Effect of laser repetition rate in the synthesis of colloidal zinc nanoparticles by pulse laser ablation method

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Abstract. Synthesis of Zinc nanoparticles (ZnNPs) has been carried out using pulse laser ablation method. In this method neodymium-doped yttrium aluminum garnet (Nd:YAG) laser pulse are used. Effect of laser repetition rate pulse was examined to produced ZnNPs. Spherical shapes of ZnNPs was produced when pulse laser beam (1064 nm, 7 ns) was bombarded onto a high purity (99.95%) zinc plate surface. The averaged diameters of ZnNPs produced in this research were 12.1 nm with standard deviation 4.4 nm for the laser repetition rate 10 Hz, the diameter of ZnNPs was 5.6 with standard deviation 4.7 nm. The spectrum of ZnNPs was obtained by ultraviolet visible (UV-Vis) spectroscopy shows that the surface plasma resonance (SPR) at the center of 300 nm wavelength, which certifies that the ZnNPs produced has the spherical shape.

1. Introduction
Recently, Nanoparticles are one of the most attractive subject of research interest. Nanoparticles are very small materials that are less than 100 nm in size [1]. Many metals has been synthesized as nanoparticles, one of them potential to be developed is zinc nanoparticles (ZnNPs). The ZnNPs have been used for biomedical application [2], revolutionizing agriculture [3], making solar cell [4], anti microbial activity and food packaging [5]. Furthermore, in medical application ZnNPs can be used for antibacterial activity and toxicity mechanism [6]. So, the synthesis of ZnNPs is very important. Several methods used to ZnNPs synthesis are spray pyrolysis method [7], wet chemical method [8], and precipitation method [9]. Those methods have some disadvantages, such as complex preparation, complex equipment, and problem for environment. In addition, the produced ZnNPs have a low purity as they require additional chemical agents during synthesis process.

In this study, colloidal ZnNPs were produced by using pulse laser ablation (PLA) method. In this experiment, the laser beam was focused on a surface of the sample located inside pure aquades. The laser beam will ablate the surface of the sample causing the evaporation of small amount of sample. The evaporated material will diffuse in surrounding liquid and forming colloidal nanoparticles. Compared to other methods described above, this method only require very simple preparation, low system cost, and ZnNPs produced have high-purity because free from stabilizer and chemical agents.

Pulse Nd:YAG laser was used as radiation source for ZnNPs synthesis in this study. The effect of laser pulse repetition rate was examined to produced ZnNPs. The scanning electron microscopy (SEM) was used for morphological characterization of produced colloidal ZnNPs. Surface plasma resonances (SPR) and nanoparticles size distributions will be shown in this paper.
2. Experimental Methods
The experimental set up used in this work is shown in Figure 1. The radiation source used was Nd: YAG (New Wave Research, Polaris II, 20 Hz) with wavelengths, energy and pulse widths used respectively 1064 nm, 30 mJ, and 7 ns. The repetition rate of pulse laser was varied from 5 Hz, 10 Hz and 15 Hz. The laser beam was focused on the high-purity (99.95%) zinc plate by using a convex lens with a 30 mm focal length. The beam was directed to the sample, which located in a petri dish containing 10 mL of aquades. The ablation process occurred for 60 minutes. During the synthesis process, zinc plate and solution were moved periodically to produce homogeneous colloidal ZnNPs.

![Figure 1. Experimental set-up used in this study](image)

Charaterization of ZnNPs produced in aquades includes morphological photograph using Scanning Electron Microscopy (SEM) (SEM, JEOL, JSM-6510 LA). The size distribution of nanoparticles was calculated using photographs obtained by SEM. The Surface plasma resonance of the resulting nanoparticles was analyzed by using Ultraviolet Visible (UV-Vis) light spectroscopy (UV-Vis, Spectroquant Pharo 300).

3. Result and Discussion
The colloidal ZnNPs produced by using PLA method with different repetition rate of pulse laser are shown in Figure 2(a). In the picture, colloidal ZnNPs solution shows brownish color. Dark-brown (left hand side), medium-brown (middle side) and light-brown (right-hand side) color of ZnNPs were produced using PLA method with repetition rates of 15 Hz, 10 Hz and 5 Hz. The change of color from pure white (aquades) to light brown indicate that the nanoparticles was produced. This is based on the results of other researcher, which showed similiar colloidal colors [10]. Therefore, it should be known that the ZnNPs produced have high-purity there are no additional agents and stabilizers used in the experiment.
Figure 2. (a) Colloidal ZnNPs in 10 mL aquades with different repetition rate of pulse laser (b) Morphological photograph of produced ZnNPs

The resulting ZnNPs morphological photograph is shown in Figure 2(b). The magnification of obtained figure was set at 5000. To get this photograph, 1 mL of produced ZnNPs was dripped on the Si sheet and then heated in an oven at 100°C for about 10 minutes. The dried Si plate is then scanned by using SEM to obtain a morphological photographs of the produced ZnNPs. It can clearly be seen that ZnNPs was synthesized with spherical shape and various size distribution. Furthermore, the size of the nanoparticles and size distribution was calculated from SEM image using imageJ software.

Figure 3 shows the size distribution particles. The averaged diameters of ZnNPs is 12.1 and standard deviation 4.4 nm for the repetition rate of laser pulse 10 Hz. The averaged diameters of ZnNPs produced in this study is 5.6 with standard deviation 4.7 nm for the laser repetition rate 15 Hz. From these results, we knew that colloidal Zn was in nano-sized.

The resulting ZnNPs absorption spectra shown in figure 4. ZnNPs spectra were taken by using UV-Vis spectroscopy. Spectrum of spectroscopy shows that the surface plasmon resonance (SPR) of the resulting nanoparticles lies approximately at 300 nm. The single SPR peak indicates that ZnNPs are produced in a spherical shape. This result is consists with the results obtained by Khumaeni et. al. [11], which shows spherical ZnNPs having a single SPR peak.
4. Conclusion
The synthesis of high-purity ZnNPs by using pulse laser ablation method has been successfully conducted. The low energy Nd:YAG laser (30 mJ) was employed to produce colloidal ZnNPs in aquades. The morphological characteristic of produced ZnNPs was obtained by using SEM. From the photograph, spherical shape with various size of ZnNPs were successfully synthesized. The averaged diameters of ZnNPs is 12.1 nm and standard deviation is 4.4 nm for laser repetition rate 10 Hz. The averaged diameters of ZnNPs produced is 5.6 and standard deviation 4.7 nm for the repetition rate of laser pulse 15 Hz. The absorbance spectrum shows that the SPR approximately at wavelength of 300 nm.

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Figure 4. Absorbance spectrum of produced ZnNPs in aquades
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