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Visual colorimetric sensing of copper ions based on reproducible gelatin functionalized silver nanoparticles and gelatin hydrogels

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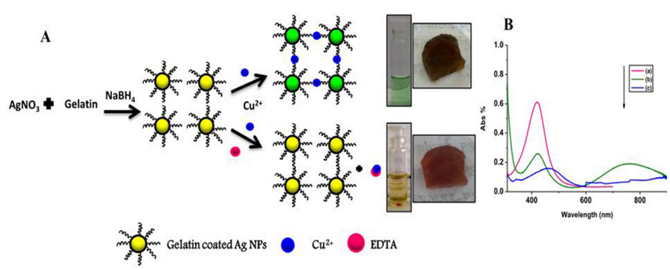
HIGHLIGHTS

- Gelatin functionalized AgNPs and AgNPs loaded gelatin hydrogels were prepared and characterized.
- Solution and solid (hydrogels) phase selective colorimetric detection of Cu^{2+} has been studied.
- AgNPs loaded gelatin hydrogels were reproduced by EDTA.
- The level of copper ion obtained using our method was in good agreement with those from AAS.
- Results are promising for environmental applications.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, we have investigated the colorimetric sensing of heavy metal ions, especially copper ions (Cu^{2+}) for multiple analyses using gelatin functionalized silver nanoparticles (AgNPs) and AgNPs loaded gelatin hydrogels. Gelatin functionalized AgNPs were prepared by chemical reduction of silver nitrate. The gelatin functionalized AgNPs showed concentration dependent color variation (yellow to green color) in the range from 1×10^{-8} to 1×10^{-4} M with lower detection limit of 1×10^{-7} M under optimal condition on interaction with Cu^{2+} ions. The selectivity response of AgNPs to various metal ions has been evaluated and found that the present method is highly selective for Cu^{2+} owing to agglomeration of gelatin functionalized AgNPs and formation of complex between Cu^{2+} and amino group of gelatin. Similarly, studies have been carried out using AgNPs loaded gelatin hydrogels for the detection of Cu^{2+}. The regeneration of AgNPs and hydrogels was carried out by using ethylenediaminetetraacetic acid (EDTA). The sensor response of real sample was evaluated with pond water and the sensitivity values are in good agreement with the value obtained by atomic absorption spectroscopy (AAS) analysis. To the best of our knowledge, the proposed sensor system is new and shows promising result for simple and low-cost sensing of Cu^{2+} which may be explored for pollution monitoring applications.

1. Introduction

Sensing and removal of heavy metal ions from water is one of the major issues in pollutant monitoring and water treatment. A variety of methods have been reported for sensing and removal of toxic metal ions from water, such as reverse osmosis, chemical sensor, ion exchange, water filtration, electro-chemical precipitation, biological treatment and adsorption method [1,2]. Among them, chemical sensor made up of metal nanoparticles was highly

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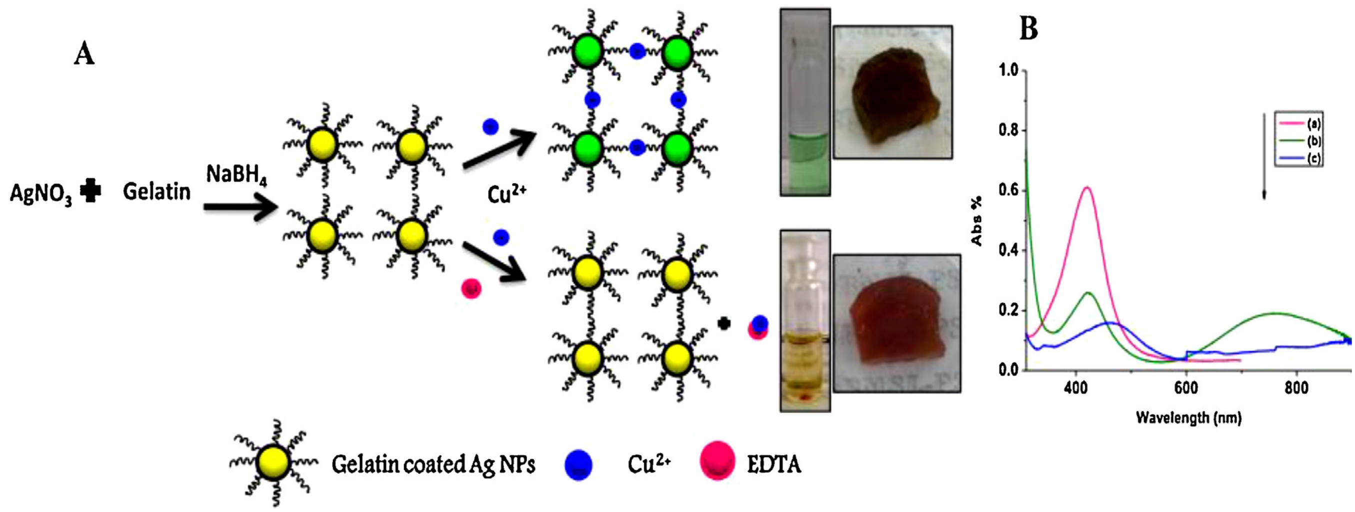

Fig. 1. (A) Schematic representation of colorimetric sensing and removal of Cu^{2+} using gelatin functionalized AgNPs and EDTA respectively (B) (a) UV–vis spectra of synthesized AgNPs, (b) colorimetric sensing of Cu^{2+} using gelatin functionalized AgNPs, (c) removal of Cu^{2+} using EDTA.

preferred due to availability of different adsorbents, high sensitivity, easy handling, rapidity and low-cost [3]. Silver and gold nanoparticles with well-controlled shape and size have received good considerations because of the color changes associated with the surface plasmon resonance (SPR). The SPR is dependent on a number of parameters such as shape and size of the particles and the dielectric properties of the surrounding medium. These characterizations have been used with great achievement for the detection of chemical and biological species [4,5]. Over the years, colorimetric assays have been developed for determination of various heavy metal ions, based on silver and gold nanoparticles due to their high extinction coefficient and SPR properties [6–10]. A wide number of colorimetric sensor assays have been reported using AgNPs for the detection of different metal ions such as Co^{2+} [11], Mn^{2+} [12], Hg^{2+} [9,13–15], Cr^{3+} [8,16], Pb^{2+} [9,17], Ni^{2+} [3,18], Cu^{2+} [19,20]. Surface modification of metal nanoparticles is the main key to develop the metal nanoparticles as colorimetric sensing probes for the detection of analyte.

Among the metal ions, copper ions play an important role in the human system. However, excess amount of Cu^{2+} in human body system could be toxic and results in liver and kidney damage, increase blood pressure and damage central nervous system. It is also related with Wilson's and Alzheimer's diseases and inflammatory disorders [21,22]. The world health organization (WHO) recommended the maximum allowable limit of Cu^{2+} in drinking water at 1.3 mg L^{-1} or 20.5 μM. Recently, AgNPs has been used as colorimetric sensor for the detection of Cu^{2+} due to high extinction coefficient and low-cost compared with gold nanoparticles. Ratnarathorn et al. [19] first developed the paper based device for the colorimetric sensing of copper ions using, homocysteine and dithiothreitol functionalized AgNPs through Ag–S bonds and they reported the lower detection limit at 7.8 nM by naked eye. Li-Jing Miao et al. [20] presented the rapid colorimetric sensing of copper ions based green synthetic approach with the lowest detectable limit of Cu^{2+} at the concentration of 0.5 μM. Feng Li et al. [23] reported the detection of Cu^{2+} and mercury ions using cysteine functionalized AgNPs based on SERS probe with the limit of detection (LOD) of 10 pM for Cu^{2+}. Ying Zhou et al. [24] investigated the colorimetric sensing of copper ions by 4-mercaptobenzoic acid modified AgNPs with a limit of detection 2.5×10^{-8} M. Despite various approaches have been developed for the detection of Cu^{2+} with good sensitivity and selectivity, but still there is a need for simple and regenerable solid phase (hydrogel) colorimetric sensor to meet the practical demand.

Development of a reproducible hydrogel sensor system is highly advantageous. In this context, we aimed to develop the colorimetric sensor for the detection of Cu^{2+} using AgNPs and the adsorbed Cu^{2+} has been removed using EDTA and also same method have been followed for sensing of Cu^{2+} using AgNPs loaded gelatin hydrogels. AgNPs was prepared through the chemical reduction method by the reduction of $AgNO_3$ with sodium borohydride in the presence of gelatin. Here, sodium borohydride used as strong reducing agent, because it requires small amount of catalyst for activation. Gelatin which can act as a stabilizer can provide stable surface and prevent the agglomeration of AgNPs due to the $-NH_2$ groups in gelatin attached over the surface of AgNPs [20]. The redox reaction would take place after addition of Cu^{2+} into AgNPs solution, so Cu^{2+} could be directly recognized by visualizing the color change of AgNPs dispersions from yellow to green by naked eye and also quantitatively measured by UV–vis spectroscopy. The recovery of AgNPs also has been investigated by using chelating agent such as EDTA. Traditionally, EDTA is widely used in the treatment of Cu^{2+} in patient with Wilson's diseases. It can be easily attached with Cu^{2+} to form complex for its removal. Based on these ideas we have developed the colorimetric sensing and removal of Cu^{2+} using AgNPs loaded gelatin hydrogels and EDTA. Compared with other reports, our detection systems provide low-cost, simple, reproducible and efficient detection of Cu^{2+} ions in water samples. The schematic representation of colorimetric sensing and removal of Cu^{2+} using AgNPs was depicted in Fig. 1A. This detection method offers a very simple, pollution-free Cu^{2+} visual detection in various environmental water samples.

2. Materials and methods

2.1. Materials required

All chemicals used were of analytical grade and used without further purification. Silver nitrate (99.98%) was procured from Sigma–Aldrich, Bangalore, India. Gelatin (99%) was purchased from Himedia chemical suppliers. Sodium borohydride (95%), copper acetate (98%), zinc acetate (98%), sodium carbonates (99.9%), nickel nitrate (97%), magnesium chloride (99%), potassium carbonate (99.9%), calcium nitrate (99.9%), barium chloride (99.9%), aluminum nitrate (99.9%), cadmium sulfate (99.9%), calcium chloride (99.9%) and ferric chloride (99.9%) were purchased from Merck. EDTA was purchased from Loba Chemia suppliers. Glutaraldehyde was