Synthesis of gadolinium nanoparticles in spinach-extracted liquid using a pulse laser ablation method

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Abstract. Colloidal gadolinium nanoparticles (GdNPs) have been produced by using pulsed laser ablation (PLA) method. The synthesis in this study used a low-power neodymium yttrium aluminum garnet (Nd: YAG) laser (45 mJ). Pulse laser beam, which has specifications of 1064 nm, 7ns, 10 Hz, was focused on high-purity metal gadolinium (Gd) surface, which was placed into a spinach-extracted liquid, to produce GdNPs colloid. It is known that the spinach naturally contains iron (Fe), which is a quite high concentration from FeSO₄·7H₂O. The magnetic characteristics of iron are ferromagnetism, likewise, gadolinium. As the contrast agent, especially in MRI, the magnetic characteristics of the material are needed to improve the image quality. Colloidal GdNPs were successfully produced at a total concentration of 71 ppm after laser bombardment. The TEM image of GdNPs shows that these nanoparticles had a spherical shape. The average diameter of GdNPs was 15 nm.

1. Introduction

Nanoparticles can occur naturally or through a process of synthesis carried out by humans. The synthesis of nanoparticles itself is the making of particles to a size of less than 100 nm while changing the nature or function of the particle. In the nanoparticle synthesis method, the synthesis process can occur physically or chemically. In general, nanoparticle synthesis will fall into two groups. The first one is the top-down approach, which is breaking up macro particles into nanometer-sized particles. The second one is a bottom-down approach that starts from atoms or molecules arranged to form nanometer-sized particles [1-4].

Nanoparticles are becoming a new trend in many fields such as technology, health, beauty, and others. The need for nanoparticles that have various benefits seems to be increasing, especially in biodiagnostic. Usually, nanoparticles are produced from metals with high purity [7]. The Gd nanoparticles have been employed for biomedical applications, especially as contrast agents [1]. In the present study, we synthesize and characterize gadolinium (Gd) nanoparticles in spinach-extracted liquid. It is known that spinach naturally contains iron (Fe), which is quite high from FeSO₄·7H₂O [9]. The magnetic characteristics of iron are ferromagnetism [2], likewise, gadolinium. As the contrast agent, especially in magnetic resonance imaging (MRI), the magnetic characteristics of the material are needed to improve the image quality. Therefore, this colloidal will be an innovation in the biodiagnostic of MRI. The contrast agent itself is a substance that helps visualize several structures in medical diagnostic
imaging. Contrast agents work on the basic principle of X-ray absorption, thereby preventing the delivery of these rays to patients [6].

Also in this study, we used the method of pulsed laser ablation synthesis (PLA). Pulse laser ablation is a method of making nanoparticles by firing laser beams at metals or other materials and can also be a solution [5]. The advantage of this method is that it has good quality nanoparticles with high-purity without adding chemical agents during nano synthesis and much faster time in the synthesis process. The use of PLA in liquids, to produce nanomaterials, has the potential to eliminate surface contamination of samples without using chemical or additive precursors, so nanoparticles with high purity can certainly produce [10].

2. Experimental Method
The experimental set up used in this work is shown in Fig. 1. The radiation source used was Nd: YAG (New Wave Research, Polaris II, 20 Hz) with wavelengths 1064 nm, energy 45 mJ, and pulse widths 7 ns. In this study, the variation liquid medium of GdNPs synthesis is using aquadest and spinach extracted liquid with repetition rate is 10 Hz. The beam was directed to the sample, which located in a petri dish containing liquids medium for 60 minutes when the ablation process occurred.

![Figure 1. The experimental setup used in this study](image)

To find out the characteristics of colloidal GdNPs, several characterization methods were used, including Ultraviolet-Visible spectroscopy (UV-Vis) and Transmission Electron Microscope (TEM). UV-Vis was used to measuring the absorbance spectrum of GdNPs in the colloids. Whereas, TEM was used to know the morphology of GdNPs.

3. Result and discussion
The colloidal GdNPs produced in 10 mL spinach extracted liquid is shown in Figure 2. After 1 hour of laser bombardment, the colloidal Gd solution shows the cloudy yellow color and the concentration of Gd nanoparticles is measured at 71 ppm (part per million). This result shows that the Gd nanoparticles are successfully produced in the liquid. Figure 3 (a) shows the image of GdNPs inside spinach-extracted liquid obtained by the TEM technique. Figure 3 (b) shows the average diameter of nanoparticles
measured by ImageJ software is 15 nm. Figure 4 shows the morphological image of GdNPs obtained by using the TEM method. The characteristic of GdNPs that used the TEM method was obtained by preparing 10 ml GdNPs colloidal sample, then put a new specimen of TEM in colloidal GdNPs. Next, place the specimen filled with GdNPs colloidal sample (facing upward) in the cartridge that located inside the holder. It can be seen in the image that the morphology of GdNPs shows the spherical shapes, which is evidence of the existence of the nanoparticles.

Figure 2. Colloidal Gd nanoparticles in the medium of spinach extracted liquid (left) and medium of spinach without Gd nanoparticles (right)

Figure 3. (a) Image of GdNPs in spinach extracted by TEM, (b) average diameter of nanoparticles measured by Image J-software
The spherical shape of the produced nano certified that the absorption spectrum has single surface plasmon resonance (SPR) peak [8]. Figure 5 shows the optical absorption spectra of GdNPs obtained by using a UV-Vis spectrophotometer. The surface plasmon resonance (SPR) can be seen at the center wavelength of 368 nm that can be indicated as the presence of gadolinium elements [3].

**Figure 4.** Morphology of GdNPs by TEM

| Normalized Absorbance | Wave length (nm) |
|-----------------------|-----------------|
| 0.001                 | 200             |
| 0.001                 | 400             |
| 0.001                 | 600             |
| 0.001                 | 800             |
| 0.001                 | 1000            |

**Figure 5.** The absorption spectrum of GdNPs in spinach extracted produced by using UV-Vis

4. **Conclusion**
Nanoparticles of gadolinium in spinach extracted liquid were successfully produced by using a pulsed laser ablation method. The results of the characterization of gadolinium nanoparticles have an average size of 15 nm measured by ImageJ software and the surface plasmon resonance (SPR) can be seen at the center wavelength of 368 nm conducted by UV-Vis spectrophotometers.

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