The effect of pH on Synthesis of ZnO-Natural Zeolite Nanocomposite by Co-Precipitation Method

T E Agustina1*, A U Prajewita1, and S A S Sinaga1
1Chemical Engineering Department, Universitas Sriwijaya, Palembang-30662, South Sumatera, Indonesia

E-mail: tuty_agustina@unsri.ac.id

Abstract. Currently, the method being developed to overcome environmental pollution generated by synthetic dyes produced from the textile industry wastewater is by photocatalysis using photocatalyst materials. Photocatalysis is a relatively inexpensive and easy method to implement. Photocatalysts that have received major attention and widely studied are metal oxide semiconductors such as ZnO. Photocatalyst activity can be increased through the development of supporting materials such as zeolites. This study aims to synthesize ZnO-natural zeolite photocatalysts nanocomposite by co-precipitation method in order to take advantage of the adsorbent and catalyst properties in the natural zeolites and the photocatalyst properties in the ZnO. To study the effect of pH, ZnO-natural zeolite nanocomposites are synthesized with different pH under alkaline conditions (pH of 8-11). Nanocomposite materials obtained then tested its photocatalyst activity in degrading of 50 ppm procion red synthetic dyes. The ZnO-natural zeolite nanocomposites produced were characterized by using XRD, SEM, and BET. The synthesized ZnO-natural zeolite nanocomposite showed the best results at pH of 10, with the ZnO crystallite size of 20.99 nm, the surface area of 134.35 m²/g, and the Zn contained of 10.05%. Procion red degradation of 75.54% was attained by using ZnO-natural zeolite nanocomposite photocatalyst after 120 minutes of UV irradiation.

1. Introduction
Many industries in Indonesia use dyes in the production processes. The manufacture of furniture, paints, varnish, housewares, and textiles need dyes to further improve the production yield. Among these industries, the textile industry is the industry that uses the greatest number of dyes in the production process. Synthetic dyes often used in the textile industry are non-biodegradable in nature, such as procion, erionyl, and auramin [1]. However, the textile industry wastewater is a hazard in the form of toxins and carcinogenic in nature, not only a danger to human health but also a bad impact on the ecosystem. Most traditional water treatment methods such as membrane filtration, adsorption, and chemical treatment are not effective for removing dyes properly. Conversely, this method also produces secondary pollutants such as poison gas and sludge as solid waste that require further treatment.

* To whom any correspondence should be addressed.
Another alternative method for treating wastewater that is cheap, relatively fast, and capable of being used in the long term is photocatalysis [2]. Photocatalysis is the process of decomposition of chemical compounds with the help of photon energy, where oxidation and reduction reactions occur on the surface of semiconductors, for example ZnO, TiO$_2$, CdS, and Fe$_2$O$_3$. When the semiconductor is affected by ultra violet (UV) light, the material can decompose organic compounds through photocatalytic reactions [3]. One of the good semiconductors used is ZnO. ZnO semiconductors are more profitable than TiO$_2$ because they are more able to absorb the spectrum of the sun and quantum rays than TiO$_2$ [4].

The weak adsorption capacity is a problem for the photocatalytic process. To cover up the deficiencies, photocatalyst material needs to be combined with an adsorbent as a matrix or dopant [5]. Zeolite is a good solid support for dispersing ZnO semiconductors because it has a number of surface area, pore volume, and relatively uniform pore and channel sizes [6]. Therefore, in this research, ZnO nanocomposite together with natural zeolite will be made, to maximize the photodegradation process accompanied by adsorption of solid particles in wastewater. The selected photocatalyst synthesis method is the co-precipitation method, which has some advantages such as the use of inexpensive raw materials, easy handling, ambient processing temperature and pressure, and a large-scale production when compared to other synthesis methods [7].

The pH is an important factor in making nanocomposite photocatalysts by co-precipitation method. Hence, the effect of pH on synthesis of ZnO-natural zeolite nanocomposite photocatalyst was studied in this research. In addition, the ability of nanocomposite photocatalyst ZnO-natural zeolite in the process of photodegradation of procion red synthetic dyes were examined.

2. Methodology

2.1. Chemicals and materials

The materials used in this study were aquadest, natural zeolite, deionized water, Zn(CH$_3$COO)$_2$.2H$_2$O, ZnO solids, 0.1 M NaOH, and procion red synthetic dyes. All the chemicals was supplied from Merck, while natural zeolite and procion red were purchased from Fajar Kimia chemical store in Jakarta. The apparatus used is a reactor equipped with UV Evaco 15W 254 nm lamp, pH meter and EMCLAB-61 UV Spectrophotometer.

2.2. Procedures

2.2.1. Synthesis of ZnO-natural zeolite nanocomposite photocatalyst

A 5 grams of activated natural zeolite are dissolved in 100 ml of 0.1 M Zn(CH$_3$COO)$_2$.2H$_2$O solution in 100 ml of deionized water. The mixture is stirred and heated at 80°C in a reflux flask for 4 hours. The mixture then washed with deionized water to remove residual acetate and dried at 60°C for 5 hours. After that 0.1 M NaOH was added to the mixture until a pH reached 8 and stirred for 2 hours with a magnetic stirrer. Then the mixture is washed by deionized water to remove sodium and dried at 60°C for 5 hours. The product is calcined for 2 hours at 450°C [8]. The procedure is repeated for the pH of 9, 10, and 11. The nanocomposite of ZnO-natural zeolite photocatalyst is characterized by using XRD, SEM-EDX and BET.

2.2.2. Photodegradation of Procion Red Synthetic Dyes

The ZnO-natural zeolite photocatalysts will be tested for the degradation of procion red synthetic dyes. To test the photocatalyst activity, photodegradation of procion red is carried out using a UV lamp reactor. As a comparison of effectiveness, the degradation was also tested using zeolite only and using ZnO only. The ZnO-natural zeolite weighed 100 mg then mixed with synthetic dye with a concentration of 50 ppm as much as 25 ml in a shaker and placed in a reactor equipped with a UV lamp. When the UV lamp was turned on, the time were recorded. The samples were taken every 30 minutes for 120
minutes of reaction. After the sample is filtered, the procion red color degradation was analysed by using UV Spectrophotometer. The procedures were repeated using only ZnO and only natural zeolite.

3. Results and Discussion
3.1. Synthesis and characterization of nanocomposite ZnO-natural zeolite
The process of synthesis of ZnO-natural zeolite nanocomposites for the degradation of synthetic dyes is carried out through several stages of the processes, which includes preparation through activation of natural zeolites, the process of co-precipitation of the production of ZnO-natural zeolite nanocomposites, calcination and catalyst characterization. This research was conducted to determine the effect of pH on the product of synthesis of ZnO-natural zeolite nanocomposite by co-precipitation method through the characterization and degradation of procion red synthetic dye.

The synthesized samples with variations in pH were characterized by BET (Brunauer Emmet Teller) analysis to determine surface area, pore area, and the ability of adsorption of nanocomposite material. Also the nanocomposite samples produced were analyzed by Scanning Electron Microscope - Energy Dispersive X-ray Spectroscopy (SEM-EDX) to determine the composition of atoms and morphology of the sample material. The composites were also characterized by X-Ray Diffraction (XRD) analysis to determine the crystal size of the sample. This will be compared to find out which conditions are the optimal one.

Natural zeolite was activated by using HCl solution. This acid treatment purposes to dissolve and remove the metal oxides that are absorbed and covered the surface of the natural zeolite, so that it is become more porous and the surface of the contact area becomes larger [9]. Activation in natural zeolites aims as a preparation process before co-precipitation process is carried out. The size of crystallites is generally determined by XRD. The crystallite size of natural zeolite before and after activation were listed in table 1. The size of the crystallites increases after activation. The size of crystallites in commercial ZnO is greater than in natural zeolite.

There is a difference between zeolites before and after the activation process; this proves that the activation process can change the surface morphology of natural zeolites, as can be seen from SEM images in Fig. 1 and Fig. 2. After the activation, natural zeolite surface looks smoother and flatter. This is caused by the loss of impurity in the activation process. In addition, the crystallite size of natural zeolites increased after the activation.

| Sample                        | Crystallite size (nm) |
|-------------------------------|-----------------------|
| Natural zeolite before activation | 42.54                 |
| Natural zeolite after activation   | 43.89                 |
| ZnO                             | 384.90                |
Figure 1. SEM images of natural zeolite before activation

Figure 2. SEM images of natural zeolite after activation

Figure 3 shows the morphological results of commercial ZnO. The surface morphology of ZnO shows homogeneous shape and distribution and has a hexagonal phase. Figure 4 demonstrates the XRD pattern of ZnO. The diffraction pattern of ZnO at 2θ (degree) with the peak of 31,950;32,707; 34,614; 36,438; 47,709; 56,755; 63,019; 66,536; 68,10; 69,248; 72,711; 76,61; and 77,130; correspond to the reflection from 100, 002, 101, 102, 110, 103, 200, 112, 201, 004, and 202. The XRD pattern is identical to the hexagonal phase with the Wurtzite structure [10]. The crystallites size of commercial ZnO is listed in table 1.

Figure 3. SEM image of ZnO

Figure 4. The XRD pattern of ZnO

The process of synthesise of ZnO-natural zeolite nanocomposites consists of a number of following steps; activation, precipitation, filtration, washing, forming, drying, calcining [11]. The natural zeolite was activated by HCl as a preliminary step. Then, co-precipitation consists of three main steps, namely, the mixing of the liquid acetate precursor with natural zeolite, the ion exchange between Zn$^{2+}$ and natural zeolite, nucleation and crystal growth to form primary particles, and aggregation of primary particles. Table 2 shows the crystallite size obtained from the XRD analysis of the ZnO-Zeolite
It has been proven that the synthesized ZnO is in nano size. In this study, the largest ZnO crystallite size occurs at pH 8, and the smallest crystallite size occurs at pH 10. Further increasing the concentration of OH− from pH 8 reduces the ZnO crystallite size. The crystallite size decreases at pH 9 and 10, but at pH 11, it increases. It can be seen that at pH 11 the co-precipitation process is no longer optimal. This is because the amount of dissolved OH− was larger during synthesis of ZnO at pH > 10. When ZnO react with too much OH−, the dissolution of ZnO occurs. The dissolution made the crystallites became smaller and agglomerated [12].

Table 2. Crystallites size of nanocomposites ZnO-natural zeolite

| Sample pH | Crystallite size (nm) |
|-----------|-----------------------|
|           | ZnO       | Zeolite    |
| 8         | 67.82     | 107        |
| 9         | 21.64     | 111        |
| 10        | 20.99     | 140.8      |
| 11        | 33.59     | 71.25      |

3.2. Degradation of procion red using nanocomposite photocatalyst ZnO-natural zeolite

To determine the effect of pH on nanocomposite synthesis, the nanocomposites are made using different alkaline pH from 8 to 11. Nanocomposites produced from this different pH are then tested for their ability to degrade procion red dyes. A procion red concentration of 50 ppm was used as a model pollutant in this study. The degradation percentage at different pH value was illustrated in Figure 5. As shown, the highest degradation percentage of 75.54% was found when using nanocomposites that synthesized at pH 10, after 120 minutes of mixing time under UV irradiation. Degradation of rocion red in the term of C/Co (C is procion red concentration at t; Co is initial procion red concentration) can be depicted in Figure 6. The lowest C/Co is also found when using the nanocomposite when synthesize at pH 10. This can be explained as follow; at pH 10 the nanocomposites have the smallest crystallite size. In addition, based on the BET test, the largest surface area of 134.35 m²/g obtained where nanocomposites was synthesized at pH 10. According to [12] the crystallite size of ZnO is relevant to the particle size. It can be considered that the smaller the particle size and the greater the surface area, the better the adsorption process. That is why the highest degradation was achieved at pH of 10. Based on SEM-EDX results, the highest content of Zn in the composites of 10.05% was also found at pH of 10.

Figure 5. Effect pH on degradation of procion red

Figure 6. Effect of mixing time on C/Co of
3.3. Comparison of degradation procion red using zeolite, ZnO, and nanocomposite ZnO-natural zeolite

Figure 7 shows the comparison of degradation percentage of procion red by using three types of materials, in this case natural zeolite, ZnO, and ZnO-natural zeolite nanocomposites (best results of pH 10) at 30 minutes of mixing time. The ZnO-natural zeolite nanocomposite produces the highest degradation compared to ZnO and natural zeolite alone. However, the longer the contact time the ability of natural ZnO-natural zeolite nanocomposites has decreased compared to ZnO, which is still able to further degrade. The specific density of ZnO-natural zeolite composite is greater than ZnO, causes this material not spread evenly during the process, so that degradation process is not optimal. Moreover, the ZnO used here is a commercial ZnO, which has a high purity and uniformity in size, so that the degradation process can be more optimal.

![Figure 7. Degradation percentage of procion red by using natural zeolites, ZnO, and ZnO-natural zeolites (procion red concentration of 50 ppm)](image)

4. Conclusion

In this research, ZnO-natural zeolite composite material was synthesized by using co-precipitation method. The material obtained was characterized by XRD, SEM-EDS, and BET. The analysis shows that ZnO and natural zeolite have been successfully synthesized to produce nano-sized composites. The pH effect significantly on the nanocomposites properties. The best physical characters were found when the nanocomposite synthesized at pH 10. At this pH the crystallite size of 20.99 nm, the surface area of 134.35 m$^2$/g, and the Zn content of 10.05% in the nanocomposite were obtained. The highest degradation percentage of 75.54% was reached when using nanocomposites photocatalyst, after 120 minutes of mixing time under UV irradiation.

Acknowledgments

The authors wishing to acknowledge the financial support from LPPM Universitas Sriwijaya through Hibah Unggulan Kompetitif 2019. The authors also thank the Integrated Research Laboratory of the Postgraduate Program of Universitas Sriwijaya and the Laboratory of Waste Treatment Technology of Chemical Engineering Department for laboratory assistances.
References

[1] Salam A, Agustina T E, and Mohadi R 2018 *International Journal of Scientific & Technology Research* 7 54-9

[2] Dhamayanti Y, Wijaya K, and Tahir I 2005 *Proceeding Seminar Nasional DIES ke 50 FMIPA UGM* 22–29

[3] Perdana D N, Wardhani S, and Khunur M 2014 *Kimia Student Journal* 2 576-82

[4] Hutabarat R 2012 *Sintesis dan Karakteristik Fotokatalis Fe^{3+}ZnO Berbasis Zeolit Alam* (Depok: Universitas Indonesia)

[5] Ruliza M, Agustina T E, and Mohadi R 2014 *Earth and Environmental Science* 10 1-7

[6] Hartini, E 2011 *Modifikasi Zeolit Alam dengan ZnO Untuk Degradasi Fotokatalis Zat Warna* (Depok: Universitas Indonesia)

[7] Chanu L A, Singh W J, Singh K J, and Devi K N 2019 *Results in Physics* 12 1230-37

[8] Fereshteh Z, Loghman M R, Estarki, Razavi R S and Taheran M 2013 *Mat Sci in Semiconductor* 16 547-43

[9] Ngapa Y D 2017 *Jurnal Kimia dan Pendidikan Kimia* 2 90-6

[10] Hamedani N F and Farzaneh F 2006 *J Sci Islamic Republic of Iran* 17 231-34

[11] Jong K P 2009 *Synthesis of Solid Catalyst* (Germany: Wiley-VCH)

[12] Alias S S, Ismail A B, Mohamad A A 2010 *J Alloys and Comp* 499 231-37