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Synthesis of ZnO-Ag Nanocomposites trough Ultrasonication-Microwave Combination Method with Clove Leaf Oil

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Abstract. ZnO and Ag nanoparticle have known their antibacterial activity especially their use in medical materials. In this study, ZnO-Ag Nanocomposite was synthesized by ultrasonication-microwave combination method with variation of reaction time using clove oil as their bioreductor. ZnO-Ag was prepared from ZnO Acetate as a source of ZnO and AgNO3 as a source of Ag. The crystallinity structure, average particle size, morphology, and composition of ZnO-Ag was characterized by X-Ray Diffraction, Scanning Electron Microscope, and Energy Dispersive X-ray Spectroscopy. X-ray diffraction pattern indicates that reaction time of 30 minutes have optimal synthesis results. The nanocomposite obtained consists of 43.2 % Ag nanoparticle, 17.5 % hexagonal Zincite, 14.6% Zinc Oxide, 14.5% wulfingite (deuterated), and 10.2% Zn(OH)2 with average particle size of 28.29 nm according to Scherer's equation. The result of scanning electron microscope showed that ZnO has an fiber shape and Ag has a round shape.

1. Introduction

Nanoparticle technology is becoming a very interesting technology to be developed. Nanoparticles are particles of 1-100 nm in size [1]. This material has broad uses because of its small particle size, one of which is the Ag and ZnO nanoparticles (AgNPs and ZnONPs). AgNPs has broad applications in the field of biomedicine, such as antibacterial [2], anticancer [3], antifungal [4], and antiviral [5]. However, the use of AgNPs with high concentrations can cause side effects because of its high toxicity [6]. Therefore, AgNPs can be combined with materials that have high biocompatibility with low toxicity on cell. ZnONPs is a metal oxide nanoparticle which has low toxicity and high biocompatibility [7], low cost, easily synthesized, and has almost the same uses as AgNPs in the biomedical field [8]–[10]. ZnO can improve some Ag capabilities, for example, increased antibacterial activity [11], photocatalytic activity so that several methods of making ZnO-Ag nanocomposites are beginning to be studied by researchers.

Research on the ZnO-Ag nanocomposite synthesis method that is environmentally friendly and economical continues to be developed until the maximum synthesis results are obtained. ZnO-Ag can be synthesized by natural materials as its bioreductor [12]. Plant extracts that have hidroxyl group (-OH), carboxyl group (-COOH), double bond, or other electron rich functional group can give a role as bioreductor [13]. Clove leaf oil is one of the essential oils from clove tree (*Syzigium aromaticum*) which is abundant in Indonesia [14]. The main content of clove leaf oil is eugenol at 60-68% [14],

[15]. Clove leaf oil has high antioxidant activity[16]. Therefore, clove oil is used as a bioreductor in the synthesis of ZnO-Ag nanocomposites in this research. So far, the method used for ZnO-Ag synthesis is conventional heating, but this method consumes time and energy. So this research uses the ultrasonication-microwave combination method for the synthesis of ZnO-Ag nanocomposites. The microwave method is a nanoparticle synthesis method that utilizes microwaves to heat the materi so that reactions occur. The advantages of this method are energy efficiency, high reaction rates, rapid volumetric heating, high reaction rates, size and shape control by tuning reaction parameters, and energy efficiency [17][18]. Meanwhile ultrasonication method use ultrasonic radiation to disperse the molecule [18]. This paper was reporting the optimal reaction time in Zn-Ag synthesis by the microwave method using clove leaf oil. The ZnO-Ag nanocomposite was characterized by X-Ray Diffractometer (XRD), Scanning Electron Microscope and Energy Dispersive X-ray Spectroscopy (SEM-EDX), while clove leaf oil was analyzed for phytochemical cost using Gas Chromatography-Mass Spectroscopy (GC-MS). XRD data analysis using Origin Pro and Match software.

2. Experimental Section

2.1 Material and Instrumentation

The chemicals used in this study were Silver Nitrate (Merck), Zinc acetate dihydrate (Merck), ethanol (Merck), clove leaf oil (CV. Nusaroma Depok), demineralized aqua (Bratachem), ammonia (Merck). The equipment used are glasses equipment, microwave reactor (Electrolux), Oven (DGG 9053A), Analytical Balance (Ohaus px224/E), ultrasonicator. The composition of clove leaf oil was analyzed by Gas Chromatography-Mass Spectroscopy (GC-MS Shimadzu QP2010). Morfology and atomic composition was observed by Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy (SEM-EDX HITACHI FLEXSEM 1000). Molecular phase was observed using X-Ray Diffractometer spectroscopy (XRD Panalytical X'Pert Pro). XRD pattern was analyzed by Match and Origin pro software.

2.2 Synthesis ZnO-Ag with clove oil

ZnO-Ag nanocomposite was synthesized according to previous report with modification [19][20]. A 15 mL of clove leaf oil was added to 50 mL of ethanol in a 250 mL of erlenmeyer flask. The mixture was ultrasonicated for 30 minute until homogen, and was further added with 100 mL of Zinc acetate dihydrate 3 x 10^{-3} M slowly. Furthermore, It was added with ammonia until pH 9 and was further ultrasonicated until homogen. Then, it was reacted in microwave reactor at power level of 300 W, temperature of 30°C for 30 minutes. Furthermore, silver nitrate was added to the mixture drop by drop while ultrasonication is taking place for 30 minutes. Then, it was reacted in microwave reactor with five variations of reaction time for 10, 15, 20, 25, and 30 minute. The mixture was filtered and washed with ethanol until a colorless filtrat was afforded. ZnO-Ag nanocomposite was obtained and further dried at 130°C.

2.3 Characterization of reaction product

ZnO-Ag characterization was carried out to the composition, morphology, particle size, and the degree of crystallinity. Phase identification, particle size, and degree of crystallinity were analyzed from XRD data. The size of nanocomposite particles is determined through the Scherrer equation. The phase composition is analyzed using the Match! Version 3.8.2, the degree of crystallinity is determined through equation (2), the XRD diffraction area is determined using the Origin pro software.

$$d_{diffr} = (0{,}9\lambda) / (\beta\cos\theta) \quad (1)$$

$$\% \text{ Crystallinity} = (\text{Area of crystalline} / \text{Total area}) \times 100\% \quad (2)$$

Furthermore, ZnO-Ag was analyzed for morphology and elemental composition using SEM-EDX.

3. Result and Discussion

3.1 Synthesis ZnO-Ag with clove oil using ultrasonication-microwave method

ZnO-Ag nanocomposite synthesis reaction is an exothermic reaction between the oxidizer with the bioreductor, ZnO acetate and AgNO3, in this study ZnO acetate and $AgNO_3$ act as oxidizing agents. ZnO and Ag synthesis process is carried out in one container or called one pot synthesis. Phytochemicals such as polysaccharides, polyphenolic compounds, vitamins, amino acids, alkaloids, terpenoids could help reducing metal ions or metal oxides to 0 valence metal NPs[21]. Clove leaf oil could worked as a bioreductor in the synthesis of ZnO-Ag nanocomposites because clove leaf oil contains several compounds that can work as Zn^{2+} ion complexing agents in solution and reduce ZnO Acetate and $AgNO_3$ to ZnO and Ag [22][23]. The clove leaf oil content was analyzed using GC-MS and the results of the analysis are shown in Figure 1. Based on the results of GC-MS, clove leaf oil consists of 71.41% eugenol; 25.96% trans-Caryophyllene; 2.63% alpha-Humulent.

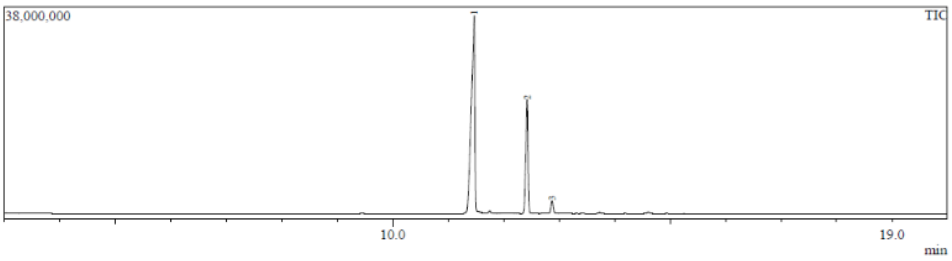

Figure 1. Total Ionic Chromatogram (TIC) of clove leaf oil.

3.2 Phase identification and Cristallinity

ZnO-Ag nanocomposites can be synthesized from ZnO Acetate and AgNO3 using a microwave-ultrasonication combination method with clove leaf oil as a bioreductor. In this research, the synthesis process was carried out with five variations of reaction time to determine the optimal reaction time. The nanocomposite was characterized by XRD to obtain a diffractogram in Figure 2. Figure 2 showed that there is a difference in peak intensity values and there is no significant 2 theta shifts in each diffractogram.

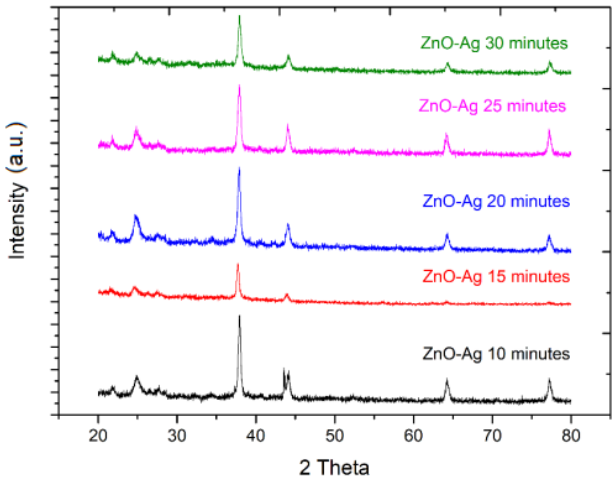

Figure 2. Diffractogram ZnO-Ag nanocomposites.

Nanocomposite phase identification was done using Match! software from the diffractogram to obtain the results that shown in Figure 3. Match! software showed that there are differences in the composition of nanocomposite elements at each reaction time variation. Globally the nanocomposite consists of five phases that is Hexagonal Zinc Oxide, Hexagonal Zinc Oxide (Zincite), Orthorhombic $Zn(OH)_2$ (Wuelfingite), trigonal (hexagonal axes) Zn $(OH)_2$, and cubic Ag. Based on the results of the phase identification, nanocomposites with the most AgNP composition were obtained at the reaction time for 20 minutes, which was 67%. While nanocomposite with the most ZnO-NP composition was obtained during the reaction time for 10 minutes, which was 44.7%. The side product of this synthesis was $Zn(OH)_2$ which is most produced during the reaction time for 15 minutes, it was consist of 23.7% trigonal (hexagonal axes) $Zn(OH)_2$ and 51.4% orthorhombic $Zn(OH)_2$ (Wuelfingite). $Zn(OH)_2$ was intermediate product of ZnO synthesis reaction. Based on these results, the composition of $Zn(OH)_2$ was inversely proportional to the composition of ZnO, so there was a possibility of an equilibrium reaction between ZnO and $Zn(OH)_2$ during the synthesis process. Hexagonal ZnO and Zincite was the best phase for antimicrobial application [24]

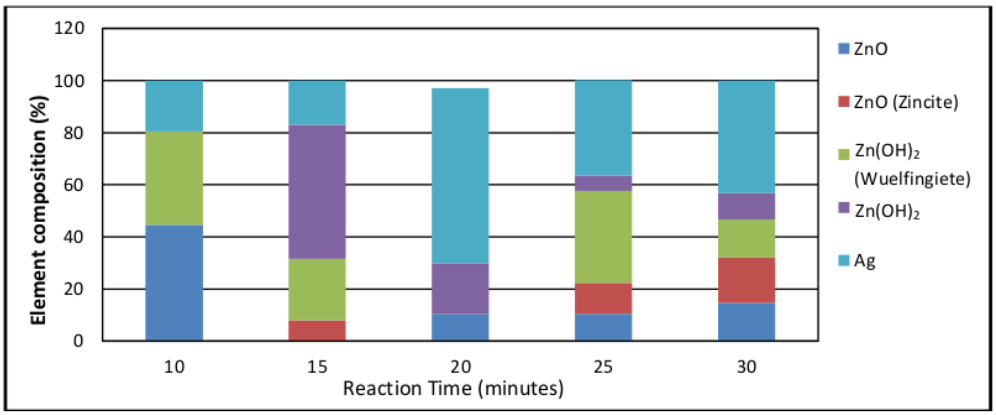

Figure 3. % Composition of ZnO-Ag nanocomposite.

The average particle size was calculated using the Scherrer equation and % crystallinity was calculated using the origin pro and Ms. Excel software. The results of the calculations are shown in Table 1. Nanocomposites with the smallest average particle size were obtained at a reaction time of 20 minutes, which was 19.66 nm. Whereas nanocomposite with the largest average particle size was obtained at a reaction time of 10 minutes, which was 36.44 nm, so the five nanocomposites meet the nanoparticle size criteria, which is 1-100 nm. The five nanocomposites have a low degree of crystallinity. The highest degree of crystallinity as much as 28% was obtained at the reaction time of 20 minutes, while the lowest degree of crystallinity of 15% was obtained at the reaction time of 15 minutes.

Table 1. Average particle size of ZnO-Ag nanocomposite.

No	Time (minutes)	Average particle size (nm)	Cristallinity (%)
1	10	36.44	23
2	15	22.64	15
3	20	19.66	28
4	25	32.64	27
5	30	28.29	20

3.3 Morphology of ZnO-Ag

Morphological studies were carried out to determine the shape of nanocomposites and the position of Ag and ZnO in nanocomposites. Morphological studies were carried out through SEM-EDX analysis on ZnOAg-NP10, ZnOAg-NP20, ZnOAg-NP30. The selection of these three nanocomposites was based on the % ZnO and Ag compositions that were successfully synthesized. Figure 4 showed the morphology of the three nanocomposites consisting of round and fiber shapes. The EDX was used to determine the location of the elements Zn, Ag, and O in the nanocomposite. The EDX results showed that Ag (round shape) can be deposited into ZnO (fiber shape). Based on Figure 4, Ag-NP in ZnOAg-NP20 is more evenly distributed on ZnO-NP with smaller particle sizes than ZnOAg-NP10 and ZnOAg-NP30. The AgNP particle was aggregated in ZnOAg-NP30 so that the average particle size is greater than the other two nanocomposites.

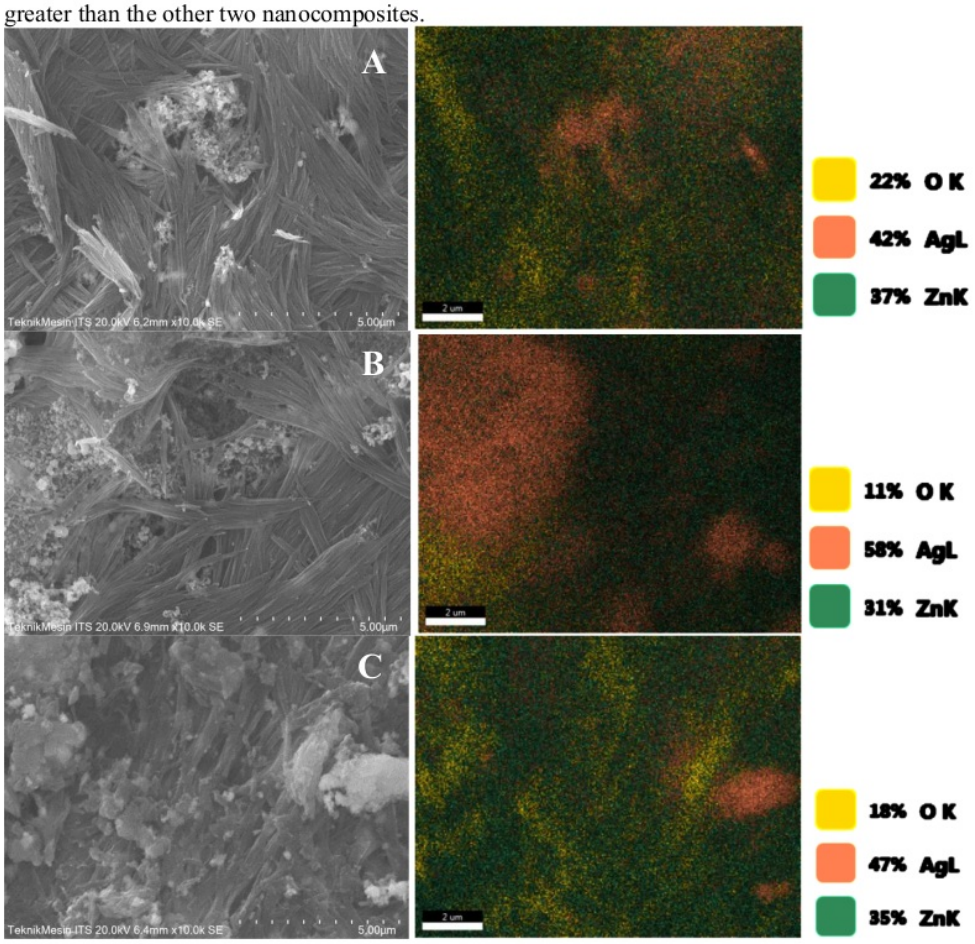

Figure 4. SEM of: (A) ZnOAg-NP10; (B) ZnOAg-NP20;(C) ZnOAg-NP30.

4. Conclusions

Ag-ZnO nanocomposite was synthesized by ultrasonication-microwave method using clove leaf oil at different reaction time 10, 15, 20, 25, 30 minutes. Characterization of ZnO-Ag nanocomposite by XRD and SEM-EDX revealed that the best Ag-ZnO nanocomposite was obtained from 20 minute

reaction time. The ZnO-Ag nanocomposite consists of 67.0 % Ag nanoparticle, 10.0 % hexagonal Zinc Oxide, 19.0% Zinc $(OH)_2$, with average particle size of 19.66 nm. The five nanocomposites have a low degree of crystallinity. Therefore, for further research, nanocomposites need to be calcined.

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