A silver nanoparticle-based colorimetric detection of Fe$^{2+}$

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Abstract. Silver nanoparticles (AgNPs) can be developed into materials for the detection of metals in the environment. The detection was carried out based on the color change AgNP colloids after reacted with metal ions, known as a colorimetric method. In this study, silver nanoparticles were obtained through biosynthesis using the aqueous extract of Diospyros discolor Willd. (Bisbul) leaves which was mixed with 1 mM of AgNO$_3$ precursor. The characterization results using a UV-Vis spectrophotometer showed a peak in the range of 300-500 nm which is the typical absorption spectrum of silver nanoparticles. Formation of AgNPs was also indicated by the solution color change from yellow to brown. After 24 hours of reaction, the formed AgNPs were tested as indicator solutions for 6 metal ions, namely Pb$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, and Fe$^{2+}$, at 1000 mg/L. The specific visual color change was observed only when AgNPs solution was added into Fe$^{2+}$ ion solution. Further testing was carried out to detect the presence of Fe$^{2+}$ ions at 0; 0.1; 1; 10; 100; 500; and 1000 mg/L. The results showed a solution discoloration ranging from brownish to greenish. The change in solution color after AgNPs were added into Fe$^{2+}$ solution was caused by AgNPs unique optical properties in the visible wavelength. Silver nanoparticles also tend to have an affinity with Fe$^{2+}$ and showed larger size based on the PSA (Particles Size Analyzer) and TEM (Transmission Electron Microscope) characterizations. The results showed that the AgNPs tend to agglomerate after the addition of a higher concentration of Fe$^{2+}$. This detection method has the potency to be developed and enhanced to detect the presence of Fe$^{2+}$ metal ions in the environment.

1. Introduction

In recent time, the process of metal identification and analysis requires less practice time and equipment. It is because the measurement cannot be directly carried out in the field. Inexpensive and rapid detection and quantification of metal cations in aqueous solutions are in high demand for environmental [1], pharmaceutical [2], and biological applications [3]. The point of interest is on how such a detection can be performed in-situ by untrained personnel using color change that is visible to
the naked eye [4,5]. Therefore, it is necessary to develop a more practical method for detecting the presence of certain metals in a straightforward, accurate, and fast manner.

In regard to this issue, nanoparticles are known to have the ability as a colorimetric indicator. Nanoparticles have unique optical properties, so they can be modified into colorimetric sensors in the presence of metals. Colorimetric sensors are quite popular because they are simple, sensitive, cheap, fast, and do not require complicated tools [1,2]. The principle of a colorimetric indicator is based on the unique nature of Localized Surface Plasmon Resonance (LSPR) of metal nanoparticles and their ability to aggregate. Nanoparticles can react to certain metal ions which cause color changes and SPR shifts. Some metal ions that can be detected using nanoparticles include Hg$^{2+}$ [1], Fe$^{2+}$ [5], Co$^{2+}$ [6], Pb$^{2+}$ and Cu$^{2+}$ [7], Zn$^{2+}$ [8]. Due to the advantages mentioned above, the colorimetric method can facilitate a real-time visual observation of the changes of metal ion analytes.

Gold nanoparticles (AuNPs) and silver nanoparticles (AgNPs) have good LSPR properties. Thus, they have distinctive color characteristics and can easily change color. The metal nanoparticles can show excellent selectivity and sensitivity as a colorimetric indicator [6]. In this study, the selectivity of AgNPs from biosynthesis using the aqueous extract of Diospyros discolor Willd. (Bisbul) [9] against Pb$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Mg$^{2+}$, Mn$^{2+}$, and Fe$^{2+}$ metal ions and their sensitivity against Fe$^{3+}$ ions were to be determined.

2. Material and methods

2.1. Silver nanoparticles biosynthesis
Silver nanoparticles were obtained from biosynthesis method using D. discolor. The synthesis procedure was based on the method from Nurfadhilah et al. 2017 [9] by using the aqueous extract of D. discolor at pH 9. One mM of AgNO$_3$ solution was added into the aqueous extract with a ratio of 2:1 (v/v).

2.2. Metal detection and image analysis
Silver nanoparticles from biosynthesis using D. discolor were used to detect the presence of several types of metal ions, namely Fe$^{2+}$, Mn$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Pb$^{2+}$, and Mg$^{2+}$. The metal ions were prepared at 1000 mg/L by dissolving FeCl$_3$, MnCl$_2$, 4H$_2$O, ZnCl$_2$, CoCl$_2$, Pb(NO$_3$)$_2$, and MgCl$_2$ in bidistilled water. All of the salts were purchased from Merck. Silver nanoparticles were then added into each metal ion solution with the ratio of 1:1 (v/v). Any color changes were compared to AgNPs solution as the standard. The ion solution with most different color change was tested further with various cation concentrations from 0, 0.1, 1, 10, 100, 500 and 1000 mg/L with the addition of the same ratio with AgNPs. The color changes that occurred were observed and the picture was taken using a Canon EOS 750D camera.

2.3. Characterization using UV-Vis spectrophotometer, Particle size analyzer, and Transmission electron microscope
Bio-synthetic silver nanoparticles, as well as the metal ions with various concentrations that had been mixed with AgNPs, were characterized using UV-Vis spectrophotometer [Thermo Genesys10S]. They were also characterized using Particle Size Analyzer (PSA) [Zetasizer Nano-ZS Nano series] to see their distribution and stability. Meanwhile, the characterization with Transmission Electron Microscope (TEM) [TEM FEI Tecnai G2 20S-Twin 200 kV] was carried out to determine the size and shape of the particles.

3. Result and discussion
Figure 1 shows that the silver nanoparticles obtained from the biosynthesis process have a brownish solution color, with an absorbance peak in the range 350-450 nm. The sizes of the nanoparticles were ranging under 30 nm and the shapes were spherical, based on the results of TEM as shown in Figure 1.c. The color and absorption spectrum show typical characteristics of silver nanoparticles [8, 9, 10],
as well as sizes that have a relatively homogeneous distribution [11]. Metal NPs used in sensor assays generally have spherical shapes. These silver nanoparticles will then be used for the detection of metal ions.

**Figure 1.** Silver nanoparticles obtained from biosynthesis using *D. discolor* aqueous extract showed a peak in the range of 350-480 nm (A) and brownish solution color (B) with size under 20 nm and spherical shape (C).

Figure 2A shows the color of the solution after AgNPs were added into Co\(^{2+}\), Mg\(^{2+}\), Mn\(^{2+}\), and Zn\(^{2+}\) ions solution. They are turned out to be not too different, which are still yellowish brown. The color of Pb\(^{2+}\) solution after AgNPs were added is not too different from the color of AgNPs. Meanwhile, the detection of Fe\(^{2+}\) using AgNPs shows the most contrast visualization compared to other metal ions. It tends to be greenish and tends to precipitate if left for a while. From this experiment, it was concluded that AgNPs tend to be sensitive to the presence of Fe\(^{2+}\) ions. Samerjai et.al. (2017) [5] tried to test L-modified AgNPs to detect several metal ions including Fe\(^{2+}\) and the result shows a color change from bright yellow to dark. Addition of other metals ions like Mn\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cu\(^{2+}\), Zn\(^{2+}\) and Cd\(^{2+}\) did not cause any color change.

**Figure 2.** Silver nanoparticles used as detector for Pb\(^{2+}\), Mn\(^{2+}\), Mg\(^{2+}\), Zn\(^{2+}\), Co\(^{2+}\), and Fe\(^{3+}\) metal ion solution, indicating some specific color change at 1000 mg/L of Fe\(^{2+}\) (A), and their absorbance spectra (B).
Figure 3. Silver nanoparticles used for the detection of Fe$^{2+}$ ions with various concentrations started to show solution discoloration from brownish to greenish at 100 mg/L.

Meanwhile, figure 2B shows the absorption spectra from the detection of Mn$^{2+}$, Fe$^{2+}$, Co$^{2+}$ and Mg$^{2+}$ ions. It shows diminishing absorbance peaks, while the detection results of Pb$^{2+}$ and Zn$^{2+}$ still show high absorbance peaks in the range of 350-450 nm. Absorption spectrum of Mg$^{2+}$ solution in the presence of AgNPs shows a decrease in the absorbance value while there is still a peak in the same range. This shows a change in the LSPR value of silver nanoparticles [1,12]. Based on the results from Figure 3, the test was carried out to determine the sensitivity of AgNPs to Fe$^{2+}$ ions at 0.1, 1, 10, 100, 500 and 1000 mg/L. The results show that the color of the solution in the detection of 0-100 mg/L Fe$^{2+}$ has a relatively similar yellowish-brown color. However, for Fe$^{2+}$ with concentrations of 100-1000 mg/L, the results show greyish green color. The photos taken show contrast color differences in both ranges of Fe$^{2+}$: 0-10 mg/L and 100-1000 mg/L (Fig. 3).

Figure 4 shows the absorption spectra of Fe$^{2+}$ solutions at various concentrations. The characterization using a spectrophotometer was carried out to see the absorbance at certain wavelengths. The results also show the same pattern. In the range of 0.1-10 mg/mL, the absorbance values are 3.382; while in the range of 100-1000 mg/mL, the absorbance values are ranging from 1.613 to 1.899. Changes in absorption patterns occur at 100 mg/L of Fe$^{2+}$ when the value of absorbance peaks in the range of 400-500 nm decrease. Meanwhile, PSA result of AgNPs show that...
they tend to be moderately stable at -26.9 mV. This value is not much different from the previous results [9], which is -28.1 mV. However, the AgNPs tend to be highly polydisperse, based on the PDI value of 0.540. Detection result for AgNPs+Fe 1 mg/L show a moderately stable zeta potential value of -29.3 mV. Meanwhile, the result from the characterization of AgNPs+Fe 100 mg/L test showed that the PDI value is 0.231, thus they tend to be moderately dispersed. Their zeta potential value is -17.6 mV, therefore they tend to be relatively stable (Table 1). Based on TEM results (Figure 5) there is a tendency for nanoparticles detected to be larger in size.

Absorption spectra and sizes of AgNP and AgNP+Fe 1 mg/L are relatively not too different. When AgNP is used to detect 100 mg/L of Fe$^{2+}$, the value of the absorbance peak decreases and the size of the nanoparticles increases. This is caused by aggregation due to a chelating process which results in AgNP size changes as shown by the TEM result (Fig. 5C) [12]. The LSPR absorption of metal NPs tends to change, also with the particle size and shape [6]. The principle of colorimetric detector is dependent on LSPR changes and aggregation between nanoparticles by metal ion analytes, hence it is also known as aggregation sensor. The aggregation between particles can be seen from the increase in the electric field on the surface of the nanoparticles. Samerjai et.al. (2017) [5], shows induced aggregation when adding Fe$^{3+}$ ions into L-modified AgNPs. The results were used for detection of Fe$^{2+}$ on multivitamin tablet samples.

**Table 1.** Size distribution and zeta potential from silver nanoparticles, before and after adding Fe$^{2+}$ ions.

| Samples | PDI Value | Zeta Potential (mV) |
|---------|-----------|---------------------|
| AgNPs   | 0.540     | -26.9               |
| AgNPs + Fe 1 mg/L | 0.636 | -29.3               |
| AgNPs+ Fe 100 mg/L | 0.231 | -17.6               |

**Figure 5.** Absorption spectra (A) and transmission electron microscope (TEM) results show morphology, shape and size distribution of silver nanoparticles, after adding 1 mg/L (B) and 100 mg/L (C) of Fe$^{2+}$ ions.

4. Conclusion
Silver nanoparticles from biosynthesis using *D. discolor* have the ability as a colorimetric indicator for Fe$^{2+}$ ions in the range 0.1-1 mg/L and 100-1000 mg/L, where the solution color changed from brown to brownish yellow and greenish. When it detects the presence of Fe$^{2+}$ ions, the absorbance spectrum will decrease, and the size of the nanoparticles will increase as the aggregation occurs. This method can be developed and optimized for further detection.
References
[1] Y. Wang, F. Yang, and Xiurong Yang. (2010) Applied Material and Interface 2(2), 339–342.
[2] P. G. Mahajan, et.al. (2015) Anal. Methods.
[3] Haibing Li, et.al. (2010). Sensors and Actuators B, 145, 194–199.
[4] N. O. Laschuk, et.al. (2016) Materials and Design, 107, 18–25.
[5] W. Samerjai, et.al. (2017) Iran J Sci Technol Trans Sci
[6] H. Sung, et. al. 5 Jun 2013. Langmuir
[7] Ja Young Cheon & Won Ho Park. (2006) Int. J. Mol. Sci. 2016, 17, 2006
[8] D. Karthiga and S. P. Anthony. RSC Adv. 2013, 10.1039/c3ra42308e.
[9] M. Nurfadhilah et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 367 012033
[10] M. Jeyaraj, et.al. (2013) Colloids and Surfaces B: Biointerfaces 106 86–92
[11] D. Philip. (2011). Spectrochimica Acta Part A 78 327–331
[12] S. Maiti, et.al. (2016) Appl. Nanosci. 6 529–538
[13] V.V. Kumar, et.al.(2014). Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 129 35-42