Influence of Activation Time on Ibuprofen Adsorption Using Zinc Oxide from Gelatin Templating Method

Maria Ulfa1, * and Umi Wahidatul Latifah1

1Study Program of Chemistry Education, Faculty of Teacher Training and Education, Sebelas Maret University, Jl. Ir. Sutami 36A, 57126 Surakarta, Central Java Indonesia

*Corresponding author: ulfa.maria2015@gmail.com

Abstract. The present work aimed to investigate the performance of activated zinc oxide for ibuprofen adsorption. The zinc oxide was synthesized by the templating method using F127 and gelatine as a soft template and sulfuric acid as a catalyst. The zinc oxide was activated by an HCl solution 1M for 1, 8, and 24 hours. The raw and activated zinc oxides were characterized by XRD and by infrared spectroscopy. The HCl treatment increases both of the numbers of Zn-O-Zn groups and peak of Zn-O from diffractogram but decreases hydroxyl group content. Ibuprofen adsorption studies of kinetics and isotherms were carried out at room temperature with solid-liquid ratio 3:5(v/v) and water-hexane solution. The adsorption properties were correlated to the activated conditions. The isotherms of adsorption were better reproduced by Langmuir–Freundlich models using activated zinc oxide by HCl at 8 hours. The best performance of ibuprofen adsorption resulted from activated zinc oxide at 8h using water-hexane 1:9 as ibuprofen solvent. The activation time and a high ratio of water-hexane both influence the adsorption of ibuprofen performance.

1. Introduction

Contamination of the water environment by natural compound waste as well as pharmaceuticals and personal care products (PPCP) is widely recognized as one of the serious environmental problems. PPCP is a substance used to treat and prevent diseases in humans and animals. The most used compound in this group is NSAIDs, including ibuprofen, diclofenac, and naproxen. The substance can enter the environment by the excretion of a compound that does not react, followed by the disposal of waste. In the long run, serious health problems can occur in humans who have consumed water that has been contaminated with waste pharmaceuticals, including ibuprofen [1]. Non-steroidal anti-inflammatory drugs (NSAIDs) are over-the-counter medications and commonly prescribed by physicians. This class of drugs has analgesic, anti-inflammatory, and anti-pyretic properties so that they are widely used. Ibuprofen is a potential hazard to human health due to this numerous pharmaceutical residue in aquatic area with [2].

Previous studies have discussed some of the methods that are used to eliminate the residual NSAIDs that contaminate water. Some of these methods are biological degradation, wet catalytic oxidation, and ozonation. Adsorption is one of the alternative methods; it is simple, of low cost, and potentially effective for eliminating residual NSAIDs, including ibuprofen, from environmental waters [3].

There are lots of materials used to eliminate the residual NSAIDs in waters, such as carbon active, biosorbentofchitin and lignin, nanoparticles silica magnetic or graphene oxide, metal-organic
frameworks, etc. Some carbon-active modifications of waste husk rice, zeolite, fly ash, and coconut shell can also be used as an adsorbent for eliminating residues of NSAIDs with low cost [4].

Photocatalytic semiconductors, such as zinc oxide, if activated to become the adsorbent, also show great adsorption ability. In maximizing the process of adsorption, adjustments were carried out, one of them by adding activator on metal oxides that aim to reach the volume of pores and the spacious surface of the adsorbent [5,6].

Zinc oxide (ZnO) could be activated in several ways, such as using photons or light so zinc oxide can be a photocatalyst, addition of activated carbon, zeolite, or certain solutions so that zinc oxide can be used as a good adsorbent [7]. Based on previous research, zinc oxide, which has been activated, can be used as an adsorbent for wastewater to adsorb toxic dyes, pollutants [8][9].

Zinc oxide is the material of metal oxides that are usually visibly white and not soluble in water and alcohol. Zinc oxide is one of the semiconductor inorganics that are not toxic and can provide mobility and height and whose thermal stability is good. Zinc oxide has a band distance of eV with a bond energy of 60 meV at room temperature, the most stable structure of zinc oxide is wurtzite [10][11].

Activation of zinc oxide is done so that zinc oxide can be used as an adsorbent. Through activation, the surface morphology of zinc oxide experiences changes, namely an increase in the size of the micropore and in the adsorption of substances. The length of time of activation affects the size of the pores of micro, making an impact on power adsorption, where the increasing size of the pores so the power adsorbed increasingly large so that will be a lot of substance that is able in adsorption application[12][13]

In this study, the formation of zinc oxide was investigated using Pluronic F127 with gelatin as co-template via the hydrothermal method. Pluronic F127 is a soft organic template with a relatively high dissolution rate and low mechanical strength. The zinc oxide was characterized using the X-ray diffraction method (XRD) and infrared analysis. The potential use of synthesized zinc oxide as an adsorbent for drug removal was investigated using ibuprofen as a probe molecule.

2. Materials and Methods

2.1. Materials

In the present research study, all of the starting materials obtained commercially from the authentic companies and used without further purification. Herein, zinc sulfate (ZnSO₄), ethanol (EtOH), F127 and gelatin as starter materials and sulfuric acid as an activation solution.

2.2. Synthesis of ZnO

EtOH is dropped into the F127 solution with a burette (1 drop of EtOH per 20 seconds) at room temperature). After the F127 has been dropped, the mixture is left in the stirrer for 4 hours 150 rpm. Closed condition (crepe plastic). When the droplet is attempted, the air is prevented from entering by making holes in the crepe plastic and covering them out with a mask. Add gelatin then stir for 60 minutes.

ZnSO₄ was dropped on the solubility of F127 with a burette (1 drop per 10 minutes) at room temperature and room conditions. After everything has been dropped, the mixture is stirred for 20 hours of 150 rpm closed condition (crepe plastic).

During the droplet, the air is prevented from entering by making holes in the crepe plastic and covering the mouth; the mixture is put in the hydrothermal reactor and then the oven at 100°C for 24 hours and then allowed to cool. The white solid is filtered and washed with distilled water so that pH=7. The solid is then dried at 100°C for 24 hours and then calcined at 550°C for 12 hours; then the solid is stored in a clear, closed bottle.

2.3. Activation of ZnO

Samples that have been synthesized, then activated using HCl solution with a variation of the time of activation are different. Sample ZnO added with HCl solution in the state is stirred using magnetic stirrer with heating for 1, 8, and 24 hours. Then the samples were washed using distilled water until a pH between 6 and 7.
Sample ZnO was subsequently filtered and then dried in an oven at a temperature of 110°C. Samples ZnO that been washed with water were dried and allowed to stand at the temperature of space in the state closed, thus the obtained samples of ZnO were activated.

2.4. Characterization
Sample ZnO was activated using a solution of HCl with the variation of time, then characterized using a Fourier Transform Infrared (FTIR) spectrophotometer brand Shimadzu 2100 resolution of 0.5cm⁻¹ X-ray diffraction (XRD). This characterization aims to determine the presence of functional groups in the ZnO sample compound as well as the crystalline from the sample. Subsequently, the samples that have been characterized were used to ibuprofen adsorption.

2.5. Ibuprofen Adsorption
To find out the adsorption of ibuprofen with activated ZnO adsorbents, the solution of ibuprofen was prepared in a solution of Water: Hexane in a ratio of 10:0; 9:1; 5:5; 1:9; 0:10 concentrates 100 ppm. The concentration of ibuprofen was monitored with a UV-Vis spectrophotometer at the wavelength of 291.5 nm. A total of 60 mg of nano-ZnO was added to the solution of ibuprofen and stirred at a temperature chamber for 60 minutes. A total of 3 mL solution of ibuprofen is taken every interval of 5 minutes for 1 hour, and then the absorbance is measured using a spectrophotometer UV-Vis spectrophotometer Hitachi U-2000 Japan.

Calibration was done by preparing a standard solution of ibuprofen with a concentration of 5 to 100 ppm. The amount of ibuprofen adsorbed by ZnO was calculated using the equation.

$$q_e = (C_0 - C_t) \left( \frac{V}{w} \right)$$  \hspace{1cm} (1)

3. Result and Discussion

3.1. Characterization of Zinc Oxide
The XRD pattern on the zinc oxide with different activation time is shown in Figure 1b. The X-Ray Diffraction pattern of the ZnO which is activated for 1 h (labelled as ZnO-1h) shows three strong diffraction peaks at of 2θ (18.862°, 26.398°, 29.394°, 35.864°), ZnO-8h show strong peaks at of 2θ (18.801°, 26.337°, 29.424°, 35.762°) and ZnO-8h shows strong peak at 2θ (20.504°, 26.435°, 31.026°, 35.901°). All the peak of sample nothing shows differences significantly which is described that crystallinity of all sample has been stable in different of activation time. All XRD of sample be indexed to the known structure of the ZnO and hexagonal phase compare to the ZnO hexagonal wurtzite phase that shown in Figure 1(c) [14]. The best diffractogram results are ZnO with a 24-hour activation time. The diffractogram results for the activation time under 24 hours show a lower peak when compared with the 24 hours activation time, as shown in Figure 1.

The FTIR spectra of all sample of ZnO show the similar peak as functional group content. in Figure 2, shows that the general peak just of ZnO-24h that means that zinc hydroxyl groups have a huge degree of an ion characteristic. FTIR of ZnO-1h and ZnO-8h not shown. The broad peak centered at 3450 cm⁻¹, which corresponded to the stretching vibration of the hydroxyl group, was observed in all carbon materials. The presence of surface hydroxyl reflects the number of carbon terminal bonded to an oxygen atom that may be due to the formation of surface defects. The peak at wavelength 1300 cm⁻¹ shown there is Zn-O-Zn which is mean that zinc oxide synthesis has been successfully done in this research.
(a) XRD pattern of ZnO with 24 hours activation time at 0-5°.

(b) XRD patterns of ZnO with 1, 8 and 24 hours activation time at 10-80°.

(c) The XRD pattern of zinc oxide hexagonal phase.

Figure 1. (a) dan (b) Diffractogram result of Zinc Oxide with XRD at 2 Theta with 24 hours activation time and (c) The XRD pattern of zinc oxide hexagonal phase.
Figure 2. Characterization results of Zinc Oxide 24 hours activation time with FTIR.

Figure 3. (a) Ibuprofen Adsorption curve on ZnO with the variation of the solvent ratio between water and hexane during 60 minutes (b) Ibuprofen Adsorption curve on ZnO with the variation of solvent ratio between water and hexane during 1440 minutes.

3.2. Adsorption studies of ibuprofen on Zinc Oxide
The adsorption profile of ibuprofen at ZnO 24 hours, as shown in Figure 3, is activated by HCl obtained from the variation of water to the hexane ratio. High adsorption of ibuprofen was observed on Zinc Oxide using solvent variation 1:9 water to hexane ratio with 77.2% of ibuprofen adsorbed from initial concentration.

The best performance of ibuprofen adsorption resulted from activated zinc oxide at 24 hours using water-hexane 1:9 as ibuprofen solvent. The activation time and a high ratio of water-hexane both influence the adsorption of ibuprofen performance. The effect of the activation time is that the activation time will open the surface of ZnO, thereby increasing the micro-pore size and thus increasing the direct absorption of ibuprofen.

4. Conclusion
The best performance of ibuprofen adsorption results from activated zinc oxide at 24 h using water-hexane 1:9 as ibuprofen solvent. The length of time will increase the micropore size of ZnO so that it can adsorb more ibuprofen. The best Ct / C0 value of each variation of the existing solvent is pure water,
hexane 10%, 50%, 90% and 100% are 0.1661; 0.0726; 0.1552; 0.1689 and 0.1678, respectively. Not only the activation time but also a high ratio of water-hexane influences the adsorption of ibuprofen performance.

Acknowledgment
Authors acknowledge the Research Collaboration Indonesian Program (PPPKI) of Sebelas Maret University 2019 under contract Number 1362/UN27.21/PN/2019 for Maria Ulfa.

References
[1] W. Phasuphan, N. Praphairaksit, And A. Imyim 2019 J. Mol. Liq. 294 111554.
[2] A. P. Zahra and Novita Carolina 2017 J. Majority 6 153–158.
[3] J. C. Lancheros, C. A. Madera-Parra, A. Caselles-Osorio, W. A. Torres-López, And X. M. Vargas-Ramirez 2019 J. Ecol. Eng. 135 89–97.
[4] F. H. Pusceddu Et Al. 2018 J. Environ. Pollut. 232 274–283.
[5] A. A. Abdullah, T. A. Saleh, S. A. Ganiyu, M. N. Siddiqui, And K. R. Alhooshani 2017 J. Anal. Appl. Pyrolysis 128 246–256.
[6] J. Saini, V. K. Garg, R. K. Gupta, And N. Kataria 2017 J. Environ. Chem. Eng. 5 884–892.
[7] C. Yang, S. Yang, H. Fan, Y. Wang, And J. Shangguan 2019 J. Colloid Interface Sci. 555 548–557.
[8] N. Ghasemi And S. Rohani 2019 J. Mol. Liq. 285 252–269.
[9] S. Chaudhary, Y. Kaur, A. Umar, And G. R. Chaudhary 2016 J. Mol. Liq. 224 1294–1304.
[10] T. E. P. Alves, C. Kolodziej, C. Burda, And A. Franco 2018 J. Mater. Des. 146 125–133.
[11] K. M. Fang, Z. Z. Wang, M. Zhang, A. J. Wang, Z. Y. Meng, And J. J. Feng 2013 J. Colloid Interface Sci. 402 68–74.
[12] L. Huber Et Al. 2019 J. Microporous Mesoporous Mater. 276 239–250.
[13] M. Sharma Et Al. 2019 Chem. Eng. J., 358 540–551.
[14] S. Karim Fatah 2018 Diyala J. Pure Sci. 14 40–47.