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Degradation of dying industry wastewater with natural zeolite-TiO_2/ZnO photocatalyst

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Abstract
The degradation process requires a photocatalyst, which is generally a semiconductor material. Photocatalyst natural zeolite-TiO_2/ZnO is used in the degradation process of dyeing industry wastewater with visible light irradiation has been conducted. To know the characteristics of natural zeolite photocatalyst-TiO_2/ZnO, such as specific surface area and amount of active sites, as well as the ability of natural zeolite-TiO_2/ZnO for degradation of dyeing industrial wastewater based on pH, COD (Chemical Oxygen Demand), TSS (Total Suspended Solid), and the concentration of the dyes. The optimum characteristics of synthesized photocatalyst were obtained that the specific surface area resulted in (1:3) optimum mass ratio of 19.172 m^2/g, and amount of active sites was 52.2384 x 10^{20} sites/g. The optimum conditions for degradation of natural zeolite-TiO_2/ZnO photocatalyst occurred at 120 minutes with the photocatalyst mass of 2.0 g, the optimum of wastewater volume of 45 mL, and the COD value of 122 mg/L, 0 mg/L TSS, and pH of 5.92. The percentage of degradation of the dyeing industry wastewater at the optimum conditions was 97.08%. The synthesized photocatalyst can be used for dyeing industry wastewater degradation.

Keywords: degradation, dyeing industry wastewater, natural zeolite-TiO_2/ZnO photocatalyst, visible light irradiation

Introduction

The development of textile industry has a problem in Indonesia, due to some fabric industries use synthetic dyes, which are azo group compounds that are very difficult to degrade conventionally [1]. An alternative method to reduce dyestuff degradation is using a semiconductor catalyst [2]. The photocatalysts when energized with photons, the photon energy will be absorbed by electrons in the valence band so that these electrons will move to a higher energy level, namely the conduction band. An alternative method currently being developed is to degrade dyes in the wastewater dyeing industry, namely degradation using a semiconductor catalyst [3].

The photocatalytic activity of the semiconductor needs to be increased by adding a matrix or dopants. The dopants can be used are natural minerals such as natural zeolite. Natural zeolite has a relatively large surface area. It has high adsorption properties so that they can degrade catalyst dyes efficiently [4]

Titanium dioxide (TiO_2) is a semiconductor material. The advantage of TiO_2 is that it has a relatively large energy gap [5]. Thus, it is suitable for photocatalysts, non-toxic, inexpensive, abundance in nature, high chemical stability over a large pH range, catalysts, and low-cost chemicals [6]. The use of TiO_2 material is still encountered in its application, namely the occurrence of a very fast recombination reaction so that the degradation process that occurs on the surface and TiO_2 has a low adsorption power to dyestuffs. Therefore, the weakness of TiO_2 can be improved by using a combination of TiO_2 with other oxides. One of the widely used oxides is zinc oxide (ZnO).

ZnO has high photocatalytic activity, is inexpensive, and has a wide bandgap energy of 3.2 eV [7]. The semiconductor band gap energy is the energy required for electrons to experience an increase in the energy of a system so that it is higher than the ground state (excitation) from the valence band to the conduction band.

The loading of ZnO on natural zeolite/TiO_2 aims to optimize its photocatalytic ability in degrading dyeing industry wastewater, because increasing the active sites of the semiconductor material. This report is expected to reduce environmental pollution due to dye wastewater [8].

Materials and Methods

All chemicals used in this research were dyeing industry waste, natural zeolite, aquadest, gauze, 96% ethanol, titanium dioxide, zinc oxide, hydrochloric acid, phenolphthalein indicator, filter paper, potassium dichromate, sulfuric acid, iron (II) ammonium sulfate hexahydrate, silver sulfate, and ferroin indicator. The tools used in the research are vials, jerry cans, boiling stones, states and clamps, magnetic stirrer, hotplate, furnace, analytical balance, sieve, burette, glassware, oven, porcelain cup, desiccator, dropper, reflux set, condenser reflux, irradiation box, Philips TUV 15W/G15 T8 lamp at 253.47 nm, Fourier Transform Infrared (FTIR) Shimadzu

Prestige-1, UV-Vis spectrophotometry Shimadzu UV-1800, and Surface Area Analyzer (SAA) Quantachrome Novatouch LX -4.

Preparation of Sample

Textile industry wastewater is taken from the fabric dyeing industry in Denpasar, Bali. Dyeing industrial wastewater is taken at three different points from the reservoir and then mixed together and put into jerry cans. The wastewater is filtered with gauze to remove solids that can interfere with the analysis, then the filtrate is collected in a beaker.

Natural Zeolite Activation

A hundred g of natural zeolite that passed a 200 mesh sieve was put into a beaker, and 1000 mL of distilled water was added while stirring with a magnetic stirrer for 3-4 hours. Natural zeolite was filtered and heated at 110ºC for 90 minutes. Adding 1000 mL of 2 M sulfuric acid and stirring for 14-16 hours. Washing with distilled water and dry at 120ºC.

Composite Synthesis

Natural zeolite and TiO_2 were mixed in a ratio (100:5), heated in a furnace at a temperature of 350ºC for 12 hours, and sieved with a size of 200 mesh. Zeolite TiO_2 was mixed with ZnO solidly in a ratio of 1:3, 1:1, and 3:1, added 10 mL of ethanol, stirred, and heated at 400ºC for 1 hour.

Light Time Optimization

Six of 250 mL Beakers glass were filled with 25 mL of industrial wastewater and 0.5 g of natural zeolite-TiO_2/ZnO. Six Beakers glass were put into the irradiation box and irradiated with variations of the LED light intensity of 20, 40, 60, 80, 100, and 120 minutes. The filtrate was centrifuged at 3500 rpm for 10 minutes. Test with UV-vis spectrophotometer, COD, TSS, and pH. The concentration value is entered into the following equation for calculating the percentage of degradation (%D) (Equation 1).

$$\text{Percentage of Degradation (\% D)} = \frac{Co - Ct}{Co} \times 100\% \qquad (1)$$

Information:
Co = initial concentration of dyeing industry effluent
Ct = final concentration of dyeing industry effluent

Catalyst Mass Optimization

Five 250 mL beakers were each filled with 25 mL of dyeing industrial wastewater and added with natural zeolite-TiO_2/ZnO with a variation of 0.5; 1.0; 1.5; 2.0; and 2.5 g and then put into the LED irradiation box with the optimum time that has been obtained in the previous procedure. The value of the irradiation time is then entered into Equation (1).

Sample Volume Optimization

Six of 250 mL beakers were each filled with dyeing industrial wastewater with a volume variation of 20; 25; 30; 35; 40, and 45 mL, then added zeolite-TiO_2/ZnO as much as the optimum catalyst mass obtained. Then put into the LED irradiation box with the optimum time that has been received in the previous procedure. The value of the irradiation time is then entered into Equation (1).

Results and Discussion

Catalyst Functional Groups

Based on Figure 1, the blue color is the natural zeolite catalyst-TiO_2, the black color is the natural zeolite catalyst-TiO_2/ZnO in the ratio (1:3), and the red color is the catalyst in the ratio (1:1), and the green color is the catalyst in the ratio (3:1). The FTIR spectra showed an absorption band in the 3600 cm^{-1} regions followed by a wide band in the 3400 cm^{-1} areas, which indicated that O-H was stretching from H_2O. This stretch indicates that dehydration has occurred due to the heating process [9]. There is also a sharp absorption band from 1600 – 1650 cm^{-1}, which is a band of asymmetrical O-H strain in the form of water deformation. There is no significant change in the FTIR spectra after adding ZnO other than changes in the characteristics of the Si-O-Si bond in wave number 1900-1170 cm^{-1} [10].

Catalyst Specific Surface Area

The specific surface area shows that a larger particle size increases a significant increase in a specific surface area [11]. The results of the measurement of the surface area of the natural zeolite-TiO_2/ZnO catalyst using the BET method carried out with the SAA tool are shown in Table 1.

From Table 1. the highest specific surface area of ZA-TiO_2/ZnO in the ratio (1:3) is 19,172 m^2/g. The data showed that the more ZnO impregnated in the zeolite, the bigger the surface area. A high surface area will increase the ability of the catalyst to adsorb dyes so that the opportunity for degradation is higher [12].

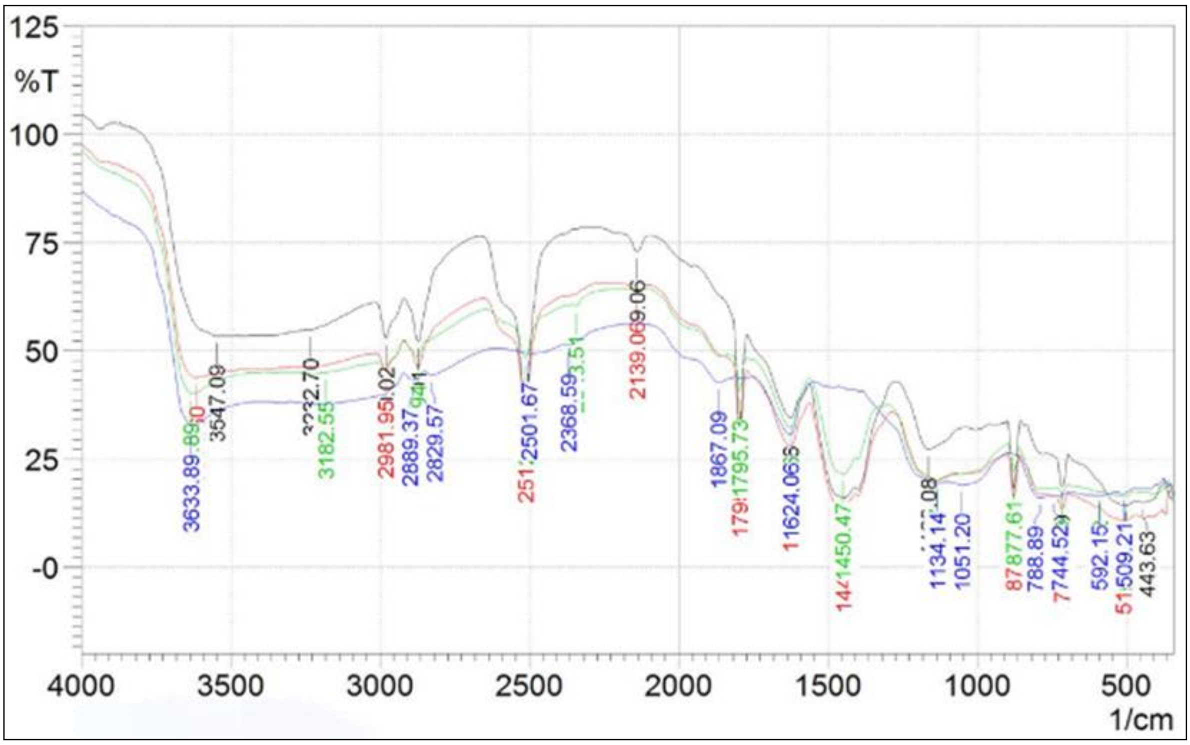

Fig 1: Initial catalysts FTIR spectras

Table 1: Photocatalyst-specific surface area result data

Composite	Surface Area (m^2/g)
ZA-TiO_2	12,019
ZA-TiO_2/ZnO (1:3)	19,172
ZA-TiO_2/ZnO (1:1)	17,636
ZA-TiO_2/ZnO (3:1)	17,624

Characteristics of Number of Catalyst Surface Active Sites

The acidity of the catalyst surface are values that express amount of Bronsted and Lewis active sites present on the catalyst surface [13]. The results of determining amount of active sites are shown in Table 2.

Table 2: Amount of catalyst active sites

Composite	Amount of Acid Active Sites (sites/g)
ZA – TiO_2	5,3012 x 10^{20}
ZA – TiO_2/ ZnO (1:3)	2,6993 x 10^{20}
ZA – TiO_2/ ZnO (1:1)	4,6010 x 10^{20}
ZA – TiO_2/ ZnO (3:1)	6,4022 x 10^{20}

The total sites selected were natural zeolite photocatalyst-TiO_2/ZnO (1:3) with amount of active sites of 2.6993 x 10^{20} sites/g. The activation process of natural zeolite will increase acidity. This is a good way to increase the acidity of the zeolite by replacing the cations bound to the zeolite with H^+ ions [14]. The active sites have an important role in heterogeneous catalytic processes and the determination of reaction properties. The high amount of surface active sites can cause an increase in the formation of ·OH radicals which play a role in the degradation process [15]. Therefore, the high amount of active sites can increase the photocatalytic degradation ability of the dyeing industry wastewater.

Light Time Optimization

Optimizing irradiation time is the shortest time needed to give the highest percentage and give a significant decrease in absorbance spectra which can be seen in Figure 2, and the curve of the relationship between irradiation time and the percentage of degradation is presented in Figure 3.

Figure 2 shows it decreased from 20 minutes to 80 minutes, then from 80 minutes to 100 minutes. This may occur because the ability of natural zeolite-TiO_2/ZnO (1:3) composites to degrade has reached its maximum point. Therefore, the 120 minutes was chosen as the optimum time to be used at the next optimum. The average percentage of the 120 minute is 99.38%. Figure 3 shows that there is a decrease in COD which is balanced with an increase in pH. The increase in COD occurs due to the length of time the sample is in the radiation box. A high COD value indicates a high content of organic compounds in the waste [16]. The increase in COD value affects the pH value. pH indicates the result is acidic. Differences in the pH conditions of the solution can cause changes in surface charge and potential shifts in the photocatalyst reaction so that it affects the degradation process of the ionic strength dye and affects the adsorption process [17]. For the TSS value, each time, the result is 0 mg/L. This may be because, after centrifugation, the residue and filtrate were separated so that there was no residue on the filter paper when the TSS test was performed.

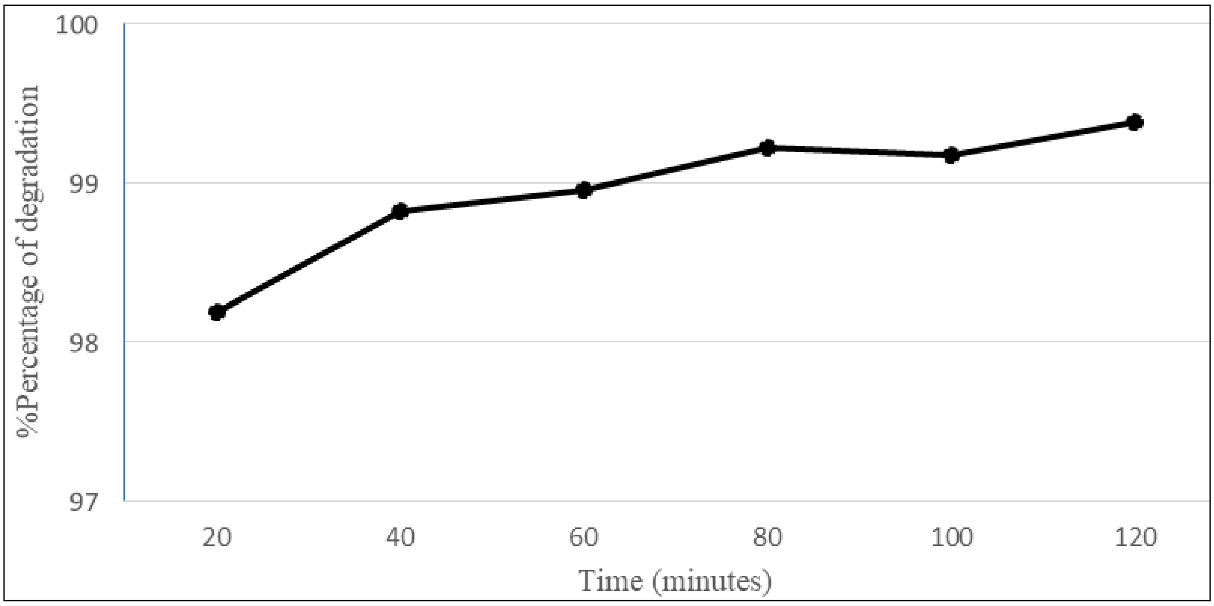

Fig 2: Curve of the relationship between irradiation time and the percentage of degradation

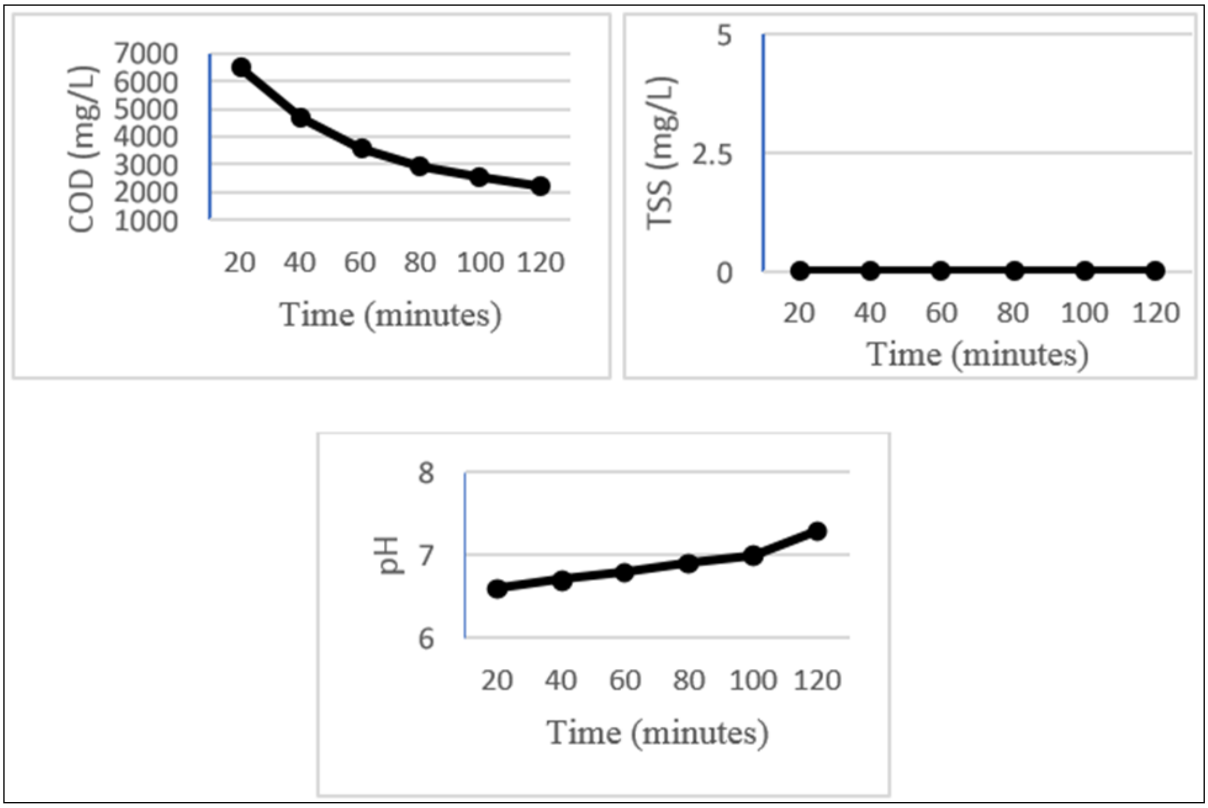

Fig 3: Graph of COD, TSS, and pH against irradiation time

Optimum Catalyst Mass

The optimization of the catalyst mass for the natural Zeolite-TiO_2/ZnO photocatalyst can be seen in Figure 4, and the curve of the relationship between the catalyst mass and the percentage of degradation is presented in Figure 5.

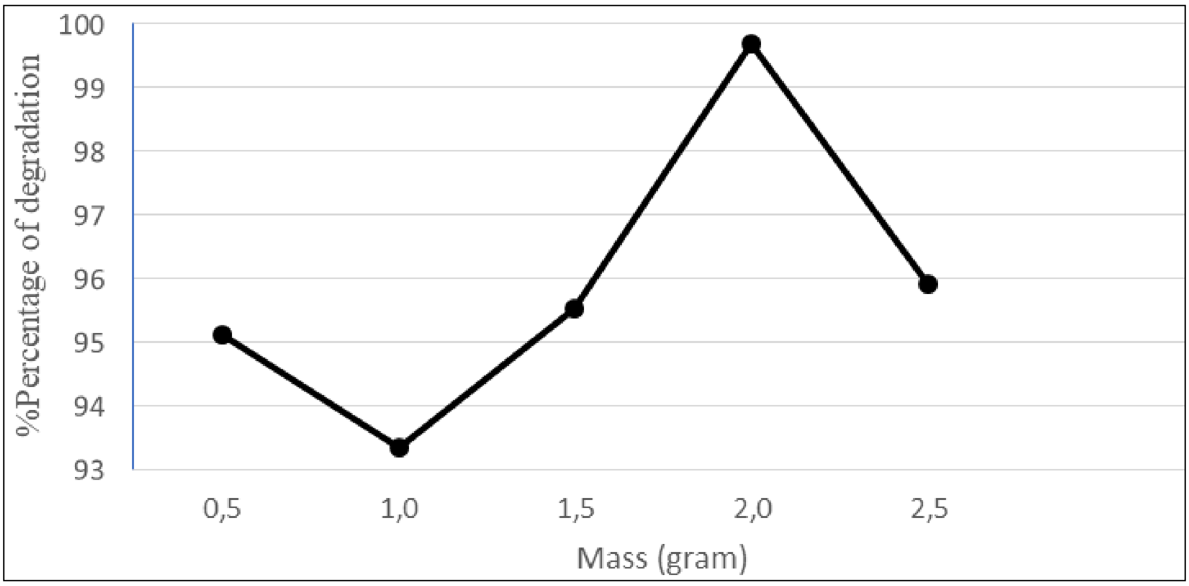

Fig 4: Curve of the relationship between catalyst mass and the percentage of degradation

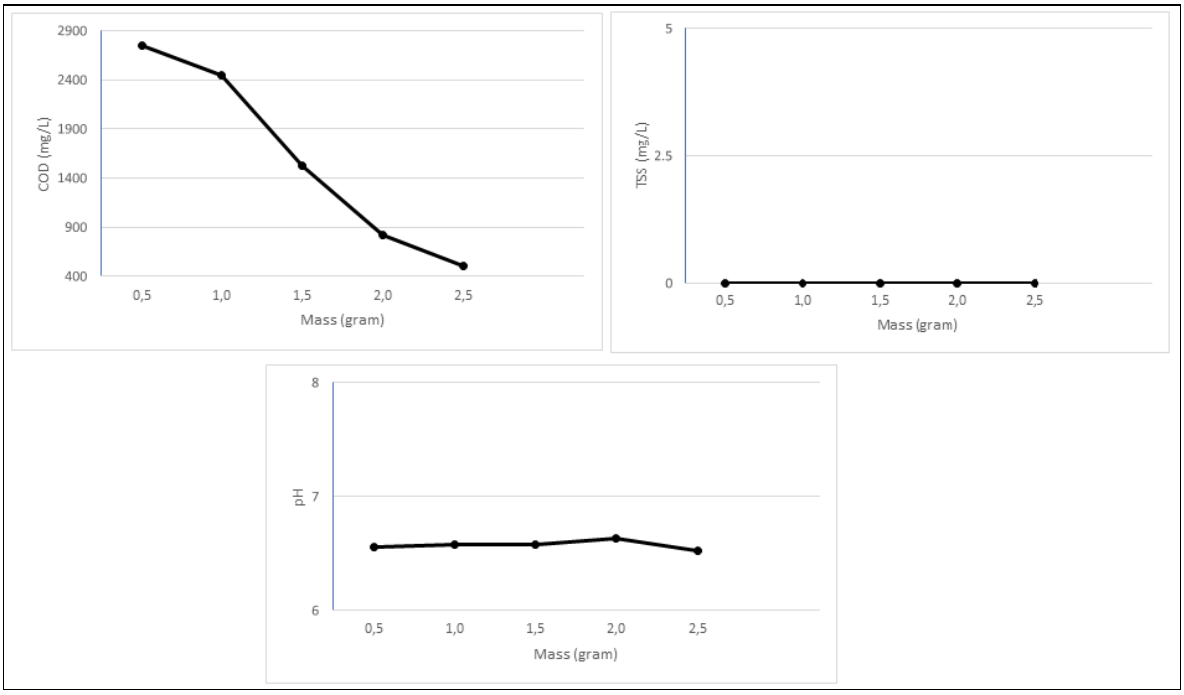

Fig 5: Graph of COD, TSS, and pH against catalyst mass

The results of the optimization of the catalyst mass in Figure 4 show an increase in the mass of 1.0 gram to a mass of 2.0 g and then a decrease in the mass of 2.0 g. This may be because the composite's ability to degrade the dyeing industry's wastewater has reached its maximum point. The average mass degradation percentage of 2.0 g was 99.70%. In Figure 5, it can be concluded that the decrease in COD and pH values is almost constant. However, for TSS, the result is still 0 mg/L because the residue has separated from the filtrate during the centrifugation process. In these results, at 2.5 g of catalyst mass, the COD reduction was not too high. Therefore 2.0 g of catalyst mass was chosen.

Optimum Liquid Waste Volume

Optimization of the volume of liquid waste against natural Zeolite-TiO_2/ZnO photocatalyst can be seen in Figure 6, and the curve of the relationship between the volume of liquid waste and the percentage of degradation is presented in Figure 7.

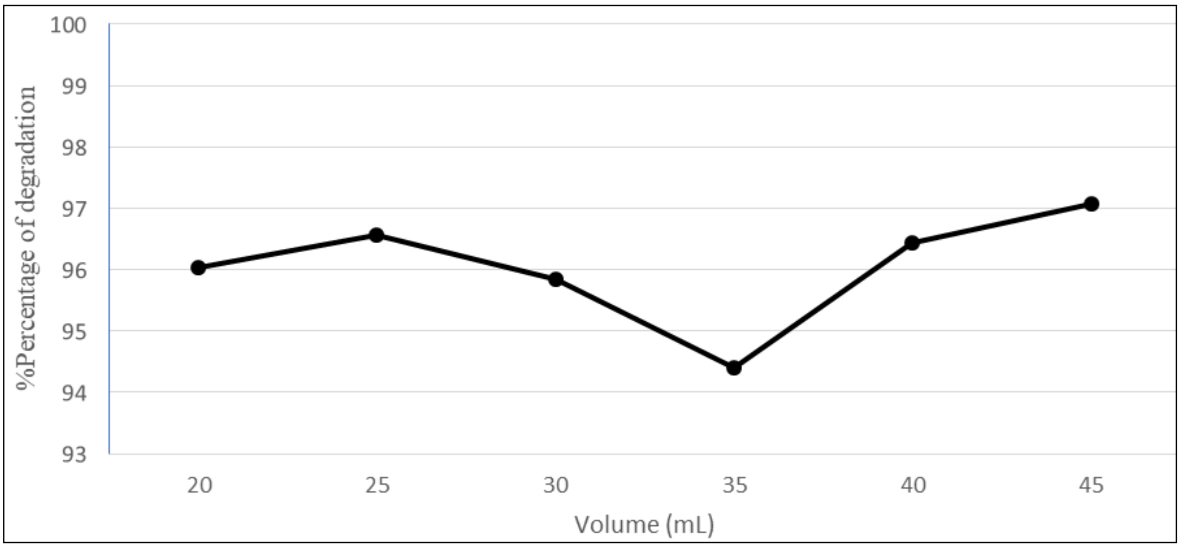

Fig 6: Curve of the relationship between liquid waste volume and the percentage of degradation

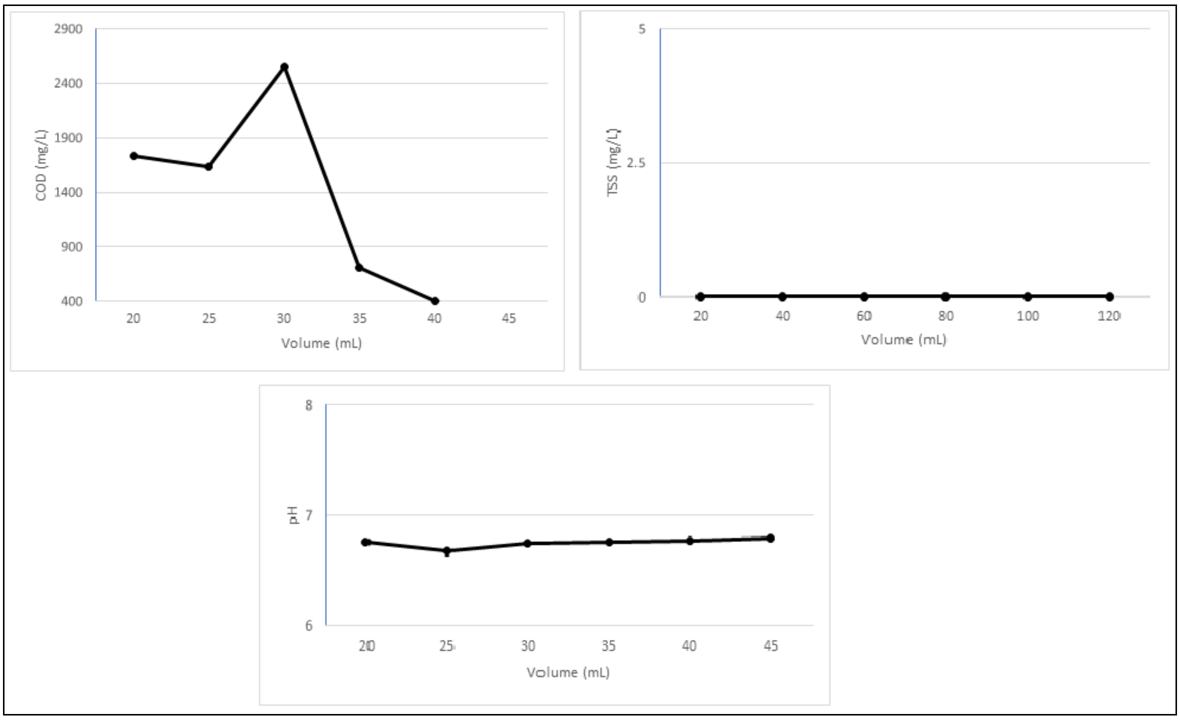

Fig 7: Graph of COD, TSS, and pH against liquid waste volume

Figure 7 shows that the optimization of the catalyst mass occurred at a volume of 35 mL to 45 mL, so that the highest optimal volume of waste is at 45 mL with a percentage of 97.08% sure. This is expected to be more waste that is degraded, but less catalyst is needed, but the results are still good. In Figure 8, using a photocatalyst can reduce COD and increase the pH value. This is due to the large volume of waste used and the large number of catalysts needed to degrade the waste properly. The volume used as the optimum volume is 45 mL because it is more effective for use in forming hydroxyl radicals and superoxide because the catalyst does not get irradiation [18].

Conclusion

The characterization of natural zeolite-TiO_2/ZnO (1:3) photocatalyst showed that the specific surface area was 19.172 m^2/g, and the number of acid active sites was 2.6993 x 10^{20} sites/g. Degradation of dying industry wastewater with natural zeolite-TiO_2/ZnO photocatalyst in the ratio (1:3) obtained optimum irradiation time of 120 minutes, catalyst mass of 2.0 g, and volume of 45 mL with UV light. These results meet the established quality standards.

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