Colorimetric detection of metal ions using greensynthesized silver nanoparticles

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Colorimetric detection of metal ions using green-synthesized silver nanoparticles

Colorimetric detection of metal ions using green-synthesized silver nanoparticles

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Abstract. Generally, the analysis of metal ions uses expensive and tedious techniques and involving complicated devices. Here, we developed a colorimetric-based detection of metal ions using green-synthesized of PVA-stabilised silver nanoparticles (AgNPs), which is simple and low cost. The linearity and sensitivity of AgNPs in detecting metal ions were determined from the absorbance and shifting of local surface plasmon resonance (LSPR) band in the visible range. The detection was carried out on Cu(II), Pb(II), Cd(II), Zn(II), and Mn(II). The most sensitive response was obtained on Cu(II) ions, among the five ions tested. The response showed a good linearity ($R^2 = 0.9886$) in the range of 0.2-1.4 ppm of Cu(II). Meanwhile, the sensitivity on Cu(II) resulted in the limit of detection and the limit of quantitation of 0.1609 $mg.L^{-1}$ and 0.5179 $mg.L^{-1}$, respectively.

1. Introduction

The presence of heavy metals in the environment in excess causes contamination of soil, water, and air. Therefore, measuring the environmental level of heavy metals is important as a means of managing pollution. There are several measurement techniques of heavy metals that are often used, such as atomic absorption spectrometry (AAS) [1-4], UV-Vis spectrophotometry [5], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [6], and ICP-mass spectrometry (ICP-MS) [7], [8]. However, such techniques are expensive, tedious, involve complicated devices, and time consuming for sample preparation. Therefore, alternative methods which are simple, selective, and cost effective are needed. Such an alternative method is a colorimetric-based sensor [9-12].

Currently, nanoparticles from noble metals such as gold (AuNPs) and silver (AgNPs) have been widely applied as chemical probes or sensor probes to detect analytes in food, pharmaceutical, and environmental samples [13-16]. This detection is based on the optical properties of AuNPs or AgNPs in aqueous solution which show a distinctive color as an effect of absorption of the local surface plasmon resonance (LSPR) band. The introduction of an analyte into nanoparticles could cause aggregation of the nanoparticles. Thus, LSPR band shift towards higher or lower wavelength in the visible region and a color change may visually observable. This can be used as a basis for detecting analytes by colorimetry. Nanoparticles-based colorimetry has been developed to detect various analytes, such as vitamins,[17] pesticides,[18] amino acids,[19] and metal ions.[12,20,21].

In this article, the green-synthesized AgNPs were used to detect heavy metal ions in aqueous solutions, colorimetrically. The absorbance and shifting of absorption bands were observed at various concentrations of Cu(II) to determine the linearity, sensitivity, and selectivity of AgNPs in detecting the ion.

2. Method

All metal salts, NaOH, and HCl were obtained from Merck. Aquademin was purchased from Bratachem Indonesia, while PVA 5,600 was obtained from Sigma Aldrich. All those chemicals were analytical grade reagents. UV-Visible spectrometer Tech Fluorostar Omega BMG Lab was used for measurement of LSPR absorption.

Synthesis of AgNPs was carried out by mixing green tea leaf extract and $AgNO_3$ 1mM (v/v) with a ratio of 1:20. The mixture was then sonicated for 15 minutes and then stirred on a hot plate and gradually added with PVA solution [22] The detection of metal ions was carried out against Cu(II) , Cd(II) , Pb(II), Zn(II), and Mn(II) with each concentration of 1000 ppm. The change of color was visually observed and the LSPR absorption was measured using a UV-visible spectrometer. The detection was further at a lower concentration, 0.1; 1; 10; 100; and 500; ppm. The determination of linearity and sensitivity of the detection was measured in the range of 0.0–1.2 ppm.

3. Result and discussion

The AgNPs used in this study were synthesized through the reduction of Ag(I) using the green tea leaf extract as a reductor and PVA as a stabilizer.[22] The synthesized AgNPs have a size distribution of 75 nm. The nanoparticles size is important because it will affect the LSPR absorption.[23]

Firstly, the detection was carried out against Cu(II) , Cd(II) , Pb(II), Zn(II), and Mn(II) with each concentration of 1000 ppm. The AgNPs respond is observed visually through the color change of the solution. Among the five solutions tested, the Cu(II) resulted the most significant color change, from brownish yellow to clear solution (Figure 1).

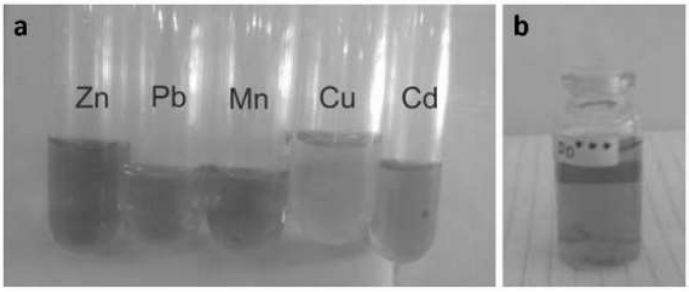

Figure 1. (a) The color of AgNPs after addition of 1000 ppm metal ions solution and (b) the initial color of the AgNPs

The analytes of Pb(II), Zn(II), Mn(II), and Cd(II) ions also showed a change in color but not as significant as Cu(II) did. This indicated that the AgNPs were more sensitive to Cu(II) ions than to other ions tested. This color shift occurred due to AgNPs aggregation that induced by the presence of metal ions. The metal ions will interfere the interaction of AgNP and oxygen of PVA [9] which then reduced the stability of AgNPs and resulted in the aggregation. In addition, Cu(II) has high standard reduction potensial (E^0) among the other analytes. This means that Cu ions oxidize Ag more easily than other metal ions. This might contribute to the AgNPs aggregation [24,25].

A significant decrease of absorbance occurred on the analyte Cu(II), as is shown in Figure 2, even AgNPs band disappeared. The detection of Cu(II) was then applied on much lower concentrations to determine the typical absorbance peaks as well as the sensitivity the detection.

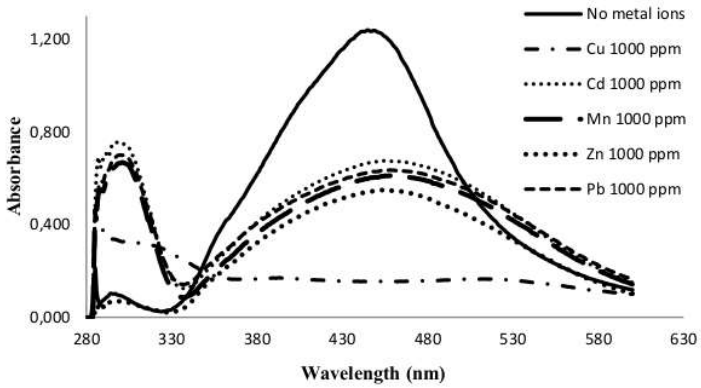

Figure 2. LSPR absorption of AgNPs and AgNPs in the presence of metal ions.

AgNPs detected Cu(II) 500 ppm clearly as the color changing from brownish yellow to colorless. However, the change in color in the case of Cu(II) 500 ppm required a longer response time (1.5 min) than that in the case of Cu(II) 1000 ppm which was only a few seconds. The same thing was observed when there was Cu(II) 100 ppm with a response time of 10 minutes. Thus, the response time of AgNPs to the Cu(II) ion was influenced by the concentration of the analyte. The absorbance of AgNPs with 1000 ppm and 500 ppm of Cu(II) was no longer exist and the solutions were colorless. In the lower concentration Cu(II), the AgNPs band was detected but the intensity was reduced and shifted to higher wavelength (Figure 3).

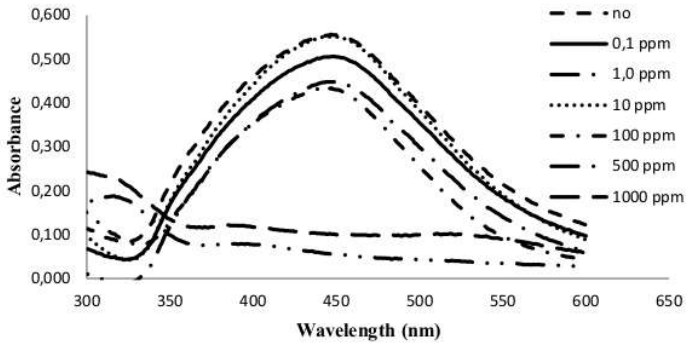

Figure 3. UV-Vis spectra on Cu(II) detection with various concentration.

Cu(II) detection at much lower concentration (0.1 - 1.4 ppm) was also conducted. In this range, the color changes were difficult to observe, thus measurement with a visible spectrometer were required. The results of this measurement were used to determine the linearity and selectivity of AgNPs on Cu(II) detection. The linearity of the AgNPs absorbance and Cu(II) concentrations in the measured range resulted in a value of R^2 of 0.9886 (Figure 4).

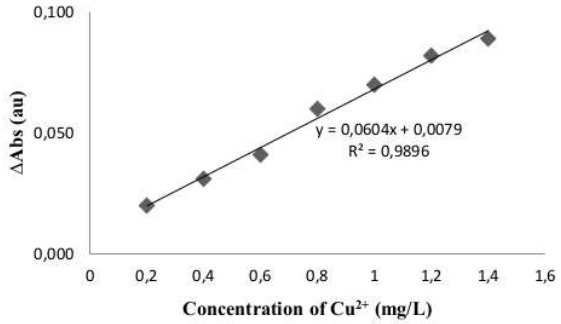

Figure 4. The decreasing absorbance (ΔAbs) of AgNPs and Cu(II) concentration curve shows the higher Cu(II) concentration, the more decreasing AgNPs absorbance.

The sensitivity of AgNPs towards Cu(II) was assessed by the limit of detection (LoD) and limit of quantitation (LoQ), which were 0.16 1 $mg.L^{-1}$ and 0.51 8 mgL^{-1}, respectively. It means that the lowest concentration of Cu(II) that can be detected by AgNPs was 0.16 1 $mg.L^{-1}$ and the lowest concentration of Cu(II) that can be precisely determined was 0.518 $mg.L^{-1}$. This result was quite promising compared to the colorimetric detection of Cu (II) using other probes (Table 1). Moreover, the sensitivity can be further improved, for example by modifying the surface of the AgNPs with a capping agent [26]

Table 1. Comparison of different colorimetric methods on the Cu(II) detection

Probe	Linear range ($mg.L^{-1}$)	LoD ($mg.L^{-1}$)	Reference
PVA stabilized-AgNPs	0.2-1.4	0.161	This work
Silver-capped AuNPs	na	$6.35x10^{-5}$	[20]
Homocysteine and dithiothreitol modified-AgNPs	na	$5 x10^{-4}$	[12]
Chrome azurol S-doped PVC membrane	5.0-1400.0	1.7	[13]
Pyrocatechol violet doped PVC membrane	5.0-200.0	1.9	[13]
Carbon dots-modified AgNPs	0.019-0.508	~0.024	[27]
ZnO@ZnS Core-Shell NPs	0-102	~0.96	[11]

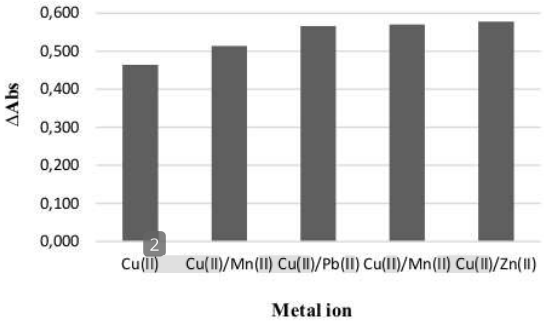

Figure 5. The decreasing absorbance (ΔAbs) of AgNPs in the presence Cu(II) alone and mixture of Cu(II) with other metal ions

LSPR absorbance measurements were also carried out in the presence of other metal ions which were Pb(II), Mn(II), Cd(II), and Zn(II), to evaluate the selectivity of AgNPs probe (Figure 5). The findings showed that the presence of the selected metal ions did not show a significant different to the absorbance decrease of AgNPs (Table 2). This means that the LSPR absorbance decrease was mainly due to the presence of Cu(II), not by other metal ions. Thus, it can be concluded that AgNPs were selective against Cu(II).

4. Conclusion

Green-synthesized AgNPs can be applied in the detection of Cu (II) with LoD and LoQ of 0.1609 mg/L^{-1} and 0.5179 mg/L^{-1}, respectively. The detection was based on the changes of LSPR absorbance of AgNPs in the visible area. The linearity of the detection resulted in R^2 of 0.9886, while the presence of Pb(II), Cd(II), Zn(II), and Mn(II) did not interfere the detection significantly.

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