ZnO INCORPORATED ON NATURAL ZEOLITE FOR PHOTODEGRADATION OF METHYLENE BLUE

N. P. Diantariani^{1,2}, I. Kartini², A. Kuncaka², and E. T. Wahyuni^{2,*}

¹Department of Chemistry, Universitas Udayana, Bali 80362, Indonesia

²Department of Chemistry, Universitas Gadjah Mada, Yogyakarta 55281, Indonesia

*E-mail: endang_triw@ugm.ac.id

ABSTRACT

Zinc oxide was incorporated into natural zeolite (ZnO-NZ) by cation exchange followed by co-precipitation and calcination processes. The effect of the amount of ZnO loaded in the zeolite framework on the properties and photoactivity was studied. The resulted photocatalysts were characterized and were examined their photodegradation efficiency for methylene blue (MB) degradation under ultraviolet light. The results showed that ZnO was successfully incorporated and well distributed into the zeolite frameworks. The ZnO-NZ photocatalysts showed a higher specific surface area and wider bandgap than the bare ZnO. The photodegradation activity of ZnO-NZ for MB is twice as high as the bare ZnO. Moreover, the photodegradation activity for MB depends on the amount of ZnO loaded in the ZnO-NZ. Optimum MB photodegradation of 83.05% was obtained by using ZnO-NZ having 6.1% of ZnO fraction.

Keywords: ZnO, Natural Zeolites, Photocatalysts, Photodegradation, Methylene Blue.

© RASĀYAN. All rights reserved

INTRODUCTION

In recent years, increasing use of dyes in industries such as textile, printing, leather, plastic, pulp mill and paper without adequate wastewater treatment methods has caused severe water pollution.^{1,2} The dyes used in industries usually are difficult to degrade naturally due to the complex and stable aromatic structures.² Methylene blue (MB) is an industrial dye that is widely used to dye silk, cotton, and wood.^{1,3,4} MB is an organic dye that is often used as a model compound for removing dyes and organic contaminants because it can represent the dyes that have stable heterocyclic aromatic structures⁴, and it is also easy to obtain and to analyze and has an economical price. Although MB is not strongly poisonous, it can have some harmful effects on humans and animals. The dye irritates the gastrointestinal tract if ingested and causes methemoglobinemia, cyanosis, convulsions, tachycardia, and dyspnea if inhaled.^{2,5}

Several treatment processes such as biodegradation⁶, bioremediation⁷, adsorption^{8,9}, and photocatalytic degradation¹⁰⁻¹² are currently used in methylene blue removal from wastewater. Among these methods, photocatalytic degradation has a high potential to develop further for its rapid degradation rate, mineralization of dyes to green products, and reduction of the toxicity of dyes.¹³

The photocatalytic degradation method uses UV light and photocatalyst semiconductors to degrade textile dyes through the formation of hydroxyl radicals ($\cdot\text{OH}$) which are highly reactive to dyes.¹⁴ These hydroxyl radicals can degrade textile dyes into small and non-toxic molecules.

Among various photocatalyst semiconductors, ZnO has been used as effective, easy synthesis, inexpensive (low production cost) and nontoxic photocatalyst for the degradation of a wide range of different pollutants in recent years.^{14,15} ZnO has high photocatalytic activity as well as TiO_2 , but it is rarely explored because of its low photostability due to its easy corrosion by light.^{16,17} The low photostability of ZnO will reduce its photocatalytic activity when it is used under long-term intensive light exposure. Also, ZnO photocatalyst has poor adsorption ability toward pollutant substances that limited its catalytic efficiency.¹⁸

To overcome shortcomings problems of ZnO so that its photocatalytic activity increase, ZnO has been supported into porous materials such as zeolites. Zeolites are very suitable as a supporting material

because they have a high ion-exchange capacity, high surface area, and high adsorption capacity.¹⁸ Moreover, the zeolite framework preserves ZnO from photo-decay.¹⁸ Incorporated ZnO into zeolites can attract the pollutant substances to the reactive surface of the ZnO particles where the hydroxyl radicals were produced and also extend the lifetime of ZnO photocatalyst under light exposure.¹⁹ The zeolites used by the previous authors were synthetic zeolites that are costly when large amounts are required. Considering their abundant, cheaper, and eco-friendly, natural zeolites seem preferable than the synthetic ones. In the present work, incorporation of ZnO into Indonesian natural zeolites for photodegradation of methylene blue is reported. The influence of reaction time, the photocatalyst dose, and MB concentration are also evaluated.

EXPERIMENTAL

Material

Zinc acetate dihydrate ($\text{ZnC}_4\text{H}_{10}\text{O}_6$), sodium hydroxide (NaOH), hydrochloric acid (HCl), methylene blue chloride ($\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$), and zinc standard solution 1000 mg/L were purchased from Merck Co. Inc. (Germany). All chemicals were of analytical grade and used without further treatment. The natural zeolite belongs to Klaten Regency, Central Java, Indonesia.

Natural Zeolite Preparation

The natural zeolite (NZ) was mechanically pretreated, by crushing the granules in a mortar and sieving using a 250 mesh sieve. Then, the NZ powder was immersed in distilled water and heated at 70 °C for 8 h under stirring at 500 rpm to remove water-soluble impurities.¹⁵ After filtration and drying in an oven at 105 °C for 18 h, the NZ powder was stored in a desiccator.

Characterization

The XRD patterns were acquired by X-ray diffractometer (XRD, Philips Analytical) operated at 30 mA and 40 kV using Cu K α radiation ($\lambda = 1.54060 \text{ \AA}$, 2θ range 5-80° and 0.02 step size). The FTIR spectra of the samples were recorded on a Fourier transform infrared spectrophotometer (FTIR-PRESTIGE 21) using the KBr pellet technique in the range of 4000-300 cm^{-1} . The morphological features were recorded by Scanning Electron Microscope which is equipped with Energy Dispersive X-Ray (SEM-EDS, JSM-6510LA). UV-Vis diffuse reflectance spectroscopy (UV-Vis DRS) measurements were done using a Shimadzu UV-2450 spectrophotometer. The concentration of zinc in the photocatalysts were determined using flame atomic absorption spectroscopy (FAAS, Analytic Jena ContrAA 300). The specific surface area and pore size of samples were examined using Quantachrome NovaWin N₂-Gas Sorption Analyzer (GSA). The degradation extent was monitored by Thermo Scientific Evolution 201 UV-Vis spectrophotometer.

Synthesis of ZnO-NZ

The synthesis of ZnO-NZ photocatalysts was carried out by the cation exchange method followed by co-precipitation. About 0.7 grams of NZ was dispersed in 50 mL of zinc acetate dihydrate solution with various concentrations (0.035M, 0.070M and 0.105M) in 250 mL round bottom flask. The mixture was refluxed at 80 °C for 5 h to allow cations exchange in zeolite cavities with Zn(II) ions. The solid was separated from the filtrate, then was washed with deionized water and added dropwise with 0.1 M NaOH solution until the pH $\cong$ 12. The mixture was stirred with a magnetic stirrer for 2 h. The resulted precipitate was washed with deionized water and separated from the liquid by centrifuging at 5000 rpm for 30 minutes. Then it was dried overnight at $\pm$ 60 °C and calcined at 400 °C for 3 h.

Photocatalytic Degradation Experiments

The photocatalytic degradation of MB in the solution was carried out in a photoreaction reactor equipped with a stirrer and 50 mL Beaker glasses. The light source used was three Sankyo Denki G20T10 UV-C lamps. For the photocatalytic degradation test, 20 mg of photocatalysts was suspended in 20 mL of 20 ppm methylene blue (MB) solution in a Beaker glass. The suspension was placed in the photoreaction equipment to be irradiated by UV light accompanied by stirring for various interval times (15, 30, 60, 90, 120, 150 and 180 minutes). After a given irradiation time, the suspension was centrifuged to remove

photocatalyst powder. Afterward, the remains MB in the filtrate was analyzed by using a Thermo Scientific Evolution 201 UV-Vis spectrophotometer at 663 nm to determine the MB concentration. The percentage of MB degradation (D), was calculated according to Eq. (1):

$$D\% = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

Where, C_0 is the initial concentrations of MB and C_t is the concentration of MB at t time.

RESULTS AND DISCUSSION

Determination of Zn Incorporated Into The Zeolite

The influences of initial Zn(II) concentration on ZnO formed on the zeolite are displayed in Table-1. It is seen in the table that increasing the initial Zn(II) concentration could increase the ZnO incorporated on the zeolite. The increase of the Zn(II) concentration, gave more Zn(II) ions in the solutions led to an increase in a collision between the ion and the zeolite active surface that can improve the effectiveness of the ion exchange toward cations in the zeolite.

XRD

The XRD patterns of bare ZnO, natural zeolite (NZ), and ZnO-NZ are presented in Fig.-1(a). In the XRD pattern of the bare ZnO, the characteristic peaks at 2θ 31.8° , 34.4° , 36.3° , 47.6° , 56.6° , 62.9° , 68.0° , and 69.1° are observed corresponding to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2) and (2 0 1) crystal planes of the ZnO with hexagonal structure, as documented in JCPDS File 89-0511.

The XRD pattern of natural zeolite (NZ) exhibits peaks at 9.9° , 11.2° , 17.3° , 19.1° , 22.4° , 26.3° , and 30.0° . These XRD peaks are matched with the corresponding data of clinoptilolite (JCPDS file 25-1349). The peak at 9.9° , 11.2° , 17.3° , 19.1° , 22.4° , 28.1° , and 30.0° are matched with the JCPDS file 53-1176 of heulandite. Also, peaks at 2θ 9.9° , 13.5° , 19.6° , 22.4° , 25.6° , and 27.7° are characteristic of mordenite (JCPDS file 29-1257). It is confirmed that Indonesian natural zeolite as composed of clinoptilolite, heulandite and mordenite zeolite types as major components.

Generally, the diffraction patterns of the natural and modified natural zeolite are similar. The positions of diffraction peaks are almost identical, indicating that ZnO loading does not change the crystal structure of the zeolite. The XRD patterns of ZnO-NZ did not show characteristic peaks of ZnO. These could due to the formation of a very small size ZnO or the presence of a small quantity of ZnO, typically below 9.0% .^{20,21}

FTIR

The FTIR spectra of the bare ZnO, natural zeolite, ZnO(3.5%)-NZ, ZnO(5.0%)-NZ and ZnO(6.1%)-NZ in the wavenumber range of $4000-300\text{ cm}^{-1}$ are presented in Fig.-1(b). In the FTIR spectrum of natural zeolite, it is seen the broad absorption band at $3700-3000\text{ cm}^{-1}$ corresponding to O-H stretching vibration which relates to $\equiv\text{Al}-\text{OH}-\text{Si}$ ¹⁵, and water molecules that are physically absorbed.²² The O-H bending vibration of the absorbed water molecule is observed at 1636 cm^{-1} .^{18,23} The characteristic band of zeolite appeared at 1049 cm^{-1} are assigned to Si(Al)-O as asymmetric stretching vibration, whereas the band at 795 cm^{-1} are assigned to Si(Al)-O as symmetric stretching vibration. The band at 471 cm^{-1} , corresponding to Si(Al)-O bending vibration.^{15,24} The presence of the absorption peak at 594 cm^{-1} indicates the double ring of external linkage of zeolite from the heulandite phase.^{24,25} The stretching vibration of ZnO appears at wavenumber $400-500\text{ cm}^{-1}$ belonged to the Zn-O bond.¹⁸

Table-1: The Influence of Initial Zn(II) Concentration on the ZnO Formed on ZnO-NZ

Initial Zn (II) Concentration (mole/L)	ZnO incorporated on Zeolite (%)	The Photocatalyst Code
0.035	3.5	ZnO(3.5%)-NZ
0.070	5.0	ZnO(5.0%)-NZ
0.105	6.1	ZnO(6.1%)-NZ

Fig-1: XRD Pattern (a) and Infrared Spectra (b) of ZnO, NZ, and ZnO-NZ

It is seen that the infrared spectra of ZnO-NZ are combination peaks of zeolite and ZnO. The broadening of the band at $400\text{--}500\text{ cm}^{-1}$ is observed, due to the stretching Zn-O band along with a vibrational band of the zeolite framework. Also, there is a slight shift in the peak position of Si(Al)-O band from 1049 cm^{-1} to 1057 cm^{-1} and from 471 cm^{-1} to 463 cm^{-1} . These wavelength shifts indicate a change in the frequency of vibration of Si-O-Al due to the bonding or strong interaction of Zn-O with the zeolites framework.

SEM-EDS

SEM-EDS is used for determining the morphology of samples and the distribution of elements in the samples. The SEM images of the photocatalysts are given in Fig.-2.

Fig-2: SEM Images of ZnO (a), Natural Zeolite (b), ZnO(3.5%)-NZ (c), ZnO(5.0%)-NZ (d) and ZnO(6.1%)-NZ (e)

The SEM image Fig.-2(a) shows that the bare ZnO has a spherical shape. The SEM image of the natural zeolite (Fig.-2(b)) shows smooth surface morphology. However, the loading of ZnO into zeolite (Fig.-2(c-e)) resulted in the coarse surface due to the formation of ZnO clusters on the surface of the zeolite. More ZnO clusters are formed upon increasing the ZnO loading. To find out how the distribution of ZnO in the sample, the SEM analysis is continued by mapping of Zn element using Energy Dispersive X-Ray Spectroscopy (EDS). The mapping images representing the distribution of Zn in the ZnO-NZ are given in Fig.-3. The result showed that the distribution of dots representing Zn is getting denser with the increasing percentage of ZnO on ZnO-NZ. Also, the results also showed that Zn is well distributed on the ZnO-NZ photocatalysts. This indicated that ZnO was well distributed in the zeolite frameworks.

Fig.-3: EDS Mapping of ZnO in ZnO(3.5%)-NZ (a), ZnO(5.0%)-NZ (b) and ZnO(6.1%)-NZ (c)

Gas Sorption Analyzer

The effect of the loading of ZnO into natural zeolite on their specific surface area, total pore volume, and average pore radius are presented in Table-2. The results show that the loading of ZnO into zeolites decreases the specific surface area (S_{BET}) and total pore volume (V_p) of the zeolites, as also observed by some researchers.^{18,26,27} The loading of ZnO into the pore of zeolite causes the narrowing and siltation of the pores. Thus, the surface area decreases.

Table-2: Pore Character of ZnO, Natural Zeolite (NZ), and ZnO-NZ based on the Adsorption-Desorption of N_2 gas

Samples	Specific Surface Area, S_{BET} (m^2/g)	Total Pore Volume, V_p (cm^3/g) $\times (10^{-2})$	Average Pore Radius, r_p ($\text{\AA}$)
ZnO	24.300	20.71	154.80
NZ	39.567	16.88	79.12
ZnO(3.5%)-NZ	34.459	14.79	80.40
ZnO(5.0%)-NZ	33.375	14.03	83.79
ZnO(6.1%)-NZ	31.835	13.17	84.10

However, compared with bare ZnO, the ZnO-NZ provided a higher specific surface area. It seems the natural zeolite confines the growth of ZnO so that resulting ZnO with small particle size. The small size of ZnO increases the gap between the valence and the conduction band, as seen in Table-3. The

decreasing of ZnO particle size increases the surface area of the photocatalyst and it gives advantages to the adsorption of pollutants on the photocatalyst surface.

DRS UV-Vis

The DRS UV-Vis spectra of the bare ZnO and ZnO-NZ in the wavelength range of 200-800 nm are presented in Fig.-4. The absorption spectrum of the bare ZnO shows the strong and large broad absorption band in the UV region due to the $O^{2-} \rightarrow Zn^{2+}$ ligand to metal charge transfer transition.^{27,28} The UV-Vis DRS absorption spectra of ZnO-NZ show similar absorption spectra to ZnO that have high absorption intensity in the UV region attributed to the ZnO particles embedded in the natural zeolite structure. The intensity of absorption in the UV region increases by rising of ZnO percentage in ZnO-NZ. This result is in good agreement with other research results.²¹

Fig.-4: The UV-Vis DRS Spectra of Bare ZnO and ZnO-NZ

The bandgap energy (E_g) can be determined based on the absorption edge wavelength (λ) from DRS UV-Vis spectra data, employing the relationship of $E_g = 1239/\lambda$.²⁹ The absorption edge wavelength (λ) and the bandgap energy (E_g) of ZnO and ZnO-NZ are shown in Table-3.

Table-3: Absorption Edge Wavelength (λ) and the Bandgap Energy (E_g) of Bare ZnO and ZnO-NZ.

Samples	λ (nm)	E_g (eV)
Bare ZnO	408	3.04
ZnO(3.5%)-NZ	371	3.34
ZnO(5.0%)-NZ	390	3.18
ZnO(6.1%)-NZ	399	3.11

The results in Table-3 confirm that the loading of ZnO into natural zeolite caused blueshifts in the edge wavelength. This blueshift indicates a decrease in ZnO particle size, as stated in the Bruss equation.³⁰ The confinement effect due to reduced particle size narrows the bandwidth. This narrowing of the bandwidth causes the distance or the gap between the valence band and the conduction band to increase so that the bandgap energy becomes higher.

The largest blueshift is at ZnO(3.5%)-NZ which is shifted from 408 nm for the bare ZnO to 371 nm for ZnO(3.5%)-NZ. Those resulted in the bandgap energy of 3.04 and 3.34 eV, respectively. Increasing the amount of ZnO in the zeolite of 5-6% produces smaller bandgap energy than 3.34 eV indicating the formation of the larger size of ZnO particles. At high ZnO concentrations of higher than 3.5%, ZnO tends to aggregate to form large ZnO particles. However, in this study, the size of ZnO in ZnO-NZ is still smaller than the bare ZnO.

Photocatalytic Activity Examination

To evaluate the effect of zeolite as supporting material on the photocatalytic activity of ZnO-NZ for MB photodegradation, several experiments have been done, namely without using photocatalyst, using the

bare ZnO, and ZnO-NZ at the same conditions. The results of the degradation at various irradiation times are presented in Fig.-5.

The un-photocatalyzed degradation of MB under UV light irradiation is found to take place with low efficiency. The degradation of MB in the presence of UV light could be caused by the distortion of the chromophore groups in the dye by the high energy of UV. The chromophores may undergo photodecomposition through the formation of radical species.³¹ The degradation caused by attacking by hydroxyl radicals ($\cdot\text{OH}$) resulted from H_2O photolysis is also possible.³² The effect of UV light and water photolysis is implied to be weaker, which is indicated by the low efficiency of the degradation.

Fig.-5: Photocatalytic degradation of MB under UV light

The increasing effectiveness of the MB over ZnO is also observed in Fig.-5. Degradation of MB can occur due to the attack of $\cdot\text{OH}$ radicals generated by ZnO during UV irradiation. The reactions are presented as equation (2-4) below:^{12,33}

In this stage, the $\cdot\text{OH}$ radicals provided by ZnO photocatalyst is much more compared to that by water photolysis. This explains the more effective degradation of MB over ZnO by the presence of UV light. Moreover, ZnO-NZ showed higher activity because ZnO supported on the zeolite structure has a smaller particle size, providing the larger surface area. The larger surface area gives more effective contact between MB and the $\cdot\text{OH}$ radicals formed on the surface of the photocatalyst^{15,19}, resulting in higher photodegradation. The high photodegradation activity of ZnO-NZ may be also promoted by effective MB adsorption on zeolite. The increasing of the specific surface area of the photocatalyst after supported into zeolite provided higher adsorption capacity of MB. Also, the high adsorption capacity of ZnO-NZ for the MB cationic dye is also due to the electronegativity properties of zeolites. This high adsorption capacity of ZnO-NZ is advantageous to the photocatalysis process because it brings more MB molecules near the ZnO surface.¹⁹ Zeolites may facilitate the photoactive species (h_{VB}^+ and e_{CB}^-) from the ZnO surface to MB molecule that adsorbed in zeolites and vice versa from zeolite to the ZnO surface. This situation promotes more degradation of the MB.¹⁸

When ZnO supported into zeolite, they form the Zn-O-Si or Zn-O-Al as shown by the FTIR spectra (Fig.-1(b)). As the characteristics of zeolite, ZnO-NZ has high thermal and chemical stability that prevents the ZnO to experience corrosion that may reduce the activity of photocatalysts. When ZnO-NZ is exposed to UV light, the electron of ZnO is excited from the valence band to conductance band (e_{CB}^-) and leaving a hole behind (h_{VB}^+). The excited electrons in zinc cations migrate to oxygen atoms and finally to Al atoms.^{18,19} This prevents the recombination of electrons and holes during photoreaction^{18,19}, thereby increasing the chance of the hole reacts with the hydroxide to produce hydroxyl radicals that plays an important role in the degradation process.^{12,34} The increasing bandgap of ZnO supported into zeolite also

increases the separation between the electrons in the conduction band (e^-_{CB}) and the hole in the valence band (h^+_{VB}), so the possibility of its recombination is getting smaller and obtain a high photocatalytic activity.

In this study, although the specific surface area of ZnO-NZ slightly decreases with the increase of ZnO percentage from 3.5% to 6.0% in the ZnO-NZ, the photocatalytic activities slightly increase. This due to the higher of ZnO amount in photocatalyst, the more radical produce so that the more MB may degrade. The photodegradation percentage of ZnO(3.5%)-NZ, ZnO(5.0%)-NZ, and ZnO(6.0%)-NZ are 76.10%, 80.13% and 83.05% respectively.

The effect of the dosage of photocatalyst on MB degradation efficiency is displayed by Fig.-6(a). The result showed that the degradation percentage of MB increases by the increase in photocatalyst dosage. This trend occurs since more amount of photocatalyst, more $\cdot OH$ radicals are provided, resulting in more effective degradation. However, at too high photocatalyst dosage, the increasing turbidity of solution causes the photon penetration to the solution reduces, thereby the photocatalyst becomes less active. As a result, at higher photocatalyst dosage is less effective to increase the degradation percentage.

Fig.-6: Effect of the Photocatalyst Dosage (a) and the Initial Concentration of MB (b) On Photocatalytic Activity of ZnO and ZnO(6.1%)-NZ under UV Light

To determine the effect of the initial MB concentration on the effectivity of photocatalyst, some experiments were carried out using 5-50 ppm of MB. The results in Fig.-6(b) showed that the degradation percentage of MB decreases with increasing the initial concentration of MB. This decrease due to the hydroxyl radicals that are produced remains constant, whereas the amount of MB molecules increases by increasing MB concentration. Also, at higher MB concentration, too many MB adsorbed in the photocatalyst surface causes the blocking of the light penetration to the surface of photocatalyst thereby reducing its activity.

CONCLUSION

Supported ZnO into natural zeolite (ZnO-NZ) has been successfully prepared by cation exchange followed by co-precipitation and calcination process. ZnO-NZ has a higher specific surface area and a wide bandgap. Methylene blue as a persistent organic pollutant was successfully photodegraded by ZnO-NZ under the irradiation of UV light. Supported ZnO into natural zeolite increases the activity of the photocatalyst more than twice compared to the bare ZnO. The highest degradation percentage of 83.05% was obtained at ZnO(6.1%)-NZ.

ACKNOWLEDGMENT

The authors are grateful to the Directorate General of Higher Education, Indonesian Ministry of Research, Technology and Higher Education for funding this research and the University of Gadjah Mada for providing the research facilities.

REFERENCES

1. M. Rafatullah, O. Sulaiman, R. Hashim and A. Ahmad, *Journal of Hazardous Materials*, **177**, 70 (2010), DOI:10.1016/j.jhazmat.2009.12.047
2. T. Liu, Y. Li, Q. Du, J. Sun, Y. Jiao, G. Yang, Z. Wang, Y. Xia, W. Zhang, K. Wang, H. Zhu and D. Wu, *Colloids and Surface B: Biointerfaces*, **90**, 197 (2012), DOI:10.1016/j.colsurfb.2011.10.019

3. S.K. Theydan and M.J. Ahmed, *Journal of Analytical Applied Pyrolysis*, **97**, 116(2012), DOI:10.1016/j.jaap.2012.05.008
4. Z. Carmen and S. Daniela, 2012, Textile Organic Dyes – Characteristics, Polluting Effects and Separation/Elimination Procedures from Industrial Effluents – A Critical Overview, in T. Puzyn and A. Mostrag-Szlichtyng (Eds.), *Organic Pollutants Ten Years After the Stockholm Convention – Environmental and Analytical Update*, InTech, Croatia, pp.55-86, DOI:10.5772/32373
5. C. Djelloul and O. Hamdaoui, *Desalination and Water Treatment*, **52(40-42)**, 7701(2014), DOI:10.1080/19443994.2013.833555
6. V. Bharti, K. Vikrant, M. Goswami, H. Tiwari, R.K. Sonwani, J. Lee, D.C.W. Tsang, K.H. Kim, M. Saeed, S. Kumar, B.N. Rai, B.S. Giri and R.S. Singh, *Environmental Research*, **171**, 356 (2019), DOI:10.1016/j.envres.2019.01.051
7. O.F. Sarioglu, N.O.S. Keskin, A. Celebioglu, T. Tekinay and T. Uyar, *Colloids and Surface B: Biointerfaces*, **152**, 245(2017), DOI:10.1016/j.colsurfb.2017.01.034
8. N. Saibaba KV and R.V. Kandisa, *Rasāyan Journal of Chemistry*, **12(4)**, 2176(2019), DOI:10.31788/RJC.2019.1245478
9. Y.A.B. Neolaka, E.B.S. Kalla, G.A. Malelak, N.K. Rukman, G. Supriyanto and N.N.T. Puspaningsih, *Rasāyan Journal of Chemistry*, **11(2)**, 494(2018), DOI:10.31788/RJC.2018.1121994
10. J. Gandhi, R. Dangi and S. Bhardwaj, *Rasāyan Journal of Chemistry*, **1(3)**, 567(2008)
11. N.P. Mohabansi, V.B. Patil and N. Yenkie, *Rasāyan Journal of Chemistry*, **4(4)**, 814(2011).
12. K.M. Lee, C.W. Lai, K.S. Ngai and J.C. Juan, *Water Research*, **88**, 428(2016), DOI:10.1016/j.watres.2015.09.045
13. C.B. Ong, L.Y. Ng and A.W. Mohammad, *Renewable and Sustainable Energy Reviews*, **81**, 536 (2018), DOI:10.1016/j.rser.2017.08.020
14. Y. Liu, S. Wei and W. Gao, *Journal of Hazardous Materials*, **287**, 59 (2015), DOI:10.1016/j.jhazmat.2014.12.045
15. A. Nezamzadeh-Ejhi and S. Khorsandi, *Journal of Industrial and Engineering Chemistry*, **20**, 937 (2014), DOI:10.1016/j.jiec.2013.06.026
16. T.T. Vu, L. del Río, T. Valdés-Solis and G. Marbán, *Applied Catalysis B: Environmental*, **140-141**, 189 (2013), DOI:10.1016/j.apcatb.2013.04.023
17. Y. Zhang, Z. Chen, S. Liu and Y.J. Xu, *Applied Catalysis B: Environmental*, **140-141**, 598 (2013), DOI:10.1016/j.apcatb.2013.04.059
18. A. Nezamzadeh-Ejhi and F. Khodabakshi-Chermahini, *Journal of Industrial and Engineering Chemistry*, **20(2)**, 695 (2014), DOI:10.1016/j.jiec.2013.05.035
19. M. Bahrami and A. Nezamzadeh-Ejhi, *Materials Science in Semiconductor Processing*, **30**, 275(2015), DOI:10.1016/j.mssp.2014.10.006
20. T. Gong, L. Qin, J. Lu and H. Feng, *Physical Chemistry Chemical Physics*, **18**, 601(2016), DOI:10.1039/C5CP05043J
21. J. Chen, Z. Feng, P. Ying and C. Li, *Journal of Physical Chemistry B*, **108**, 12669(2004), DOI:10.1021/jp048746x
22. B.J. Saikia and G. Parthasarathy, *Journal of Modern Physics*, **1(4)**, 206(2010), DOI:10.4236/jmp.2010.14031
23. Z. Liu, Z. Liu, T. Cui, J. Li, J. Zhang, T. Chen, X. Wang and X. Liang, *Chemical Engineering Journal*, **235**, 257(2014), DOI:10.1016/j.cej.2013.09.022
24. K. Byrappa and B.V.S. Kumar, *Asian Journal of Chemistry*, 2007, **19(6)**, 4933(2007).
25. E.P. Favvas, C.G. Tsanaktidis, A.A. Sapalidis, G.T. Tzilantonis, S.K. Papageorgiou and A.C. Mitropoulos, *Microporous and Mesoporous Materials*, **225**, 385 (2016), DOI:10.1016/j.micromeso.2016.01.021
26. B. Lin, J. Wang, Q. Huang, M. Ali and Y. Chi, *Journal of Analytical and Applied Pyrolysis*, **128**, 291 (2017), DOI:10.1016/j.jaap.2017.09.021
27. O. Sacco, V. Vaiano and M. Matarangolo, *Separation and Purification Technology*, **193**, 303 (2018), DOI:10.1016/j.seppur.2017.10.056

28. L. Wang, S. Sang, S. Meng, Y. Zhang, Y. Qi and Z. Liu, *Materials Letters*, **61**, 1675(2007), DOI:10.1016/j.matlet.2006.07.097
29. E.T. Wahyuni and R. Roto, 2018, Silver Nanoparticle Incorporated Titanium Oxide for Bacterial Inactivation and Dye Degradation, in D. Yang (Eds.), *Titanium Dioxide: Material for a Sustainable Environment*, Intechopen, pp. 331-348, DOI:10.5772/intechopen.70290
30. E.O. Chukwuocha, M.C. Onyeaju and T.S.T. Harry, *World Journal of Condensed Matter Physics*, **2**, 96 (2012), DOI:10.4236/wjcmp.2012.22017
31. J. Albaigés, J.M. Bayona and J.R. Radović, 2016, Photochemical effect on oil spill fingerprinting, in S.A. Stout and Z. Wang, *Standard Handbook in Oil Spill Environmental Forensics*, 2nd edition, Academic Press, New York, pp. 917-959, DOI:10.1016/B978-0-12-803832-1.00020-9
32. J.L. Wang and L.J. Xu, *Critical Reviews in Environmental Science Technology*, **42**, 251(2012), DOI:10.1080/10643389.2010.507698
33. R.E. Adam, G. Pozina, M. Willander and O. Nur, *Photonics and Nanostructures - Fundamentals and Applications*, **32**, 11(2018), DOI:10.1016/j.photonics.2018.08.005
34. K. Akhil, J. Jayakumar, G. Gayathri and S.S. Khan, *Journal of Photochemistry & Photobiology, B: Biology*, **160**, 32(2016), DOI:10.1016/j.jphotobiol.2016.03.015

[RJC-5597/2019]