Research Article

Green Silver Nanoparticles (AgNPs) probe for the selective detection of metal ions in the aqueous system

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ABSTRACT

The search for energy-efficient, cost-effective and environmentally sustainable synthetic routes for metal NPs with highly defined properties and biocompatibility is an extremely important and challenging task. Nanoparticles (NPs) functionalization by the use of biologically important substances through a green route is a novel feature of colorimetric sensor architecture. In this work, we mainly discuss about colorimetric sensors. Colorimetric sensors have been extensively studied in sensing biomolecules, metal ions, and so on because their response signals are visible, that is, the results can be directly observed by naked eye. In this study, we use the bifunctional Pomelo (Citrus Maxima) stabilized silver nanoparticles (P–AgNPs) for simultaneous colorimetric detection of Al(III) and the disinfection of synthetic and actual polluted groundwater samples. Under natural sunlight irradiation, the P-AgNPs were prepared using Pomelo leaves extract (PLE) as both the reducing agent and the stabiliser. The on−site analysis from these sensors can be easily observed via the naked eyes or with the help of UV−Vis spectrophotometer. With the recent development in the field of nanotechnology, nanoparticles based colorimetric sensors have emerged as a noteworthy analytical tool for the detection of the metal toxicants. As they possess all the required characteristics and appeared as an excellent substitute for the water remediation. As far as we know, this is the first study to use natural sunlight as a source of energy for the generation of P–AgNPs in an aqueous medium, allowing the process Eco friendly, attractive and effective.

Key words: *Pomelo leaves extract, Silver nanoparticles, Al(III) detection, Colorimetric Sensor*

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INTRODUCTION

In science and technology, one of the quickest developing concepts in the recent years is nanotechnology, which has brought fabulous development. The nanomaterial which comprises distinctive physicochemical properties has the potential to develop incipient systems, structures, devices, and nanoplatforms with impending bids in extensive variety of disciplines**[1,2].**

Nanomaterials are particles that are in nanoscale size, and they are very small particles with improved thermal conductivity, catalytic reactivity, nonlinear optical performance, and chemical stability due to their large surface area-to-volume ratio **[3].** This quality has attracted many researchers to locate novel techniques for their synthesis. Modern industrialization has played a greater role in exacerbating the water quality by contaminating the limited natural water resources throughout the world. The improvement of water quality has become an important area of research for the analytical chemists and scientists. The toxicant present in the water includes volatile organic compounds, inorganic gases, heavy metal such as Pb, Mn, Hg, Ar, Cr, Co, Cd, Zn etc. It is well known that short and long term exposures of these heavy metal ions even at very trace level may cause various dangerous diseases like cancer, skin disease, kidney problems, lungs problem and have also been linked with premature mortality and reduced life expectancy. As a result there is an urgent need for their on-site detection. The use of conventional methods as trace metal detector exhibited major limitations such as complex preparation, expensive, high time consumption and sample preparation which limit the sensor application. Hence, a growing worldwide demand for chemical sensors that accurately and rapidly detect and selectively recognized pollutant species exists. Through conventional techniques (physical and chemical methods) use less time to synthesize bulk amount of nanoparticles. However, they required toxic chemicals like protective agents to maintain stability, which leads to toxicity in the environment. Keeping this in mind, green technology by using plants is rising as an eco-friendly, nontoxic, and safe option. Since plant extract-mediated biosynthesis of nanoparticles is economically advantageous and offers natural capping agents in the form of proteins. **[4]** The use of environmentally benign material like plant extract (leave, flower, bark, seed, peels etc.), fungi, bacteria and enzyme for the synthesis of nanoparticles offers numerous benefits of Eco friendliness and compatibility for pharmaceutical and other biomedical applications as they do not use toxic chemical for the synthesis protocol. Engineered nanoscale materials with particular sizes, shapes, compositions and functions have recently played a leading role in sensor design because of their unique properties such as ultra-small size, low toxicity, conductivity, magnetism, long term stability and show good selectivity and sensitivity for detection of marker even at very trace level i.e. ppm or ppb level. In this work, we mainly discuss about colorimetric sensors. Colorimetric sensors have been extensively studied in sensing biomolecules, metal ions, and so on because their response signals are visible, that is, the results can be directly observed by naked eye. The special equipment for read out results are not indispensable in colorimetric sensors and thus the cost of sensors and hence of tests can be significantly reduced. Application of NPs as sensors are usually based on detecting the shifts in SPR peaks. The on–site analysis from these sensors can be easily observed via the naked eyes or with the help of UV−Vis spectrophotometer. With the recent development in the field of nanotechnology, nanoparticles based colorimetric sensors have emerged as a noteworthy analytical tool for the detection of the metal toxicants. As they possess all the required characteristics and appeared as an excellent substitute for the water remediation.

MATERIALS AND METHODS

Chemical and materials:

Fresh leaves from Pomelo plant were obtained from Kehri Gaon, Premnagar, Dehradun, Uttarakhand, India. Silver nitrate (AgNO3) was obtained from Sigma-Aldrich. Salts of different metals have been bought from Merck Pvt. Ltd and Sigma-Aldrich and were used as provided. The glassware's were washed with aqua-regia and rinsed well with Milli–Q water before using them.

Preparation of P–AgNPs:

For preparing Pomelo leave extract (PLE), firstly pomelo leaves are cleaned with Milli-Q water and then cut into fine pieces. These small pieces were then dried in an oven. Now 3g of dried leaves were crushed into fine powder by mortar pestle and then transferred into a beaker containing 100ml of Milli-Q water. The extract was prepared by boiling leaves at about 37 ° C for 4 hrs.The prepared extract was held for cooling, filtered, and then stored in the refrigerator prior to its use in P–AgNPs synthesis.

For synthesizing the P-AgNPs, a 50 ml of silver nitrate solution (0.001M) was added to various concentrations of PLE (50-1200 μL). The resulting mixture solution was then kept undisturbed in ambient sunlight radiation 13 minutes. The colour of the solution changes from colorless to yellowish brown. This solution was used as a detection probe, which was further characterized and used for the colorimetric detection of aluminium.

Colorimetric detection of Al(III) ions:

For the colorimetric detection of Al(III) ions, 300 µL aqueous solutions of Al(III) of different concentrations were added to a 400 µL of P–AgNPs solution. The mixtures were then kept at room temperature and then characterized by approaches viz. colorimetric and spectrometry.

Instruments:

UV–vis spectra were recorded using a UV–vis spectrophotometer containing double beam in each compartment with a 1 cm path length quartz cell cuvette. The morphology of the surface of P – AgNPs was determined by means of a high-resolution transmission electron microscopy (HRTEM) performed on TENAI instrument at 200 kV. Studies of the zeta potential and dynamic light scattering (DLS) were performed on a Nano series – ZS 90, a Malvern instrument. Fourier transforms infrared spectral experiments were performed using FTIR spectrometer (Shimadzu) to investigate the functional group involved in the synthesis of P–AgNPs and detection of Al(III). This was achieved by drying the samples at room temperature and mixing them with KBR to form a pellet. The FTIR spectra were then recorded in the range 4000 to 400 cm^{-1}The Thermo K Alpha XPS instrument was used to determine the elemental surface composition of the samples. Cyclic voltammogram (CV) was recorded using a computer-controlled 400A electrochemical analyser using Pt electrode as the reference electrode. SERS spectra were recorded with a thermo scientific instrument equipped with Ar laser (λ¼532 nm) and a charge-coupled device (CCD) as the detector. Samples for Raman spectroscopy were prepared on gold-coated slides.

Application of the sensor:

For confirming the practical applicability of developed probe, tap water samples were collected from our research laboratory and used as such without filtration.

RESULTS AND DISCUSSIONS

Selectivity study of the detection probe:

To calculate the selectivity of P-AgNPs towards various metal ions, 300 µL of each metal ion was added to the as-prepared P–AgNPs. After adding various environmentally important metal ions, namely Ba(II), Ca(II), Cd(II), Cr(III), Cr(VI), Hg(II), Co(II), Mn(II), Ni(II), Pb(II) and Zn(II), Mg(II), Fe(II), Cu(II) to the AgNPs solution, no major changes were observed in the SPR spectra of test solutions. However, a significant shift in the size of the SPR band was observed when Al(III) was added. This can be further confirmed by a change in color of the solution of nanoparticles from yellowish brownish to yellow which can be easily detected by the naked eye. However, after addition of other environmentally important metal ions, there is no change in color of the nanoparticles solution. Additionally, the selectivity of the synthesized probe for the Al(III) ions was further confirmed in the synthetic water samples. We have prepared two different types of synthetic water samples with all the metal ions listed above (Sample a & b). The difference between sample a and b was the presence of additional Al(III) ions. Sample a has all of the above mentioned metal ions except Al(III) ions.The prepared water samples a and b were then treated with the P – AgNPs. It is very evident from the fact that P – AgNPs detected Al(III) ions in the sample even in the presence of other important environmental metal ions and gave negative results with the sample a. The results confirm that the this method is highly selective for Al(III) ions even in the presence of other metal ions. However, the method was found to give false positive results when the concentration of other metal ions was higher than 3 ppm in synthetic water samples.

Sensitivity study of the detection probe:

Various concentrations of Al(III) ions were applied to the P – AgNPs to estimate the appropriate detection limit for the prepared nanosensor. The colorimetric results show that a continuous color change from yellowish brown to colorless was observed with an rise in Al(III) concentration from 0.001 to 10 ppm. The change in the peak strength of the UV-vis spectra of the detection probe can be seen after interaction with different Al(III) ion concentrations. A gradual decrease in the SPR intensity along with line broadening and shift towards longer wavelength as a function of Al(III) concentration was observed. The lowest detection limit of the synthesized probe is 0.01 ppm which makes it suitable for the quantitative detection of Al(III) ions in the aqueous systems.

Using Raman spectroscopy the interaction between the P – AgNPs and the Al(III) ions was further explored.The nanoparticles which are largely sized are more sensitive, their stability is lower and this limits their application**.**

Ritu Painuli , Priyanka Joshi and Dinesh Kumar (2018) studied the Cost-effective synthesisof bifunctional silver nanoparticles for simultaneouscolorimetric detection of Al(III) anddisinfection.**[5]**

PRACTICAL APPLICATION

The field application of the synthesized P – AgNPs has been tested in real water samples. The samples were spiked with a known Al(III) concentration and added to solution for AgNPs. UV–vis spectroscopy then analyzed the responses. There is colorimetric response of the P–AgNPs in tap water with Al(III). With the increase in Al(III) ion concentration, the response of the detection probe was linearly increased. The detection probe 's response was somewhat comparable to tap water and to the Milli – Q water. The detection limit of the present method is lower or comparable to other reported Al(III) ion methods. Thus, the present method used for biosynthesizing AgNPs is specific, green and reliable and could be applied in real water samples to detect Al(III).

COST ANALYSIS OF PRESENT NANOSENSOR

The materials required for the synthesizing of the nanosensor were easily available which includes $AgNO_3$. It also includes easily available and inexpensive Pomelo leaves. The estimated average cost for nanosensor (100 ml) is approx. $0.003 USD. This proves that the cost of the developed nanosensor is very much affordable even in the areas having limited-resource setting.

CONCLUSION

We have created a cheaper and greener method for AgNPs synthesis using Pomelo leaves extract under ambient solar energy in an aqueous media. The size of the AgNPs has been changed by altering the capping agent concentrations, the reaction time and the pH of the reaction medium. The pomelo leaves extract acted as the reducing as well as the capping agent for stabilization of the synthesized AgNPs while the stability of the synthesized particles lasts up to 40 days. In aqueous media, the synthesized P – AgNPs were used as colorimetric nanosensors for selective detection of Al(III) over the other heavy metal ions. Due to the color change of the solution, Al(III) could be detected with the naked eyes with a visual detection limit of about 0.001 ppm. However, when the simultaneous presence of other metal ions is more than 3 ppm, then this sensor gives the false positive results. The developed method has many advantages over the other existing methods for detection of Al(III) ion which don't require any modification, difficult instrumentation and is cost-effective which make simple the operation and reduces associated costs. This method provides a new economic, fast , and simple route for potential applications in the analysis of samples of environmental water.

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