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Colorimetric detection of Pb^{2+} ions using PVP-capped silver nanoparticles

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Abstract

Colloidal silver nanoparticles (AgNPs) have been synthesized using polyvinylpyrrolidone (PVP) as a capping agent. The particles were characterized using UV-visible absorption spectroscopy and transmission electron microscopy (TEM). The particles were 4-12 nm in diameter. The surface plasmon resonance (SPR) band of the AgNPs at 400 nm was quenched in the presence of 1 μM Pb^{2+} *ions at pH 9.6. Additionally, a new absorption band was formed around 600 nm. The colour of the colloidal solution was found to change from yellow to green. The addition of metal ions such as* Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Mg^{2+}, Ni^{2+}, Sm^{3+} *and* Zn^{2+} *did not alter the SPR band of the AgNPs significantly. The limit of detection (LOD) of* Pb^{2+} *ions by the colorimetric method was found to be 14.4 nM. The mechanism of the aggregation of the AgNPs in the presence of the* Pb^{2+} *ions has been discussed.*

Keywords: Colorimetric; Colloidal; Nanoparticles; Aggregation; Sensing

Introduction

Lead is categorized as a Class B metal that falls under non-essential trace elements which are highly toxic (Nagajyoti *et al.,* 2010). The contamination by heavy metal ions, particularly Pb^{2+}, poses a serious threat to human health and to the environment. Lead poisoning is known to causes renal malfunction and inhibits brain development particularly in children causing various neurotoxic effects. As lead is nondegradable, it would be persistent in the environment and can produce toxic effects in plants and animals (Chai *et al.,* 2010). It is also known that even long exposure to very low levels of lead can cause neurological, reproductive, cardiovascular, and developmental disorders (Kim *et al.,* 2012). The source of lead in urban areas is mainly the combustion of tetraethyl lead in gasoline, local pollutants from mines and lead based paint pigments (Huheey *et al.,* 2013). Various methods for the detection of Pb^{2+} ions in drinking water or river water have been reported. These include atomic absorption spectrophotometry (Chen *et al.,* 2005, Siraj *et al.,* 2013, Bertenshaw *et al.,* 1981) , voltammetry (Dai *et al.,* 2017) , plasma optimal emission spectrometry (Bispo *et al.,* 2005) , flotation spectrophotometric (Shiri *et al.,* 2011) and fluorescence spectroscopy (Ali *et al.,* 2007; Fu *et al.,* 2012; Li *et al.,* 2013; Singh *et al.,* 2019).

Although several techniques has been employed for the determination of Pb^{2+} ions, the colorimetric methods based on the aggregation of gold (Liu *et al.,* 2003; Liu *et al.,* 2004; Peng *et al.,* 2014; Ratnarathorn *et al.,* 2015) and silver (Qi *et al.,* 2012; Kumar *et al.,* 2014) nanoparticles have attracted considerable attention due to their cost efficiency, rapidity and simplicity. The strategy for designing bifunctionalized gold nanoparticles that can be used for detection of lead have also reported (Zhu *et al.,* 2012). They used two peptide ligands, glutathione and pentapeptide for the selective sensing of lead under physiological conditions. The colorimetric detection of lead using gold nanoparticles is in quite good reported numbers. However, silver nanoparticles based colorimetric methods are fewer.

Herein, we have presented a simple method for the synthesis of the silver nanoparticles using sodium borohydride ($NaBH_4$) as a reducing agent and polyvinylpyrrolidone (PVP) as the capping agent. The colorimetric studies were carried out in the presence of several metal ions such as Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Mg^{2+}, Mn^{2+}, Ni^{2+}, Pb^{2+}, Sm^{3+}, Zn^{2+} and Pb^{2+} to ascertain the selectivity of the probe.

Materials and methods

Materials

Aluminium sulphate, calcium chloride, cobalt chloride, cadmium chloride, copper chloride, magnesium sulphate, manganese chloride, lead nitrate, samarium nitrate, mercuric chloride, nickel chloride, polyvinylpyrrolidone, silver nitrate and zinc chloride were obtained from Himedia. Sodium borohydride was obtained from Sigma Aldrich. All other chemicals were of analytical grade. The water used for preparing the solutions was purified through distillation.

Instrumentation

UV-visible absorption spectra were obtained using PerkinElmer 25 spectrophotometer. TEM measurements were carried out using a JEOL 100 CX transmission electron microscope operating at 100 kV.

Synthesis of the PVP-capped AgNPs

200 ml distilled water was taken in a conical flask. Subsequently, 0.2 ml of 0.1 M $AgNO_3$ solution was added and the solution was stirred for 10 minutes. Then 0.02 g of solid $NaBH_4$ was added at room temperature to yield yellow colloidal solution. The solution was stirred and allowed to stand for 10 minutes for the completion of the nucleation process. It was followed by the addition of 1 ml of 1×10^{-3} M PVP solution. The solution was then stirred for 10 minutes and stored in the dark. The pH of the colloidal solution was 9.6.

Results and discussion

Characterization of the PVP-capped AgNPs

The UV-visible absorption spectrum of the PVP-capped AgNPs has been displayed in Figure 1.

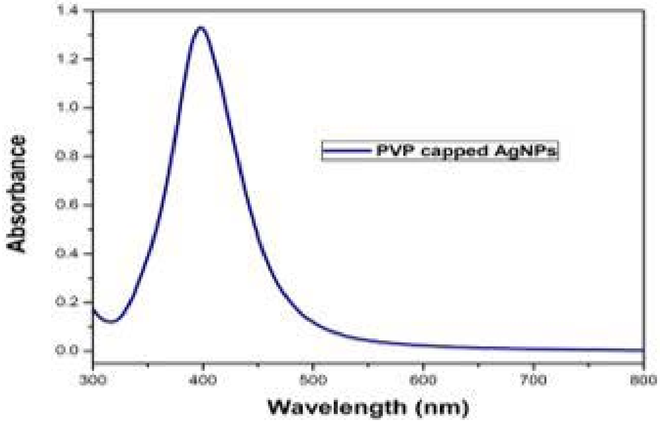

Figure 1. UV-visible absorption spectrum of the PVP-capped AgNPs.

The SPR band of silver was positioned at 400 nm. The intensity and position of the band remained unchanged for a period of two weeks. The morphology of the synthesized AgNPs was determined using the TEM measurements. Figure 2 shows the TEM images of the colloidal PVP- capped AgNPs.

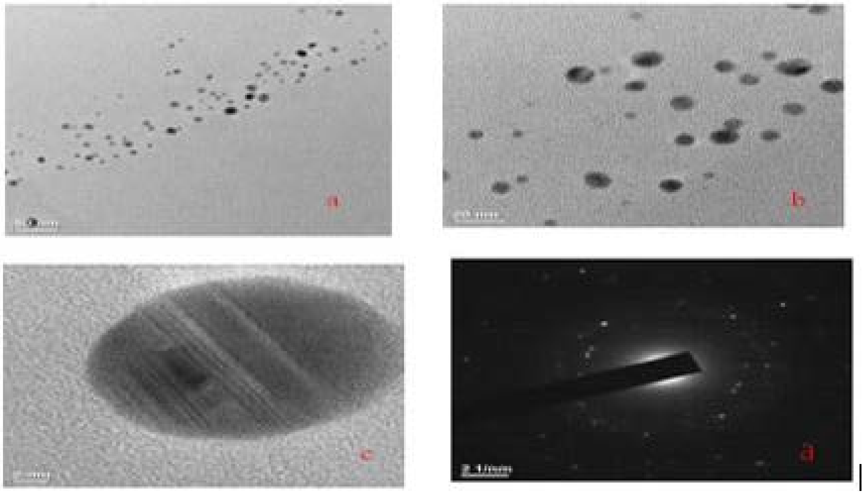

Figure 2 (a) & (b): TEM images of the PVP-capped AgNPs. **(c)** High resolution TEM image of the AgNPs **(d)** SAED pattern of the AgNPs.

The particles were nearly spherical in shape with the diameter ranging from 4 to 12 nm. The high resolution TEM image of the AgNPs has been shown in Figure 2(c). The selected area electron diffraction (SAED) pattern gives information on the crystalline nature of the material (Diamai *et al.,* 2019). The concentric rings in images confirm the crystalline nature of the synthesized AgNPs.

Effect of the addition of various metals ions on the SPR band of the PVP capped AgNPs

It is well known that the metals ions can induce aggregation of the silver or gold nanoparticles (Saha *et al.,* 2012). The aggregation of the NPs can be confirmed by the change in the colour of the silver NPs from yellow to green. We investigated the effect of the different metal ions such as Al^{3+}, Ca^{2+}, Cd^{2+}, Co^{2+}, Cu^{2+}, Hg^{2+}, Mg^{2+}. Mn^{2+}, Ni^{2+}, Pb^{2+}, Sm^{3+} and Zn^{2+} on the SPR band of the AgNPs. The absorption spectra of the PVP-capped AgNPs in the presence of 1 μM concentration of various metal ions at pH 9.6 have been displayed in Figure 3.

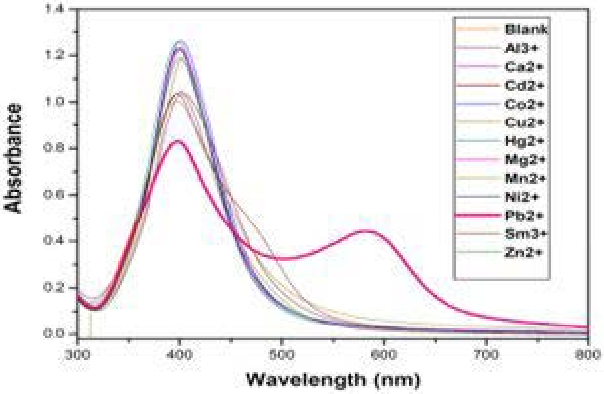

Figure 3. UV-visible spectra of the AgNPs upon the addition of 1 μM concentrations various metal ions at pH 9.6.

It is evident from Figure 3 that the addition of Pb^{2+} ions to the AgNPs resulted in quenching of the 400 nm band and the formation of a new peak around 600 nm. The addition of the other metal ions quenched the SPR band of silver, although not to the same extent as Pb^{2+}. Significantly, no longer wavelength absorption band was observed upon addition of the other metal ions. The colour of the AgNPs turned green upon addition of the Pb^{2+} ions (Figure 4). However, there was no change in the colour upon addition of the other metal ions. Therefore, the PVP-capped AgNPs can be used as a colorimetric probe for the selective detection of Pb^{2+} ions in aqueous medium.

Figure 4. Photograph of the AgNPs in the absence and presence of 1 µM concentrations of the various metal ions.

Selectivity and sensitivity of the colorimetric probe for the Pb^{2+} ions

The plot of the ratio of the absorption intensity response (A_{600}/A_{400}) of the probe for the Pb^{2+} ions against other metal ions at 1 µM have been shown in Figure 5.

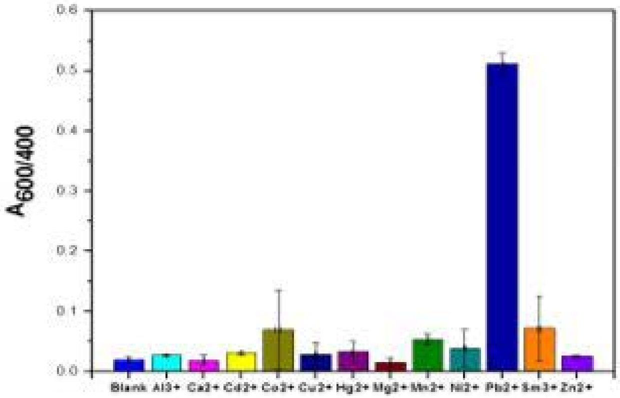

Figure 5. Plot of the response of the PVP-capped AgNPs (A_{600}/A_{400}) in the presence of 1 µM concentration of the various metal ions at pH 9.6.

As can be observed from the figure, the response of the probe was the maximum for the Pb^{2+} ions. The response indicates that Pb^{2+} ions can cause a maximum red shift of the SPR of the probe compared to the other competing metal ions. Thus, aggregation of the AgNPs can be strongly and selectively induced by the Pb^{2+} ions which indicates that the probe is selective for the Pb^{2+} ions. The aggregation of the AgNPs induced by Pb^{2+} ions was confirmed from the TEM measurements as shown in Figure 6. The limit of detection (LOD) was calculated as per the formula $3\sigma/S$, where σ is the standard deviation of the blank and S corresponds to the slope of the calibration curve. The LOD was found to be 14.4 nM.

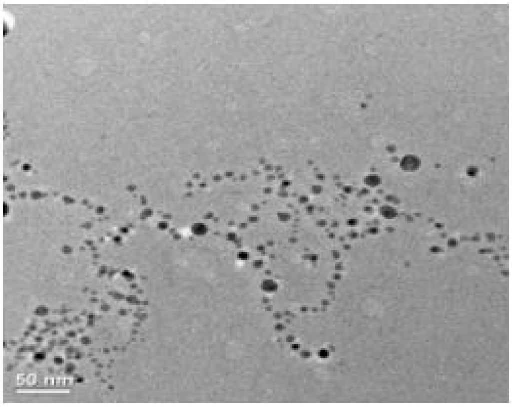

Figure 6. TEM image of the PVP-capped AgNPs upon the addition of 1 μM Pb^{2+} ions.

Mechanism for the aggregation of the PVP-capped AgNPs in the presence of Pb^{2+} ions

The selectivity of the probe towards the Pb^{2+} ions can be explained on the basis of the unique character of this metal ion. The Pb^{2+} ions have highly flexible bond length and geometry with a maximum coordination number up to 12 (Yoosaf *et al.,* 2007). Due to these properties, the Pb^{2+} ions have a high tendency to coordinate with the polymer PVP to form assembly of the AgNPs. Pb^{2+} ion is a borderline acid which can bind to different group of ligands. Thus, when the Pb^{2+} ions are added to the PVP-capped AgNPs, the metal ions coordinate with the N and O group of the PVP as displayed in the inset of Figure 7. Consequently, an assembly of the AgNPs was formed. The other metal ions interact very less or not at all with the ligand due to rigid coordination geometry of these ions. Hence upon the addition of these metal ions, there was little or no change on the absorption spectrum of the AgNPs.

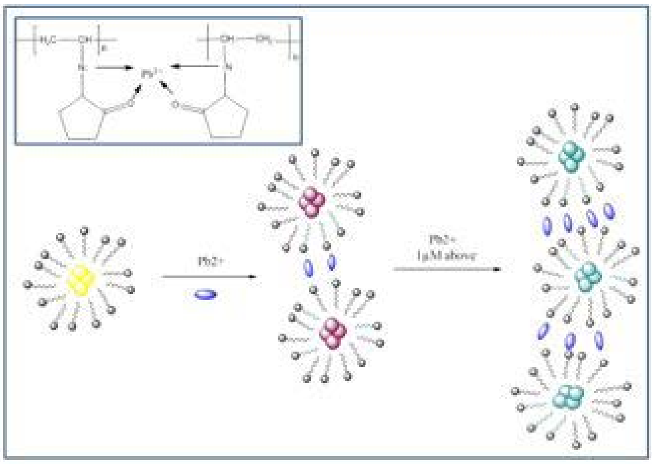

Figure 7. Pictorial representation of the aggregation of the PVP-capped AgNPs in the presence of the Pb^{2+} ions.

Conclusions

The PVP-capped AgNPs have been demonstrated to be a colorimetric probe for the selective detection of the Pb^{2+} ions in the aqueous medium. The LOD of the probe was calculated to be 14.4 nM. The aggregation of the AgNPs in the presence of the Pb^{2+} ions was due to the preferred coordination of Pb^{2+} with the N and O ligand groups of PVP. The present method has potential for the sensing of Pb^{2+} ions in water bodies such as lakes as streams.

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