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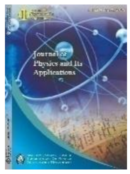

Zinc Oxide Nanoparticles (ZnONPs) photocatalyst using pulse laser ablation method for antibacterial in water polltude

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A B S T R A C T

Pulsed laser ablation method had been successfully performed to produce high-purity zinc oxide nanoparticles. A low-energy Nd:YAG laser beam, of 30 mJ, was bombarding the zinc plate surface followed by ablating the plate to produce zinc oxide nanoparticles (ZnONPs) solution. Synthesis was carried out in aquades medium with a repetition rate variation of 5 Hz, 10 Hz and 15 Hz. Characterization of the ZnONPs was performed by employing XRD, FTIR, SEM-EDX, imageJ software, and UV-Vis spectroscopy. The image of SEM result that ZnONPs have around shape . The characterization results revealed that most of the ZnONPs are small size spherical particles with average diameter decreased from 23.63 nm, 12.13 nm and 5.59 nm as the repetition rate increased. Energy band gap of ZnONPs in range 3.1-3.2 eV verified of ultraviolaet absorbance. ZnONPs is activated by irradiating UV light so that photocatalyst reaction occurred. The testing of the antibacterial activity of ZnONPs using a liquid dilution method with nanoparticle concentrations of 40 ppm, 60 ppm and 80 ppm. The test results showed the percentage of degradation of Escherichia coli bacteria at concentrations of 40 ppm, 60 ppm and 80 ppm respectively at 89.60%, 97.76% and 98, 70%.

1. Introduction

Water pollution is one of the most serious concerns in environmental management. Water pollution is contributed by several pollutants originating from household, agricultural, medical, and industrial waste [1]. The polluted material accumulates in rivers and the sea in the form of hazardous waste such as bacteria [2-3]. On the other hand, water pollution by pathogenic bacteria is characterized by the presence of bacterial resistance. Water pollution by bacteria is triggered by a variety of pathogenic bacteria such as *Escherichia coli* (E coli)[4].

Solution of water pollutants polluted by E coli can be treated using the photocatalyst method. The photocatalyst method has proven to be effective in describing heavy metal and bacterial waste in a relatively short and clean time [5-8]. Photocatalyst material generally used to decompose bacterial and heavy metal waste is Zinc oxide nanoparticles (ZnONPs) [9-10].

Zinc oxide nanoparticles (ZnONPs) are one type of metal oxide that is widely used to overcome the problem of water pollutants [11-14]. ZnONPs have strong oxidation ability, good photocatalytic properties, chemical stability and recombination with other materials, bicompatibility, non-toxic, high light sensitivity [15] which is more effective, economical and environmentally friendly. Nanoparticles are able to increase specific surface area so that absorption of pollutants increases [16]. ZnONPs have the ability as antibacerial, self cleaning and heavy metal reduction [17].

The prevalent methods used to synthesize ZnONPs are precipitation method, sol-gel synthesis, sonochemical reactions, hydrothermal reactions and wet chemical method. All of those chemical methods can produce spherical and monodispersed nanocrystals with adjustable size and composition by controlling the nucleation and growth mechanisms during particle formation. However, the methods require complicated and expensive chemical processes [18].

The other method used to produce ZnONPs is pulse laser ablation method. Pulse laser ablation is a simple method for fabricating the metal nanoparticles without surfactant or chemical addition. In this method, Nd: YAG laser is used as an energy source for ablation a solid target material [19].

Synthesis of ZnONPs using pulse laser ablation methods has been done by Singh (2007). In this research, a high energy Nd: YAG laser with 100 mJ and repetition rate laser is 10 Hz was used. Yu (2017) also conducted research using a pulse laser ablation method which has an energy laser 300 mJ and repetition rate 15 Hz. In that study, ZnONPs were able to produce particle size 40-120 nm. However, this researches has not tested the effect of using repetition rate laser and is still using high laser energy [20-21].

In this study, ZnONPs synthesized using the pulse laser ablation method as E coli antibacterial in polluted water. The synthesis process was conducted to investigate the laser repetition rate on the ZnONPs size at low laser energy. The lower laser energy was utilized to prevent the agglomeration.

2. Methodology

2.1. Synthesis Zinc Oxide Nanoparticles

In this study, zinc oxide nanoparticles was produced by pulse laser ablation method. A high-purity (of about 99.95%) zinc plate was immersed into 10 ml of deionized water in a petri dish. The target irradiation was done by using Neodymium yttrium aluminum garnet (Nd:YAG) laser beam (New Wave Research, with wavelength of 1084 nm, and pulse duration of 7 ns) focused on the zinc plate surface with energy of the laser arranged to 30 mJ. The laser pulse repetition rate was varied to 5 Hz, 10 Hz and 15 Hz to produce zinc oxide nanoparticles colloidal solution. The experimental set up used in this work is shown in Figure 1.

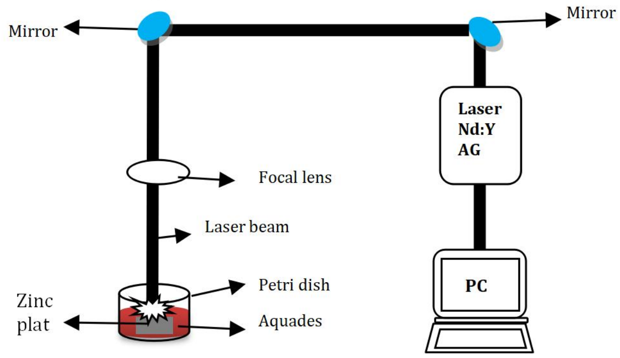

Fig. 1: Experimental set-up

The laser beam will bombarded the sample surface during 60 minutes for any sample. In the synthesis process, the laser beam will be deflected with a mirror to the convex focus lens which has a focal distance of 3 cm. During the shooting process, the petri dish containing the zinc plate is moved slowly to obtain homogeneous nanoparticles.

2.2. Characterization Zinc Oxide Nanoparticles

The synthesized ZnONPs were then characterized. To find out the absorbance level and energy band gap of ZnONPs, Ultraviolet Visible Light Spectroscopy (UV-Vis) test was performed. The X-Ray Diffraction test is performed to identify the crystalline phases and various oxides contained in ZnONPs. Fourier Transform Infra Red Spectrophotometer (FTIR) test was also carried out with the aim of identifying functional groups and compounds contained in ZnONPs.

In addition, morphological photograph of the ZnONPs was generated by utilizing Scanning Electron Microscopy – Energy Diffraction X-ray (SEM-EDX, JEOL JED-2300). The resulting image from SEM-EDX is then processed with imageJ software to determine the distribution size of the ZnONPs produced.

2.3. Application of ZnONPs

ZnONPs testing as antibacterial in water polluted is carried out by utilizing the photocatalysts mechanism. This mechanism will function if ZnONPs have been activated. The activation process is carried out by making a ZnO nanoparticle solution from sample water to be tested with a concentration variation of 40 ppm, 60 ppm and 80 ppm. The solution is then irradiated with Ultraviolet (UV) light. The irradiation process will occurred for 90 minutes and during the irradiation takes place, the solution will be stirred using a magnetic stirer.

3. Results and Discussion

ZnONPs were successfully synthesized using pulse laser ablation method with low energy laser and various repetition rate. The color of ZnONPs colloidal was changed from light to brown along with increasing number of repetition rate.

3.1 Samples

ZnONPs were produced from zinc plate (Nilaco, 99.95%). ZnONPs synthesis by pulse laser ablation method begins when the Nd: YAG laser which has a wavelength (1064 nm, 7 ns) is focused with a convex lens. The darker color of ZnONPs colloidal proves that a higher concentration of nanoparticles were produced [27]. ZnONPs synthesized shown in figure 2.

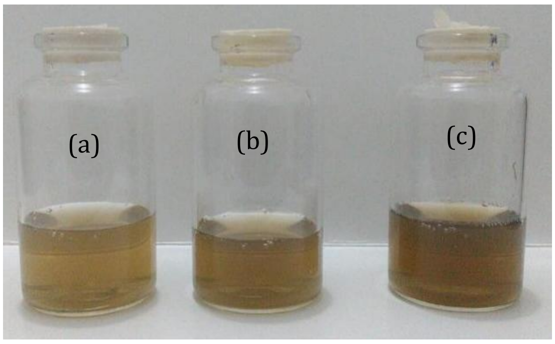

Fig. 2: ZnONPs synthesized with laser pulse frequency (a) 5 Hz, (b) 10 Hz and (c) 15 Hz

3.2 XRD analysis

The chemical composition of samples is provided in Table 1. The XRD pattern obtain for the samples with 15 Hz repetition frequency. The difraction peak at 31.32o, 34.2o, 36.1o, 47.3o, 56.4o, 62.7o, 66.1o, 67.7o, and 68.9o . The Crystal Planes respectively in (100), (002), (101), (012), (110) and (013). The corresponding XRD pattern show the formation of pure ZnONPs.

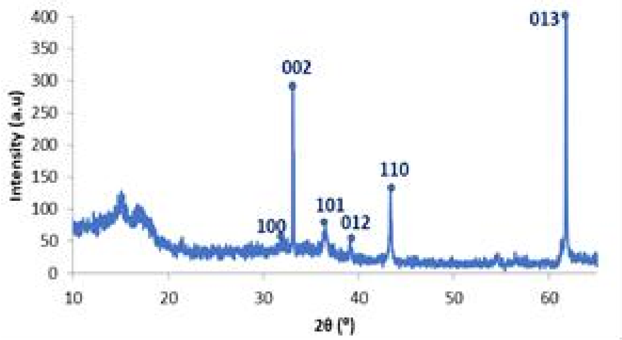

Fig. 3: The XRD spectrum of ZnO colloid nanoparticles results from the synthesis of the pulse laser ablation method

3.3 Morphology Analysis of ZnONPs

To find out the morphology of ZnONPs synthesized by the laser laser ablation method, Scanning Electron Microscopy (SEM) test was performed. The SEM test was carried out by dropping colloidal ZnONPs into a 1 mm x 1 mm silicon carbide (SiC) wafer plate. Previously, the SiC plate was cleaned first. Then the colloidal ZnONPs are dripped with room temperature (around 30o C) for 24 hours.

ZnONPs that have been deposited on a SiC plate are then tested by SEM. SEM test result that the particles produced for each laser shot frequency produce spherical shapes.

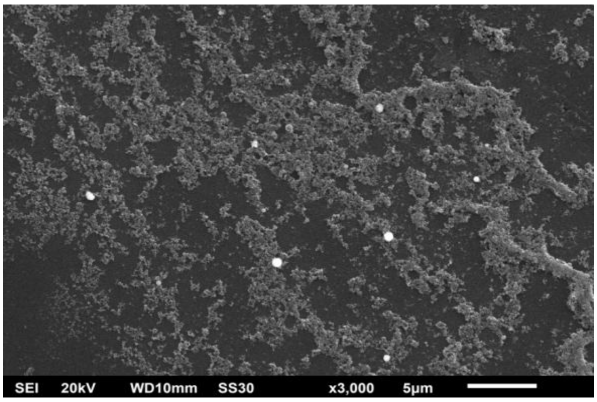

Fig. 4: SEM image for ZnO nanoparticles

3.4 Effect of laser repetition rate

Analysis of ZnONPs size distribution was utilized by imageJ software. The calculation technique is done by Otsu tresholding technique to measure the diameter of each circle pattern produced from SEM images in Figure 5. The higher repetition rate used can produce the smaller nanoparticles. This is because the greater repetition rate was used, it will cause particles in the colloid to experience fragmentation and decrease the size of the particle distribution. The surface of the sample and the synthesis medium through which the laser beam passes with a high level of laser shot repeatability will result in colloids being hit more often by laser pulses each time unit. This results in more photon energy hitting the surface of the sample and particles will be more fragmented compared to the low rate of laser shot repeatability. Therefore, particles produced with the use of high frequency laser shots have smaller sizes [28].

Table 1. The average diameter of the size of ZnONPs from processing ImageJ software

Sample	Repetition Rate (Hz)	ZnONPs diameter	
		Average diameter (nm)	Deviation standart (nm)
A	5	23.63	5.75
B	10	12.13	4.41
C	15	5.59	4.74

3.5 Purity of ZnONPs

ZnONPs content can be determined by Energy Dispersive X Ray (EDX) test. EDX analysis results show the presence of Zink (Zn), Oxygen (O), Carbon (C) and Silicon (Si) in ZnONPs colloid. These results of EDX characterization verified that the colloidal nanoparticles produced are high-purity zinc oxide nanoparticles because no others elements were detected on the surface of SiC sheet, except zinc and oxygen.

Zinc was detected in the EDX spectrum because the material used in the synthesis of ZnO nanoparticles was a zinc plate which had a high purity of 99.95%. Silicon and Carbon peaks derived from those elements are main components of silica carbide (SiC) sheet. Oxygen contained in colloidal ZnO nanoparticles indicates the formation of ZnO compounds which are bonds between Zn and O. This is due to the absence of impurities in the EDX spectrum. The EDX spectrum of SiC sheet poured with ZnONPs is presented in Figure 5.

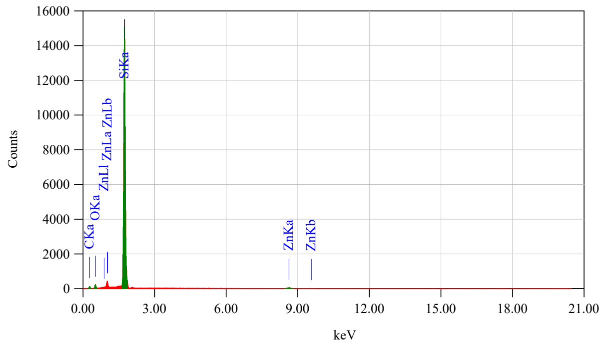

Fig. 5: EDX analysis

3.6 FTIR analysis

ZnO colloid nanoparticles showed transmittance bands at wave numbers 545 cm-1 and 457 cm-1. This corresponds to the peak of ZnO transmittance. The functional groups detected were the O-H group in the band 3361 cm-1 and the C = O group in the band 1646 cm-1. The O-H group that was detected came from the synthesis medium in the form of aquades (H2O) that interact with the sample.

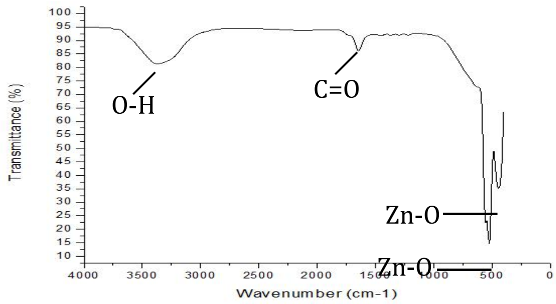

Fig. 6: The FTIR spectrum of ZnO colloid nanoparticles results from the synthesis of the pulse laser ablation method

3.7 Photocatalys Mechanism of ZnONPs

ZnO photocatalytic activity produced from electron and hole which come from semiconductor material. Energy band gap of ZnONPs in range 3.1-3.3 eV verified of ultraviolaet absorbance. ZnONPs is activated by irradiating UV light so that photocatalyst reaction occurred. Width of the energy band gap causes ZnONPs to capture more photon energy from UV light. In this study, energy band gap ZnONPs can be known from absorbance unit using Tauc plot method. Energy band gap of ZnONPs synthesized by pulse laser ablation method shown in Figure 7.

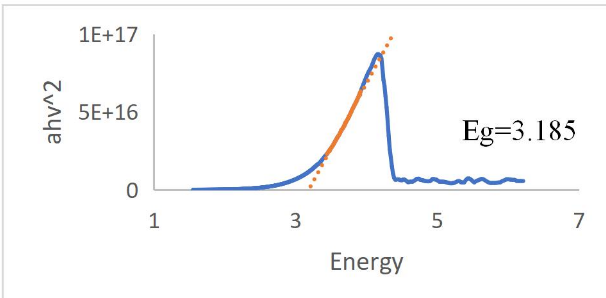

Fig. 7: Energy band gap of ZnONPs synthesized with (a) 5 Hz, (b) 10 Hz and (c) 15 Hz

The results of energy band gap verified that the colloidal ZnONPs correspondence with ultraviolet (UV) absorbance. ZnONPs semiconductor is irradiated with UV light during 90 minutes. UV rays come in contact with ZnONPs particles so they are able to excite electrons in a ground state.

In nanoparticles condition, the surface energy of ZnO activation is greater so that the energy produced is greater. The energy resulting from the excitation of these electrons caused the position of the electrons in the conduction band by producing electron (e) and hole (+) pairs so that they are referred to as photo excitation semiconductors. Photocatalyst reactions cause the formation of superoxide compounds releasing O2 and OH- radicals which can oxidize pollutants of heavy metals and bacteria [29].

3.8 Activation in Escherichia coli

ZnONPs can be used as antibacterial Escherichia coli. ZnO nanoparticles can damage the Escherichia coli membrane which causes leakage of cytosolic components and kills bacterial cells. ZnO can damage the bacterial cell membrane with hydrogen peroxide produced by ZnO or the proximity between ZnO and the surface of the bacteria [29].

The antibacterial activity test of ZnO nanoparticles against Escherichia coli bacteria was carried out by the liquid dilution method. The liquid dilution method was chosen because it is a simple method and is able to provide quantitative results showing the amount of ZnO nanoparticles needed to inhibit or kill Escherichia coli bacteria [29].

Antibacterial activity test using the liquid dilution method is done by dilution technique. Before making the test media, the first step is to determine the amount of Escherichia coli in agar nutrient media. The dilution process is carried out with a liquid medium in a row on tubes arranged in one rack. Each tube contains a mixture of media and colloidal ZnO nanoparticles with different concentrations of 40 ppm, 60 ppm and 80 ppm. The tube is then planted with a bacterial suspension containing 5.0 x 108 CFU / mL bacterial cells. Furthermore, it was cultured in a tube medium and incubated at 37oC for 2 x 24 hours. Bacterial growth was observed by looking at turbidity in the tube caused by a bacterial inoculum [29].

Table 3. The amount and percentage of degradation of Escherichia coli bacteria

Sample	ZnONPs concentrate (ppm)	The number of Escherichia coli (CFU/mL)	Persent degradation (%)
Control	-	5,00 x 108	-
1	40	5,20 x 107	89,60
2	60	1,12 x 107	97,76
3	80	0,65 x 107	98,70

Increasing ZnONPs concentrations indicate the number of ZnONPs in colloids is increase. As a result, nanoparticles interact more with Escherichia coli bacteria. The degradation process of Escherichia coli bacteria occurs by means of ZnONPs passing through the peptidoglycan bacteria Escherichia coli and is very susceptible to killing bacteria. Therefore, the higher the concentration of ZnO nanoparticles given, the more degraded Escherichia coli bacteria [29].

4. Conclusions

ZnONPs were synthesized using a pulse laser ablation method of varying the frequency of laser shots of 5 Hz, 10 Hz and 15 Hz. The higher the frequency of laser shots used, the ZnONPs produced have a more concentrated color. The concentration of ZnONPs produced is higher with the use of higher laser shot frequencies as well. The XRD analysis results observed several peaks, namely at a value of 31.32o; 34,93o; 36.28o; 40.07o; 47,77o and 63,19o which are diffraction patterns by fields (100), (002), (101), (012), (110) and (013). The SEM image of ZnONPs shows that the ZnONPs produced have a spherical shape. The frequency of laser shots 5 Hz, 10 Hz and 15 Hz produces ZnONPs with diameters of 23.63 nm, 12.13 nm and 5.59 nm. The results of the EDX spectrum analysis show that there are only Zn and O atoms in the synthesized colloidal ZnONPs. FTIR results were observed that ZnONPs produced transmittance bands at wave numbers 457 cm-1 and 545 cm-1. The antibacterial activity test of ZnONPs on Escherichia coli bacteria was carried out by the liquid dilution method with variations in the concentration of ZnONPs at 40 ppm, 60 ppm and 80 ppm. ZnONPs with concentrations of 40 ppm, 60 ppm and 80 ppm produced the percentage of degradation of Escherichia coli bacteria respectively at 89.60%, 97.76% and 98, 70%.

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