Synthesis of silver nanoparticles (AgNPs) using Sodium Chloride (NaCl) for Iron (III) ions detection based on colorimetric and optical changes

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Abstract. Iron ions (Fe³⁺) is one of the most hazardous metals found in the water supply. The contamination of that metal originated from the corrosion process of pipes and cracks from waste disposal sites. High levels of iron would affect a bad impact to the environment. The current study aimed to synthesize silver nanoparticles (AgNPs) for heavy metals detection using a method which depends on colorimetric and optical changes. The approach to synthesize AgNPs adapted from polyol reduction method, i.e. by mixing polyvinyl alcohol (PVA), sodium chloride (NaCl) and silver nitrate (AgNO₃). The colorimetric response of AgNPs to Fe³⁺ ions was observed visually and measured quantitatively by a spectroscopic method using a UV-Vis spectrophotometer. This work shows that the colloidal AgNPs were sensitive to identify Fe³⁺ ions.

1. Introduction

Nowadays, metal nanoparticles have a wide area of interest in many fields such as renewable energy, cosmetics, medicine, environment needs, sensors, optoelectronics, mechanics, and surface-enhanced Raman scattering (SERS) [1-10]. Nanoparticles were known as the vast application in environmental issues such as ions detection in water supply, adsorbent materials, and water purification [11]. In the previous study, we found that Silver Nanoparticles (AgNPs) and Gold Nanoparticles (AuNPs) have been of current research interest due to its unique optical properties, such as surface plasmon resonance (SPR) absorption and scattering [12].

Regard to environmental issues, stated by the Inter-Agency and Expert Group on SDG Indicators (IAEG-SDGs) in 2016, there are environment world focus that prioritize to achieve in 2030. IAEG-SDGs said state the global indicator framework include improving water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally. Nowadays, the number of untreated wastewaters were found from industrial process as heavy metals [13]. According to Banfakvi (2011), heavy metals defined as an atom that has high weight and density five times greater compared to water [14]. The most common heavy metals that can be found in the water supply are Fe³⁺, Mn²⁺, Zn²⁺, Co²⁺, Pb²⁺, Mg²⁺, Cu²⁺, Ni²⁺, and Fe²⁺. The afore mentioned heavy metals cause serious health issues to humans and mammals [15].

AgNPs contribute excellence parts for the development colorimetric sensors to detect heavy metals such as Fe³⁺, Mn²⁺, Zn²⁺, Co²⁺, Pb²⁺, Mg²⁺, Cu²⁺, Ni²⁺, and Fe²⁺. The reaction can be seen obviously by...
displaying a color change of AgNPs solution. The colour changes seen on the localized surface plasmon resonance (LSPR) peak depend on the size, shape and aggregation state of AgNPs. The use of AgNPs for colorimetric sensors exploits the interparticle gap in LSPR [12]. In advanced, the properties could be modified by various metal concentrations.

2. Materials and Methods

2.1. Materials
Silver nanoparticle was synthesized using a polyol reduction method [16] using silver nitrate (AgNO₃) Mw = 169.87 g/mol from Merck, sodium chloride (NaCl) from sigma aldrich, deionized water used throughout the experiment were collected from Direct-Pure® EDI (Direct-Q 5UV-R, Ultrapure (type1) water), polyvinyl alcohol (PVA) fully hydrolized (Mw = 60,000 Da ) was purchased from Merck Co. Several of metal salts, i.e. Fe₂Cl₃, Fe(NO₃)₂, MnCl₂.4H₂O, CuCl₂, ZnCl₂, NiCl₂. CoCl₂, Pb(NO₃)₂, and MgCl₂ were purchased from Merck.

2.2 Silver nanoparticles using chemical reduction method
To synthesize the particles, first, 9.9 mL of PVA (3%) as a capping agent [17], 0.1 mL of AgNO₃ (10mM) were mixed with PVA. Second, 2 μL of NaCl 0.5 M were added to the solutions. The total volume of the solution was adjusted into 10.0 mL by adding a certain amount of H₂O. This solution was stirred for 5 min at 180 rpm and kept it the oven at 30°C for 96 h.

2.3. Characterization of AgNPs
The as prepared AgNPs were characterized using a UV-Vis spectrophotometer (Thermo Scientific™ GENESYS™) and then washed by centrifugation at 5000 rpm for twice to remove an excess number of reactants. The particles were collected and dropped about 5-7 μL on a Carbon Film 200 Mesh coated Copper TEM grid, followed by evaporation at room temperature. The particles were characterized using Transmission Electron Microscope (TEM, Tecnai, 200 kV).

2.4. Metal detection
The stock solution of metal ions was prepared with the concentration of 1000 ppm (mg/L) by dissolve their salts, i.e. Fe₂Cl₃, Fe(NO₃)₂, MnCl₂.4H₂O, CuCl₂, ZnCl₂, NiCl₂. CoCl₂, Pb(NO₃)₂, and MgCl₂ in deionized water. Each metal solution with a certain concentration was added to the colloidal solution of AgNPs with the volume ratio 1:3. The colour change observed during the reaction was compared to their original colour of AgNPs and measured using a UV-Vis spectrophotometer. Limit of detection (LOD) of each metal was obtain by measuring its sensitivity for various concentration, i.e. 0.1, 10, 10, 100, 500, and 1000 mg/L.

3. Results and Discussion
Figure 1a. shows the UV-Vis spectrum of the as prepared of colloidal AgNPs. The localized surface plasmon resonance (LSPR) peak maximum was observed at 448 nm which is typical for AgNPs [18]. It can be seen that a broadening peak was formed, i.e between 330 nm to 650 nm suggesting the formation of AgNPs with rather polydisperse in size. This result is in agreement with the previous results [19]. The colour of the solution is dark brown as shown in Figure 1b. In this research, 1% of NaCl was used during synthesis hypothetically to induce a faster reaction, probably through a heterogeneous nucleation. The exact role of NaCl is still under investigation by our group. TEM image of AgNPs is shown in Figure 1c. It can be seen the shape of AgNPs is rather rounded and the average size is about 15 nm.
Figure 1. (a) PVA coated AgNPs spectrum synthesized using polyol reduction method using 1% NaCl (b) a dark brown colloidal solution of PVA coated AgNPs solution, and (c) the corresponding TEM images of the particle.

In the polyol method, PVA which is rich of hydroxyl groups acts as a capping agent. These hydroxyl group could be utilized to detect metal ions through the formation of a polymer-metal complex [20]. Thus, in this experiment, the ability of PVA coated AgNPs to detect various metal ions was investigated. Figure 2a shows the UV-Vis spectra of PVA coated AgNPs-metal complex for various metal ions, i.e Fe$^{3+}$, Mn$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Pb$^{2+}$, Mg$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, and Fe$^{2+}$. Among the metal ions used in this experiment, only the LSPR peak maximum for PVA coated AgNPs-Fe$^{3+}$ complex shifted to the lower wavelength significantly (from ca. 448 nm to 350 nm). This could indicate that the PVA coated AgNPs used in this experiment were sensitive to the detect Fe$^{3+}$ ions. This result was also observed visually by the colour change shown in Figure 2b. The colour of PVA coated AgNPs metal complex for Fe$^{3+}$ was rather reddish, meanwhile for other metal complex were still brown (original PVA coated AgNPs) or yellowish.

Figure 2. (a), UV-Vis spectra and (b) colorimetric responses of PVA coated AgNPs in the presence of various metal ions, [M$^{n+}$] = 1000 mg/L (Fe$^{3+}$, Mn$^{2+}$, Zn$^{2+}$, Co$^{2+}$, Pb$^{2+}$, Mg$^{2+}$, Cu$^{2+}$, Ni$^{2+}$, and Fe$^{3+}$)
To know the LOD of Fe$^{3+}$, various concentration of Fe$^{3+}$ was complexed with PVA coated AgNPs. The concentration of Fe$^{3+}$ used to measure the LOD is 0.1, 10, 100, 500, and 1000 mg/L. The UV-Vis spectra and their corresponding colour are shown in Figure 3a and 3b, respectively. The result shows that as the concentration of Fe$^{3+}$ increases, the colour of the solution gradually changes from dark brown into reddish. The intensity of UV-Vis spectrum is decreasing when the concentration of Fe$^{3+}$ concentration 0.1 and 10 mg/L, while their LSPR peak position is slightly blue shift. Meanwhile, at higher concentration of Fe$^{3+}$, i.e. 100, 500, and 1000 mg/L, the LSPR peak becomes broadening, while its intensity is increasing.

![Figure 3](image1.jpg)

**Figure 3.** (a) Uv-Vis spectra and (b) colorimetric responses of AgNPs in the presence of various concentration Fe(III) ions, [M$^{3+}$] = 0.1, 10, 100, 500, and 1000 mg/L

![Figure 4](image2.jpg)

**Figure 4.** The correlation between absorbance and the Fe$^{3+}$ concentration at three different wavelengths ($\lambda$: 450, 480, and 500 nm)
The correlation between absorbance and Fe\(^{3+}\) ions concentration at function of wavelength shown in Figure 4. The absorbance of PVA coated AgNPs with the presence of Fe\(^{3+}\) has rapidly increased from 0.1 to 500 mg/L. However, the absorption was found to be diminished when the concentration of Fe\(^{3+}\) was 1000 mg/L. The change in intensity was ascribed due to the interaction of PVA coated AgNPs with Fe\(^{3+}\) ion forming a metal ion complex [8]. The detection limit of PVA coated AgNPs for the analysis of Fe\(^{3+}\) was determined from the calibration curves (Figure 5). The results indicate a non-linear relationship \((A-A_0)/A_0=2-2e^{(x/186)}, r^2=0.99\). It can be seen that the spectral responses of the complex formation were exponential proportional to the concentration of Fe\(^{3+}\) between 0 to 1000 mg/L \((r^2 = 0.99)\). This is shows that the lowest iron ion detection limit at 100 mg/L [21]. Those conditions support based on differences in the absorption spectrum besides the visually observe colour. For detecting the iron ion concentration at 0; 0.1, 10 and to 100 mg/L, the visual colour, and the UV-Vis spectrum also did not show any differences. Meanwhile, when detecting the 500 mg/L iron ion, the solution colour formed visually almost the same with the solution colour when detecting the iron ion from 0-100 mg/L.

![Figure 5](image)

**Figure 5.** Exponential relationship between the absorbance intensity of PVA-AgNPs vs Fe\(^{3+}\) ion concentration at 448 nm

4. Conclusions
PVA coated AgNPs have been successfully synthesized using a polyol reduction method using 1% NaCl. The particles showed the ability as a colorimetric sensor for specific Fe\(^{3+}\) ions in the range of 0.1-1000 mg/L through the formation of polymer (PVA) metal complex. The formation of the complex between PVA coated AgNPs and Fe\(^{3+}\) was visually observed by colour change of the colloidal solution and measured using a UV-Vis spectrophotometer. The Lowest detection of Fe\(^{3+}\) ions was 100 mg/L.

Acknowledgments
This work was supported by Universitas Indonesia by Hibah Publikasi Internasional Terindeks untuk Tugas Akhir Mahasiswa (Hibah PITTA) 2018, No. 2225/UN2.R3.1/HKP.05.00/2018.

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