

Mild temperature synthesis of Zinc oxide frameworks before and after calcination

Maria Ulfa^{1*}, Didik Prasetyoko², and M. Fajar P³

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

²Department of Chemistry, Faculty of Mathematics and Natural Sciences, Institute of Technology SepuluhNopember, JlKeputih, Surabaya, 61115, East Java Indonesia.

³Department of Chemistry, Faculty of Mathematics and Natural Sciences, Gadjah Mada University, 61115, Sleman, Indonesia

ABSTRACT

Room temperature synthesis of s zinc oxide has been developed for four well-known ZnO. In this work, character of zinc oxide compared by uncalcined zinc oxide using XRD, FTIR and SEM. The mild temperature can be applied as an efficient tool obtain ordered shape of ZnO before and after calcination. zinc oxide before and after calcination could be completely performed adsorption of metilen blue as the model dye by 30 mg of catalyst. The obtained results indicated that the conversions of methylene blue achieve 92% after 15 min in ambient temperature.

Keywords: zinc oxide; mild temperature, calcination; methylene blue; adsorbent

Introduction

Methylene blue is widely used in industry for dye paper, cotton, silk, wool and for hair coloring. The use of methylene blue causes human health problems, such as damage to the respiratory tract, eye, digestion and mental disorders [1]. The removal of methylene blue in waste has been researched recently. Methyl blue removal methods that are widely used are enzymatic processes, degradation reactions, electrochemistry, chemical coagulation, membrane filtration and physical adsorption methods [2]. The adsorption method is the most preferred method because it is cheap, easy and requires low energy[3]. In adsorption, the right adsorbent is needed so that the removal process of methylene blue can run well. One of the adsorbents that attract attention is zinc oxide [4]

Zinc oxide has attracted the attention of many researchers because it has physical, chemical stability and is able to act both as an active center in catalysis and adsorption. Synthesis of ZnO is carried out by various methods such as hydrothermal, sonication, microwave and sol gel. Previous research synthesized ZnO through the hydrothermal method in which zinc-acetate in methanol solution is reacted with NaOH with a concentration of 1M at 60C with the results obtained showing various sizes of ZnO particles at that temperature [5]. Other research

synthesized ZnO using the hydrothermal method stated that the increase in temperature during synthesis had an effect on reducing the hydroxyl (OH) group [6]. The presence of calcination is also believed to increase crystallinity. To the best of the authors' knowledge, the synthesis of ZnO at room temperature has rarely been investigated for its influence on its structure, functional groups and crystallinity. The difference in ZnO structure before and after calcination has never been studied before.

In addition to temperature, another factor that can affect the ZnO structure is the pore formation process and the ZnO space frame. Synthesis of ZnO with surfactants (anionic, cationic, and nonionic) is more effective than without surfactants [6]. Good surfactants are those that can be degraded in nature which are then called natural surfactants. Examples of natural surfactants are starch, gum, gelatin. Gelatin is effective as a natural surfactant because it has the ability to reduce surface tension [7]. Previous research using gelatin as a co-template has succeeded in making a regular carbon microsphere structure. Previous researchers believed that the presence of an amine group was capable of being a center for molecular rearrangement as well as a soft mold for the synthesis of various materials [8]. Therefore gelatin in this study is used for the synthesis of zinc oxide. Based on the description above, this study will examine the effect of room temperature on zinc oxide synthesis in ZnO before and after calcination using bovine bone gelatin extract for the application of methylene blue adsorption as a model molecule.

Experimental Material

The materials used in the study were zinc sulphate, cow bone gelatin, ibuprofen, ethanol, poly (ethylene-glycol) -block-poly (propylene-glycol) -block-poly (ethylene-glycol) -poloxomer F127, and aquades purchased by Sigma Aldrich

Synthesis ZnO

The synthesis of ZnO was initiated by dropping the ethanol solution (water: ethanol = 1: 3) into the F127 solution with a burette drop by drop at room temperature. Then the mixture plus 1M HCL is stirred for 4 hours with a stirring speed of 150 rpm in a closed condition (crepe plastic) to prevent entry. Then put the gelatin solids and stir for 60 minutes. After that, ZnSO₄ was put in a solution with a burette (1 drop per 10 minutes) at room temperature and room conditions. Ration of ethanol solution: gelatin: F127: Zn Sulfate: HCl is 125: 0.12: 12: 27: 0.001 (v / w / w / w / v). After everything is dripping, the mixture is stirred for 20 hours at a stirring speed of 150 rpm in closed conditions (crepe plastic). The mixture is then put into a hydrothermal reactor and then oven at 100 ° C for 24 hours and then allowed to cool. The white solid was filtered and washed with distilled water so that the pH = 7. The solid was then dried at 100 ° C for 24 hours and then calcined at 550 ° C for 6 hours; then the solid is stored in a clear and closed bottle.

Characterization

Instruments for zinc oxide characterization include: Fourier Transform Infrared Spectrophotometer (FTIR), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD). For the methylene blue adsorption test using Ultra Violet-Visible (UV-Vis).

Adsorption Methylene Blue

The adsorption equilibrium was observed by batch method. Adsorption was carried out using an initial concentration of 200 ppm with 30 mg of adsorbent at neutral pH and room temperature. The methylene blue solution was contacted with the adsorbent for 20 minutes and then 5 ml was taken every minutes. The concentration was determined using UV-vis which was studied at the absorbance peak of 670nm. The percentage of removal of methylene blue is calculated from the difference between the initial concentration (C_0) and the concentration at t (C_t) so that the % removal Mb is the result $(C_0 - C_t)$ divided by C_0 multiplied by 100%

Result and Discussion

Figure 1 is an X-ray diffractogram of ZnO before and after calcination. The XRD diffractogram showed a typical peak for ZnO which appeared at 2 theta 18.8; 27.9; 29.5; 35.6 and 41.4 which are in accordance with the results of previous studies [9-10]. At that peak both samples have images in depicting wurtzite crystals with diffraction fields (100), (200), (101), (110) and (103) respectively. The XRD ZnO uncalcined pattern shows a lower uncrack than ZnO Calcined because it is guaranteed that a high temperature after calcination results in the crystallinity of the sample and increases the purity of the material. The higher the X-ray diffraction peak, the higher the crystallinity level of the ZnO nanoparticles. It can be seen in the graph that ZnO calcined have higher peak than ZnO uncalcined as the higher the crystallinity level of the ZnO nanoparticles due to the high temperature treatment. Synthesis of ZnO, initiated by dropping a solution of ethanol F127 and gelatin at room temperature, showed success because the ZnO wurtzite structure was successfully formed with low energy. However, compared to standard ZnO, the synthesized ZnO results in this study showed changes due to pore enlargement that occurred when F127 pluronics coordinated with gelatin as the pore directing agent. This was confirmed by FTIR data

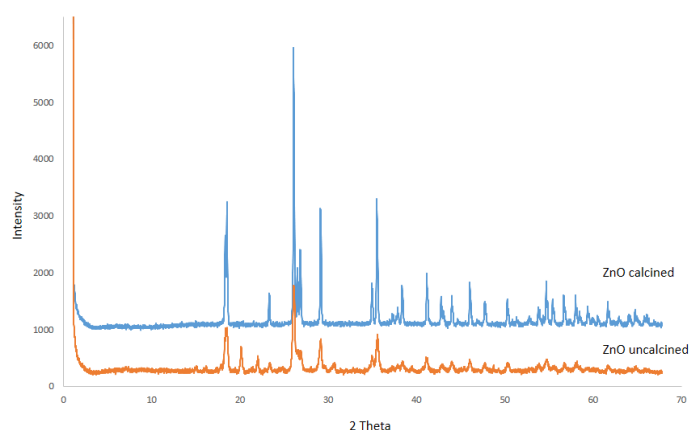


Fig 1. XRD of a. ZnO uncalcined and b. ZnO calcined.

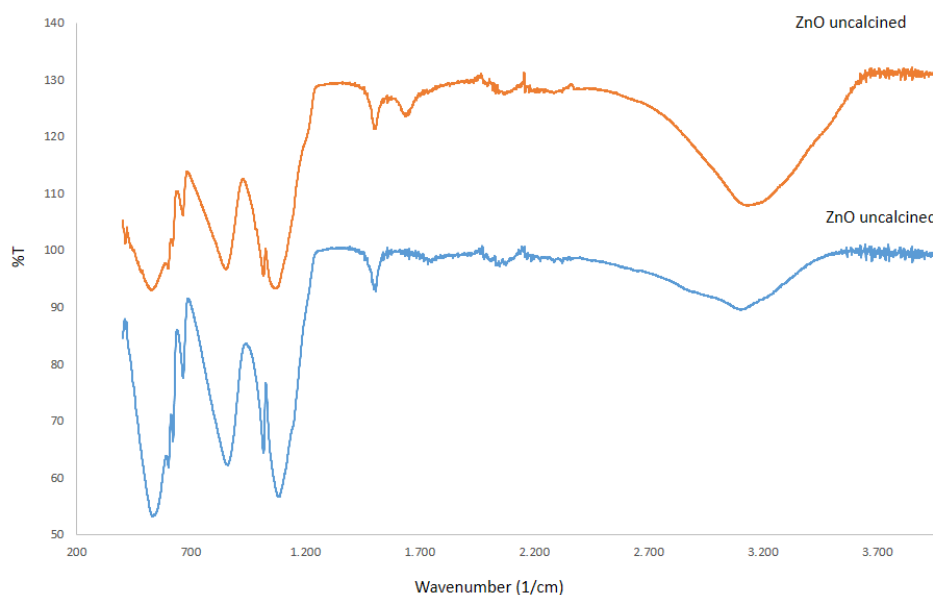


Fig 3. FTIR of a. ZnO uncalcined and b. ZnO calcined

Figure 2 is the FTIR ZnO spectra before and after calcination. There is a wide absorption at a wave number 3200-3500 cm⁻¹ which indicates a stretching vibration of -OH from Zn-OH and water molecules trapped in the ZnO surface. Meanwhile, the spectra with a peak at the wave number of 1650 cm⁻¹ are the Zn-O-Zn stretching vibrations as the main backbone of the ZnO material. This is supported by the sharp absorption at wave numbers 1230, 970 and 798 cm⁻¹, which indicate the presence of Zn-O and Zn-OH vibrations. In general, the ZnO spectra are in accordance with the absorption in previous studies. The synthesis of ZnO mild temperature has been proven to be successful, starting with the rearrangement of Zn atoms with micelles formed from the combination of the work of the F127 and gelatin molecules with the stability of the main function groups on the ZnO structure both before and after calcination. The difference is

clear in uncalcined ZnO which has a wide absorption at 3300 cm^{-1} which indicates the dominance of water molecules on the ZnO surface. Whereas in calcined ZnO the absorption is sharper and narrower. In other wave numbers such as in 1200-700 the uncalcined absorption is higher in intensity because the distance between atoms and groups is more tenuous than the calcined ZnO structure which is more solid, the distance between the groups so that the absorption is lower. This is confirmed by SEM data.

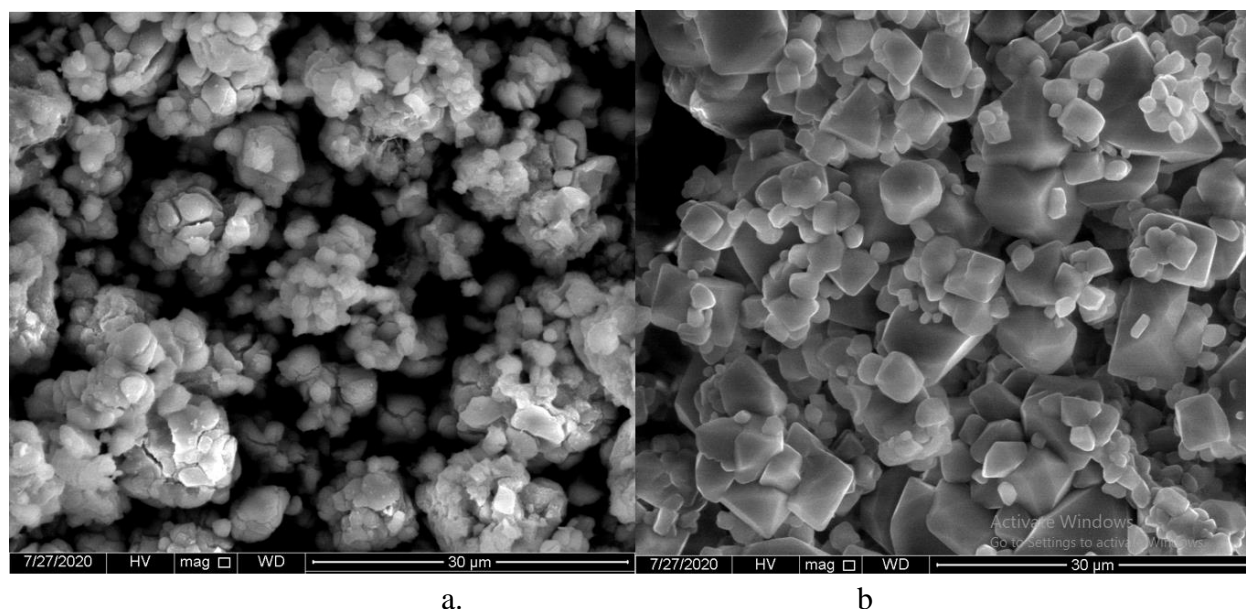


Fig 3. SEM of a. ZnO uncalcined and b. ZnO calcined

Figure 3 is a SEM of the calcined and uncalcined ZnO sample. It can be seen in the SEM image that the uncalcined ZnO sample has a disordered shape in the form of fractures and cracks of round and cube-shaped material about 5-10 μm . There is agglomeration in several parts but still dominated by regularity of shape between particles. The synthesis of ZnO at mild temperature has succeeded in producing regular ZnO forms due to the Zn pore directing process from the combined work of the F127 and gelatin molecules through electrostatic interactions on the ZnO structure both before and after calcination. This is predicted to arise due to the role of gelatin and pluronics F127 as a pore guide that maintains the rearrangement of the zinc precursor molecules to lead to a uniform size wurtzite. It is predicted that the agglomeration that appears in the SEM ZnO image before calcin is still covered with gelatin molecules and F127 pluronics so that it looks like a crack. This logically occurs because the pore directing agent has not undergone decomposition so that the pore directing molecule is still fused with the ZnO particles which have formed a structure that is different from its precursor shape. Whereas in calcined ZnO the surface of the material appears smoother with the loss of coarse cracks that were previously found in many ZnO calcined. Besides that, in ZnO calcined, the shape is dominated by cubes.

Small cubes measuring 2-5 μm with smooth surface on calcined ZnO are spread evenly over the larger ZnO cubes with a size of 7-12 μm which are predicted to come from the fusion of ZnO aggregates due to high temperature heating to form solids with regular structures. It appears that after calcination, ZnO regularity improves even though the pore alignment process has been completed. The ZnO surface was also dominated by Zn and there were no traces of carbon or other impurities from the gelatin residue or F127 copolymer block which showed that the pore-leading agent was completely decomposed after calcination.

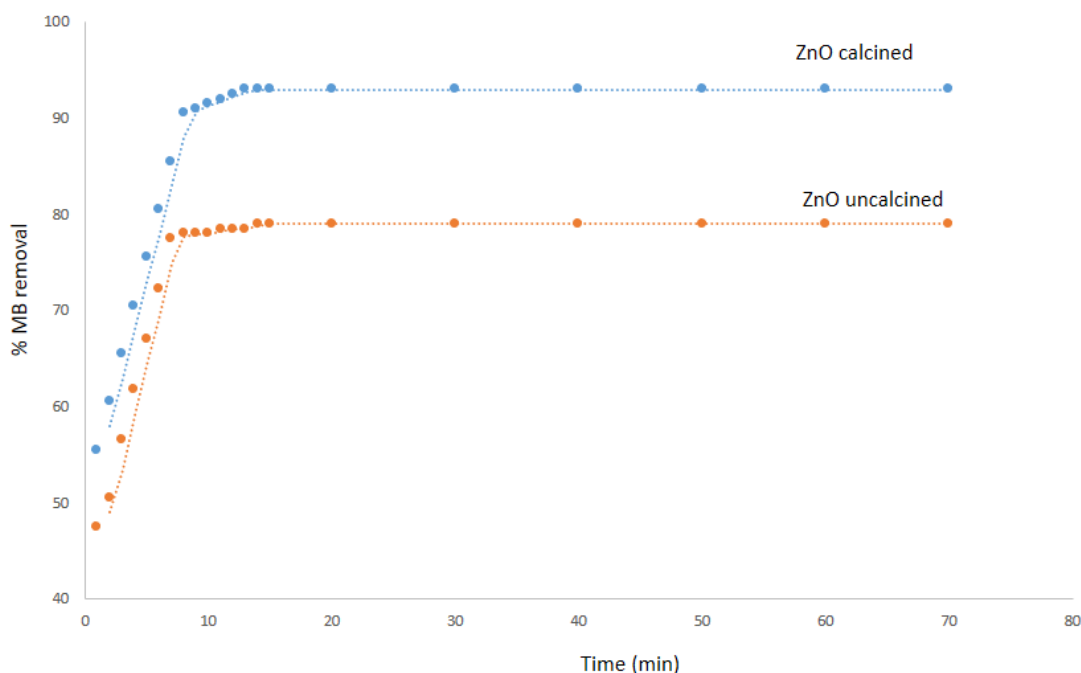


Fig 4. methylene blue Removal by Adsorption using ZnO calcined and ZnO uncalcined

Adsorption of methylene blue with calcined ZnO showed a higher removal percentage than ZnO which was not calcined (Figure 4). This happens because in the adsorption of methylene blue there is a physical bond between the Zn surface and the -OH group on the dye. In addition, the presence of Zn as an active center which has high affinity through the interaction of Lewis acid and electrostatic forces when the ZnO structure is formed well without blocking from gelatin or pluronic F127 as a pore-controlling agent. The percentage of methylene blue removal of calcined ZnO was higher by about 15 % compared to ZnO uncalcined which is not calcined which is predicted to come from the dominant role of electrostatic interactions, Van der Waals forces or hydrogen bonding can occur between Zn + and methylene blue via carboxylate anions through electrophilic and nucleophilic attack.

Conclusion

The synthesis of ZnO at room temperature has been successfully carried out using F127 pluronics and gelatin by hydrothermal method. The crystallinity, chemical functional groups and morphological properties of calcined ZnO were better than ZnO which were not calculated from the XRD, FTIR and SEM results. This happens because in the calcined ZnO there is no space barrier from the pore-guiding agent that closes the structural ordering. The adsorption of methylene blue as a dye model was successfully carried out with a percentage of removal of methylene blue as much as 92% in the first 15 minutes using calcined ZnO due to the electrostatic interaction effect between the ZnO surface and the -OH group on the dye and the interaction of Zn cationes as Lewis acid with alkaline dyes. Meanwhile, the adsorption of methylene blue with ZnO which was not calcined was lower than that of calcined ZnO because the active center of Zn was partially covered by the pore-guiding agent.

Acknowledgment

Authors would like to acknowledge funding from Program Penelitian Kolaborasi Indonesia (PPKI 2020) which consists of collaborators from Sebelas Maret University, Gadjah Mada University and Institut Teknologi Sepuluh Nopember , Indonesia.

References

- [1] O. Pezoti Jr., A.L. Cazetta, I.P.A.F. Souza, K.C. Bedin, A.C. Martins, T.L. Silva, V.C. Almeida, Adsorption studies of methylene blue onto ZnCl₂-activated carbon produced from buriti shells (*Mauritia flexuosa* L.), *J. Ind. Eng. Chem.* 20 (2014) 4401e4407, <https://doi.org/10.1016/j.jiec.2014.02.007>
- [2] Asfaram, M. Ghaedi, S. Hajati, M. Rezaeinejad, A. Goudarzi, M.K. Purkait, Rapid removal of Auramine-O and Methylene blue by ZnS: Cu nanoparticles loaded on activated carbon: a response surface methodology approach, *J. Taiwan Inst. Chem. Eng.* 53 (2015) 80e91, <https://doi.org/10.1016/j.jtice.2015.02.026>.
- [3] O. Pezoti Junior, A.L. Cazetta, R.C. Gomes, E.O. Barizão, I.P.A.F. Souza, A.C. Martins, T. Asefa, V.C. Almeida, Synthesis of ZnCl₂-activated carbon from macadamia nut endocarp (*Macadamia integrifolia*) by microwave-assisted pyrolysis: optimization using RSM and methylene blue adsorption, *J. Anal. Appl. Pyrolysis* 105 (2014) 166e176, <https://doi.org/10.1016/j.jaap.2013.10.015>
- [4] Santoso, E., Ediati, R., Kusumawati, Y., Bahruji, H., Sulistiono, D. O., & Prasetyoko, D. (2020). Review on recent advances of carbon based adsorbent for methylene blue removal from waste water. *Materials Today Chemistry*, 16, 100233. <https://doi.org/10.1016/j.mtchem.2019.100233>

- [5] G. Eshaq, A.E. Elmetwally, Bmim[OAc]-Cu₂O/g-C₃N₄ as a multi-function catalyst for sonophotocatalytic degradation of methylene blue, *Ultrason. Sonochem.* 53 (2019) 99e109, <https://doi.org/10.1016/j.ultsonch.2018.12.037>.
- [6] A. Mosbah, H. Chouchane, S. Abdelwahed, A. Redissi, M. Hamdi, S. Kouidhi, M. Neifar, A.S. Masmoudi, A. Cherif, W. Mnif, Peptides fixing industrial textile Dyes : a new biochemical method in wastewater treatment, *Hindawi J. Chem.* 2019 (2019), <https://doi.org/10.1155/2019/5081807>.
- [7] P. Senthil Kumar, S.J. Varjani, S. Suganya, Treatment of dye wastewater using an ultrasonic aided nanoparticle stacked activated carbon: kinetic and isotherm modelling, *Bioresour. Technol.* 250 (2018) 716e722, <https://doi.org/10.1016/j.biortech.2017.11.097>.
- [8] V. Katheresan, J. Kansedo, S.Y. Lau, Efficiency of various recent wastewater dye removal methods: a review, *J. Environ. Chem. Eng.* 6 (2018) 4676e4697, <https://doi.org/10.1016/j.jece.2018.06.060>
- [9] Ulfa, M., Prasetyoko, D., Mahadi, A. H., & Bahruji, H. (2020). Size tunable mesoporous carbon microspheres using Pluronic F127 and gelatin as co-template for removal of ibuprofen. *Science of the Total Environment*, 711, 135066. <https://doi.org/10.1016/j.scitotenv.2019.135066>
- [10] M.J. Ahmed, S.K. Dhedan, Equilibrium isotherms and kinetics modeling of methylene blue adsorption on agricultural wastes-based activated carbons, *Fluid Phase Equilib.* 317 (2012) 9e14, <https://doi.org/10.1016/j.fluid.2011.12.026>