Development of Metal Nanoparticles Based Sensing Platform for Lead in Aqueous Samples †

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Abstract: Lead (Pb) is one of the highly persistent and major toxic health hazards listed by various health organizations. A stable, specific, and simple sensor which can rapidly detect Pb in drinking water is required urgently. To this end, we have prepared stable and uniformly sized colloidal silver nanoparticles (AgNPs) using citric acid for the color-based sensing of Pb in water samples. The synthesized AgNPs are characterized by UV-vis spectroscopy, DLS-Zeta, and TEM to access their optical and morphological properties. The cit-AgNPs have shown a great affinity/selectivity towards Pb over Cd, Mn, Cr, Fe, Co, Pb, Hg, Zn, and Ti ions. Thus, based on the interaction of cit-AgNPs and Pb, a colorimetric sensor for selective, specific, and expeditious detection of Pb ions has been developed.

Keywords: heavy metals; sensing; lead; health; toxic; functionalization

1. Introduction

Metals are an important component of dietary intake and play a major role in the metabolism and functioning of the human body [1]. Metals such as zinc (Zn), copper (Cu), and manganese (Mn) serve as essential minerals which are a part of biochemical pathways, whereas metals such as mercury (Hg), lead (Pb), and arsenic (As) are non-essential, and can be lethal even if trace amounts are ingested by living organisms [2]. Pb has is of the most devastating metals that can lead to several health risks. In humans, it can cause increases in blood pressure, neuropathy, fatigue, fertility disorders, and, in severe cases, encephalopathy or even death [3]. Considering such outcomes, the WHO has enlisted Pb as one of the toxic metal pollutants [4]. The interference of such toxic heavy metals can be avoided if sensed in a timely manner.

Nanomaterials, especially nanoparticles (NPs), can serve as an indicator for the presence of heavy metals in food and water samples [5]. The unique optical properties and characteristic surface plasmon resonance (SPR) signals of NPs provide an edge over using classical analytical techniques (such as atomic absorption, ICP-MS) for being feasible, rapid, and cost effective [6].

Among different NPs, silver nanoparticles (AgNPs) are one of the promising candidates suitable for the color-based detection, because of efficient electronic, physical, and chemical properties [7]. The colloidal solution of spherical AgNPs is of yellow color, exhibiting characteristic SPR signal at 350–400 nm [8]. In this study, the SPR properties of stable citrate-AgNPs (cit-AgNPs) were utilized for the specific qualitative sensing of Pb ions.
2. Materials

Silver nitrate (AgNO₃) was purchased from MP Biomedicals (P) Ltd, India. Trisodium citrate (TSC), sodium borohydride (NaBH₄), sodium ascorbate, lead chloride (PbCl₂), zinc chloride (ZnCl₂), ferrous chloride (FeCl₂), chromium chloride (CrCl₂), manganese chloride (MnCl₂), cobalt chloride (CoCl₂), titanium oxide (TiO₂), mercury chloride (HgCl₂), and cadmium chloride (CdCl₂) were purchased from Sigma-Aldrich, USA. All the purchased chemicals were of analytical grade. All the aqueous solutions were prepared using Milli-Q (MQ) water with 18 MΩ cm resistivity.

3. Method

The citrate-AgNPs were prepared by a chemical reduction method [9]. Briefly, 10 mM AgNO₃ was dropwise added to an ice-cold solution containing 1 mM NaBH₄ and 0.30 mM TSC. The solution was stirred continuously until it turned yellow. The synthesized nanoparticles were washed and redispersed in Milli-Q (MQ) water for further use.

4. Results and Discussion

The synthesis of cit-AgNPs was completed when the colloidal solution turned yellow (Figure 1). The synthesis of cit-AgNPs was further confirmed by the appearance of characteristic SPR signal for AgNPs at 398 nm [8] (Figure 1). The cit-AgNPs particles were stable and exhibited −24 eV zeta potential due the presence of negatively charged citrate group as the capping agent (Figure 2). TEM imaging revealed the uniform distribution of cit-AgNPs, with 20 nm average size (Figure 3).

An interaction of different metal ions (10 ppm each) with cit-AgNPs was performed. An equal volume of metal salt solution was individually mixed with AgNPs solution. Out of the tested metal ions (e.g., Cd, Mn, Cr, Fe, Co, Pb, Hg, Zn, and Ti), only Pb ions were capable of turning the cit-AgNPs solution from yellow to colorless (Figure 4). The specific sensing of Pb was also performed spectroscopically by UV-vis spectroscopy. The solution containing Pb loses its stability and aggregates the AgNPs and, correspondingly, there is a clear change observed in the UV-Vis spectrum (Figure 5).

![Figure 1. The AgNPs synthesized by chemical reduction (inset). The characteristic SPR signal (398 nm) of citrate-AgNPs as obtained in UV-Vis.](image-url)
Figure 2. Size and zeta potential of cit-AgNPs, as measured using dynamic light scattering (DLS).

Figure 3. The TEM image for the citrate-AgNPs.
5. Conclusions

Lead (Pb) ions have been listed as one of the most toxic pollutants for the environment. Herein, we have prepared and used well-characterized AgNPs for the colorimetric and spectroscopic sensing of Pb ions. The use of AgNPs helped in the quick detection of Pb, which would be highly beneficial for point-of-care qualitative detection. The developed cit-AgNP displayed color change and shift in SPR signal after interaction with Pb. Notably, these NPs did not show any color change in the presence of interfering heavy metals, e.g., Cd, Mn, Cr, Fe, Co, Hg, and Zn.
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