Materials Letters 333 (2023) 133614

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Colorimetric and plasmonic detection of Hg^{2+} in water by biogenic Ag nanoparticles synthesized with *Opuntia joconostle*

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ARTICLE INFO

Keywords:
Ag nanoparticles
Biosynthesis
Sensing
Hg^{2+}

ABSTRACT

Silver nanoparticles (AgNPs) have been synthesized, for the first time, using the pulp of *Opuntia joconostle* fruit as reducing reagent of Ag^+ ions. The reported method is wholly green, since no temperature or infusion preparation were required. AgNPs with a 428 nm plasmon absorbance, a quasi-spherical morphology, a mean size of 17.7 nm, and an FCC crystal structure were obtained. These biogenic AgNPs, without further chemical functionalization, could sense easily (naked eye) and selectively the presence of Hg^{2+} ions in aqueous solution and in tap water.

1. Introduction

Even though many plasmonic and colorimetric nanometric-sensing systems have been reported in recent years, there is still plenty of room to continue investigating in this field, mostly, to create novel sensors which could be easily prepared, with a low-cost, and having a simple way of noxious chemicals detection [1]. Noble metal nanoparticles have been one of those novel sensing systems which can offer relatively simple, selective, and sensitive detection of metal ions, particularly of heavy-metal ions. One of the easier and greener ways to synthesize metal nanoparticles is the so-called bio-reduction methodology using plant or fruit extracts, where the biomolecules present in these eukaryotic products function as both, reducing reagents of the metal ions and passivating agents of the nanostructures [2]. Although some *Opuntia* spp. species, such as *Opuntia ficus-indica* [3], have been employed to produce AgNPs, there are no reports regarding the use of *Opuntia joconostle* for such purpose. *Opuntia joconostle* grows in central regions of Mexico, and its fruit has an acidic taste due mainly to the high content of ascorbic acid [4]. Detection of Hg^{2+} are amid the most described metal ion detection experiments using AgNPs; nonetheless, in many of the reported studies the AgNPs are activated, or functionalized, with different chemicals to work properly as sensors of Hg^{2+} [5].

Herein, AgNPs were formed throughout a green bio-reduction of Ag^+ ions methodology using *Opuntia joconostle* fruit, and these, non-functionalized, biogenic nanoparticles were successfully proved as efficient sensors for the colorimetric and selective detection of Hg^{2+} in water.

2. Experimental

2.1. Materials

The fruit of *Opuntia joconostle* was obtained in Jocotitlán, State of Mexico, Mexico. $AgNO_3$, $Cu(NO_3)_2$, $Pb(NO_3)_2$, $Co(NO_3)_2$, $ZnCl_2$, $Hg(CH_3COO)_2$, $Cd(NO_3)_2$, $Ni(NO_3)_2$, $FeCl_2$, As_2O_5 and $K_2Cr_2O_7$, were acquired as analytical-grade reagents from Sigma-Aldrich and used without further purification.

2.2. Preparation of aqueous extract of Opuntia joconostle

The fruit was washed with tap water, the peel and the central part of the fruit were removed, leaving only the pulp, which was macerated. 10 g of pulp was weighed in a beaker, followed by the addition of 90 mL of deionized water. The solution was kept under stirring for 20 min, then it was filtered to remove suspended solids.

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https://doi.org/10.1016/j.matlet.2022.133614
Received 18 August 2022; Received in revised form 11 November 2022; Accepted 27 November 2022
Available online 2 December 2022

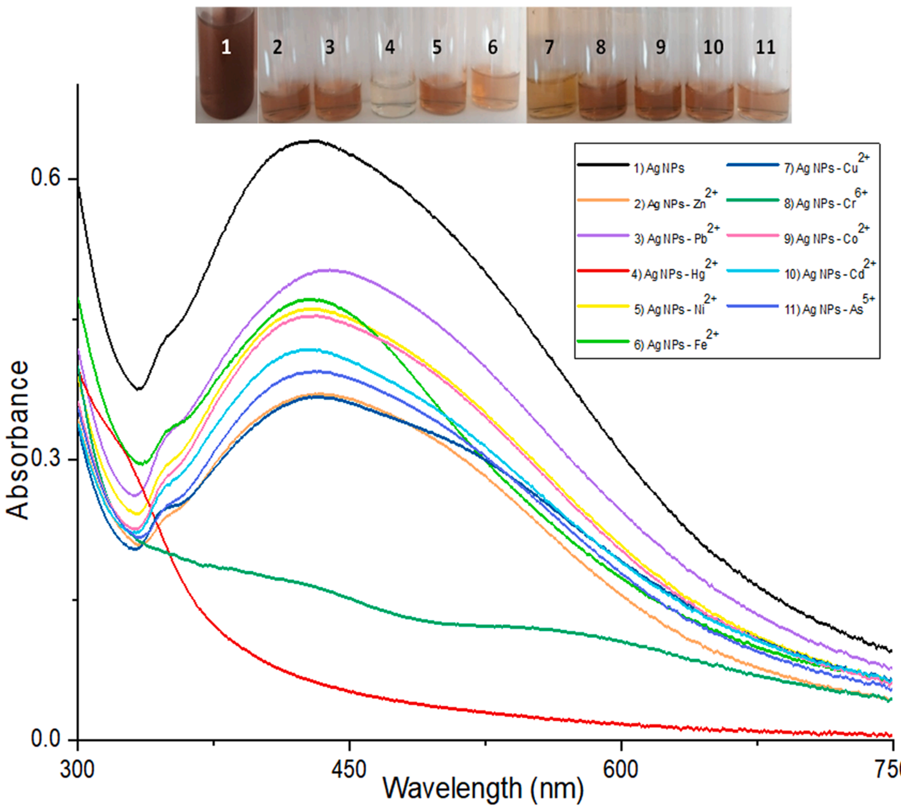

Fig. 1. UV–vis spectra of biogenic AgNPs and the interaction of AgNPs with the different metal ions surveyed. Pictures of vials containing (1) AgNPs and (2–11) the mixture of biogenic AgNPs with the different metal ions probed.

2.3. Biosynthesis of AgNPs

An aqueous solution of 10^{-3} M $AgNO_3$ was prepared. The volume ratios of 10^{-3} M $AgNO_3$ solution to extract were 1:1 and 1:2. An aliquot of the admixture was sampled at given times to monitor the progress of AgNPs biosynthesis by UV–vis spectrophotometry. The biosynthesis was carried out under ambient conditions.

2.4. Characterization

Absorption spectra were measured using a Thermo-Scientific UV–vis spectrophotometer Evolution 220. TEM observations were performed in a JEOL 2100 microscope. For IR studies, an aliquot of 20 mL *Opuntia joconostle* extract and biogenic AgNPs was allowed to dry at ambient conditions. The powders were analyzed from 4000 to 500 cm^{-1} using a Bruker Tensor 27 spectrophotometer.

2.5. Sensing studies

Selectivity sensing experiments were performed by adding 1 mL of 100 ppm solution of $Cu(NO_3)_2$, $Pb(NO_3)_2$, $Co(NO_3)_2$, $ZnCl_2$, $Hg(CH_3COO)_2$, $Cd(NO_3)_2$, $Ni(NO_3)_2$, $FeCl_2$, As_2O_5 and $K_2Cr_2O_7$, separately, to 1 mL of the AgNPs solution, at room temperature. For sensitivity studies, solutions with different concentrations of Hg^{2+}: 1, 10, 25, 50

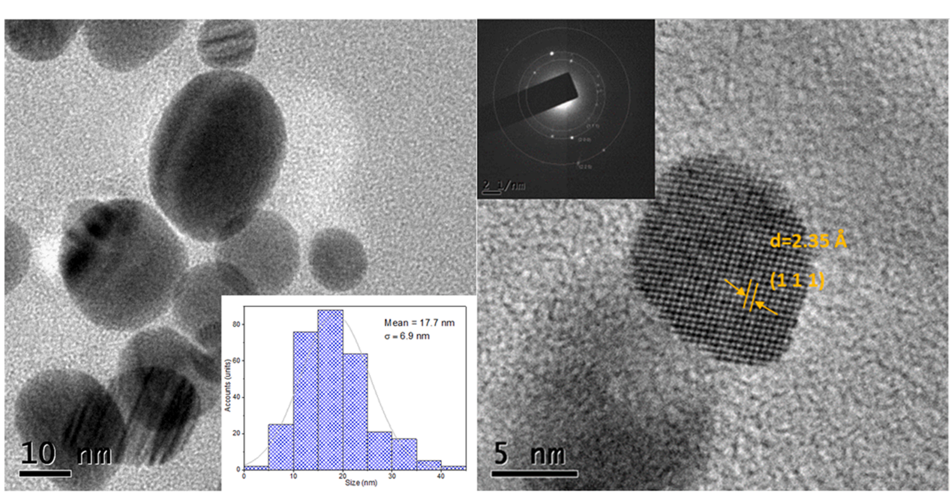

Fig. 2. A) Tem image of biogenic AgNPs with average diameter of 17.7 nm accordingly to histogram (inset). b) HRTEM micrograph of a biogenic AgNPs; SAED pattern (inset).

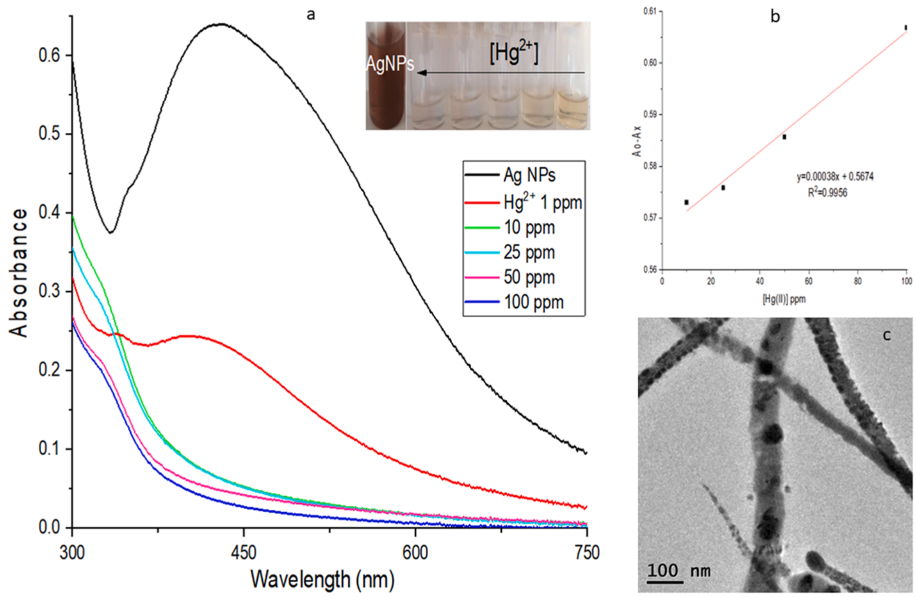

Fig. 3. A) UV–vis spectra of AgNPs colloidal solution after addition of various concentrations of Hg^{2+} ions; AgNPs solution color loss with increasing Hg^{2+} ion concentration (picture). b) Change in absorption intensity as a function of concentration of Hg^{2+} showing the linear behavior in the concentration range 10–100 ppm. c) TEM image of biogenic AgNPs after contact with Hg^{2+} ions.

and 100 ppm, were added to the AgNPs solutions. Selectivity and sensitivity sensing studies were performed by UV–vis spectroscopy.

2.6. Colorimetric and plasmonic detection in tap water

Tap water samples were collected and filtered, separately, before use. Known concentration of Hg^{2+} solutions (1, 10, 25, 50, 75 and 100 ppm) were added, individually, to these tap water samples. Then, each one of these solutions were combined with 1 mL of freshly prepared 10^{-3} M AgNPs. Absorption spectra were recorded using a UV–vis spectrophotometer.

3. Results and discussion

3.1. Synthesis and characterization of AgNPs

Opuntia joconostle species contain several compounds such as ascorbic, protocatechuic, malic, citric, fumaric acids, besides other polyphenolic compounds [3]. These biomolecules contribute to favor the synthesis of AgNPs under ambient conditions, throughout the bioreduction of Ag^{+} ions and passivating the AgNPs formed. Although each ratio of 10^{-3} M $AgNO_3$ solution to fruit extract seem to produce AgNPs, the best proportion was 1:2 due to the larger amount of AgNPs produced, accordingly to the higher intensity of the surface plasmon resonance (SPR) obtained. Under these conditions the resultant colloidal

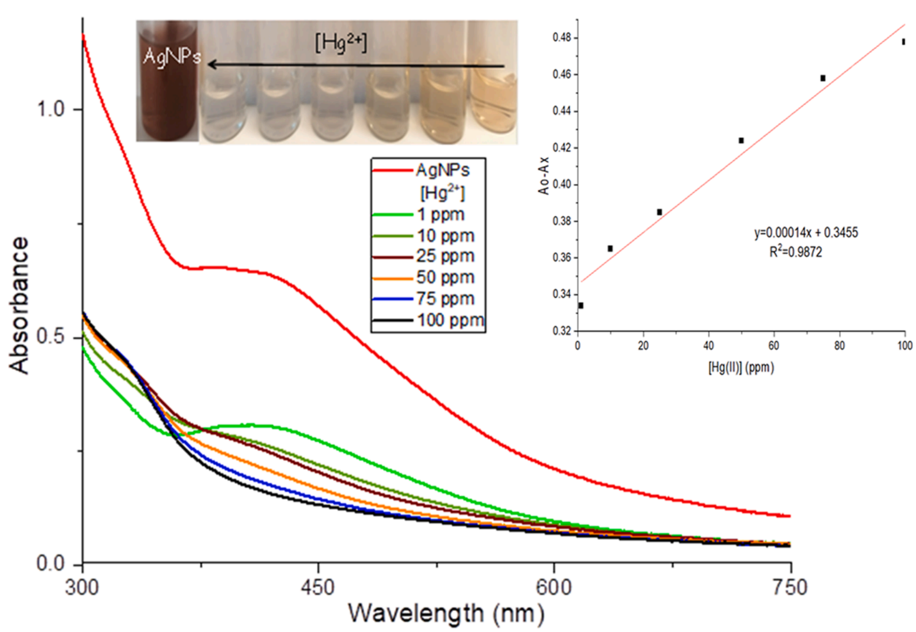

Fig. 4. UV–vis spectra of biogenic AgNPs and of AgNPs after addition of different concentrations of Hg^{2+} ions in tap water. AgNPs solution color loss with increasing Hg^{2+} ion concentration (picture). Change in absorption intensity as a function of concentration of Hg^{2+} showing the linear behavior in the concentration range 10–100 ppm (right hand plot).

solution of AgNPs had a brown color (inset picture Fig. 1). The absorption maximum at 428 nm observed in the UV–vis spectrum (Fig. 1, black line spectrum) evidences the presence of AgNPs, this signal can be related to the SPR of AgNPs.

AgNPs are mostly quasi-spherical (Fig. 2a) with an average size of 17.7 ± 6.9 nm (inset Fig. 2a). The SAED pattern (inset Fig. 2b) denotes the formation of monocrystalline AgNPs. An interplanar distance of 2.35 Å was obtained from HRTEM micrograph in Fig. 2b, which can be associated to the lattice plane (1 1 1) of the crystalline silver with face-centered cubic (FCC) structure (JCPDS 004-0783).

3.2. Sensing studies

The sensing capability of the biogenic AgNPs was probed with ten ions, of which Zn^{2+}, Pb^{2+}, Ni^{2+}, Fe^{2+}, Cu^{2+}, Co^{2+}, Cd^{2+} and As^{5+} showed small spectral changes and slight reductions in the SPR intensity (Fig. 1); conversely, for Hg^{2+} and Cr^{6+} the loss of the characteristic AgNPs SPR absorption is observed (Fig. 1). Consequently, there is a colorimetric response in the AgNPs colloid in the presence of Hg^{2+}, changing from a brown color solution to a discolored one (inset pictures in Fig. 1). In many reported studies [5], the AgNPs need to be activated with different chemicals, such as calixarene-capped [6] or AgNPs stabilized with sodium 3-mercapto-1-propanesulfonate [7], to work properly as sensors of Hg^{2+}. There are only few examples where no functionalization of AgNPs was performed to achieve the sensing of Hg^{2+} [8]. A preliminary sensitivity study of the AgNPs capability for detection of the Hg^{2+} was performed by UV–vis spectroscopy, and the results are shown in Fig. 3a. Hence, as the concentration of Hg^{2+} increases from 1 to 100 ppm the SPR absorbance diminishes until practically disappear. Colorimetrically, a complete fading of the solution color is observed at a Hg^{2+} concentration of 25 ppm (inset picture Fig. 3a). In Fig. 3b, the plot of Ao-Ax, which is the difference in the absorbance of the sample without and with Hg^{2+} at SPR peak maximum, *versus* the [Hg^{2+}] shows a linear relationship in the 10 to 100 ppm interval. In analogous sensing studies using biogenic AgNPs, the reported detection limits of Hg^{2+} varies from 2.00 to 0.85 μM [9,10,8]. TEM image in Fig. 3c was obtained after addition of a 25 ppm Hg^{2+} solution to a AgNPs solution. The nanoparticles lost their quasi-spherical shape, and they are no longer separated, rather they are aggregated forming rodlike-shape structures. This is in agreement with the observed disappearance of the SPR absorption (Figs. 1 and 2). Therefore, it is possible that a spontaneous oxidation–reduction reaction is being generated, provoking that the solution changes from a brown color to colorless. Comparable results and mechanism proposals for the Hg^{2+} sensing by AgNPs have been described by other authors [6].

It was also possible to detect colorimetrically, and plasmonically, Hg^{2+} ions added to tap water samples by means of the biogenic AgNPs. Fig. 4 shows the SPR absorbance of AgNPs, which tends to diminish, and practically disappear as the concentration of Hg^{2+} augments. The fast colorimetric change from brown to colorless of the AgNPs solution can be detected (inset picture Fig. 4); therefore, it seems that the metal ions existing in tap water do not interfere with this facile naked eye method of detection of Hg^{2+}. AgNPs produced by *Garcinia indica* (Kokum fruit) were able to detect Hg^{2+} in tap water until reaching a concentration above 120 ppm [8], whereas our AgNPs can detect, both colorimetrically and plasmonically, Hg^{2+}ions in tap water at lower concentrations.

4. Conclusions

Crystalline FCC AgNPs with an average size of 17.7 nm, and a quasi-spherical shape, can be obtained by a facile and green biosynthesis using the pulp of *Opuntia joconostle* fruit straight, without the need of an infusion preparation. Furthermore, aqueous dispersion of these biogenic nanoparticles demonstrated to be an efficient probe for Hg^{2+} sensing in water, both colorimetrically and plasmonically. Thus, this detection method of Hg^{2+} is simple (naked eye), selective, low-cost and portable; it is also worth stating that, unlike other reported methods, additional chemical functionalization of the AgNPs was not required in the sensing experiments.

CRediT authorship contribution statement

Rosa Gómez-Sánchez: Methodology. **Victor Sánchez-Mendieta:** Investigation, Writing – review & editing. **Raúl A. Morales-Luckie:** Investigation, Methodology. **Alfredo R. Viclhis-Néstor:** Methodology. **Fabián Ruíz-Ruíz:** Methodology.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The authors are thankful to M. en C. Lizbeth Triana Cruz and L. I. A. Maria Citlalit Martinez Soto (CCIQS UAEM-UNAM) for FTIR analysis and computing assistance, respectively. Funding for this work was provided by Universidad Autonoma del Estado de México and CONACYT (Grant A1-S-34533). FRR thanks *Acción Cátedras COMECYT* program, No. CAT2021-0231.

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