HEXADECYLAMINE FUNCTIONALIZED GOLD NANOPARTICLES FOR THE DETECTION OF LEAD IN WATER SAMPLES

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1. INTRODUCTION

Nanometer sized colloidal suspension gold particles are referred as Gold Nanoparticles. These Nanoparticles have been synthesized either physical or chemical methods. Physical methods include the exploding wire technique, plasma, pulsed laser ablation, chemical vapor deposition, gamma radiation, supercritical fluids, microwave irradiation, sono-chemical reduction etc [1-2]. Chemical methods includes the polyol process, the alcohol reduction process, the chemical reduction of metal salts, electrochemical synthesis, the thermal decomposition of metal salts, microemulsions, etc [3,4].

Gold Nanoparticles synthesis based on the reduction of chloroauric acid in the presence of a stabilizing agent is one of the famous techniques. Reduction of chloroauric acid using trisodium citrate resulting into the formation of Gold Nanoparticles was reported by many authors [5-7]. The size of Gold Nanoparticles is mainly depends on the salt concentration, temperature and rate of addition of reactants of the solution. One more commonly used method employs toluene using the tetra-octanyl ammonium bromide as a phase transfer reagent [8]. Several modifications of the basic methods have resulted into a range of techniques to synthesize and manipulate these nanoparticles satiating the needs of a specific research objective [9–11]. Chemical reduction using L-Tryptophane as a reducing agent for ionic gold and polyethylene glycol was used to produce $AuCl^{4\,-}$ ions to provide higher stability and uniformity in size, shape, and particle distribution [12]. Another method used methanol extract of medicinal plants as reducing agent to produce the environmental friendly Gold Nanoparticles [13]. Serrapeptase is an amino acid derivative has been used as stabilizing and reducing agent to synthesize stable “eco-friendly” Gold Nanoparticles [14].

Gold nanoparticles (GNPs) and their biomedical applications have been reviewed recently indicating enormous growth in this field [15,16]. In the present work, Gold Nanoparticles capped with hexadecylamine were synthesized and these Nanoparticles were used to determine lead pollutant in various environmental water samples. Various parameters such as Ligand concentration, Nanoparticle concentration, and reaction time were studied.

2. MATERIALS AND METHODS

2.1 Chemicals

Gold Chloride (HAuCl4.3H20) was purchased from Research Lab fine chem. Industries, India Limited. Chemicals used in this study included Hexadecylamine, methanol, ethanol, Silica (10-50 nm), Lead nitrate, which were of analytical purity grade and procured from Sigma-Aldrich Company. Double distilled water was used throughout the experiment.

2.2 Instrumentation

Scanning Electron Microscopic (SEM) image was taken using a FEI QUANTA-200 SEM instrument. High Resolution Transmission Electron Microscopy (HRTEM) was carried out using a 300 kV JEOL-3011 instrument with a ultra high resolution (UHR) pole piece. Shimadzu model Ultraviolet-Visible Spectrophotomer is used for spectral analysis.

2.3 Synthesis of Gold Nanoparticles

Amine group capped Gold nanoparticles were synthesized by the reduction of Chloroauric acid with NaBH4. In this method, 5 mL of 1 mM HAuCl4.3H2O was diluted with 80 mL of distilled water and heated until it begins to boil. An amount measuring 5 mL of 1% NaBH4 solution along with 10 ml of Hexadecylamine was added and continued heating until the solution turned wine red.

2.4 Detection of Lead Contaminant in Water Samples

Different concentrations of Lead standard solutions have been prepared freshly using double distilled water. Add 2 ml of hexadecylamine capped Gold Nanoparticles solution to these standard solutions and mix these solutions for five minutes. The performance of the synthesized hexadecylamine Gold nanoparticles was studied using Tap water and Lake water samples collected from Amara raja Batteries, Karakambadi, Tirupati, Chittoor district, Andhra Pradesh, India. This sample was spiked with the known Lead contaminat chosen for the present study.

2.5 Preparation of the Silica Column Loaded with Hexadecylamine Capped Gold Nanoparticle

Silica was treated with an ethanol–hydrochloric acid–water (2:1:1) solution overnight. Later, the Silica was rinsed with double distilled water until supernant water pH became neutral. The packing of the column was done using ethanol as eluent since water makes silica beads float. The silica was saturated by passing 2.5 mL of a 0.01% hexadecylamine capped Gold Nanoparticle solution at a flow rate of 0.75 mL min-1. All experiments were done in a funnel-tipped glass tube as a column for preconcentration. It was plugged with glass wool and then filled with the silica to the height of 1.0–1.2 cm. Before sample loading the column was preconditioned by passing a buffer solution.

2.6 HR TEM Analysis

Structural and Morphological changes of Gold Nanoparticles capped with amine group were done using HRTEM and shown in Figure 1.

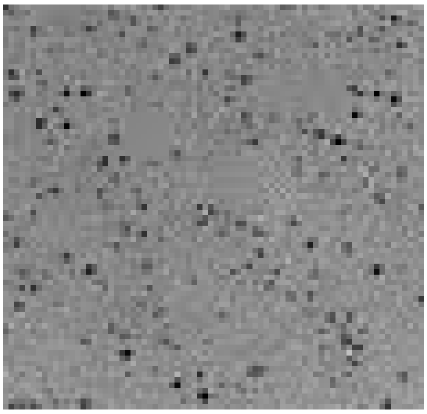

Fig 1. HRTEM images for hexadecylamine capped Gold Nanoparticles

3. RESULTS AND DISCUSSION

During synthesis, the author studied a number of parameters like the length of hexadecylamine chain, reaction time, ratio of hexadecylamine to gold ratio. As per previous literature [17,18] the size of synthesized Gold Nanoparticles decreased with increased in the length of the hexadecyl amine chain. Figure 2 shows UV-Visible spectrum of aqueous solution of hexadecylamine capped Gold Nanoparticles. The hexadecylamine capped Gold Nanoparticles exhibit a Plasmon resonance peak at 540nm. Hexadecylamine capped Gold Nanoparticles results in a positive charge on their surface. Due to this the spectrum wavelength was shifted and increased. It clearly shows that hexadecyl amine concentration was increased during synthesis of Gold Nanoparticles. The effect of hexadecylamine which act as a capping and stabilizing agent shows more capping agent results small Gold Nanoparticles. The result also shows more hexadecylamine direct more surface on Gold Nanoparticles, thereby limiting the growth of Gold Nanoparticles and ultimately leads smaller Gold Nanoparticles.

The size of Gold Nanoparticles capped with hexadecylamine also depends on the rate of reaction time. If rate of reaction time increased led to an increase in the size of the hexadecylamine stabilized Gold Nanoparticles. This procedure provides a reasonably narrow size distribution and control of average particle diameter while allowing for simple changes of surface functionality.

The author further characterized the Gold Nanoparticles capped hexadecylamine using HRTEM are shown in Figure 1. The formation of Gold Nanoparticles capped hexadecylamine is clear from the HRTEM images. The mean diameter of the Nanoparticles as observed from the TEM images is 50 nm.

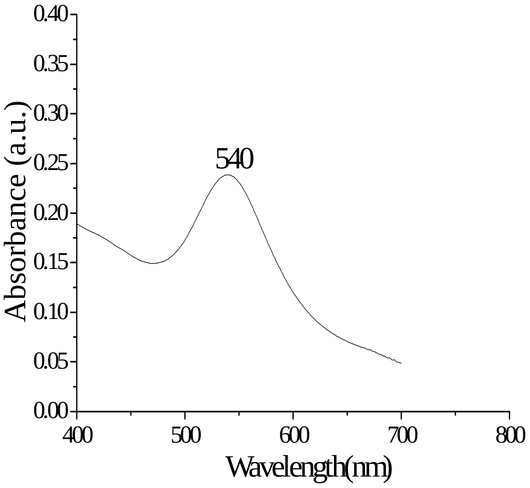

Fig 2 shows UV-Visible spectrum of hexadecyl amine capped Gold Nanoparticles

To assess hexadecylamine capped Gold Nanoparticles practically, these Nanoparticles was employed for real samples to detect Lead concentrations in tap and lake water samples. 10ml of the sample solution was passed through the column filled with silica along with hexadecylamine capped Gold Nanoparticles at a flow rate of 0.75 mL min-1. The trace Pb content of the acidified tap and lake water samples was in between 0.12 to 30 ng mL-1 levels based on FAAS analysis, respectively. Consequently, a certain amount of Lead was spiked into each actual sample to determine the recovery using Hexadecylamine capped Gold Nanoparticles. As shown in table 1 the recovey was from 93% to 99% for the tap water and from 93% to 98% for the lake water samples, respectively. The results are in good agreement with that of existed literature, indicating that the developed hexadecylamine capped Gold Nanoparticles are successfully applied for the determination of lead species in various environmental water samples.

Table 1 shows determination of Lead in water samples using hexadecylamine capped Gold Nanoparticles

Sample	Added(uM)	Found	Recovery (%)	RSD (%)
Tap water	0.6	0.56±0.02	93.3%± 2.0	3.0
	1.0	0.99 ±0.03	99.0%± 4.0	2.7
Lake water	0.6	0.56±0.04	93.3%± 4.0	3.0
	1.0	0.98±0.02	98.0%± 3.0	4.2

CONCLUSIONS

The hexadecylamine capped Gold Nanoparticles provides a novel approach towards the integration of separation, enrichment and detection of target pollutants. The method is simple, sensitive, rapid, and effective. The hexadecylamine capped Gold Nanoparticles gave a good exponential relationship in the lead concentration range of 0.12–30 ng mL-1 with the detection limit of 60 ng mL-1. The hexadecylamine capped Gold Nanoparticles can also be expanded for the detection of other toxic pollutants, present in various environmental samples. This novel approach using hexadecylamine capped Gold Nanoparticles opens a whole new area that could enhance analytical technology for pollutants analysis and for environmental applications.

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