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Photodegradation of rhodamine B over natural zeolite/ZnO

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ABSTRACT
Rhodamine B is dye compound commonly used in the textile industry that consisted of azo compound. Azo compound generally difficult to be degraded. Undegradated azo compound in rhodamine B make it danger for the environment. An effective effort to handle rhodamine B waste must be conducted. Natural zeolite/ZnO is a material that can be used to degrade rhodamine B to be simpler compound based on photodegradation procces. Based on the analysis, the particle size of natural zeolite/ZnO is 16.92709 nm and the band gap energy 2.92 eV. The highest degradation percentage of rhodamine B over natural zeolite/ZnO under UV irradiation is 99.54%.

Keyword: Rhodamine B, natural zeolite/ZnO, percentage of degradation

1. INTRODUCTION

Rhodamine B (Figure 1) is one of various kind of dyes that generally used in textile industry. In commercial world, rhodamine B also known as tetraetilrhodamine; rhodamine B klorida C.I basic violet 10, Cl. 45170, D&C Red No 19. Chemically, rhodamine B is named as N-[9-(2-carboxyphenyl)-6-(diethylamino)-3H-xanthen-3-ylidene]-N-ethylethanaminium and the formula is $C_{28}H_{31}C_1N_2O_3$. Rhodamine B consists of chlorin group, poli aromatic hydrocarbon (PAH), alkylating compound, i.e. compound that consist heavy metal residual. Molecular weight and melting point of rhodamine B are 479.06 g/mol and 210 - 211°C. Rhodamine B is water soluble compound and slightly soluble in NaOH and HCl (Sumantri, 2007). In textile and paper industries, rhodamine B is used to make the product better in colour and appearance. The presence of chlorine bond in rhodamine B make it reactive and toxic for human being and environment (Masthura, 2019).

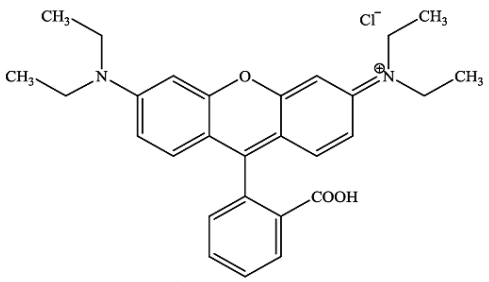


Figure 1. The structure of rhodamine B

Several procedurs have been proposed to reduce industrial textile waste, such as coagulation, precipitation and adsorbtion. These methods are simple and cheap in cost but still have

several shortages. Alternative methods are needed to overcome those shortages. One of the alternative methods to reprocess rhodamine B waste, especially in water areas, is photodegradation.

Photodegradation is a process to decompose a compound to be simpler compound with the presence of catalyst and photon energy. Generally, catalyst in the form of semiconductor material, such as ZnO. Photodegradation is based of the electron movement from valence band to conduction band in the presence of photon energy. Holes in valence band are formed due to electron jump form valence to conduction band. Holes may promote the forming of radicals that actively break the target to be simpler compound (Kurniadi, 2000). The dedragation of rhodamine B, is shown in Figure 2.

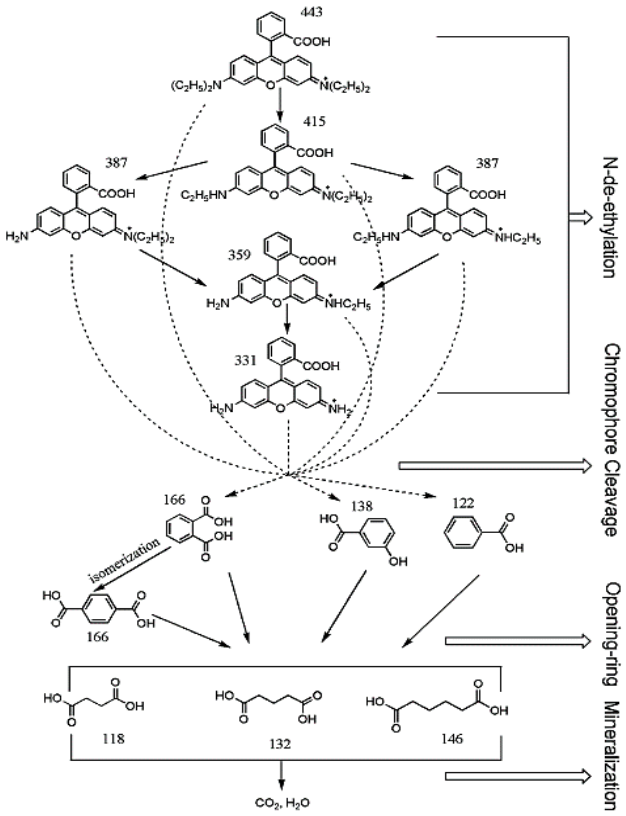


Figure 2. The mechanism of the degradation of rhodamine B

Zinc oxide (ZnO) is n-typed semiconductor with high transmittance, chemical and mechanical stability (Maryanti et.al., 2012). ZnO may adopt cubic, cubic rocksalt and hexagonal forms, where hexagonal is the most stabil form. The lattice parameters of zinc oxide wurtzite are a = b = 0.3249 nm and c = 0.52042 nm with the ratio of c/a = 1.602, the angle α = 109.46° and the density = 5.675 g/cm^3 (cm^3 (Tüzemen & Gür, 2006). The structure of ZnO wurtzite is shown in Figure 3.

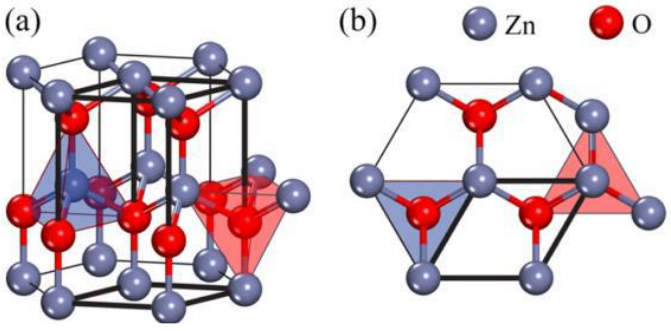


Figure 3. Structure of ZnO wurtzite a) side view, b) top view

The advantages of ZnO for photocatalyst are cheap, absorb sun radiation in broader scale, has higher photocatalyatic activity than other metal oxide (Saravanan *et al*., 2013), non-toxic and high chemical stability (Kusdianto *et al*., 2019). The photocatalysist activity of zinc oxide may be increased by dopping it to the support, such as zeolite. Zeolite is a tetrahedral alumina silicate mineral. Based on the structure, zeolite may be used as an adsorbent, thermal catalyst, ion exchange and catalyst support (Sutarti and Rahmawati, 1994). When metal oxide, such as TiO_2, ZnO, CuO and CaO, are dropped onto the zeolite surface, may degrade the organic compound. Based on the fact, zeolite is extensively used to process liquid waste. Before used, natural zeolite must be activated by strong acid or base solution.

2. RESEARCH METHOD

The grinded zeolite was sieved by 150 mesh siever, and then dispersed into aquadest with the ratio of zeolite to aquadest was 1:3. The mixture was then stirred and heated at 90 ^oC for 2 hours. The resulted precipitation was dried at 120 ^oC for 5 hours in an oven, and then calcined at 300 ^oC for 2 hours in muffle furnace. The precipitation was immersed into 1 M NaCl solution with the ratio of precipitation to NaCl solution is 1:4 and heated at 80 ^oC for 2 hours. The precipitation was decanted and dried in an oven at 120 ^oC for 5 hours, and then calcined for 3 hours at 300 ^oC. The physically and chemically activated zeolite was characterized by using XRD and FTIR.

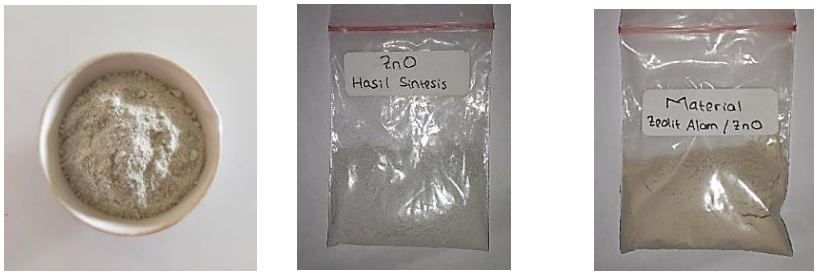
Zinc oxide was prepared by dispersing 18 g of $Zn(CH_3COO)_2.2H_2O$ into 32 mL of ethanol solution. The mixture was then stirred and heated in a flask for 2 hours at 76 ^oC. A 90 mL NaOH 2M was slowly added into the mixture and stirred for 1 hour and then decanted with filter paper to get ZnO. The precipitation was dried for 1 hour at 110^oC in an oven, and then calcined at 450 ^oC for an hour in muffle furnace. The synthesized ZnO was then characterized by using XRD and FTIR.

Natural zeolite/ZnO was prepared by mixing activated zeolite with $Zn(CH_3COO)_2.2H_2O$ powder and ethanol with the ratio 4:2:15 respectively. The mixture was stirred and heated at 50 ^oC for 2 hours. A 60 mL of 0.1 M NaOH solution was added to the mixture and stirred for an hour. The resulted precipitation was separated, dried at 120 ^oC for 5 hours and then calcined at 400 ^{o} C for 2 hours. Nature zeolite/ZnO material was characterized by using XRD, FTIR, UV-Vis and SEM-EDX.

Protodegradation of rhodamine B over natural zeolite/ZnO was conducted under UV irradiation. A 0.1-gram natural zeolite/ZnO was immersed into 10 mL of 10 ppm rhodamine B solution. The UV irradiation was taken at -30 (dark condition), 0, 30, 60, 90 and 120 minutes. After UV irradiation, the mixture was centrifused and analyzed by UV-Vis spectrometer at maximum wavelength to obtain the absorbance of rhodamine B after the photodegradation process.

3. RESULTS AND ANALYSIS

The natural zeolite/ZnO material (Figure. 4) is successfully synthesized by precipitation methode use activated natural zeolite and $Zn(CH_3COO)_2.2H_2O$ as the precursors. The activated natural zeolite, synthesized ZnO and natural zeolite /ZnO are shown in Figure 4.



a) b) c)

Figure 4. a). Activated natural zeolite, b). synthesized ZnO and c). natural zeolite /ZnO

3.1. The characterization of natural solite/ZnO material

a. X-Ray Diffraction

Characters of activated and unactivated zeolite, synthesized ZnO and natural zeolite/ZnO was investigated by using XRD Miniflex 600, range 4° – 80°, radiation CuKα 1.5406 Å, voltage 40 kW and current 15 mA. Diffraction pattern of unactivated and activated natural zeolite are shown in Figure 5 and Figure 6.

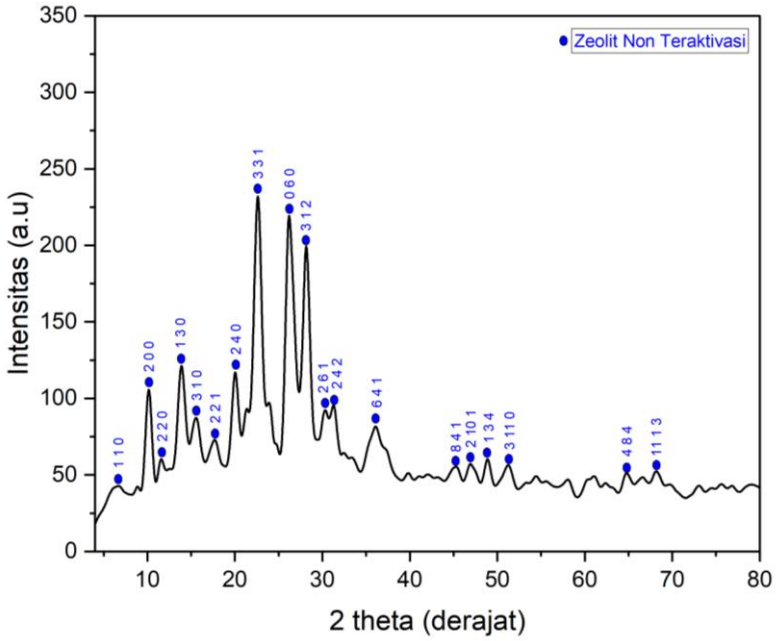


Figure 5. Difractogram of unactivated natural zeolite

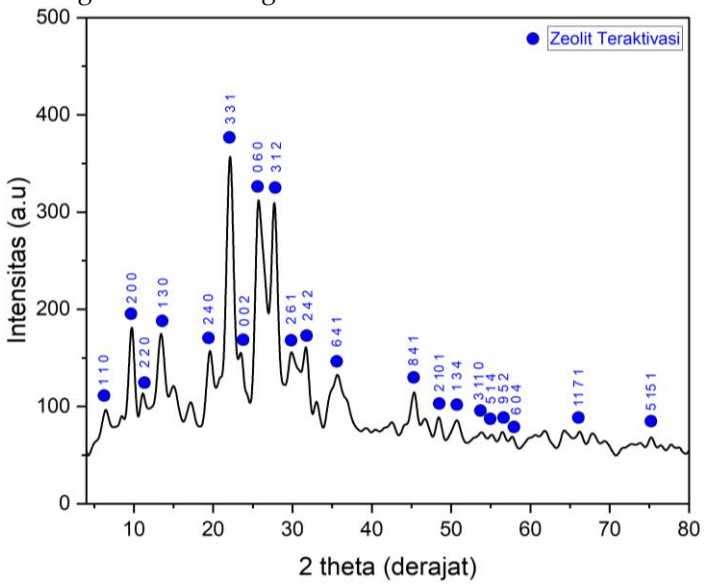


Figure 61. Diffraction pattern of activated natural zeolite

Based on Figure 5 and Figure 6, there is no significant difference between diffraction pattern of unactivated and activated natural zeolite. It indicates that the physically and chemically activation to the zeolite do not change the original structure of natural zeolite. By the QualX application, comparing to COD (Crystallography Open Database) data, the 2θ values of unactivated and activated zeolite match to data No. 00-900-3355 indicates that the zeolite is mordenite. The crystal size of unactivated and activated zeolite, based on Scherrer equation are 20.61324 and 16.9167 nm.

The diffraction peaks of refinement of activated zeolite by Rietica software are shown in Figure 7. The result of refinement process is fitted with the diffraction pattern data of American Mineralogist Crystal Structure Database (AMCSD). Based on Rietveld analysis for activated zeolite result the Rp = 10.52%, Rwp = 14.91% and GoF = 0.4982%. The lattice parameters of natural zeolite are a = 19.9572, b = 20.4920 and c = 7.5209 Å. Based on the AMCSD data No. 0003444, natural zeolite is classified as orthorhombic mordenite and space group Cmc21.

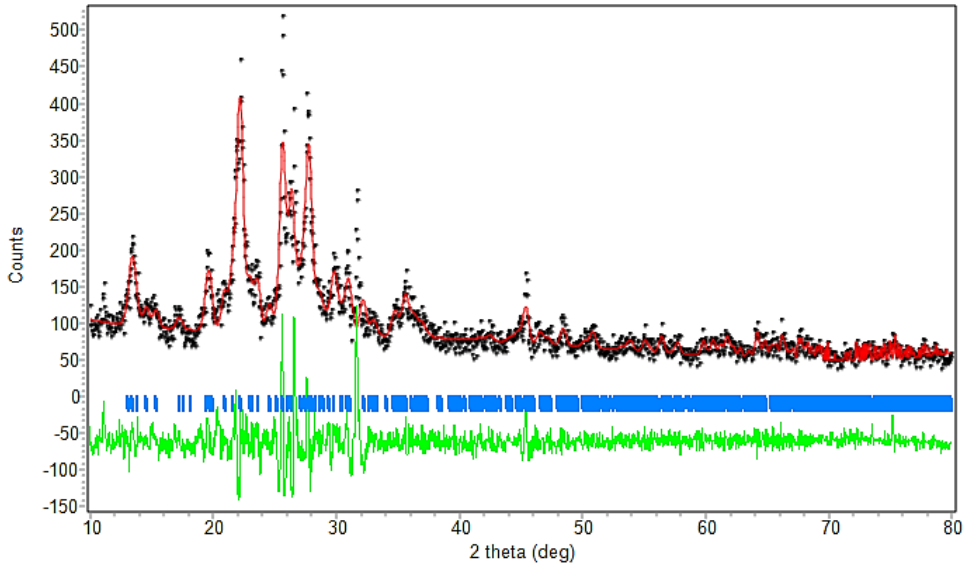


Figure 7. refinement pattern of activated zeolite

Diffraction pattern on ZnO (Figure 8) shows that the value of 2θ = 31.69°; 34.36°; 36.17°; 47.49°; 56.50°; 62.77°; 66.32°; 67.84°; 68.98°; 72.48° and 76.84°. The 2θ values of the synthesized ZnO are matching with COD (Crystallography Open Database) data No. 00-101-1258 and indicates that the peaks are characteristic of ZnO hexagonal. Based on Scherres equation, crystal size of ZnO is 25.8998 nm and can be classified as nano particle. The high peaks indicates that ZnO is a crystallin.

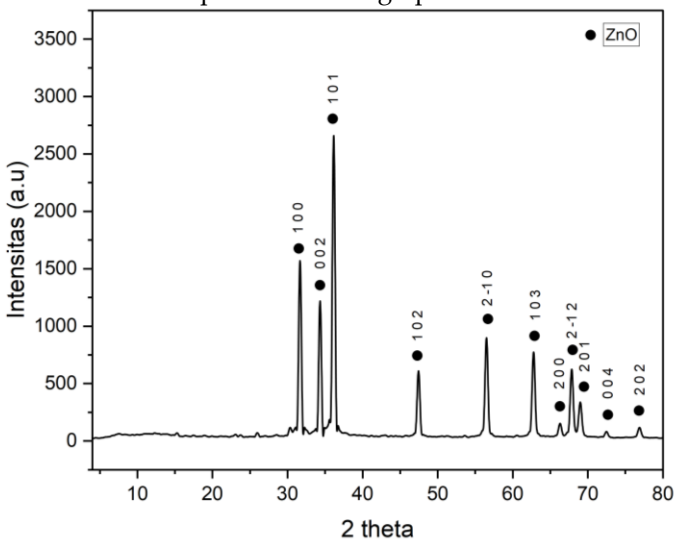


Figure 82. Difractogram of synthesized ZnO

Diffraction pattern of natural zeolite/ZnO is shown in Figure 9.

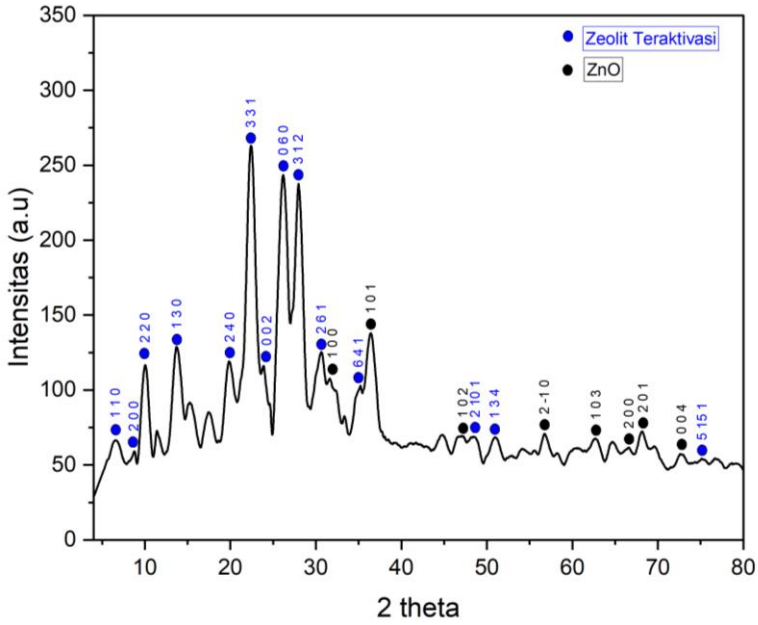


Figure 9. Diffraction pattern of natural zeolite/ZnO material

The 2θ values of natural zeolite/ZnO match with the data of COD No. 00-900-3355 (mordenite zeolite) and No. 00-101-1258 (ZnO), with the percentage of modernite and ZnO are 63.64 % and 36.36 % respectively. Based on Scherrer equation, the crystal size of natural zeolite/ZnO is 16.92709 nm. It can be concluded that the crystals are nanoparticles in category.

b. FTIR

The FTIR spectra of natural zeolite/ZnO is shown in Figure 10, whereas the interpretation in Table 1.

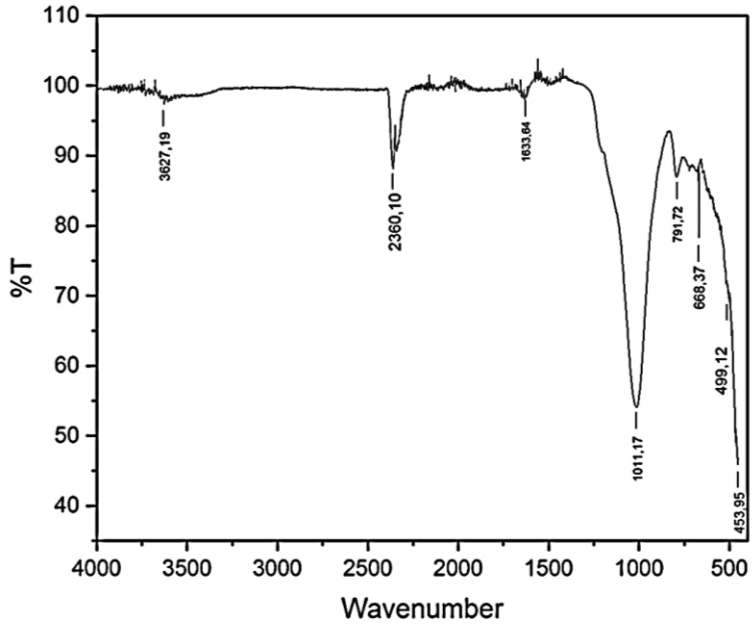


Figure 10. FTIR spectra of natural zeolite/ZnO

Table 1. Intepretation of FTIR spectra of natural zeolite/ZnO

Wave number (cm^{-1})	Intepretation
453,95	Si-O or Al-O bench vibration
499,12	Zn-O stretching
668,37 and 791,72	Vibrasi ulur simetri O-Si-O or O-Al-O
1011,17	Si-O-Si or Zn-O-Si stretching
1663,64	Zn-O-Zn stretching
2360,10	Si-OH vibration
3627,19	O-H stretching

Based on Table 1, it`s showed that ZnO is successfully dopped onto natural zeolite surface.

c. UV-Vis Spectroscopy

Absorbance spectrum of natural zeolite/ZnO is shown in Figure 11.

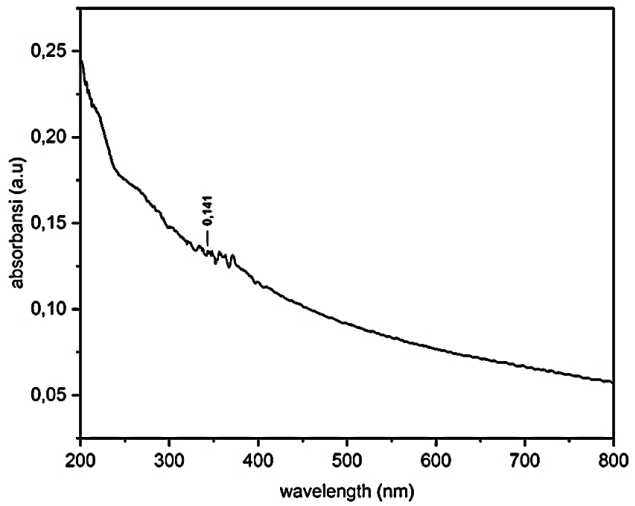


Figure 11. Absorbance spectrum of natural zeolite/ZnO

Natural zeolite/ZnO absorp energy in UV area, with maximum wavelength and absorbance are 343 nm and 0.131 respectively. Band gap energy of natural zeolite/ZnO is determined based on the absorbancy data by using Tauc Plot methode (Figure 12)

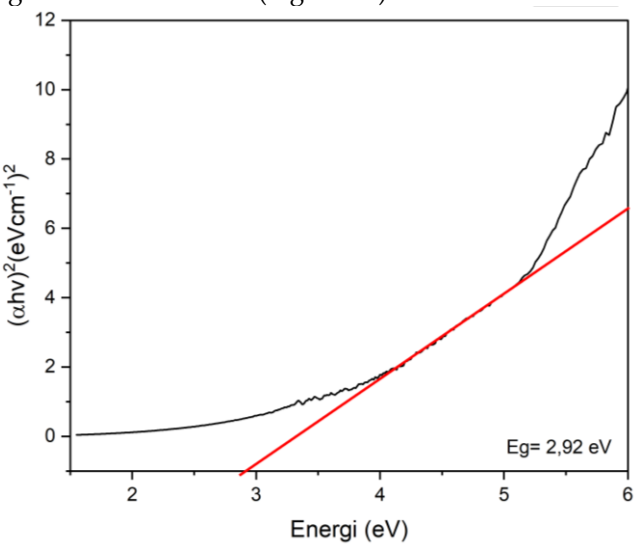


Figure 12. Graph of determining of band gap energy of natural zeolite/ZnO

Based on Figure 14, the band gap energy of natural zeolite/ZnO is 2.92 eV and indicates that the dopping of ZnO onto zeolite surface decrease the band gap energy of ZnO (3.3 – 3.7 eV). Zeolite disperses ZnO onto the surface and increase the surface area of photocatalyst, so the band gap energy is decrease.

d. SEM-EDX

The magnification of 1000, 3000, 5000 and 10000, depth of field 4 – 0.4 mm and resolution1-10 nm are conducted in SEM analysis of natural zeolite/ZnO (Figure 13)

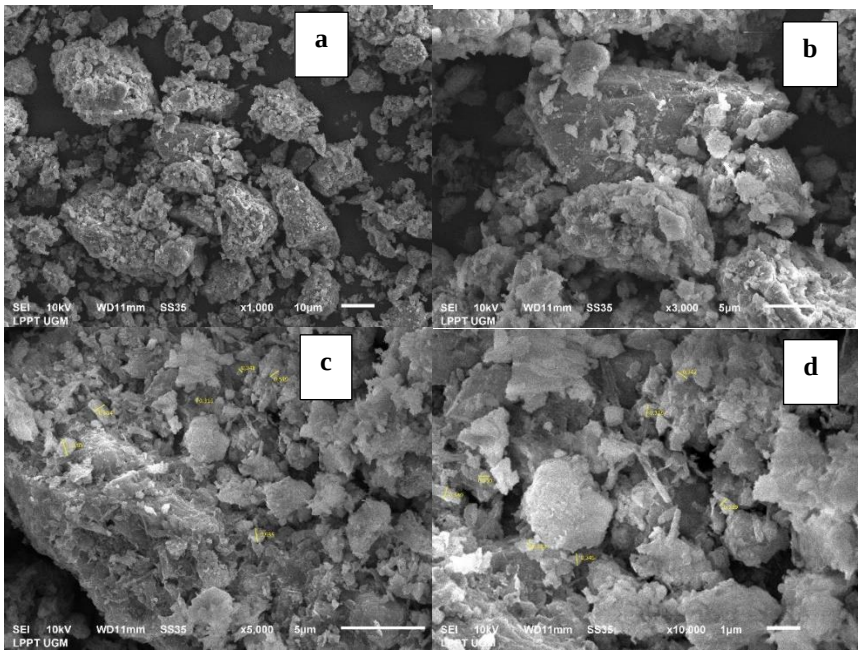


Figure 13. SEM analysis of naturalzeolit/ZnO with the magnification a)1000, b) 3000, c) 5000 and d) 10,000

Morphology analysis shows that there are agglomerates (0,439 – 1,13 μm in size, supposed to be zeolite) and small particles (0,31 – 0,35 μm in size, supposed to be ZnO) dispersed randomly around it. The EDX spectrum of natural zeolite/ZnO is shown in Figure 14.

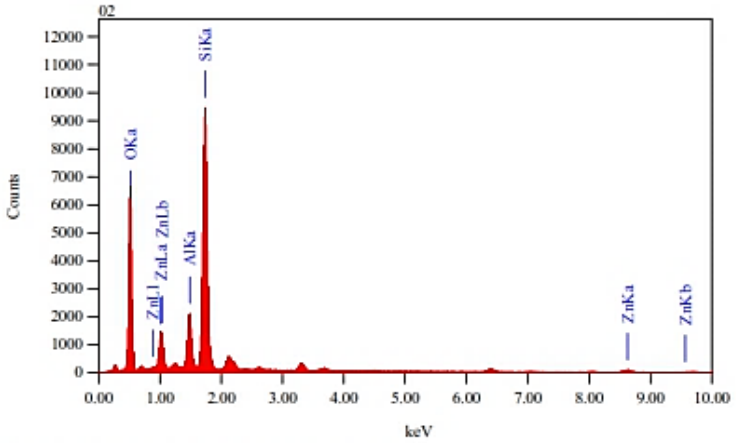


Figure 14. EDX spectrum of natural zeolite/ZnO

The mass percentage of the element in natural zeolite/ZnO, based on EDX analysis, are:O = 53.81%, Al = 6.27%, Si = 32.14%, Zn = 7.78%. Based on the fact, it can be concluded that ZnO is successfully dopped onto the zeolite surface.

3.2. Activity test of natural solite/ZnO material on the photodegradation of rhodamine B

Maximum wavelength of rhodamine B is shown in Figure 15.

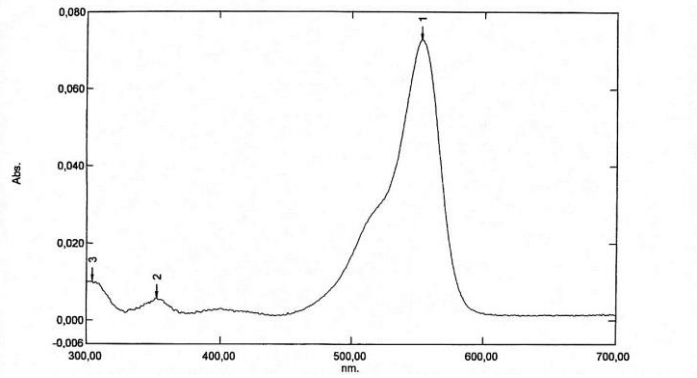


Figure 15. Maximum wavelength of rhodamine B

Based on Figure 15., maximum wavelength of rhodamine B is 553 nm and the absobance is 0.073. The absorbance of standard rhodamine B solution is shown in Table 2 and the standard curve of rhodamine B is shown in Figure 16.

Tabel 2. The absorbance of rhodamine B solution

Concentration (ppm)	Absorbance
0	0.000
1	0.034
2	0.071
3	0.110
4	0.137
5	0.162

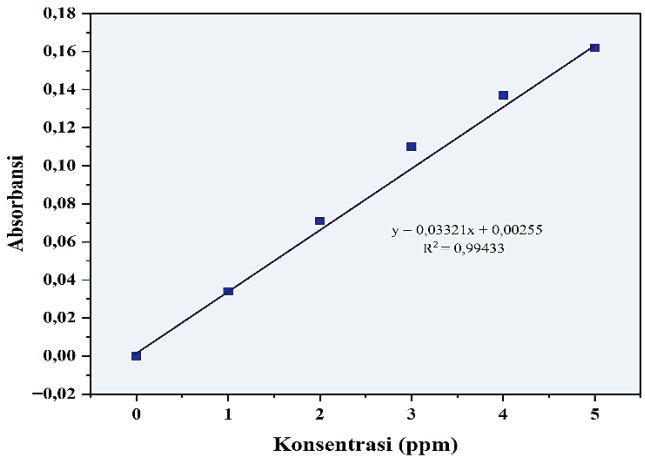


Figure 16. Standard curve of rhodamine B

The linear regression of standard curve of rhodamine B is y = 0,03321x + 0,00255, with correlation coefficient (R^2) is 0,99433. It means, the standard curve of rhodamine B fulfil the SNI 06-6983.31-25 with the correlation coefficient ≥ 0,97.

The result of rhodamine B photodegradation over natural zeolite/ZnO is shown in Table 3 and Figure 17.

Table 3. The degradation of rhodamine B under UV irradiation

No.	Irradiation time (minute)	Absorbance	Final concentration (ppm)	Degradation percentage (%)
1.	-30	0.089	2.6031	72.78%
2.	0	0.320	9.5589	0.00%
3.	30	0.071	2.0611	78.43%
4.	60	0.036	1.0072	89.46%
5.	90	0.021	0.5556	94.18%
6.	120	0.004	0.0436	99.54%

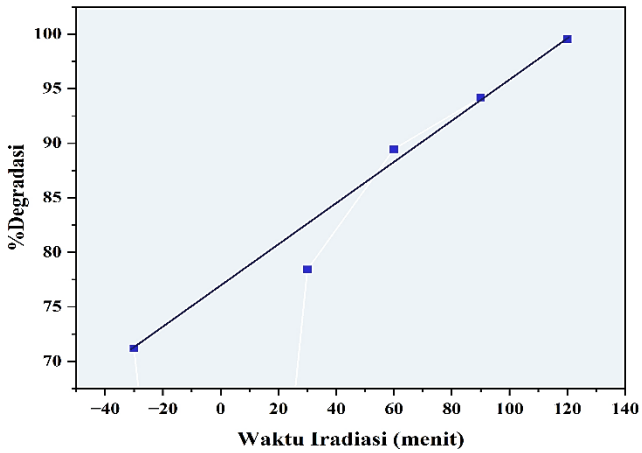


Figure 17. Degradation curve of rhodamine B over natural zeolite/ZnO

In dark conditions (-30 minute), the degradation is 72.78 %, due to the adsorption on the catalyst surface. The absence of photons makes no hydroxyl radical formed. Under UV irradiation, the greater the irradiation time, the greater the hydroxyl radical formed. Hydroxyl radical is a strong oxidazing agent that contributes to the degradation process. The greater the hydroxyl, the greater the rhodamine B degradated. The highest percentage of photodegradation of rhodamine B is obtained at 120th minute, with the degradation percentage 99.54%. based on the photodegradation values, it can be concluded that material of natural zeolite/ZnO has a good catalytic activity on the photodegradation of rhodamine B under UV irradiation.

4. CONCLUSION

The particle size and band gap energy of natural zeolite/ZnO are 16.92709 nm and band gap energy 2.92 eV. The highest degradation percentage in degradation of rhodamine B over natural zeolite/ZnO under UV irradiation is 99.54%.

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