio2.

Abbreviations: zinc oxide (ZnO), titanium dioxide (TiO₂), X-Ray Diffraction (XRD), Fourier Transform Infra-Red (FTIR), Scanning Electron Microscope (SEM), Diferensial scanning calorimetry (DSC)

Introduction

In the era of industrial development, there are many agricultural industries, medicinal industries, textile industries, and chemical industries that play a role in supporting the economy, science and economy of the country. In addition to having a good impact, the industry has a harmful impact on the environment where waste disposal and the use of dyes can cause water and soil pollution. Water pollution has a definition as the entry or inclusion of living things, substances, energy and or other components into water by human activities, so that water quality drops to a certain level so that water loses its function (Agustiningasih, 2012).

In reducing the impact of water pollution, the use of bioremediation methods from both plants and beneficial bacteria is considered to have a positive impact because it does not leave harmful

residues. One of the technological developments in the utilization of living things, especially plants, is the synthesis of nanoparticles. In recent years, the development of the nano field has been very rapid which has made significant progress in the field of science. When compared to other sizes, nanoparticles have a size of $\pm 1-100$ nm. One example of a nano-sized molecule is deoxyribonucleic acid (DNA). With a size of 2 nm (Manurung, 2018).

Silver nanoparticles have a variety of uses including as antimicrobials, biosensor materials, composite fibers, cryogenic superconducting materials, cosmetic products to electronic components (Korbekandi, 2014).

The chemicals used in the manufacture of synthetic dyes are generally toxic, carcinogenic, and flammable. If these synthetic dyes are contained in waste, it will be very difficult to remove because they contain organic compounds,

are resistant to aerobic treatment, stable to light and heat. This makes synthetic dyes an ecological problem. Therefore, it is necessary to remove organic contaminants from waste before disposal so as not to damage the surrounding ecology (Mun et al, 2015).

One of the dyes used in industry is methylene blue (MB) in the textile industry, methylene blue is one of the most widely used thiazine dyes because it is economical and easy to obtain. MB dye is an important basic dye in the process of dyeing leather, mori fabrics, cotton fabrics and tannins. The use of methylene blue can cause several effects, such as gastrointestinal irritation if ingested, cyanosis if inhaled, and skin irritation if skin contact occurs. These side effects are the reason for the importance of treating industrial waste containing methylene blue. There are many methods used to overcome this color waste problem, such as chlorination, biodegradation and ozonation methods (Raganata et al, 2019). these methods are considered less effective because they require large operational costs and are considered less effective.

One method that is relatively cheap and easy to implement in Indonesia is photodegradation, and photocatalysts. The principle uses photocatalysts derived from semiconductor materials, such as TiO_2 , ZnO , Fe_2O_3 , CdS , and so on. One of the substances that can be used in photocatalysts is ZnO and TiO_2 , both of which are non-toxic inorganic semiconductors that can provide high mobility and good thermal stability. ZnO is often used either in photocatalysts, or as a monocatalyst, ZnO doped with fellow metals (metal metal) or doped with non-metal compounds (metal-nonmetal) because of its versatility, ease of manufacture, and relatively low cost. TiO_2 nanoparticles used as methylene blue adsorbents are based on semiconductor properties, crystallinity, crystalline phase, and surface active side (Jin et al, 2018). MB photodegradation is a degradation process using visible light.

TiO_2 nanoparticles are non-toxic metal oxides, have high thermal stability, and have high oxidizing ability. The photodegradation process is used to remove organic substance pollutants into

compounds that are more environmentally friendly. Due to their very small size (the specific surface area is very large) nanomaterials have strong adsorption capacity and reactivity. The adsorption strength of these two substances can be optimized through nanoparticle technology, nanoparticles have a strong adsorption capacity and reactivity.

Materials and Methods

Study area

This study aims to synthesize nanoadsorbents that have a particle diameter size of 1-100 nm. Preparation of TiO_2 nanoparticles was carried out by dissolving PVA surfactant, TTIP, ethanol, and acetic acid. Characteristic analysis using crystal phase test, Ti-O and Ti-O-Ti bond characteristics, thermal analysis, and application as methylan blue adsorbent (Thahir et al, 2019). While in the preapi sinsythesis ZnO tools and materials used are distilled water, $\text{Zn}(\text{NO}_3)_2$, methylene blue, NaOH , Polyvinylpyrrolidone (PVP). The tools used are glassware (iwaki pyrex), UV-Vis spectrophotometer (UV-1800 Shimadzu), photodegradation reactor, UV-A lamp (Himawari T8-20W), SEM test equipment (JOEL JSM-6510 LA), XRD (Rigaku SmartLab 3kV), Oven (Memmert), furnace (IND88), sonicator (Eyela), sudip, pH Scherrer (Raganata et al, 2019).

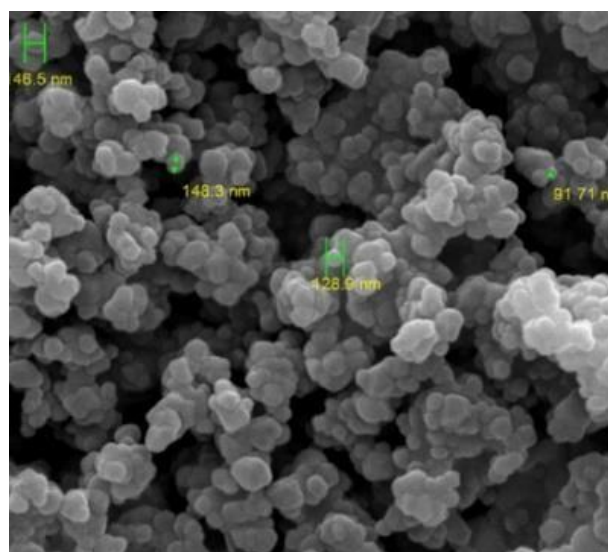


Figure 1. Nanoadsorbent image

Procedures

Preparation of TiO₂ and ZnO for Nanoparticle Manufacturing

Preparation of TiO₂ nanoparticles was carried out by dissolving PVA surfactant, TTIP, ethanol, and acetic acid. Characteristic analysis using crystal phase test, Ti-O and Ti-O-Ti bond characteristics, thermal analysis, and application as MB adsorbent. The fixed variables in this study are the volume of TTIP precursor 15 mL, weight of PVA 2.4 grams, volume of ethanol 60 mL, volume of acetic acid 6 mL. The variable changes are calcination temperature 400°C (TiO₂ 400 sample) and calcination at 600°C (TiO₂ 600 sample) (Thahir et al, 2019). Then in ZnO preparation used distilled water, Zn (NO₃)₂, methylene Polyvinylpyrrolidone (PVP), blue, NaOH, The tools used are glassware (iwaki pyrex), UV-Vis spectrophotometer (UV-1800 Shimadzu), photodegradation reactor, UV-A lamp (Himawari T8-20W), SEM test equipment (JOEL JSM-6510 LA), XRD (Rigaku SmartLab 3kV), Oven (Mettler), furnace (IND88), sonicator (Eyela), sudip, pH Universal (Merck), analytical balance (AE Adam), dropper, filter paper, ruler, scissors (Raganata et al, 2019).

Synthesis of TiO and ZnO Nanoparticles

In both synthesis methods, the same method is used with the method of adding chemical compounds. In the synthesis of TiO, 2.4g of PVA was dissolved in 15 mL of hot distilled water (70°C), stirred until PVA dissolved completely. Add 15 mL TTIP, 60 mL ethanol, and 6 mL acetic acid. Homogenize for 1 hour using a magnetic stirrer, continue using an ultrasonic cell disruptor for 1 hour. The solution was then put into a closed Teflon container and heated at 105°C for 17 hours. The gel formed was washed to pH 5 and calcined at 400 and 600°C (Thahir et al, 2019).

Furthermore, the synthesis of ZnO used the same method with the addition of a chemical solution in the form of PVP. 4H₂O 0.2 M, weighed as much as 2.6148 grams, put into a 100 mL beaker and added distilled water to the 50 mL limit mark. Add 2 mL of PVP, sonicate the solution while dripping with 0.2 M NaOH solution until it

reaches pH 11 and forms a white precipitate. The precipitate was filtered, washed with distilled water until pH 7, then centrifuged at 3000 rpm for 15 minutes. The precipitate was taken and then dried in an oven at 100°C for 2 hours, then annealed at 300°C for 2 hours to produce ZnO crystals (Raganata et al, 2019).

ZnO Photocatalyst Activity Testing

Weighed ZnO samples (1%, 3%, 5%, 7%, and 10% of the weight of Zn (NO₃)₂ · 4 H₂O) as much as 0.01 grams were put into each of the seven glass tubes, then 5 ppm methylene blue solution was put into the seven glass tubes as much as 10 mL each. The seven glass tubes were then placed in a reactor and irradiated with a UV-A lamp for 30 minutes. The remaining dye concentration was analyzed by UV-Vis spectrophotometer at the maximum wavelength of methylene blue 664.50 nm. In the same way, it was done for time 60 min, 120 min, 150 min, 180 min. The percentage (%) of MB degradation can be calculated using the following equation (3):

$$\text{Degradasi (\%)} = \left(\frac{C_0 - C_t}{C_0} \right) \times 100\% \dots (1)$$

C₀ is the initial concentration and C_t is the concentration after irradiation.

Absorbent power test on TiO Nanoparticles

Prepared 50 mL of MB solution at a concentration variation of 20-100 ppm into a 100 mL beaker. A total of 0,1 g of TiO₂ nanoparticles was put into the MB solution, then the adsorption process was carried out in a box equipped with a 150 watt Hg lamp. The adsorption process is carried out at an optimum time of 1 hour while stirring using a magnetic stirrer. After reaching the optimum time of 1 hour, the solution was filtered and analyzed for the final concentration using a uv-vis spectrophotometer at a wavelength of 664 nm.

Characterization of TiO Nanoparticles and Characterization of ZnO Synthesis Results

In the characterization of TiO nanoparticles, the FTIR (Fourier Transform Infra-Red) analysis instrument is used to identify the spectrum of bonds that occur in the Ti-O and Ti-O-Ti functional groups, then the analysis of the characteristics of

particle size, phase and shape of the TiO₂ nanoparticle crystal structure is carried out using XRD (X-Ray Diffraction), and to determine the thermal characterization of TiO₂ nanoparticles using DSC (Differential scanning calorimetry) measured at a temperature of 25-250°C for 20 minutes. In the characterization of ZnO synthesis results used XRD (X-Ray Diffraction) instrument to determine the size, as well as the use of SEM (Scanning Electron Microscope) to determine the morphological shape of the ZnO.

Results and Discussion

Photocatalyst Effectiveness Test Results

The contact time profile between the photocatalyst and methylene blue on % degradation can be seen in Figure 1. From Figure 1, it can be seen that the methylene blue dye is well degraded. When the contact time is from 30 minutes to 150 minutes, the degradation ability of ZnO to methylene blue increases with increasing irradiation time.

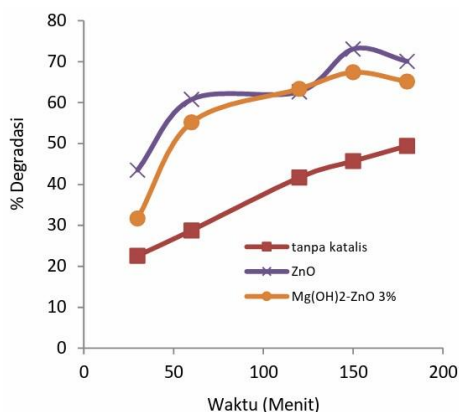


Figure 2. Contact time between photocatalyst and methylene blue on % degradation.

Seen with the rise of the graph. However, there was a decrease in % degradation on each photocatalyst when the contact time was 180 minutes which indicates that the optimum irradiation time occurred at 150 minutes contact time.

Methylene Blue Photodegradation Adsorption

The adsorption isotherm process was carried out to reduce the concentration of methylene blue in solution. The method used was photodegradation

from 150 watts Hg lamplight in a closed box for 60 minutes (optimum conditions for MB sorption using TiO₂ adsorbent). The weight of TiO₂ adsorbent used was 0.1 g. The concentration of methylene blue solution is 20, 40, 60, 80, and 100 ppm. Determination of initial and final concentrations was carried out using a uv-vis spectrophotometer. Table 1 shows the calculation data of the adsorption power of TiO₂ nanoparticles against methylene blue.

Table 1. Adsorption Power Calculation Data (Thahir et al, 2019).

Sample	Co	Ce	Co-Ce	Adsorption efficiency %
TiO ₂ -400	20	3,96	16,04	80,2
	40	8,04	31,96	79,9
	60	12,30	47,70	79,5
	80	16,71	63,29	79,1
	100	21,30	78,70	78,7
TiO ₂ -600	20	3,80	16,20	81,0
	40	7,68	32,32	80,8
	60	11,62	48,38	80,6
	80	15,60	64,40	80,5
	100	19,60	80,40	80,4

Then the data in Table 2 were used to create straight line equations, R² values and Langmuir and Freundlich constants. To determine the adsorption capacity of TiO₂ samples, the amount of MB adsorbate adsorbed per gram of adsorbent was first calculated. Furthermore, the adsorption capacity of TiO₂ was determined through a linear equation by comparing Langmuir and Freundlich adsorption isotherms. Adsorption test parameters of TiO₂ nanoparticles are adsorption capacity (a, mg/g), R² value, and determination of single-layer or multi-layer adsorption type through comparison of Langmuir and Freundlich adsorption isotherm equations.

Table 2. Freundlich and Langmuir adsorption isotherms (Thahir et al, 2019)

Sample	X/m	Cec	Log Ce	Log (X/m)
TiO ₂ -400	8,02	0,494	0,60	0,90
	15,98	0,503	0,91	1,20
	23,85	0,516	1,09	1,38
	31,64	0,528	1,22	1,50
	39,35	0,541	1,33	1,59
TiO ₂ -600	8,10	0,469	0,58	0,91
	16,16	0,475	0,89	1,21
	24,20	0,480	1,07	1,38
	32,20	0,484	1,19	1,51
	40,20	0,487	1,29	1,60

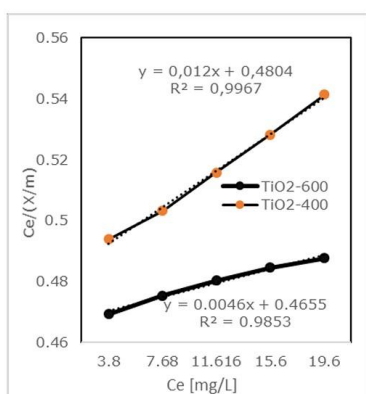


Figure 3. Langmuir adsorption isotherm of TiO sample.

In Figure 3, the R2 value of Langmuir adsorption test is close to 1 (R2 of TiO2-600 sample is 0.9853 and R2 of TiO2-400 sample is higher at 0.9967), while the R2 value of Freundlich adsorption is lower at about 0.94. It can be concluded that MB adsorption can occur on single-layer or multi-layer surfaces. Adsorption capacity. TiO2 nanoparticles to MB is very large, about 83-217 mg/g. This is due to the very small particle size of TiO2 so that the surface area in contact with MB is also greater. Langmuir and Freundlich isotherm equations of TiO2-400 nanoparticle adsorbent can be known Langmuir constant value is KL 0.025 L/mg and Freundlich constant Kf 6.48 L/mg, while TiO2-400 nanoparticle adsorbent has KL value 0.01 L/mg and Kf 6.535 L/mg.

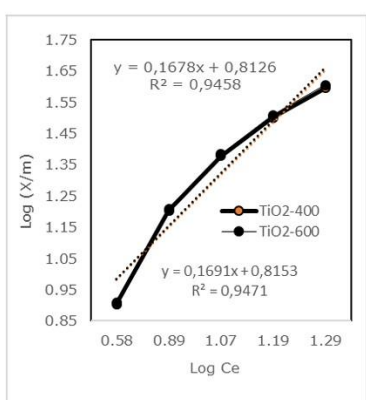


Figure 4. Adsorption Isotherm Freundlich of TiO2 sample (Thahir et al, 2019).

Synthesis Characterization of ZnO and TiO Nanoparticles

The formation of the crystallite phase is shown through XRD measurements. The formation of

ZnO particles has been proven through XRD data, namely the appearance of characteristic ZnO peaks at 2θ 31.760; 34.430; 36.240; 47.530; 65.80; 62.850; 66.360; and 69.070. These peaks are similar to the ZnO standard peaks from ICSD number 29272 which are at 2θ 31.75°; 34.73°; 36.33°; 47.68°; 56.63°; 63.00°; 68.00°; 69.31°.

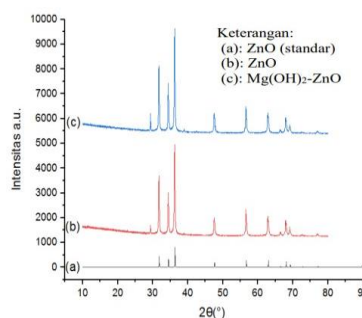


Figure 5. ZnO nanoparticles diffractogram (Raganata et al, 2019)

SEM is used to determine the surface morphology of a material. Observation of ZnO particle morphology with a magnification of 10,000 times. The SEM image shows that the morphology of ZnO particles is spherical and attached to each other (Hosseini et al, 2015).

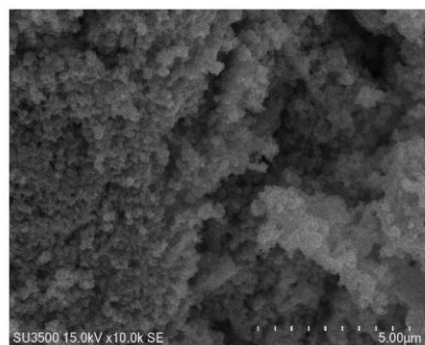


Figure 6. SEM image of ZnO nanoparticles (Raganata et al, 2019)

FTIR analysis was used to identify the spectrum of bonds that occur in the Ti-O and Ti-O-Ti functional groups. Figure 7 shows the spectrum of Ti-O at wave numbers 400-700 cm⁻¹, while Ti-OH is in the spectrum of 2500-3800 cm⁻¹ (Khalaf et al, 2018). The 1616-1624 spectrum shows hydroxyl groups and water absorption on the TiO2 surface (Bakre & Tilve, 2018).

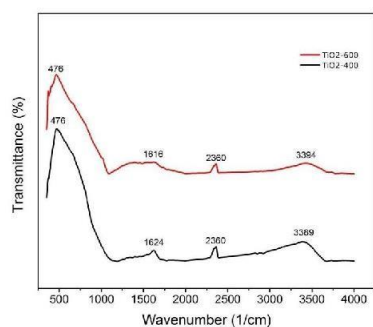


Figure 7. FTIR spectrum of TiO₂ sample (Raganata et al, 2019)

In Figure 8, it can be seen the determination of crystal size using the Scherrer equation by taking the three highest peaks ($2\theta = 25.3^\circ, 37.8^\circ$ and 48.1°) contained in the XRD diffractionogram. The crystal size of the TiO₂-400 sample is 3.15 nm and TiO₂-600 are 1.66 nm. diffraction peaks of TiO₂ samples in Figure 3 occur at $2\theta : 25.3^\circ, 37.8^\circ, 48.1^\circ, 53.9^\circ, 55.1^\circ,$ and 62.9° which correlate with the intensity of hkl (101), (004), (200), (105), (211), and (204). The position and intensity of the TiO₂-600 sample peak is narrower and sharper, so the crystalline properties are more perfect (Lu et al, 2017).

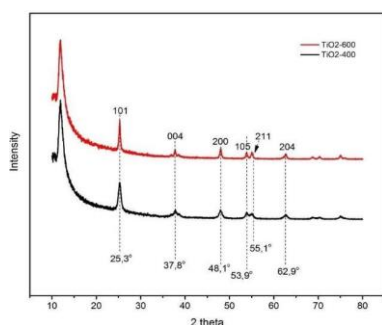


Figure 8. XRD Spectrum of TiO₂ Sample (Raganata et al, 2019)

Thermal characterization of TiO₂ nanoparticles using DSC measured at 25-250°C for 20 minutes. Figure 9 shows the heat absorbed or released by the material when a phase change occurs. Glass transition phase change ($T_g = 60.77\text{-}72.33^\circ\text{C}$) releases 0.10-0.18 J/g heat. While the sharp peak is the crystal point at 158°C , it requires heat of about 33-38 J/g.

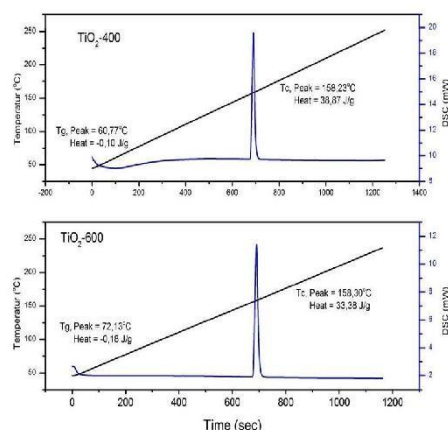


Figure 9. DSC diffractogram of TiO₂ sample.

A sharp peak at the crystal point indicates the material obtained has high purity. The DSC diffractogram has no melting point peak. This indicates that the TiO₂ nanoparticle sample has not melted at 250°C .

Discussion

There are many types of nanoparticles that can be used in wastewater treatment, including zero-valence metal nanoparticles. Logan nanoparticles include silver nanoparticles (AgNPs), iron nanoparticles, and zinc nanoparticles. Then there are metal oxide nanoparticles, specifically TiO₂ nanoparticles and iron oxide nanoparticles. In the field of photocatalysis, in addition to TiO₂ NPs, ZnO NPs have emerged as another effective candidate in water and wastewater treatment due to their unique properties including direct and wide band gap in the near UV spectrum, as well as strong oxidation ability and good photocatalytic properties. ZnO NPs are environmentally friendly photocatalysts, which are biocompatible or in other words, make microorganisms can be used for water and wastewater treatment. In addition, the photocatalytic ability of ZnO NPs is similar of TiO₂ NPs because they have almost the same energy range. The advantage is that ZnO NPs have a lower cost than TiO₂ NPs. In addition, ZnO NPs can absorb a wider solar spectrum than some metal oxide semiconductors. However, similar to TiO₂ NPs, the light absorption ability of ZnO NPs is also limited to the ultraviolet light region due to the large energy band gap. In addition, the application

of ZnO NPs is hindered by photocorrosion, which will cause rapid recombination of photogenerated charges and thus lead to low photocatalytic performance. To improve the photodegradation performance of ZnO NPs, metal doping is a common strategy. Various types of metal dopants were tested, including anionic dopants, cationic dopants, rare earth dopants (dopants containing elements rarely found on the earth's surface) and co-doping. In addition, many studies show that grafting using other semiconductors, such as CdO, CeO₂, SnO₂, TiO₂, graphene oxide (GO) and reduced graphene oxide (RGO), is a feasible method to improve the photodegradation performance of ZnO NPs. When testing the photocatalytic activity of ZnO, positive results were obtained with the increase of contact time from 30 minutes to 150 minutes. The ability to decompose ZnO into methylene blue increased as the contact time increased. Then the TiO₂ nanoparticles showed good results while at 250°C the TiO₂ nanoparticles did not melt which shows the resistance of TiO₂ nanoparticles at high temperatures.

Conclusions

TiO₂ nanoparticles can be synthesized using PVA surfactant and TTIP precursor through sol-gel method followed by hydrothermal method at calcination temperature of 400-600°C. The characteristics of TiO₂ produced are tetragonal structure, anatase phase and particle size of 1.66-3.15nm. The binding spectrum of Ti-O group is 476 cm⁻¹. DSC analysis shows that TiO₂ nanoparticles have high thermal stability. The adsorption capacity of TiO₂ nanoparticles on MB is 81%, the adsorption capacity is about 83-217 mg/g. The adsorption process of MB on the TiO₂ surface can use the Langmuir or Freundlich isotherm adsorption equation with a correlation coefficient value of R² 1. ZnO nanoparticles can be synthesized by the mass coprecipitation method of 0.3489. The activity of ZnO photocatalyst on methylene blue decomposition increases with the increase of contact time.

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