International Journal of Technology (2018) 6: 1159-1167
ISSN 2086-9614

ENHANCED ACTIVITY OF TiO_2/NATURAL ZEOLITE COMPOSITE FOR DEGRADATION OF METHYL ORANGE UNDER VISIBLE LIGHT IRRADIATION

Arif Rahman[1*], Muktiningsih Nurjayadi[1], Rika Wartilah[1], Eny Kusrini[2],
Eko Adi Prasetyanto[3], Volkan Degermenci[4]

[1]*Department of Chemistry, Faculty of Mathematics & Natural Sciences, Universitas Negeri Jakarta, Rawamangun 13220, Indonesia*
[2]*Department of Chemical Engineering, Faculty of Engineering, Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia*
[3]*Faculty of Medicine and Health Sciences, Universitas Katolik Indonesia Atma Jaya, Jl. Pluit Raya 2, Jakarta 14440, Indonesia*
[4]*School of Engineering, University of Warwick, Coventry, CV4 7AL, United Kingdom*

(Received: August 2018 / Revised: September 2018 / Accepted: October 2018)

ABSTRACT

A series of titanium dioxide nanoparticles anchored on mordenite zeolite from an Indonesian natural deposit were prepared by the sol-gel route using a titanium isopropoxide sol as the precursor. Mordenite was incorporated during the sol-gel process by dispersing mordenite powder into the titania sol-gel precursor. The resulting titanium dioxide nanoparticles were in the anatase and rutile form, as confirmed by X-Ray diffraction (XRD) spectroscopy. Diffuse reflectance ultra violet visible (DR-UVVis) spectroscopy analysis indicated a red shift for the band gap energy, which enabled the materials to absorb ultraviolet to visible light. Subjecting the material to photodegradation in a reactor under ultraviolet and visible radiation gave better dye degradation under visible light than ultraviolet irradiation and the yield was proportional with the content of TiO_2 nanoparticles incorporated into the zeolite.

Keywords: Natural zeolite; Photocatalysis; TiO_2 photocatalyst

1. INTRODUCTION

The various applications of photocatalysis based on titanium dioxide is driving rapid growth in this research (Alvarez et al., 2018). One of the prominent applications in this field is the decomposition of organic pollutants. The photocatalytic activity of TiO_2 for organic pollutant decomposition is mainly influenced by the crystallinity, particle size, crystal phase, and surface area of the TiO_2. A study conducted by Yener et al. (2017) revealed that the anatase form of TiO_2, which has a small particle size and high crystallinity, is needed to obtain high photocatalytic activity. However, the presence of a certain amount of TiO_2 in the rutile phase can increase photocatalytic activity. This is related to the creation of holes and electrons on the surface of TiO_2 for reaction with the substrate and the lifetime of these holes and electrons (Sun et al., 2015).

Many synthesis methods have been developed to obtain TiO_2 nanoparticles, such as aerosol pyrolysis, amorphous TiO_2 calcination, and colloidal surfactant synthesis (Sun et al., 2015). In general, these methods have the disadvantage of generating products that do not perform

---

[*] Corresponding author's email: arifrahman@unj.ac.id, Tel. +62-21-4898486, Fax. +62-21-4898486
Permalink/DOI: https://doi.org/10.14716/ijtech.v9i6.2368

sufficiently for photocatalytic applications. However, several methods of synthesis of TiO_2 nanoparticles, such as hydrothermal, solvothermal, and microwave methods, can produce TiO_2 nanoparticles with high crystallinity and controlled size. Nevertheless, these methods are relatively complicated and require high temperatures and pressures. All three methods require the conversion of the precursors into colloidal forms through the sol-gel process and special equipment to facilitate the TiO_2 crystal formation.

In the sol-gel process, metal alkoxides are hydrolyzed by alcohol to metal hydroxide. The sol-gel method has been widely used for the synthesis of oxide materials or other materials, such as SiO_2 and PbI_2 (Lalena & Cleary, 2005). Using this method, anatase, rutile, and brookite TiO_2 nanoparticles have been successfully synthesized (Zhang et al., 2014). Zhang et al. (2018) successfully made rutile and anatase TiO_2 nanoparticles, whereas Yener et al. (2017) successfully produced TiO_2 nanoparticles in the mordenite structure.

The use of porous material as a host to control the metal oxide particle size has been reported. TiO_2, CdO, and ZnO have been successfully synthesized by an ion exchange method using NaY zeolite as a host (Zhao et al., 1996). The use of clinoptilolite natural zeolites as host materials for biogas purification was reported by Kusrini et al. (2016). Efforts to utilize Indonesian natural zeolite for catalysis applications were made by Hidayat et al. (2018). The utilization of zeolite as a carrier in TiO_2 synthesis results in smaller particle sizes of TiO_2 than can be obtained with pure TiO_2 (Hadjltaief et al., 2016), making this zeolite use more desirable in the synthesis of TiO_2 nanoparticles. This is because the photocatalytic activity of the TiO_2-zeolite system increases when compared to the TiO_2 system (Chang et al., 2015).

Zeolite is a porous aluminosilicate material with a unique three-dimensional structure. It is widely used as a catalyst, adsorbent, and ion exchanger. Its pore structure also allows zeolite to be used as a host material. The utilization of zeolite is limited by the high cost of basic materials in industrial scale applications (Maraschi et al., 2014)

In this report, we incorporate TiO_2 nanoparticles onto zeolite pores through sol-gel and impregnation processes to enhance the reactivity of the particles. We characterized the catalyst system and examined it for photocatalytic dye degradation under visible light than ultraviolet irradiation.

2. METHODS

2.1. Materials

Titanium (IV) isopropoxide 97% (Aldrich), nitric acid 65% (Merck), Methyl Orange (MO), and 2-propanol (Merck) were used directly without purification. Demineralized water (aqua DM) was used as the solvent. Mordenite type natural zeolite (150 mesh) was obtained from Lampung, Indonesia.

2.2. Synthesis TiO_2 Sol-gel

The TiO_2 sol solution was made from titanium (IV) isopropoxide. A total of 67.5 mL of titanium (IV) isopropoxide and 16 mL of 2-propanol were combined in a 100 mL beaker. The resulting solution was added slowly to 223.5 mL of demineralized water in a 500 mL beaker, with constant stirring using a magnetic stirrer. The solution was homogenized with stirring for 10 minutes and then added slowly to 3 mL of 65% HNO_3. This mixture was then heated to 80ºC for 8 hours with constant stirring. A white TiO_2 solution was produced and was used to make zeolite-TiO_2.

2.3. Synthesis of TiO_2/Natural Zeolite

The desired amounts of natural zeolites were dispersed in water and then slowly added to a sol-gel solution of TiO_2 with constant stirring. Stirring was continued for 2 hours to generate homogeneous TiO_2/zeolite preparations with a concentration of 2.5%, 5%, and 10%. The TiO_2/zeolite obtained was then dried at 100ºC for 4 hours. Some samples were calcined at 500ºC for 6 hours. Dried and calcined samples were characterized by fourier-transform infrared spectroscopy (FTIR), specific surface area (SSA), XRD, and DR-UVVis techniques. The quantitative analyses were done on a Biospec 1601V (Shimadzu) spectrophotometer, FTIR instrument (Perkin Elmer), DR UV-Vis Spectroscopy instrument (Pharmaspec UV 1700 UV-VIS Spectrophotometer with a Specular Reflectance Attachment), and an XRD instrument (Shimadzu X-Ray Diffractometer 7000).

2.4. Photocatalysis Experiments

A total of 1 gram of sample was dispersed in 200 ml of demineralized water, and then homogenized by constant stirring using a magnetic stirrer. A 60 mL volume of 30 ppm MO solution was then added to the sample. The decomposition rate of MO was observed by removing 10 mL of the mixture every 30 minutes for 5 hours and measuring the absorption with the spectrophotometer at maximum wavelength of 464 nm. The experiments to evaluate photocatalysis performance were carried out in the dark, in natural sunlight, and under UV lights.

3. RESULTS AND DISCUSSION

3.1. TiO_2/Natural Zeolite Characterization

The loading of low concentrations TiO_2 into zeolites produced relatively small amounts of TiO_2, this was confirmed by atomic absorbance spectroscopy. Loading of titanium dioxide onto natural zeolites does not damage the structure of the zeolites, although high loading of TiO_2 onto zeolites will usually cause some damage to the zeolite structure (Li et al., 2005). We observed the interaction of titanium dioxide on zeolite by FTIR spectroscopy and examined the effect of the loaded TiO_2 on the zeolite structure, the TiO_2 phase, and the effect of the concentration of the precursor. The samples were analyzed by X-ray diffraction.

Table 1 Effect of precursor concentrations on loaded TiO_2 into natural zeolite

Samples	Concentration of TiO_2 in precursor solutions (% ^{m}/m)	TiO_2 loaded onto zeolites samples (% mass)
Zeolite	-	0.26
Zeolite-TiO_2 2.5%	2.5	9.5
Zeolite-TiO_2 5%	5	18.1
Zeolite-TiO_2 10%	10	28.6

The presence of a pore system in the zeolite structure increased the amount of TiO_2 loaded onto the zeolite. The interaction between TiO_2 and zeolite can be observed by investigating the transmission spectra of FTIR for zeolite and TiO_2-zeolite. The FTIR zeolite spectra have peaks in the regions of 3622, 3640, 1634, 1051, 790, 607, 523, and 467 cm^{-1}. The typical peaks for zeolites are 1051 and 467 cm^{-1} for the zeolite internal tetrahedral system, as well as 790, 607, and 523 cm^{-1} for the zeolite external system. The peaks at 3622, 3640, and 1634 cm^{-1} are the peaks that show the –OH stretch vibration.

The most common peak is in the area of 950–1250 cm^{-1} and 420–500 cm^{-1}. The area of 950–1250 cm^{-1} shows the asymmetric stretch vibration of T-O-T (T; Al or Si) in the double ring and pore interactions in the zeolite external system, whereas the area of 420–500 cm^{-1} is the internal tetrahedral system (Lechert, 1984).

The FTIR spectra of the 2.5% Zeolite-TiO_2 samples were similar to the zeolite spectra but had new peaks at 2426 and 1384 cm^{-1}. The new peaks show the bond between C-H and C-O from the alkoxide compounds that were used as precursors. As well as these new peaks, we also observed peak widening and shifting. The widening and shifting peak at 1055 cm^{-1} occurs due to the presence of TiO_2 attached to the zeolite (Chen et al., 1999). Peak shifts also occurred from the 790 cm^{-1} area in the zeolite to 789 cm^{-1}. We found a change in the shape of the shoulder at an area of 600–700 cm^{-1}. A change in the shape of the spectrum in the region of 600–790 cm^{-1} indicates the interaction of TiO_2 with the zeolite external pore system. The interaction of TiO_2 with the zeolite system occurs in the formation of Ti-O-Si and / or Ti-O-Al bonds, as reported by Li et al. (2005).

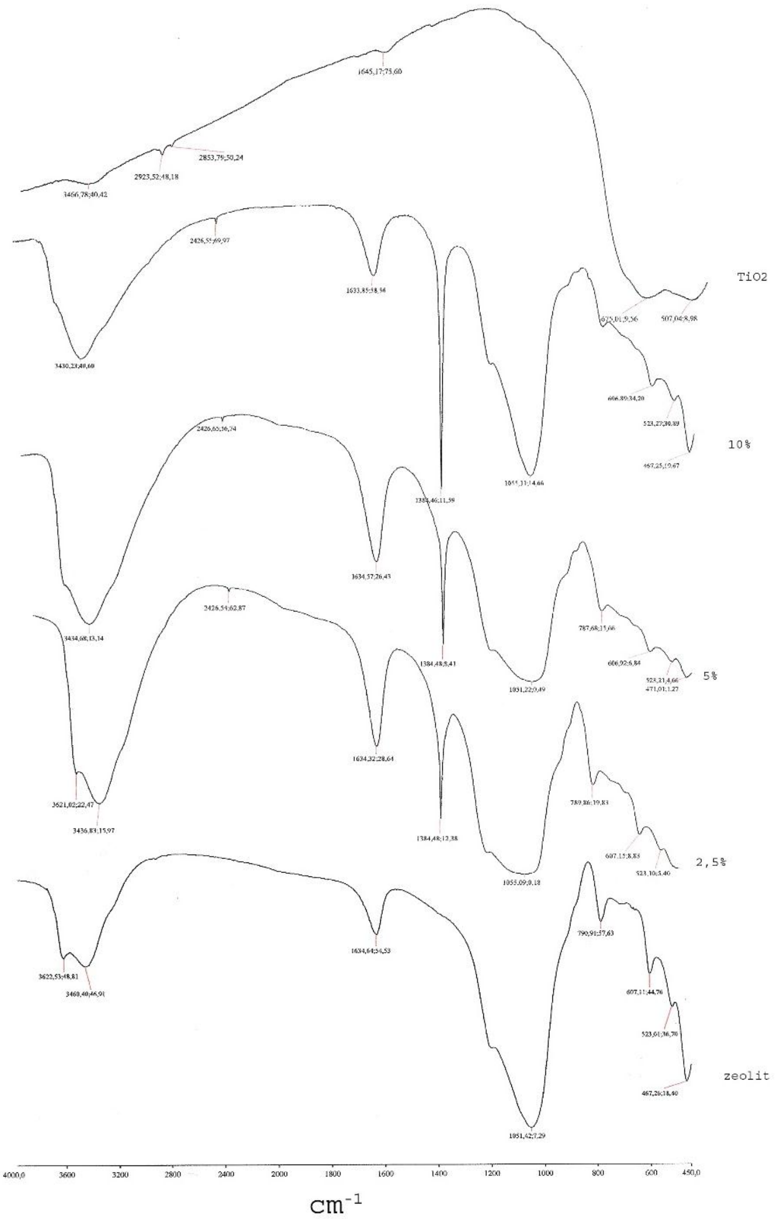


Figure 1 FTIR spectra of TiO_2 loaded onto a natural zeolite structure via the sol-gel route

The diffraction pattern of TiO_2-zeolite samples in Figure 2 shows that the TiO_2 precursor does not damage the zeolite structure. This can be observed from the presence of a typical peak for mordenite at 2θ = 22° and this peak does not decrease in intensity over various concentrations of TiO_2 precursor. The XRD patterns also exhibit TiO_2 crystalline phases in the anatase and rutile form. The typical peak is in the area of $2\theta = 25°$ for anatase, and $2\theta = 28°$ for rutile. The XRD pattern reveals that each loading concentration has both anatase and rutile TiO_2 phases. The intensity of both the anatase and rutile peaks increases with increasing TiO_2 concentration.

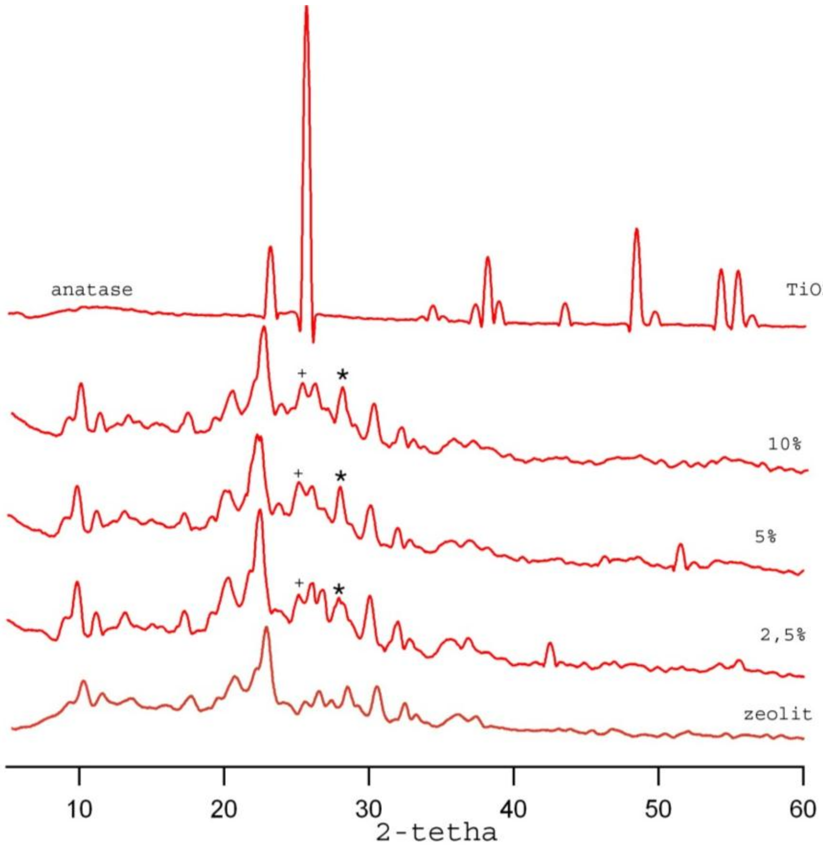


Figure 2 X-ray diffractogram from loaded TiO_2 into natural zeolite ($^+$: anatase TiO_2, *: rutile TiO_2)

Band gap energy measurements were carried out by DR UV-Vis spectroscopy analysis. The aim of band gap energy measurement is to determine whether a shift has occurred in the edge absorption to a smaller wavelength. This would occur as a result of the reduced size of the TiO_2 particles and is referred to as the quantum size effect (Zhao et al., 1996).

Table 2 Band gap energy of composite TiO_2/natural zeolite

Sample	λ (nm)	Eg (eV)
TiO_2	404	3.07
Zeolite-TiO_2 2.50%	360	3.44
Zeolite-TiO_2 5%	368	3.37
Zeolite-TiO_2 10%	375	3.30

Figure 3 shows a shift in the absorption edge of the Zeolite-TiO_2 sample towards a shorter wavelength (blue shift) when compared to the TiO_2 bulk uptake. A shift in edge absorption also occurs, indicating the widening of the valence band and conductance bands. This widening of these bands occurs because of the reduction in particle size, again indicating the quantum size effect, as stated by Hoffmann et al. (1995).

Figure 3 shows the maximum peak in the area 360–375. In addition to the maximum peak, peaks are also evident at longer wavelengths. These peaks show the hydroxide species of Ti. The peaks are formed to a greater extent as the concentration of the sol-gel precursor increases. Thus, the Ti hydroxide species are formed to a greater extent by increasing the concentration of the sol-gel precursor.

Because of the difference in size between the bulk TiO_2 and the TiO_2 produced, the size of the Eg for both TiO_2 forms is also quite different. This difference in Eg values occurs because of the quantum size effect or QSE, where a smaller sized material will have a greater Eg value (Linsebigler et al., 1995). This is due to the increasing distance between the valence band and the conductance band in the smaller material. The Eg values can be determined from the results of spectroscopic analysis by DR UV-Vis.

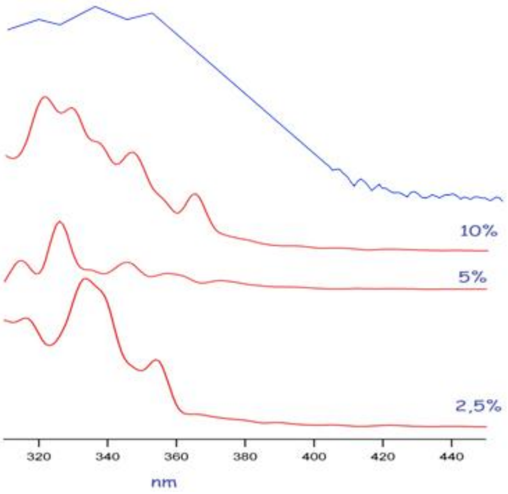
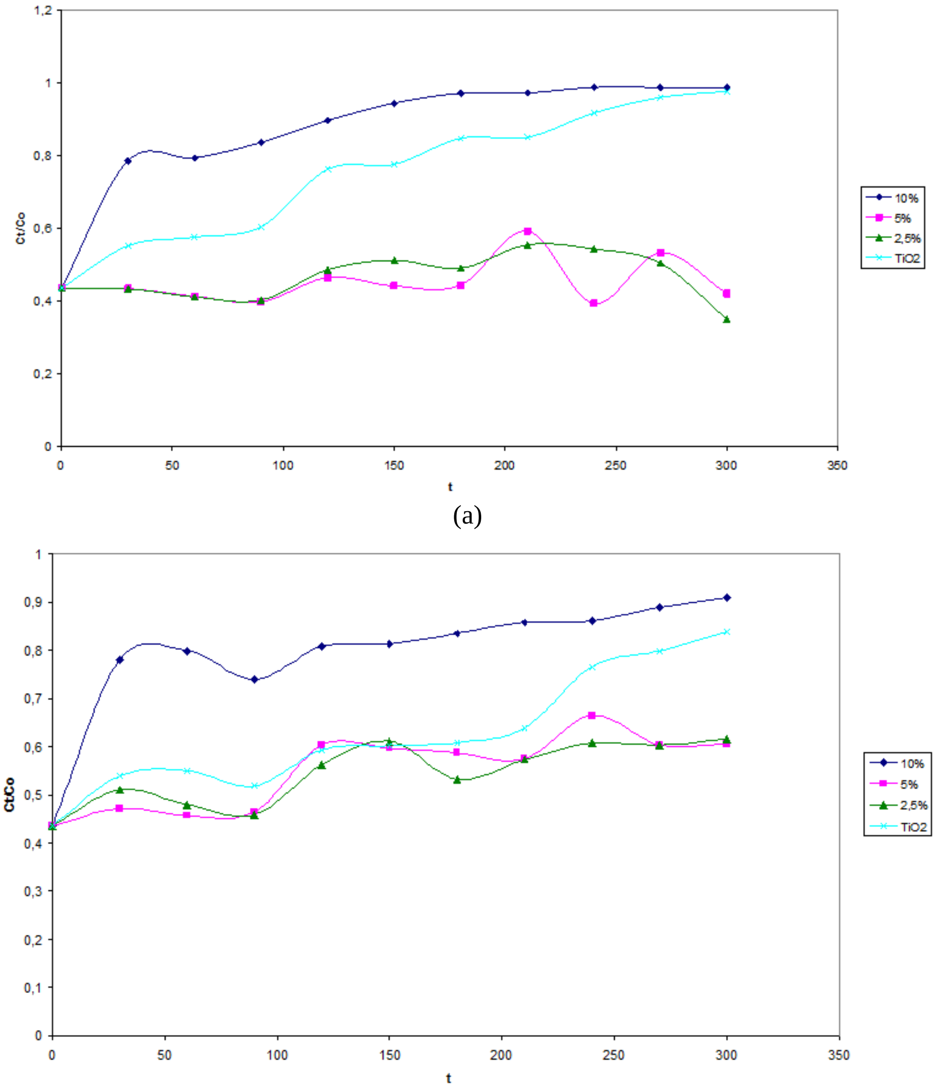


Figure 3 Diffuse reflectance spectroscopy spectra of composite TiO_2/natural zeolite

3.2. Photocatalysis Performance

The effect of the amount of TiO_2 on photocatalysts has been reported by Chatti et al. (2007). In that report, an increase in MO reduction was observed both with visible light and sunlight by increasing the amount of TiO_2 in the photocatalysts from 5% to 10%. The presence of light and the light sources themselves affect the photocatalytic process. The results from the present study confirmed that the photocatalysis process does not occur in the dark. This is because, in the dark condition, recombination occurs between the holes + (h +) and electrons (e-) that form when the excitation occurs. This recombination can occur inside the particle or on the surface of the particle. The occurrence of this recombination causes a reduction or even a loss of photocatalytic activity from the photocatalysts (Chatti et al., 2007). The difference in the light source used also affects the photocatalysis that occurs. In the present study, the photocatalysis process occurs with the use of UV light and sunlight as a light source. The photocatalysis process is better with sunlight as a light source than with UV light. This is because sunlight has greater energy when compared to UV light, so it causes more electron excitation to occur.

The influence of light sources on the photocatalysis process has been observed by several researchers. For example, Rashed and El-Amin (2007) reported that the MO degradation process is very good in the presence of sunlight when compared to the use of halogen lamps or fluorescent lamps as light sources. Kansal et al. (2007) reported that MO removal occurs faster in the presence of sunlight than in UV light.



(a)

(b)

Figure 4 Photocatalytic performance under solar light (a) and under UV light (b)

The effect of the TiO_2 system and TiO_2-zeolite system on the photocatalysis process was also examined in this study. The results show that the MO degradation process occurs better with the TiO_2-zeolite systems than with the TiO_2 systems. This is because of the super adsorption ability of zeolites (Li et al., 2005). In addition, the electron zeolite TiO_2 system from the conductance band moves rapidly out of TiO_2 particles before recombination occurs, because the surface of the electron-rich zeolite functions as an h + inhibitor. This is the reason why TiO_2-zeolite systems have better photocatalytic activity than TiO_2 systems (Anandan and Yoon, 2003). Zhang et al. (2018) and Sayilkan et al. (2007) reported photocatalytic activity on Rhodamine B for pure SiO_2 / TiO_2 and TiO_2 oxide mixtures. The SiO_2 / TiO_2 had better photocatalytic activity than pure TiO_2 because the addition of a number of SiO_2 molecules to TiO_2 will increase the thermal stability, the surface area, and the surface acidity, which then influence the addition of active sites that support the occurrence of photocatalytic processes.

4. CONCLUSION

Taken together, the results of this study indicate that TiO_2 nanoparticles synthesized using the impregnated sol-gel method in natural zeolites have a smaller size than the bulk TiO_2, which is in the nanometer range. The interaction of TiO_2 with zeolite occurs on the external surface of the zeolites, where the TiO_2 crystalline phase is a mixture of anatase and rutile. The TiO_2-zeolite produced has photocatalytic activity. The photocatalytic activity increases with increasing concentration of the titanium dioxide precursor.

5. REFERENCES

Alvarez, K.M., Alvarado J., Soto, B.S., Hernandez, M.A., 2018. Synthesis of TiO_2 Nanoparticles and TiO_2-Zeolite Composites and Study of Optical Properties and Structural Characterization. *Optik*, Volume 169, pp. 137–146

Chatti, R., Rayalu, S.S., Dubey, N., Labhsetwar, N., Devotta, S., 2007. Solar-based Photoreduction of Methyl Orange using Zeolite Supported Photocatalytic Materials. *Solar Energy Materials and Solar Cells*, Volume 91(2), pp. 180–190

Chang, C.-T., Wang, J.-J.. Ouyang, T., Zhang, Q., Jing., Y.-H., 2015. Photocatalytic Degradation of Acetaminophen in Aqueous Solutions by TiO_2/ZSM-5 Zeolite with Low Energy Irradiation. *Materials Science & Engineering B*, Volume 196, pp. 53–60

Chen, H., Matsumoto, A., Nishimiya, N., & Tsutsumi, K. (1999). Preparation and characterization of TiO_2 incorporated Y-zeolite. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 157(1-3), 295–305. doi:10.1016/s0927-7757(99)00052-7

Hadjltaief, H.B, Zina, M., Galvez, M., Da Costa, P., 2016. Photocatalytic Degradation of Methyl Green Dye in Aqueous Solution over Natural Clay-supported ZnO–TiO_2 Catalysts. *Journal of Photochemistry and Photobiology A: Chemistry*, Volume 315, pp. 25–33

Hidayat, A., Mukti, N.I.F., Handoko, B., Sutrisno, B., 2018. Biodiesel Production from Rice Bran Oil over Modified Natural Zeolite Catalyst. *International Journal of Technology*, Volume 9(2), pp. 400–411

Hoffmann, M.R., Martin, S.T., Choi, W., Bahnemann, D.W., 1995. Environmental Aplications of Semiconductor Photocatalysis, *Chemical Reviews*, Volume 95(1), 69-96

Kansal, S., Singh, M., Sud, D., 2007. Studies on Photodegradation of Two Commercial Dyes in Aqueous Phase using Different Photocatalysts. *Journal of Hazardous Materials*, Volume 141(3), pp. 581–590

Kusrini, E., Lukita, M., Gozan, M., Susanto, B.H., Widodo, T.W., Nasution, D.A., Wu, S., Rahman, A., Siregar, Y.D.I., 2016. Biogas from Palm Oil Mill Effluent: Characterization and Removal of CO_2 using Modified Clinoptilolite Zeolites in a Fixed-bed Column. *International Journal of Technology*. Volume 7(4), pp. 625–634

Lalena, J. N., Cleary, D.A., 2005. *Principles of Inorganic Material Design*. John Wiley & Sons, Inc., USA

Lechert, 1984. The Physical Characterization of Zeolites. *In:* Ramôa, Ribeiro, F.R., Rodrigues, A.E., Rollmann, L.D, Naccache, C. (eds.). Zeolites: Science and Technology. Springer, Netherlands, pp. 163–164

Li, F.-F., Jiang, Y.-S., Yu, L.-X., Yang, Z.-W., Hou, T.-Y., Sun, S.-M., 2005. Surface Effect of Natural Zeolite (Clinoptilolite) on the Photocatalytic Activity of TiO_2. *Applied Surface Science*, Volume 252(5), pp. 1410–1416

Linsebigler, A.L., Lu, G., Yates, T., 1995. Photocatalysis on TiO_2 Surface: Principles, Mechanisms, and Selected Results. *Chemical Reviews*, Volume 95(3), pp. 735–758

Maraschi, F., Sturini, M., Speltini, A., Pretali, L., Profumo, A., Pastorello, A., Kumar, V., Ferretti, M., Caratto, V., 2014. TiO_2-modified Zeolites for Fluoroquinolones Removal from Wastewaters and Reuse after Solar Light Regeneration. *Journal of Environmental & Chemical Engineering*, Volume 2(4), pp. 2170–2176

Rashed, M.N., El-Amin, A.A., 2007. Photocatalytic Degradation of Methyl Orange in Aqueous TiO_2 under Different Solar Irradiation Source. *International Journal of Physical Sciences,* Volume 2, pp. 73–81

Sayilkan, F., Asilturk, M., Sener, S., Erdemoglu, S., Erdemoglu, M., Sayilkan, H., 2007. Hydrothermal Synthesis, Characterization and Photocatalytic Activity of Nanosized TiO_2 Based Catalysts for Rhodamine B Degradation. *Turkish Journal of Chemistry,* Volume 31, pp. 211–221

Sun, Q., Hu, X.-L., Zheng, S.-L., Sun, Z.-M., Liu, S.-S., Li, H., 2015. Influence of Calcination Temperature on the Structural, Adsorption and Photocatalytic Properties of TiO_2 Nanoparticles Supported on Natural Zeolite. *Powder Technology,* Volume 274, pp. 88–97

Yener, H.B., Yılmaz, M., Deliismail, Ö., Özkan, S.F., Helvacı Ş.Ş., 2017. Clinoptilolite Supported Rutile TiO_2 Composites: Synthesis, Characterization, and Photocatalytic Activity on the Degradation of Terephthalic Acid. *Separation and Purification Technology,* Volume 173, pp. 17–26

Zhang, G.-G., Song, A.-K., Duan, Y.-W., Zheng, S.-L., 2018. Enhanced Photocatalytic Activity of TiO_2/Zeolite Composite for Abatement of Pollutants. *Microporous and Mesoporous Materials,* Volume 255, pp. 61–68

Zhang, J.., Zhou, P., Liu, J., Yu, J., 2014. New Understanding of the Difference of Photocatalytic Activity among Anatase, Rutile and Brookite TiO_2. *Physical Chemistry & Chemical Physics,* Volume 16(38), pp. 20382–20386

Zhao, X.S., Liu, G.Q., Millar, G.J., 1996. Encapsulation of Transition Metal Species into Zeolites and Molecular Sieves as Redox Catalysts: Part I-Preparation and Characterization of Nanosized TiO_2, CdO, and ZnO Semiconductor Particle Anchored in NaY Zeolite. *Journal of Porous Materials,* Volume 3, pp. 61–66