

Research Article

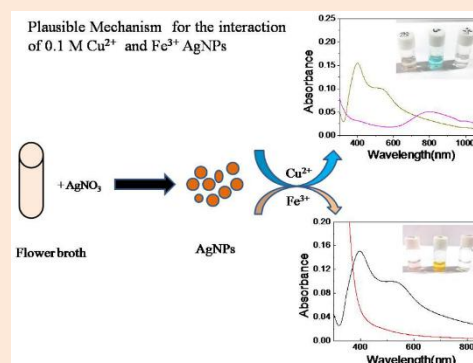
Non-Aggregation Based Colorimetric Detection of Cu (II) and Fe (III) Using Biosynthesized Silver Nanoparticles

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Abstract

Nanoparticles based colorimetric detection of metal ions has attracted great attention, due to its advantages, such as convenience, efficiency and simple equipment method. In this report we focus on the colorimetric assay of Cu^{2+} and Fe^{3+} ions using green synthesized and unmodified silver nanoparticles (Ag NPs). The sensing of Cu^{2+} ions was based on the fact that addition of metal ions to nanoparticles solution changes its color along with the SPR band which may be due to the complex formation. We observed good linearity in this method by varying concentrations of Cu^{2+} ions (0.0006 to 0.0036 M). A new peak at around 802 nm was observed in addition to the peak of Ag NPs at 399 nm. The original color of Ag NPs was yellowish brown, which resulted into decolorization with 60 μl of Cu^{2+} (0.1 M) and 20 μl of Fe^{3+} (0.1 M) ions. This study reveals that these Ag NPs are more sensitive towards Fe^{3+} ions rather than Cu^{2+} ions.



Keywords: Colorimetry, Non-aggregation, AgNPs, copper ions, ferrous ions.

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Introduction

Copper is one of the vital micronutrients in human diet to ensure good health [1]. But excessive use of this can cause adverse health effects including dizziness, headaches, diarrhea, skin irritation, stomach cramps and nausea. Excessive intake of copper may also lead to kidney mal function and liver damage [2-5]. Unlike copper ion is another important transition metal in all living organisms including human body. Iron plays vital role in various cellular metabolism processes, enzyme catalysis and also acts as an oxygen carrier in hemoglobin in many enzymatic reactions [6-7]. Therefore, fabrication of more selective and sensitive methods to monitor the levels of these ions in water is becoming a matter of interest. They are detected by using several analytical techniques such as inductively coupled-plasma atomic emission spectrometry (ICP-AES) [8] inductively coupled plasma mass spectrometry (ICPMS) [9], atomic absorption spectrometry (AAS) [10,11] and voltammetry [12]. Despite all these available detection methods there is still a lot of scope to develop new practical assays for detection of Cu^{2+} and Fe^{3+} ions. Recently, gold and silver nanomaterial based sensors have proved to exhibit exceptional sensing properties owing to their distinctive optical properties. They can yield eye-sensitive color change in the visible region (390-750nm) for colorimetric assay [13-15]. The high extinction coefficient of silver nanoparticles, make them useful for colorimetric sensors. Zhan et al reported pyridyl-appended calyx [4] arene modified silver nanoparticles as Fe^{3+} colorimetric sensor [16]. Ma et al reported colorimetric detection of copper ions in tap water during the synthesis of silver/dopamine nanoparticles [17]. Lou et al reported colorimetric detection of trace copper ions based on catalytic leaching of silver-coated gold nanoparticles [18]. Swarnali et al reported detection of heavy metals (Cu^{2+} , Hg^{2+}) by biosynthesized silver nanoparticles [19]. Barman et al reported the detection of Cu^{2+} ions by synthesis of biomass-silver nanoparticle nanocomposite [20]. Motivated by above mentioned outcomes we attempted colorimetric detection of Cu^{2+} and Fe^{3+}

ions in aqueous samples using biosynthesized unmodified silver nanoparticles of average particle size of 10nm which were previously reported by Ankamwar and co-workers [21] with a low detection time of 2 min.

Experimental

Chemicals

The metal salts Copper chloride CuCl_2 and Ferric chloride FeCl_3 were purchased from Merck Company. All experiments were performed in MilliQ water.

Instruments and apparatus

The changes in absorbance spectra were examined using double beam UV-Visible spectrophotometer [UV-1800 (Shimadzu)] having 3.5cm quartz cuvette.

Synthesis of Silver Nanoparticles

Silver nanoparticles applied here were green synthesized by using flower broth of *Neolamarckia cadamba*. For this purpose 15 μl of flower broth was added in 2ml of $1 \times 10^{-3}\text{M}$ AgNO_3 solution along with 15 μl of ammonia solution. The silver nanoparticles thus prepared were centrifuged at 12,000 rpm for 14min. and collected after decanting the supernatant. These particles were then washed with deionized water several times in order to get purified pellets. The pellets were kept as it is for further possible applications.

Colorimetric detection of Cu^{2+} and Fe^{3+} ions

The colorimetric detection of aqueous Cu^{2+} ions was studied at room temperature by adding varied amounts of Cu^{2+} (20 μl , 30 μl , 40 μl , 50 μl and 60 μl) of 0.1 molL^{-1} Cu^{2+} ions in 3ml of AgNPs and absorbance values were recorded immediately at 399nm. The colorimetric determination of Fe^{3+} was also investigated at room temperature. In this case there is instant decolorisation of AgNPs solution at 20 μl of 0.1 molL^{-1} concentration of Fe^{3+} ions at 399nm.

Results and discussion

Interaction of Cu^{2+} with AgNPs

It is widely accepted that colloidal solution of AgNPs yields yellowish brown color due to the presence of the specific SPR peak of silver [22]. **Figure 1** shows UV-Visible spectrum of as synthesized AgNPs exposing two absorbance bands one sharp at 399nm followed by a tail at about 507nm indicating monodispersity of these bio synthesized AgNPs.

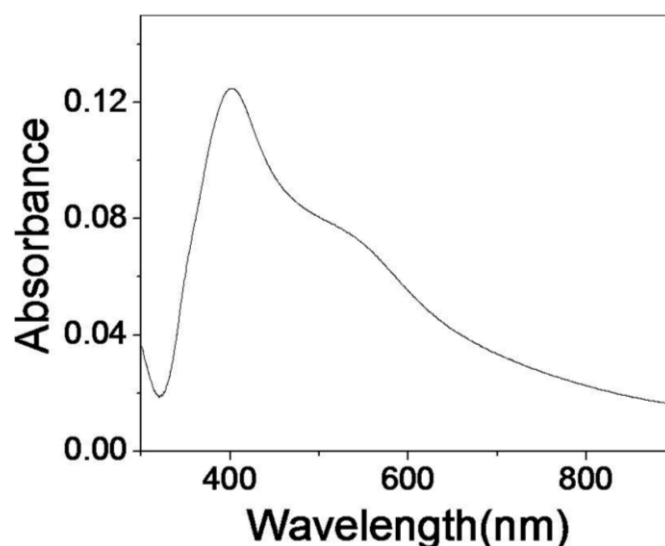


Figure 1 UV-Visible spectrum of AgNPs synthesized from flower extract of *Neolamarckia cadamba*.

After addition of different amounts of Cu^{2+} in AgNPs solution a decrease in absorbance intensity of AgNPs was observed. With increase in concentration, the peak at 399nm decreased and that of 802nm increased gradually as shown in **Figure 2**. The linearity of the proposed method was studied by plot of $A_0 - A$ versus concentration of Cu^{2+} ions [where A_0 is absorbance in absence of Cu^{2+} ions and A is the absorbance in presence of Cu^{2+} ions]. After addition of Cu^{2+} ions to silver nanoparticles color of solution goes on decreasing along with the change in shape of SPR band indicating that there was binding of Cu^{2+} with AgNPs. Absorption spectra of AgNPs in presence of changing concentrations of Cu^{2+} are shown in Figure 2 (left). The colorimetric response of this assay with varied concentration of Cu^{2+} ions is highly linear with $R^2 = 0.9841$ Figure 2 (right).

Interaction of Fe^{3+} with AgNPs

When 20 μl of Fe^{3+} ions solution was added into 3ml AgNPs, there is instant decolorization of NPs solution as shown in (Figure 3).

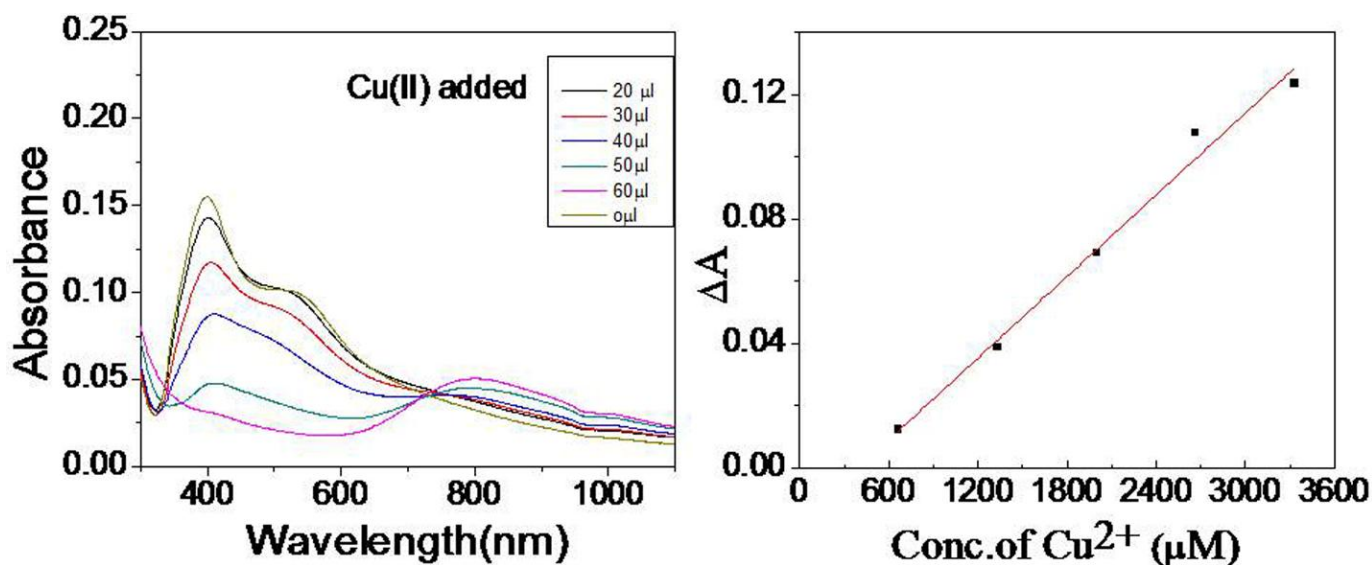


Figure 2 UV-Visible absorption spectra of AgNPs after addition (0-60 μl 0.1 molL^{-1}) of Cu^{2+} [Left]; a plot of ΔA versus Cu^{2+} concentration [Right].

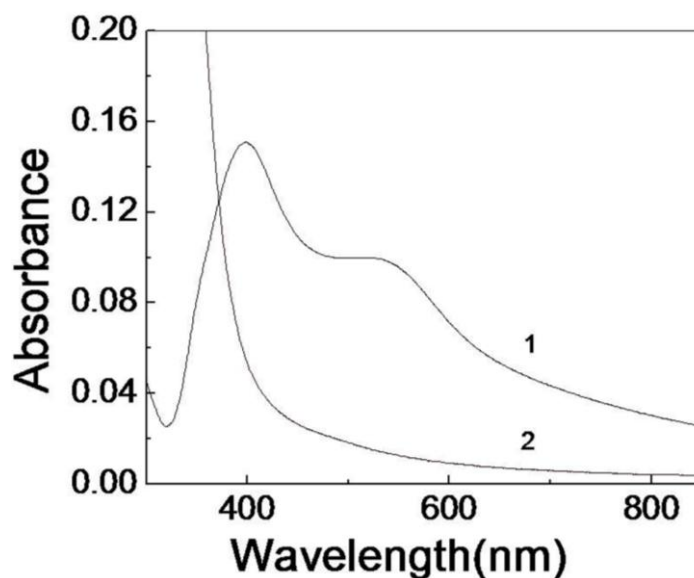
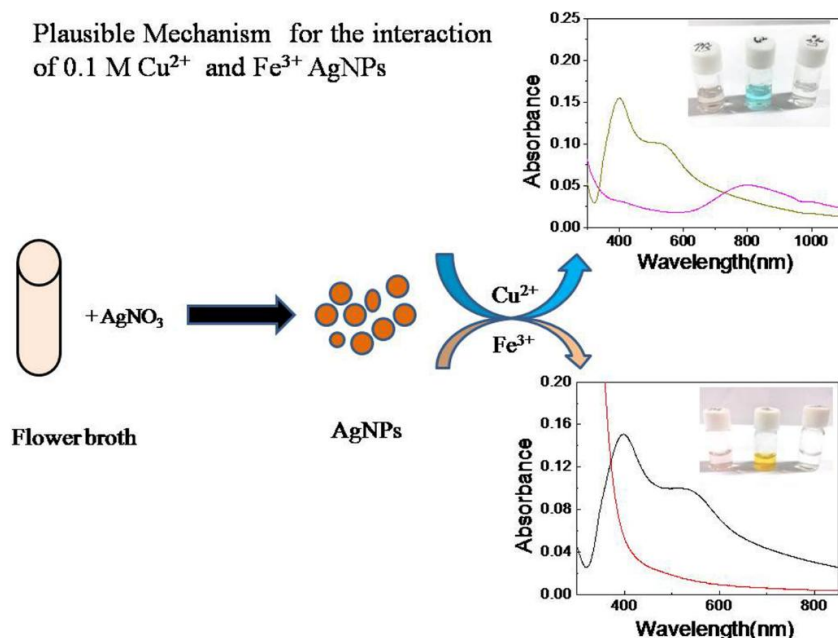


Figure 3 UV-Visible absorption spectra of pure AgNPs (1) and AgNPs after addition of 20 μl 0.1 molL^{-1} of Fe^{3+} ions (2).

Plausible mechanism

The mechanism of the interaction can be explained on the basis of formation of complex of Cu^{2+} ions with AgNPs. The original flower broth contains strong peaks characteristic of hydroxyl group in alcoholic and phenolic compounds which may be responsible for the stabilization of AgNPs. The original broth also contains peak due to phenol containing amine group. This-NH₂ linkage of phenolic group may form complex with Cu^{2+} [23]. This formation of the complex is also evidenced from the visible color change and appearance of new peak at around 802 nm (Berman et al 2014). In case of Fe^{3+} binding of these ions with AgNPs occurs through -OH and -COOH linkage as Fe^{3+} ions shows great affinity to -OH and -COOH groups (vaibhav kumarmehta) hence Fe^{3+} ions may get adsorbed on the surfactant layer of AgNPs through these bonds producing drastic color change when added in nanoparticles solution. The schematics of interaction are given below:



Conclusions

Here we have reported colorimetric determination of Cu^{2+} and Fe^{3+} ions using biosynthesized, unmodified silver nanoparticles in aqueous solution. The detection is based on the changes in color accompanied by corresponding changes in UV-Visible spectra due to the complex formation with metal in case of Cu^{2+} and due to adsorption of metal ions on the surface of AgNPs in case of Fe^{3+} ions. These studies can be extended further for the estimation of amount of these ions present in water at μM level.

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Publication History

Received	18 th Jun 2016
Accepted	25 th Jul 2016
Online	30 th Sep 2016

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