

Synthesis and Application of 12-Mercaptododecanoic Acid AuNPs and C-SNSs Sensors for Sensing of Heavy Metal Ions in Water Samples

Anjali, Anamika Srivastava, Shubhangi Yadav,
Shubhangi Singhal, Sakshi

Department of Chemistry, Banasthali Vidyapith, Banasthali, Rajasthan, India

Manish Srivastava

Department of Chemistry, University of Allahabad, Prayagraj, U.P., India

Corresponding Email: sagermanish1@gmail.com

(Received November 21, 2024, Accepted December 05, 2024)

Abstract: Heavy metal pollution is amongst one of the foremost severe environmental downside that results in declination in overall sustainability around the globe. Various efforts are created to construct transportable sensors for analyzing these metals in our surrounding. Insertion of nanomaterials into sensors results in substantial advancement in the efficiency of devices with respect to selectivity, sensitivity, portability and multiplexed detection capability. This review paper presents the efficient sensor for heavy metal detection and further highlights different types of nanosensors and their application in sensing. Out of which Plasmon based nanosensors are the most efficient one. Recent advancement in plasmonic nanosensors has signified modern and extraordinary options towards highly sensitive biological and chemical sensors, and in our perspective, plasmonic nanosensors has wide scope.

Keywords: Nano sensor, MDA (12-mercaptododecanoic acid) –AuNPs, Heavy metal ions, clove silver nanospheres.

1. Introduction

The particles which exist on a nanometer scale are known as **nanoparticles** (i.e. below 100 nm in at least 1D). They can possess various physical characteristics like conductance, uniformity and special optical characteristics that is a boon to materials science and biology.

A common problem encountered today in many countries is water contamination by heavy metal ions. The origin of heavy metal ions in environment is industrial activities. Heavy metals particularly cadmium,

mercury, arsenic, chromium and lead are perilous and destructive even in minute levels. They get easily accumulated in the food chain since they are non-biodegradable, which puts a dreadful menace to humans alongside our environment. Since it has become a matter of consideration for worldwide viability, therefore it is necessary to track down ions of heavy metals in our domain. Some arbitrarily determined methods for measuring heavy metals are mass spectrometry, plasma emission spectroscopy, atomic emission spectrometry, atomic absorption spectroscopy, UV spectroscopy, etc. Since they need tiresome sample fabrication, high-priced instruments etc. so above mentioned characteristics are highly sensitive and selective. Moreover, for on-site determination they cannot be used as portable devices. In contrast to them, sensors are highly competent of on-site detection of multiple heavy metal ions. Active development in nanotechnology has improved the efficiency of sensors w.r.t selectivity, sensitivity and limit of determination. The device that detects the physical or electrical changes and results in an output based on the current conditions or pre-set values is known as a **SENSOR**.

The thiophilic nature of both Au^{3+} and Hg^{2+} has attracted scientists to explore the need of thiol groups for detecting and synthesizing various heavy metal ions. Taking this into consideration, Xue et al proposed selective, water compatible process for detecting trivalent aluminium 5-MMT-Au nanoparticles. These tetrazole functionalized gold nanoparticles were cheaper and readily available. More importantly, with high sensitivity of $0.53 \mu\text{M}$ probe is applicable in water and human urine samples¹. A label free method has been reported for carbon dioxide detection i.e. by persuading aggregation of thiosulphate stabilized gold nanoparticles along with EDTA. Reported system has demonstrated high selectivity and excellent sensitivity with LOD of 2.36 ppb ranging from $0.1 \mu\text{M}$ to $0.7 \mu\text{M}^2$. Gold nanoparticles capped with dopamine dithiocarbamate (DDTC) were stated for detecting bivalent copper ions. Reported probe provide rapid, straightway in situ detection of bivalent copper ions and the colorimetric deviation can be easily visualized by unaided eyes³. 4-amino3- hydrazino-5-mercapto-1, 2, 4-triazole altered AuNPs has been discovered for the selective and sensitive determination of cadmium ion. This criterion provides high limit of detection of 30 nanometre and was effectively used for detecting bivalent cadmium in samples of tap and lake water⁴. Kailasa et al reported malonamidedithiocarbamate (MA-DTC) functionalized gold nanoparticles for detecting bivalent mercury and bivalent copper ions colorimetrically. Reported probe shows LODs 41 nm for bivalent copper and 45 nm for bivalent mercury. The proposed probe was successfully applied in canal, tap, river as well as drinking water samples⁵. Moreover,

silver nanoparticles have also been employed for detecting Ni^{2+} , Co^{2+} , oxalate and phosphate colorimetrically⁶ by using different functional group. However, two to three metal ions were detected in aforementioned methods. Wu et al reported a novel reagent of gold nanoparticles functionalized by hexadecyltrimethyl ammonium bromide (CTAB) and dithizone product for concurrent detection of ten heavy metal ion, hexavalent chromium, bivalent lead, trivalent chromium, bivalent copper, bivalent nickel, bivalent manganese, bivalent cobalt, bivalent cadmium and bivalent mercury. The spontaneous and recognizable change in color of heavy metals provides rapid and easy process for sensing. The color deviation in the solution of nanoparticles is due to various factors which includes cation- π interactions, coordination bond formation, electronic transitions and manganese-induced accumulation of AuNPs⁷. Recently, Kailasa et al reported 5-sulfoanthranilic acid dithiocarbamate (SAA-DTC) functionalized silver NPs for the simultaneous detection of bivalent manganese and bivalent cadmium. LOD for bivalent manganese is 1.7 mM and for bivalent cadmium is 5.8 mM. Both metal ion induced accumulation of Ag nanoparticles results in colour deviation from yellowish to orange⁸. In determination of heavy metal ions amino acid modified nanoparticles were highly sensitive. Since amino acids are easily available so Rajendiran et al reported L-tyrosine stabilized Ag and AuNPs for simultaneous detection of bivalent mercury, bivalent lead and bivalent manganese. These synthesized silver nanoparticles were strongly sensitive to bivalent lead and bivalent mercury ions with LOD of 16 nm under optimized conditions. Although, gold nanoparticles were sensitive to bivalent lead (LOD is 16 nm) and bivalent mercury (LOD is 53 nm)⁹. Another colorimetric test proposed by Guan et al for the sensing of mercury by electrostatic self-assembly strategy by using PGA capped CTAB-gold nanoparticles. Mercury behaves as a cross linker for PGA capped gold nanoparticles causing the aggregation of nanoparticles, established by color deviation from light red to dark purple. This colorimetric assay was extremely sensitive and selective with a LOD of 1.9 nm in real water samples¹⁰. A facile colorimetric test was proposed by Denizli et al using 11- mercaptundecanoic acid-Au NPs for discrimination of seven metal ions when 5 monomers of protein (amino acids (AA)) that were tyrosine, cysteine, histidine, lysine, and arginine were present. The probe showed good selectivity since AA bind to Au nanoparticles and formed complexes with metal ions via groups like amino and carboxyl¹¹. In the synthesis of AgNPs it was theorized that the use of amino acid appended phenolic ligands would ensure interaction of metal ions and functionality of its surface for establishing specific colorimetric sensing. Taking advantage of this fact, Anthony et al developed N-(2-

hydroxybenzyl)-valine and N-(2-hydroxybenzyl)-isoleucine reduced and capped silver nanoparticles for detecting bivalent lead, bivalent mercury and bivalent cadmium. The sensitivity and LOD were regulated by adding distinct co-stabilizing agents like poly vinyl alcohol in N-(2-hydroxybenzyl)-valine-silver nanoparticles and N-(2-hydroxybenzyl)-isoleucine –silver nanoparticles solution¹². Ye *et al* recited in his report, mononucleotide-metal nanoparticles as a detection assay for monitoring of trivalent aluminium under physiological conditions on living cellular surfaces. Aggregation of nanoparticles on addition of Al^{3+} can easily regulate by naked eyes¹³. Wu *et al* recited in his report the aggregation induced probe for the sensing of trivalent chromium by utilizing triphenylphosphate (5-P3O10) functionalized gold nanoparticles. These synthesized particles were greatly stable at room temperature for over half a year and showed a good LOD of 1×10^{-7} M. But working of probe at acidic pH (3.2) limits its application¹⁴. Instantaneous detection of various ions in minute quantities by single probe for various sampling is of immense use. Wu *et al* established and reported modern silver nanoparticles-based system for detecting bivalent manganese and bivalent copper at pH 12.0 and 1.9 respectively. They used hydroxyl propyl methyl cellulose (HPMC) and sodium pyrophosphate ($\text{Na}_4\text{P}_2\text{O}_7$) for stabilizing Ag NPs. Although, LODs was less than the national drinking water standards but the synthesis procedure was time consuming¹⁵. Utilizing the fact that Al^{3+} has high stability constant with citrate, Yang *et al* proposed citrate capped gold nanoparticles for sensitively detecting Al^{3+} at pH 2.9 but its timing was difficult to control rigorously, because¹⁶ after two min nanoparticles aggregate even without Al^{3+} . A method was reported for detecting hexavalent chromium ion in liquid solution by Rajendiran *et al*. The probe was based on the principle that in presence of excess of reductant in Ag NPs, Cr^{6+} gets reduced to Cr^{3+} . Further these Ag NPs underwent aggregation by Cr^{3+} showing a red shift in absorption spectra. The method enables us to detect toxic Cr^{6+} up to nanomolar concentration¹⁷. For instantaneous detection of Cr^{3+} and Cr^{6+} , a new method has been reported by using citrate capped gold nanoparticles. As prepared Au NPs showed good stability in HCl-glycine buffer (3-6) which allowed determination of Cr species in acidic media and eliminate the possibility of metal ion precipitation in neutral or basic media¹⁸. Wang *et al* demonstrated an assay for the sensing bivalent copper ions considering catalytic etching of Au nanoparticles in ammoniacal solution which is hazardous for unaided eyes. The LOD was 0.32 ppb ranging from 10-80 nm but the sensing procedure is quite tedious¹⁹. Bi *et al* proposed Tween gold nanoparticles in three fashions (nano-plates, nano-rods and nano-spheres). In this method, for obtaining a remarkably reduced reaction, sodium

borohydride was utilized to reduce Hg^{2+} to Hg^0 . A solid amalgam-like structure formed when reduced mercury bound with the AuNPs which depicted the topographical features of gold NPs and it decreased its intensity and showed blue shifting of its resonance band. This probe showed a good selectivity and easily applicable on real water samples²⁰. A new method has been reported for the detecting bivalent mercury depending on breakdown of gold NPs after being induced by MPBA. The recognition mechanism showed color deviation from blue to red because of self-dehydration condensation of 4-mercaptophenylboronic acid. The limit of detection using UV-Vis spectrophotometric was insignificant to WHO standard²¹ i.e. 8 nm. An anti-aggregation-based detection probe for Cu^{2+} by using penicillamine-gold nanoparticles was reported by Abbasi- Moayed. Under optimized conditions reported probe show high LOD of 30 nm of L-1 with high selectivity²². Recently, Anthony et al proposed extremely selective detection of bivalent mercury by making use of Au NPs for a wide pH, ranging from 2.0 to 10.0. AA act as reducing agent for different stabilizing agents viz. poly ethylene glycol (PEG), polystyrene sulphonate, Polyoxyethylene (20) sorbitanmonooleate, sodium dodecyl sulphate (SDS), poly(vinyl pyrrolidone) (PVP) and PVA. They showed high selectivity for Hg^{2+} across a wide pH range. System allowed the detection up to ppb level without any interference from other environmentally relevant metal ions²³. Biogenic engineered procedures derived naturally (e.g. from single-celled organisms to higher plants) which utilized non-hazardous, multifunctional reactants (possessing reducing and stabilizing characteristics) are encouraging options for the fabrication of biologically acceptable metal nanoparticles. Over the past decade, different pharmaceutical plants and their derivatives has been used for the fabrication of nanoparticles which makes its use in biomedical, catalysis and biosensors fields and as colorimetric sensors²⁴. Najeed et al proposed a system where they used leaf extract of *Amomum Subulatum* for synthesizing silver nanoparticles. They utilized the synthesized particles for detecting Zn^{2+} with limit of determination²⁵ as 3.5×10^{-6} M. Biocompatible fabrication of silver and gold NPs by making use of citrus fruit residues (like *Citrus limetta*) was revealed by Anthony et al. The synthesized probe showed high selectivity ranging from pH 3.2-8.5 and allowed the detection of Hg^{2+} up to micro molar level²⁶. Anthony et al proposed the fabrication of Ag-nanoprobes for detecting various toxic metal ions in our environment. They used different plants extract for synthesizing silver based nanoprobes, Based on interaction of organic functional group present in residue alongside ions of metal. The superiority of the process was specific determination of toxic metal ions at a vast potential of H range and an excellent sensitivity in the

micro molar range²⁷. Later, Shi et al proposed a new criterion for determining Cr^{3+} by using Xanthocerasorbifolia tannin (XT) attached Au NPs. This new method uses remarkable optical and biocompatible properties of Au NPs made stable by using a natural material and provides a potential medium for rapid identification of Cr^{3+} for analyzing it environmentally²⁸.

2. Classification of Sensors

2.1 Fluorescent Sensors

The basis of fluorescence sensing is the changes induced by analyte in physical and chemical properties of the fluorophores including anisotropy, intensity and lifetime of fluorescence related to the transfer of energy²⁹. While developing light emitting sensors for detecting heavy metals, researchers emphasized on the FRET process. FRET occurs during dipolar coupling of an acceptor and an energy donor³⁰⁻³², with a separation distance of $1/d_6$. The Forster distance or the effective interaction distance is approximately 6 nm. Generally, Forster resonance energy transfer needs spectral overlapping of acceptor's absorbing spectra with donor's emission band³³. One pondered advancement of Forster resonance ET sensors for detecting heavy metal ions^{34,35}. He linked a quencher and a fluorophore to two terminals of a molecular beacon to establish a structure *i.e.* Forster resonance energy transfer sensor (refer to Figure 2.1.1).

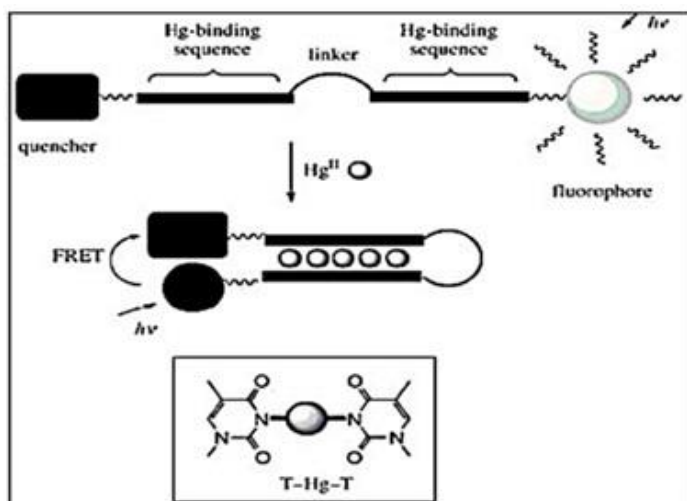


Figure 2.1.1: Sketch of Forster resonance ET sensor on basis of molecular beacon; existence of bivalent mercury ions leading to quenching of light emitting fluorescein.

Small sized (that minimizes steric hindrance) with well entrenched labeling protocols organic dyes, are generally employed as fluorophores in Forster resonance energy transfer sensors because of commercially available toolbox. Although, organic dyes experience fading and show a reduced excitation spectra^{36,37}. Due to their distinct and unique properties, carbon dots, cluster of metals, QDs, GO, and up converted luminescent NPs have been developing as a substitute to organic dyes.

The energy transfer mechanism of Au NPs depends on plasmonic nature when in a fluorophore-quenching method; the organic dye quenching is altered with gold nanoparticles. In case somehow, gold nanoparticles exhibits SPR then the ET from the fluorophore (a quantum dot or an organic dye) to the Au nanoparticles is being followed by the FRET mechanism³⁸. The FRET mechanism is replaced by NSET when no surface plasmon resonance is shown by gold nanoparticles³⁸. Nano metal surface ET induced from the dipole-induced inter-band electronic conversion in a narrow layered semi-infinite metal hemisphere, unlike FRET, that needs profound or sonorous interaction between electrons^{38, 39}. The nano metal surface ET method tracks a separation distance of $1/d^4$ and also poses prolonged effective interaction distance³⁹⁻⁴² i.e. approx. 30 nm. Gold nanoparticles are found to be great light emitting quenchers across varied wavelength and prolonged intervals as compared to organic acceptors^{38, 40, 41}.

Substituting gold nanoparticles in nano metal surface ET sensors, graphene oxide is a fascinating light emitting quencher⁴³⁻⁴⁵ since it is cheaper and can be produced in bulk. It has a facile surface-functionalization feature and admirable water solubility because of intrinsic O-containing functional groups⁴⁶⁻⁴⁹. Further, it also has super fluorescence quenching ability.

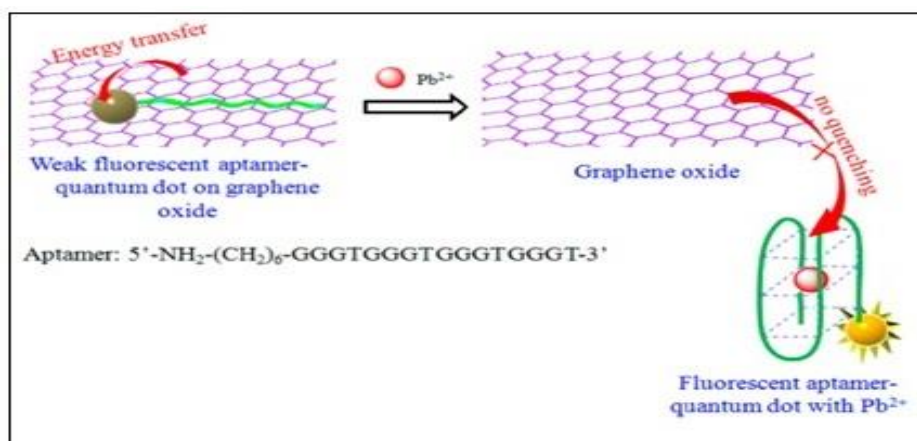


Figure 2.1.2: Diagram depicting a “turn on” fluorescent quantum dot–aptamer – GO sensor for detecting bivalent lead.

Beyond FRET and NSET based conventional fluorescent sensors, chemiluminescent sensors have also gained attention in heavy metal detection^{50,51}. In Chemiluminescence resonance ET sensors, donor's luminescence is transmitted through chemical process which can reduce background noise and rationalize instrumentation of sensing. ET processes have been operated for creating light emitting sensors for detection⁵²⁻⁵⁴. It processes through varied mechanisms including the intramolecular photo induced ET, Dexter interaction, and interfacial ET. The rate coefficient of ET is inversely proportional to distance from nucleus. At lower separation distance (< 1 nanometre) ET is effective⁵⁵⁻⁵⁶. A Quantum Dot-based fluorescent sensor was established for detecting Ag (II) ions and Hg (II) ions by ET mechanism⁵³.

Due to large scattering cross-section of Plasmon's in comparison to its magnitude, large absorption and strong local electromagnetic field, the insertion of Plasmon into Forster resonance energy transfer provides great flexibility for controlling ET mechanism⁵⁷⁻⁵⁹.

Two distinct functions of plasmon in Forster resonance energy transfer are:

- (i) To act as energy acceptor to performs fluorophore quenching.
- (ii) To serve as the third party to modulate ET between an acceptor and the donor⁶⁰⁻⁶⁴.

When plasmon acts as acceptor ideally, it intends to utilize nanoparticles with intense local fields and high absorption cross-sections but with little scattering. This ensures the quenching of fluorescence and further ensures that the plasmon refuse to enhance the fluorescence intensity^{65-67, 72}.

Plasmonics provides two key merits as an acceptor. Firstly it offers the large absorption cross-section that permits excellent quenching efficiencies leading to double the distance as compared to fluorophore-fluorophore Fourier Resonance ET system^{73,74}. Secondly, it does not re-radiate energy when designed properly, hence reducing the background signal levels.

2.2 Plasmonic Sensors: Plasmonic Sensors are two types 1. Nanoparticles - Based Colorimetric Sensors and 2. Chip-Based SPR Sensors.

2.2.1 Nanoparticles -Based Colorimetric Sensors:

The mutual vibration of free conduction e^- within inert gas elements resonating with EMR of incidence which gives rise to Surface Plasmon Resonance^{75, 76}. For example, mono dispersed Au NPs of around 20 nm size show characteristic SP resonance spectra (absorption spectra) in aqueous medium and becomes "red wine". Further it will show any change in color when there will be aggregation of gold nanoparticles to some extent because of shifting in the SPR peak.

Considering this theory, for determining multiple analytes, sensors have been established colorimetrically⁷⁷⁻⁸². Such sensors provide visual, direct, and rapid detection of analyte hence minimizing its cost. The advancement of colorimetric sensing has been established by Joseph⁸³. Till now, the use of colorimetric detection method is for monitoring various heavy metal ions e.g. bivalent Pb, bivalent Cu, bivalent and bivalent as⁸⁴⁻⁹³. Liu et al. proposed a method for detecting bivalent Hg calorimetrically by making use of oligonucleotide-functionalized gold nanoparticles (Figure-3)⁹¹. When bivalent mercury selectively binds to the T-T mismatches there is accumulation of gold nanoparticles which further show color deviation because of coupled SPR spectra of Au nanoparticles in close proximity. This is the reason for the selectivity of Hg^{2+} .

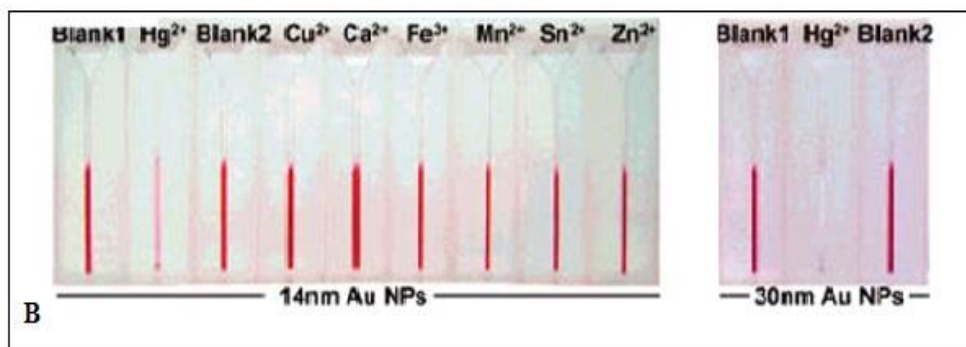
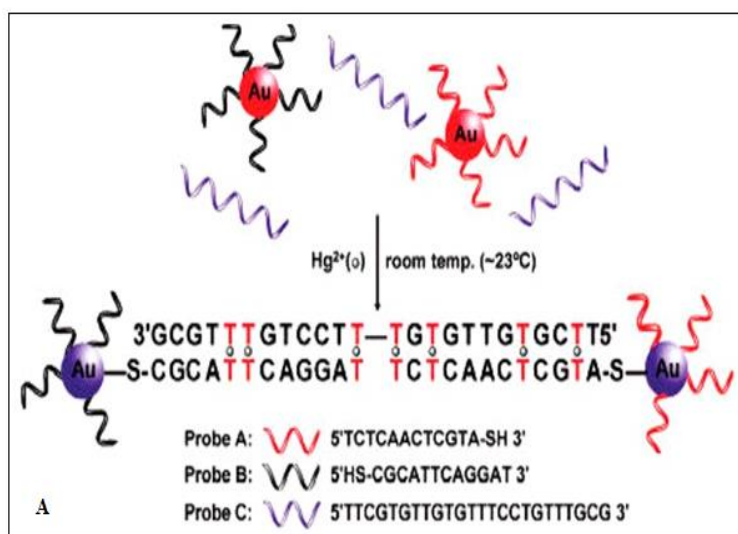


Figure2.2.1: (a) A sensor for the detecting of Hg^{2+} calorimetrically. **(b)** Modification in color of Au nanoparticles {14 and 30 nanometre} on adding ions (bivalent mercury, bivalent copper, bivalent calcium, trivalent iron, bivalent manganese, bivalent tin, bivalent zinc; 10 μM each) to it.

2.2.2 Chip-Based SPR Sensors:

The spectra are sensitive to deviation in the position and intensity of surrounding environment along with the nearby plasmonic field coupling⁹⁴⁻⁹⁶. On this basis the transmission localized SPR has been conducted via plasmonic substrate which specifically seizes metals. During capturing of metal ions on the substrate in refractive index there would be a deviation in resulting SPR spectra⁹⁵.

Three distinct advantages of plasmonic chip-based sensors are:

(i) The simplification in operation and the configuration of the sensor is because of label-free detection, and it further eradicates the utility of various antibodies as engaged in ELISA⁹⁷.

(ii) If we insert plasmonic chip in a flow-cell there would be real time measurement of kinetics of a reaction, which acts as a dynamic means for understanding the binding concept^{98, 99}.

(iii) Formation of long-range SPP modes, resulting in less damping orders of magnitude¹⁰⁰. Small damping in long range SPP results in higher FOM, narrower bandwidths and a perforation depth 1.0 mm onwards¹⁰¹ which specifically analyze life forms¹⁰². LRSP modes are possible only if we insert narrow metal film between two dielectrics of same refractive indexes¹⁰³.

2.3 SERS Sensors

Broadly SERS sensors are used for medical diagnostics, and biological and chemical sensing^{104,105}. Some of the papers have recited the detection of heavy metal ions¹⁰⁶⁻¹¹³. Although it may give the spectral fingerprint signature of analytics as molecular spectroscopy but it is incapable of detecting metal ions directly. Accumulation of gold nanoparticles can be done for detecting them colorimetric ally. Side by side, it may cause plasmonic field coupling of surrounding nanoparticles that would lead to formation of “hot spots” for intensifying SER scattering. Considering previously mentioned criteria, Chen et al. constructed a SER spectroscopy sensor for detecting trivalent arsenic. Surface-enhanced Raman spectroscopy gives information about the element and its chemical structure which is a judicial view in studying the toxicity of metals since many distinct complex structures of heavy metals contain different toxicity levels towards living organisms.

2.4 Optofluidic Sensors

The condensed microfluidic systems that combine microfluidics with optical sensors possessing exclusive characteristics are termed as Optofluidic devices¹¹⁴⁻¹¹⁸. They assist multiple analyte detection in a single chip and further enables real-time disclosure within a reduced volume of sample instantaneously¹¹⁸. The SER spectroscopy substrates in microfluidic surface-

enhanced Raman spectroscopy devices can be inserted into microfluidic ducts in two forms¹¹⁴.

- (i) The nanoparticles of metal acting as substrates of surface-enhanced Raman Spectroscopy are released in the fluid which passes via the passage.
- (ii) At the bottom of a microfluidic passage a nanostructure of metal is fixed as surface-enhanced Raman spectroscopy substrate.

2.5 Electrochemical Sensors

Instead of detecting optically the signal of sensing in case of these sensors is gathered via conducting wires as compared to electrochemical sensors may be wrapped into a dense system easily. Furthermore, the selection criteria towards précised heavy metals can be gained via unconcealed electrodes without the demand of recognition probe because heavy metal ions have the characterized redox potential. Various criteria have been applied in sensing electrochemical sensors (amperometrically, potentiometrically, voltammetrically, impedemetrically, and conductometrically)¹¹⁹⁻¹²¹. The most viable method for determining the heavy metal ions is ASV.

Anodic stripping voltammetry analysis usually consists of two main criteria¹²²⁻¹²⁴:

- (i) Electrochemical sedimentation or aggregation of heavy metal ions electrochemically at a persistent potential to focus onto the surface of electrode.
- (ii) Dispersal of the analyte deposited on the surface of electrode.

First electrode that came into spotlight for detecting heavy metal ions electrochemically was Hg-based electrode because it was remarkably reproducible and has high sensitization power and varied cathodic potential range for detection^{125,126}. Since Hg-based electrode is highly hazardous so eco-friendly Bi-based electrode manifesting similar behavior was preferred over it^{127,128}. Unfortunately, Bi-based electrodes do not have wide cathodic potential range as that of Hg and that's why it becomes unstable when come in contact with air since it gets easily oxidized¹²⁹. Other than Hg and Bi electrodes, glassy C, Au-doped diamond, B-doped diamond electrodes have been considered during anodic stripping voltammetric analysis¹³⁰⁻¹³¹.

2.6 Field effect transistor Sensors

Field effect transistor sensors have been developed when a semiconductor resistor interact with an analyte¹³². They can detect heavy metals label-free in a certain period. Semiconducting nanomaterials specifically 1D and 2D attract field electron transistor sensors as they are highly sensitive due to higher surface to volume ratio^{133,134}. For detecting heavy metal ions, a silicon nano-wire was used to develop a field effect transistor sensor¹³³. This silicon wire prepared sensor possessed high sensitization with limit of detection as

10^{-4} M for bivalent cadmium and 10^{-7} M for bivalent mercury. Using SWCNTs another field effect transistor sensor was developed on the basis of change in conductance due to simultaneous oxidation and reduction between single walled carbon nanotubes and bivalent mercury, which was both selective and sensitive in nature¹³⁵.

3. Fabrication of Gold nanosensors

3.1. Fabrication of MDA (12-mercaptododecanoic acid) -AuNPs

435 microlitres of 0.01087 Molar $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ solutions was mixed in 50 milliliters of water and stirring continued for 10 minutes. Further 10mL of 0.0038 M 12-MDA in ethanol was swiftly poured into gold mixture and stirred continuously (half an hour). The mixture showed yellowish to reddish color deviation which indicated preparation of gold NPs. Now these fabricated gold NPs were kept for centrifugation at 5000 rpm for half an hour to exclude any ionic scum present in the solution and then re-disposed in Millipore water. Lastly, the solution was sonicated for 20min to increase the dispersity of gold NPs.

3.2. Stability and characterization of MDA-AuNPs

MDA-Au NPs were fabricated in one pot by reducing Au^{3+} with MDA which also acts as protecting agent for the fabricated Au NPs. Analogous to the ruby red color of MDA-Au NPs, a characteristic absorption peak was observed at 520 nm (Figure 3.2.1a). The resulting peak was different from the absorption peak of pure MDA (Figure 3.2.1b) which indicates the evolution of nanoparticles.

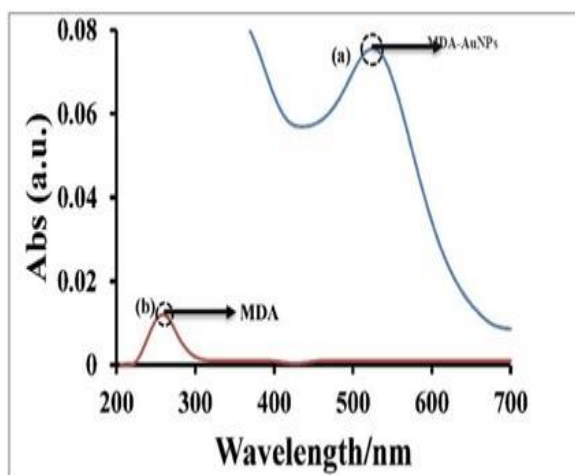


Figure 3.2.1: Ultra Violet-Visible spectra of (a) MDA-Au NPs (b) MDA.

Figure 3.2.2 depicts the FTIR spectra of pure MDA, and MDA-Au NPs. It is apparent from the FTIR spectrum of pure MDA (Figure 3.2.2a), that characteristic peaks at 1699 and 1226 cm^{-1} shows carbonyl and CO stretching oscillation of carboxylic group elements. 1109 and 2851 cm^{-1} spectral peaks are correlative to bent and stretched oscillation of -C-S and -S-H respectively. However, in FTIR spectrum of MDA-AuNPs peak corresponds to -S-H group disappeared (Figure 3.2.2b) which confirms attachment of MDA onto the surface of nanoparticles in such a way that COO^- extruding out from the surface which provides electrostatic stability to the nanoparticles.

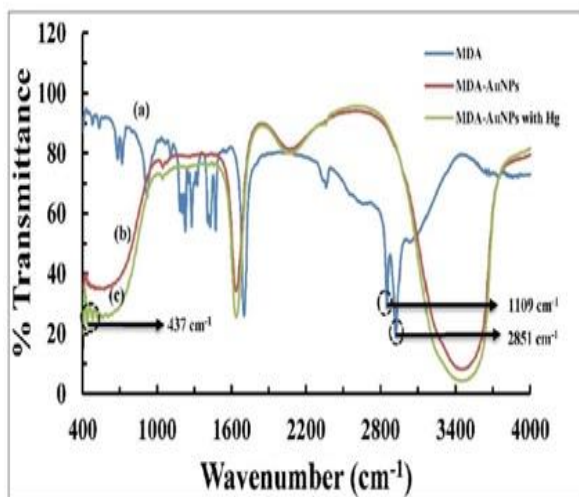


Figure 3.2.2: Fourier Transform Infrared spectra of (a) MDA (b) MDA-gold nanoparticles

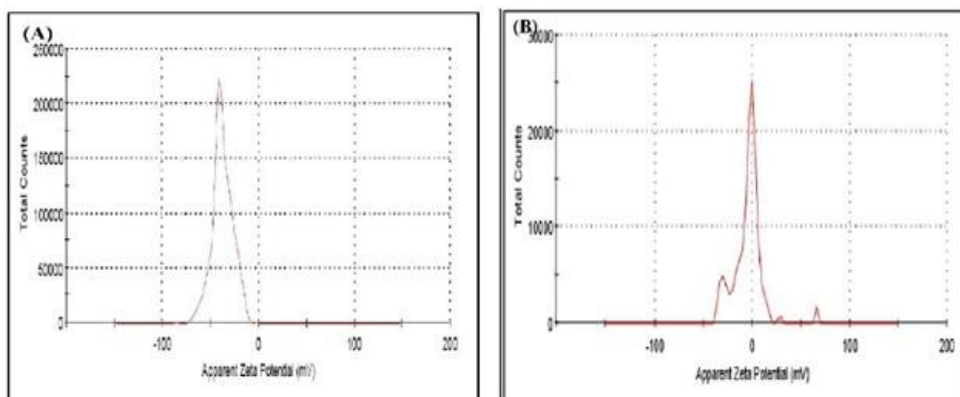


Figure 3.2.3: Zeta potential measurement of (a) Gold nanoparticles and (b) MDA-gold nanoparticles.

Zeta potential of the fabricated nanoparticles was -37 mV (Figure 3.2.3), which shows the electrostatic stability of nanoparticles¹³⁶. SEM image of MDA-AuNPs revealed that the formed AuNPs were well separated, uniform and spherical (~30 nm) (Figure 3.2.4a). DLS measurement was propelled out to show the dispersability and hydrodynamic diameter of MDA-gold NPs. The average diameter of MDA-gold NPs was 52 nm (Figure 3.2.4b).

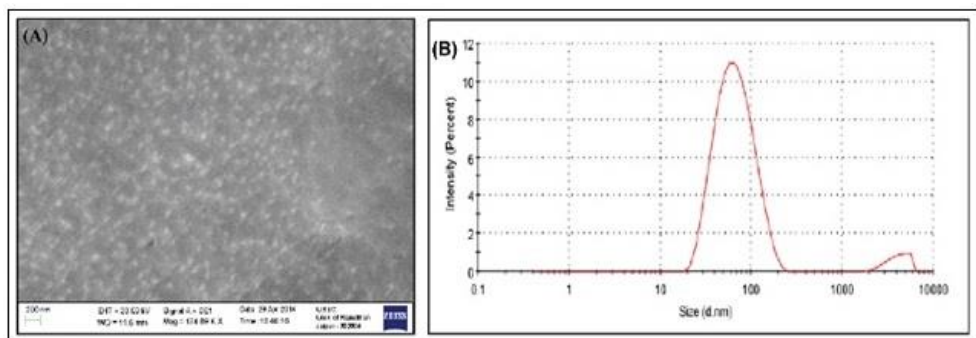


Figure 3.2.4: (a) SEM image (b) Distribution of size of MDA-gold NPs

4. Application of MDA-gold NPs for removal of Hg in water samples

Different concentrations of Hg^{2+} solutions were prepared. From each concentration, 100 μL was added to a tube containing 500 μL of gold NPs and the reaction mixture was kept at ambient condition. After interaction, the solution showed color deviation from red to blue, and SPR spectra was analyzed using Ultra Violet-Visible spectrometer. It was experimented in triad.

For calculating selectivity of MDA-Au NPs, 100 microlitres of different metal ions were added into the 500 microlitres of MDA-gold NPs solution, and their Ultra Violet-Visible spectra were recorded. It is apparent from Figure 4.1a that characteristic peak of MDA-gold NPs not only blue shifted but also decreased in intensity with broadening, when interacted with Hg^{2+} ions. While any remarkable effect on the Ultra Violet-Visible spectra of MDA-gold NPs solution was not shown by other metals. Figure 4.1b presents the sensing response of MDA-gold nanoparticles about various metal ions expressed as absorption difference ($A_0 - A$). The difference of $A_0 - A$ for Hg^{2+} was much higher than that for a panel of other cations which also shows the high selectivity of MDA-gold NPs towards Hg^{2+} . Accumulation of MDA-gold nanoparticles in the presence of Hg^{2+} confirmed by SEM image (Figure 4.2c), and increase in size from 52 nm to 139 nm (Figure 4.2d), further confirm the selectivity of the probe.

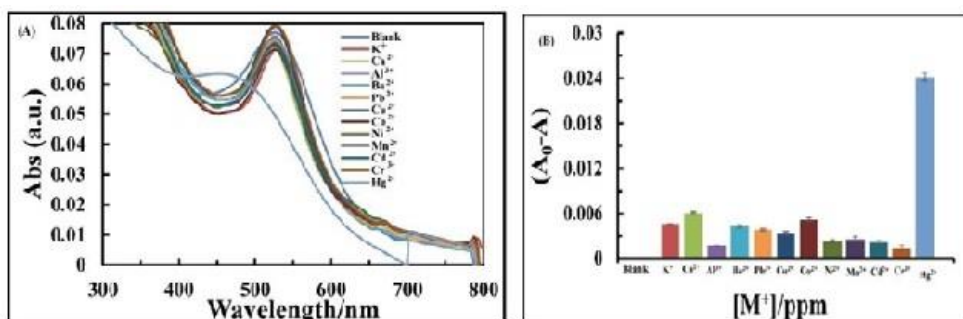


Figure 4.1: (a) Ultra Violet-Visible absorption spectra of the MDA-AuNPs on adding various metallic ions, (b) Corresponding bar graphs ($A_0 - A$) when different metals were present.

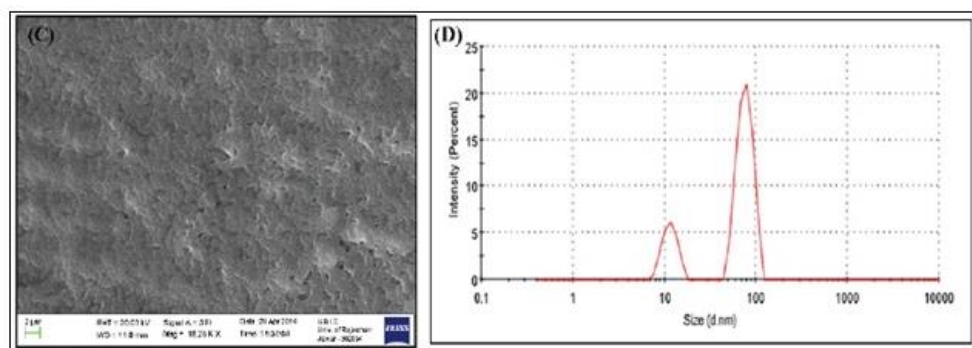


Figure 4.2: (c) Scanning electron microscope image (D) Distribution of size of MDA- gold NPs when $Hg(II)$ ions were present.

Qualitatively demonstrates potentiality of MDA-gold nanoparticles for Hg^{2+} ion, the Ultra Violet-Visible spectra of nanoparticles recorded when distinct concentrations of bivalent mercury were present. As shown in the Figure 4.3a, color of MDA-gold NPs gradually becomes purple which finally become blue as the function of Hg^{2+} ion concentration that can be seen by unaided eye. Additionally, the absorption peak at 520 nm shows blue shift with decreased intensity. At final concentration i.e. 20 ppm the peak completely disappears (Figure 4.3b), which confirms that at higher concentration higher degree of aggregation takes place. Calibration graph was constructed using intensity of absorption band at 520 nanometre (Figure 4.3c). The précised relationship was obtained from 0.1 ppm to 10 ppm range with the correlation coefficient value (R^2) as 0.9907. The LOD was 0.1 ppm for Hg^{2+} ions. The mechanism of detection was based on FTIR analysis and theoretical studies. A new peak appeared at 420 cm^{-1} in FTIR spectra of MDA-Au NPs with Hg , which confirms the interaction of Hg^{2+} with Au NPs. Heavy metal ions like Hg^{2+} ($5d^{10}$) and Au^+ ($5d^{10}$) have very strong relativistic effects causing high

specificity and great dispersion forces between closed-shell metal atoms^{137,138}. As a result of specific d¹⁰-d¹⁰ metallophilic interactions, Hg²⁺ adsorbs on the surface of the Au nanoparticles. On the contrary, the enormously high affinity of thiol containing ligands¹³⁹ for Hg²⁺ may cause the breakage of Au-S bonds.

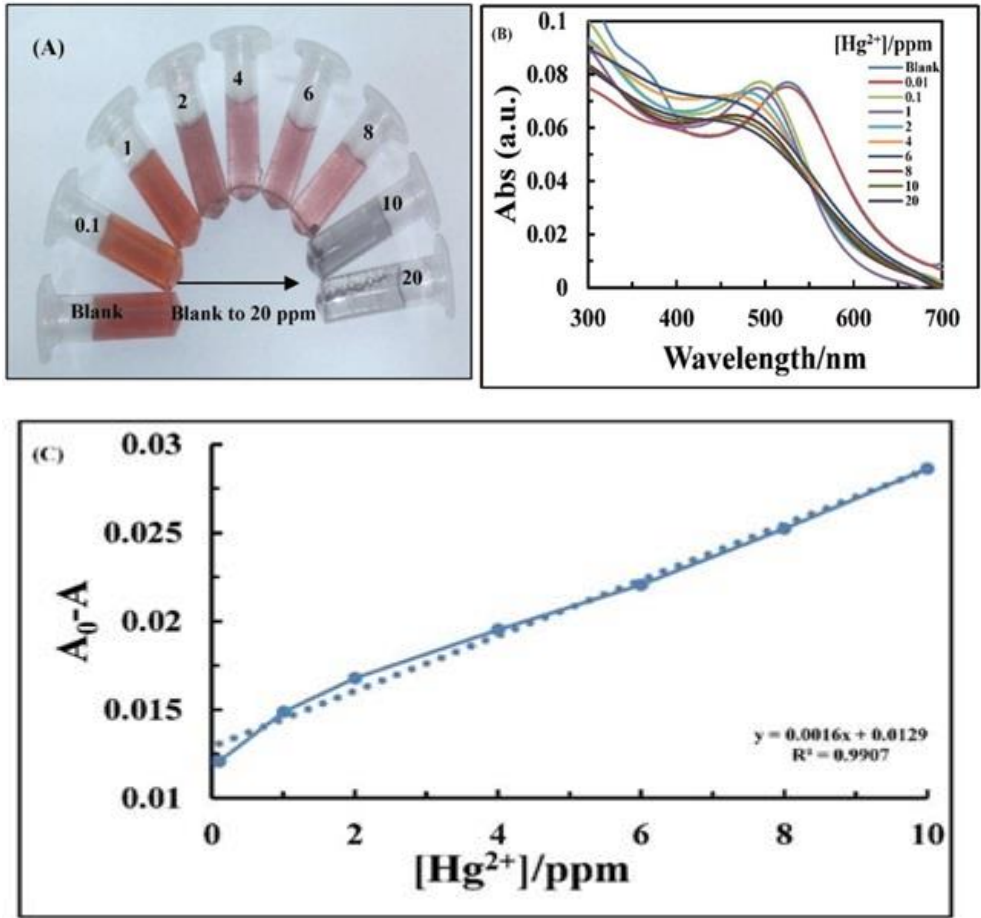


Figure 4.3: (a) Visible change in color (b) Ultra Violet-Visible spectra of MDA-gold NPs in response of Hg²⁺ (c) Corresponding linear calibration plot for different concentrations of Hg²⁺ from 0.1-10 ppm A₀-A.

To calculate the practical suitability of MDA-gold nanoparticles as sensor, Hg²⁺ (0.2 and 5.0 parts per million) was perforated with the tap water samples and analyzed by aforementioned procedure. Results of tap water sample are shown in table below. These outcomes revealed that present strategy demonstrates good recuperations in the range of 90-105 % Hg²⁺ ions. Hence, this process can be used for detecting Hg²⁺ with accuracy and precision.

Table-1: Hg²⁺ detection in tap water sample by above prepared MDA-gold NPs probe.

SAMPLE	ADDED AMOUNT (ppm)	FOUND AMOUNT (ppm)(mean $\pm$ E, n=3)	RECOVERY (%)
Domestic tap water	Blank	0	-
Hg ²⁺	0.19	0.18 $\pm$ 0.01	94 $\pm$ 5
	4.9	4.8 $\pm$ 0.22	98.6 $\pm$ 4.4

5. Fabrication of Silver nanosensors

5.1 Fabrication of C-SNSs (clove silver nanospheres)

Seeds of clove were bought from the domestic market. Seeds were grounded into powdered form and stirred up in a 250 milliliters beaker with 100 milliliters of Millipore water at 35 degree Celsius for two hours. After turbulence, it changed to dark brown color. By making use of Whatman filter paper (25 μ M pore size) the solution was filtered, and kept under cold conditions for storage before using it for preparation of Ag nanospheres. Clove-SNSs were fabricated at pH 4.5 and 11.5 with little alteration in aforementioned report¹⁴⁰ by reducing AgNO₃ at room temperature with clove seed extract. 50 mL solution of AgNO₃ with varied volumes (50-850 μ L) of clove extract was mixed at pH 4.5 for synthesizing the detection probe and further stirred for few hours. The color showed deviation from transparent to light yellow. Similarly, by adjusting pH value at 11.5 detection probes was synthesized using sodium hydroxide. The color showed deviation from transparent to dark yellow. Until their use the prepared solutions were kept in encompassing environment.

5.2. Stability of Clove-Silver Nanospheres

The detection system is meant to be stable during colorimetric analysis. So, the stability of nanospheres was examined using Ultra Violet-Visible spectroscopy in reference with pH, time and volume of clove extract.

Starting with pH, ranging from 4.5 to 13. While adjusting the pH range, it deviated to pH 11.5 and no further deviation was examined after it, even up to pH 13. Surface Plasmon Resonance Spectra reflected the difference in color. On increasing pH from 4.5 to 11.5, the intensity and the sharpness of Surface Plasmon band too showed increment from 424 to 407 nm with a blue shift. This confirms the stability of nanospheres at pH 11.5. Initial pH of prepared silver nanospheres was 4.5 and as mentioned earlier and was maximum stable at pH 11.5, so their felicity was checked at pH 4.5 and 11.5 for detecting them colorimetrically.

Moving on to the effect of volume of extract, various volumes of the clove extract was poured into AgNO_3 solution ranging from 50 to 850 μL . With change in volume, the color showed deviation from transparent to yellow (Figure 5.2.1a). This was examined using Surface Plasmon Resonance spectra. As the Figure 5.2.1b clearly depicts the increment in the intensity of the peak with volume (50 to 450 μL). Further increase in volume 650 to 850 μL leads to an immense color deviation from yellow to reddish brown with a broadened peak. That's the reason for selecting 450 μL of extract over 850 μL for the stabilizing the clove silver nanospheres.

Lastly, the reaction time was meant to be controlled while preparing nanospheres. With increase in reaction time from 5 to 120 minutes, colorless solution of AgNO_3 darkened (Figure 5.2.1c). Figure 5.2.1c confirmed that no optical absorption was seen after 5 minutes in 400 to 500 nanometre range; only a shoulder appeared at 385 nm which disappeared with time. With time, a new peak appeared at 424 nm which sharpened at 65 minutes, it showed increase in intensity from 65 to 120 minutes without any remarkable change in its place. It depicts that Ag^+ ion reduced to Ag atoms with a time lapse of 65 minutes.

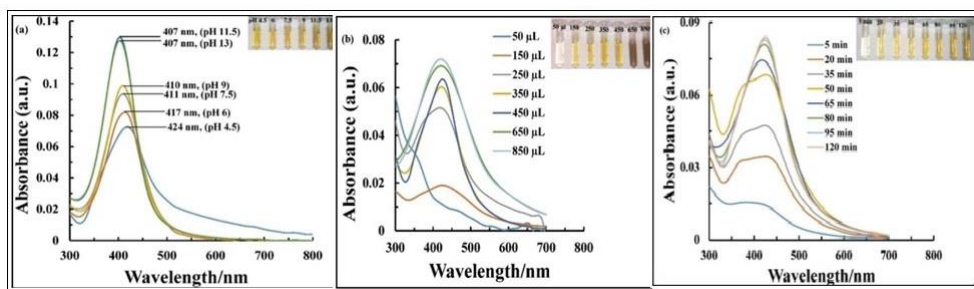


Figure 5.2.1: Surface Plasmon Resonance spectra of clove nanospheres presenting effect of (a) pH (b) volume of extract (c) reaction time. Inset images show deviation in color accordingly.

5.3. Characterization of Clove-Silver Nanospheres

Ultra Violet-Visible spectra of AgNO_3 , extract of clove seed, and solution of clove silver nanospheres represented in Figure 5.3.1. In 350-500 nm regions, AgNO_3 and clove extract did not show any peak. The Ag^+ ions were reduced to nanospheres when clove extract was present and this was confirmed when a new SPR peak arose at 424 nm at pH 4.5 and 407 nm at pH 11.5. The internal structure and the size of the nanospheres were analyzed by SEM and Transmission electron microscope images at pH 4.5 (Figure 5.3.2a) and pH 11.5 (Figure 5.3.2c) respectively. The mean diameter of nanospheres was analyzed as 38 nm and 24 nm at pH 4.5 and 11.5 respectively. The particles were spherical and well distributed in aqueous medium was confirmed by

TEM and SEM images. The charge on the surface of nanospheres was calculated using zeta analyzer. The zeta potential of nanospheres inclined from -35 mV at pH 4.5 to -46.3 mV at pH 11.5 (Figure 5.3.3 a & c). The increment in charge resulted in aggregation on the surface of nanospheres and its (nanospheres) electrostatic stability¹⁴¹. The most important component for extract is eugenol¹⁴². In this, methoxy and allyl (electron withdrawing groups) are presented at ortho and para position of hydroxyl group because of which eugenol can release a $-\text{OH}^+$ and convert into an anion. The resonating structures further stabilize this anionic form. Because of +I effect of withdrawing groups and their capability of forming stable resonating structures, eugenol discharge 2e^- instantaneously, 1e^- from $\beta\text{-C}$ and 1e^- from CH_2 group present just after double bond. They cause reduction of Ag^+ ions into Ag^0 atoms, which again collide to make nanospheres.

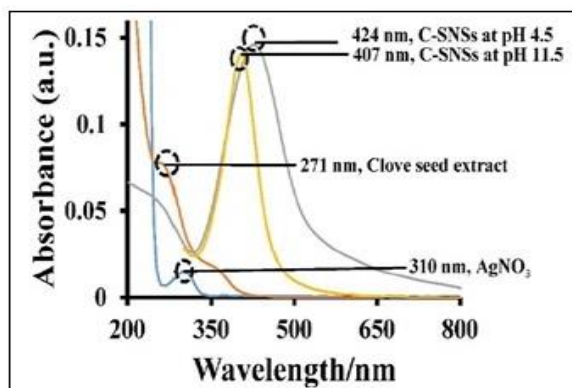


Figure 5.3.1: Spectra of Surface Plasmon Resonance of AgNO_3 mixture, clove extract, Clove-Silver Nanospheres at pH 4.5 and 11.5.

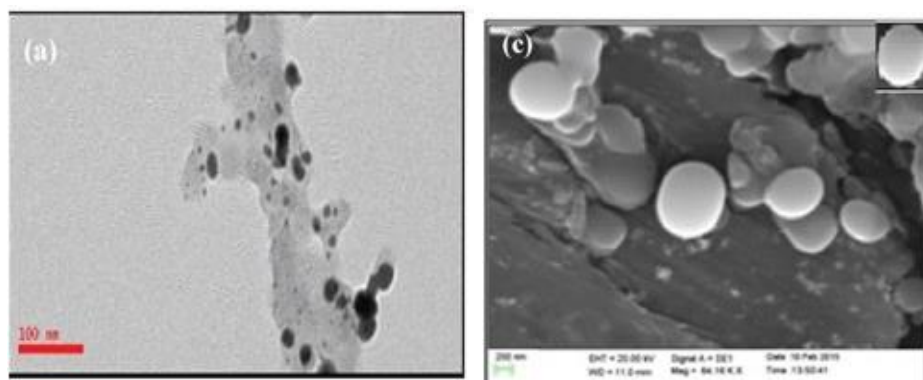


Figure 5.3.2: Transmission electron microscope images of Clove nanospheres at pH 4.5 in (a) When Cr^{3+} ions were absent. Scanning electron microscope images of Clove nanospheres at pH 11.5 in (c) When Mn^{2+} ions were absent; inset (spherically shaped spheres)

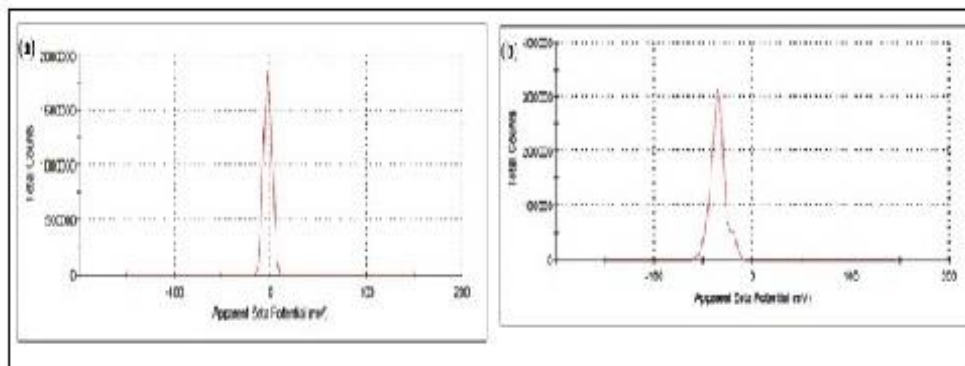


Figure 5.3.3: (a) Distribution of zeta potential of nanospheres at pH 4.5 (c) Distribution of zeta potential of nanospheres at pH 11.5

6. Application of Clove-Silver Nanospheres for detecting Cr^{3+} and Mn^{2+} ions colorimetrically in water samples

By preparing detection probe at pH 4.5 and 11.5, the colorimetric detection of Cr^{3+} and Mn^{2+} was accomplished respectively. In $800\ \mu\text{L}$ of respective detection probe solutions, $200\ \mu\text{L}$ aqueous solutions of both Cr^{3+} and Mn^{2+} of varied concentrations were poured individually. For about half an hour, the detection systems were stored at room temperature and later their characterization was done colorimetrically and spectrometrically.

The selection was calculated for Cr^{3+} and Mn^{2+} along with other salient metal ions present in our environment which involves bivalent calcium, bivalent cadmium, bivalent copper, bivalent mercury, bivalent zinc, bivalent nickel, bivalent lead, bivalent cobalt, potassium, trivalent iron, trivalent and hexavalent chromium, bivalent barium, bivalent manganese and trivalent aluminium. Experiments were carried out three times to check their selectivity.

Figure 6.0(a) shows that on adding Cr^{3+} at pH 4.5, a new peak generates at 596 nm and the presence of metal ions does not affect the spectra. On plotting absorption intensity ratio ($A_{596/424}$) of nanospheres against concentration of metal ions (Figure 6.0b), the selection of Cr^{3+} at pH 4.5 was quantified. As compared to other metals, Cr^{3+} induced value of $A_{596/424}$ was higher which represents its distinct interaction with nanospheres. Although, absorption ratio for Al^{3+} ion is greater than other metals but significantly lower than Cr^{3+} ion, which signifies its less selection towards Al^{3+} compared to Cr^{3+} . When Cr^{3+} interacts with nanospheres, there is enhancement of value of $A_{596/424}$ and a new peak generates, affirmed by color deviation from yellow to transparent which can be seen by unaided eyes (Figure 6.0c).

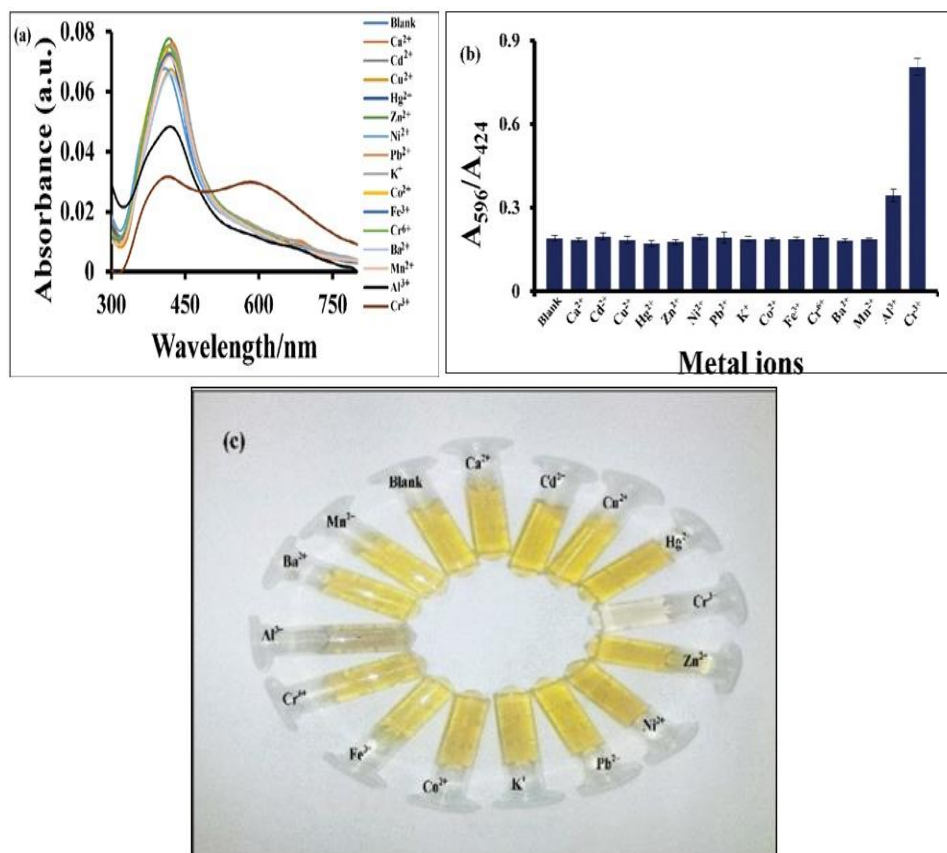


Figure 6.0: Selection of prepared nanospheres probe at pH 4.5 for the Cr^{3+} .

(a) Surface Plasmon spectrum of various metals (b) Bar diagram showing specificity of nanospheres based probe for the Cr^{3+} , error bars showing change due to repetition of experiments (c) Optical images of nanospheres when different metal ions were present.

Clove extract composes compound having phenol as functional group e.g. eugenol, flavanoids, hydrolysable tannins, gallic acid and hydroxyl cinnamic acids¹⁴³. Compounds containing phenol and $-\text{OH}$ group possess great tendency to bind with Cr^{3+} ion¹⁴⁴. According to the outer electron configuration of $3d^3 4s^0 4p^0$, Cr^{3+} ion is small-sized, a strong chelating agent and have higher effective nuclear charge. Therefore, it falls in category of hard Lewis acids and can form bonds with oxygen (having negative charge) of poly phenols and its binding decrease zeta potential of nanospheres from -35 to -2.0 mV. This declination in potential depicts the strong binding capability of Cr^{3+} ion with nanospheres which completely neutralizes the nanospheres and initiates their accumulation. Similarly, on adding Mn^{2+} at pH 11.5, Surface Plasmon spectra shows deviation while the presence of other

metals does not affect the spectra (Figure 6.1a). On plotting various metals against A_0-A (A_0 = absorbance of nanospheres when other metal ions were absent, A = absorbance of nanospheres when other metal ions were present), its selection was checked thoroughly (Figure 6.1b). The value of A_0-A for Mn^{2+} is larger as compared to other metals which suggests selection of nanospheres for Mn^{2+} ions. Figure 6.1c clearly depicts that accumulation of nanospheres caused by Mn^{2+} results in deviation in color from yellowish to reddish brown while no deviation in color was observed due to other metal ions. Mie proposed a theory based on the fact that with decrease in distance of particles, their radii and SPR band possessed decreased intensity and broadening^{145,146}. This internal change depicts that on adding Mn^{2+} , the spherical morphology made of ionic interactions was distressed¹⁴⁷.

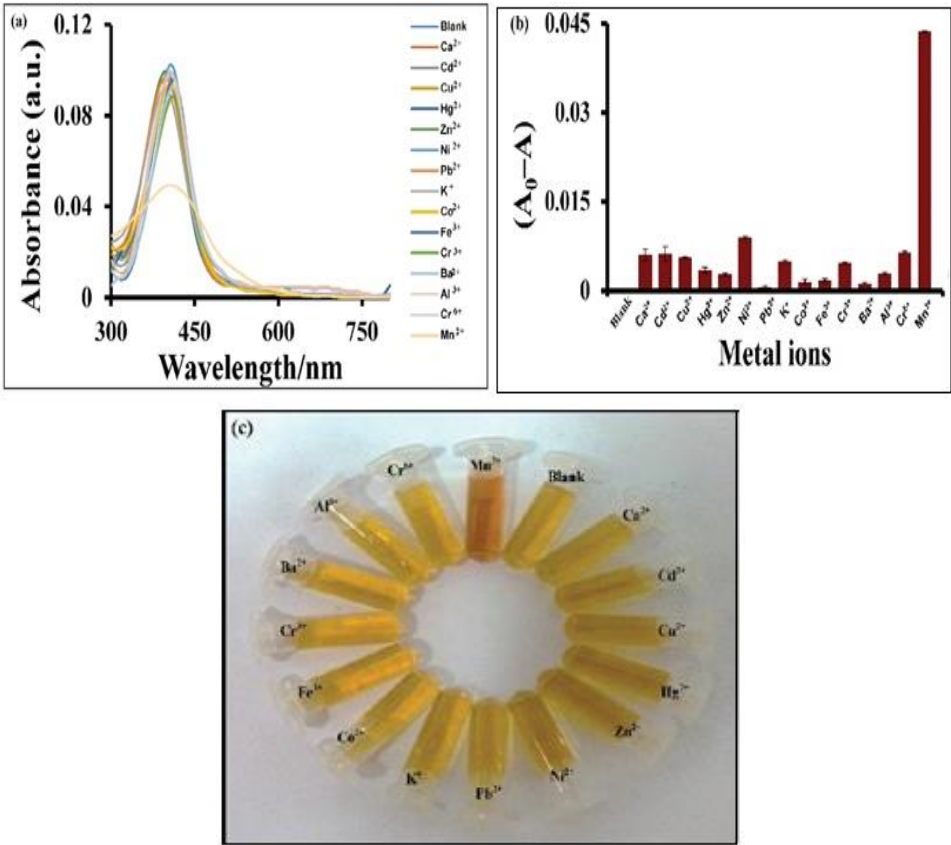


Figure 6.1: Selection of prepared nanospheres at pH 11.5 for the Mn^{2+} ions (a) Surface Plasmon Resonance spectrum (b) Bar diagram showing the specificity of nanospheres for Mn^{2+} comparative to other metal ions, error bars showing change due to repetition of experiments (c) Optical images of nanospheres, while metals were present.

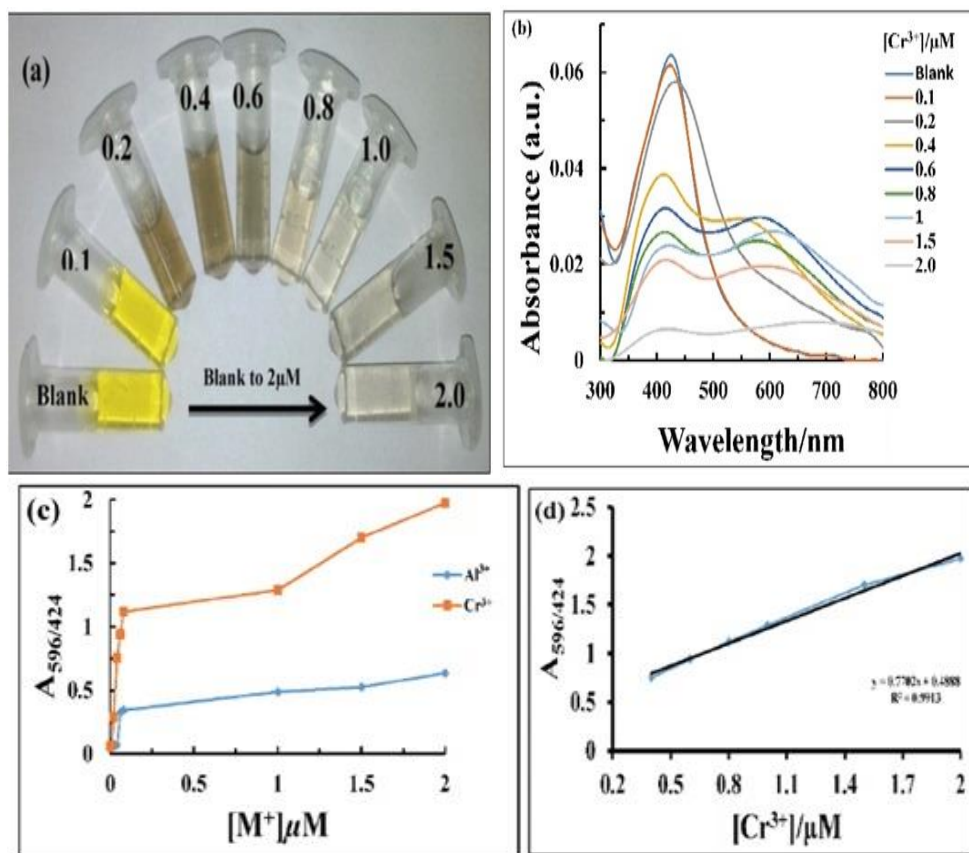


Figure 6.2: (a) Optical images (b) Surface Plasmon Resonance peak of nanospheres when varied concentrations of Cr^{3+} (0.1–2.0 μM) at pH 4.5 were present. (c) Response of $A_{596/424}$ as means of concentration of various metal ions (trivalent aluminium and trivalent chromium) (d) Plot of $A_{596/424}$ as means of concentration of Cr^{3+} depicting linearity of $A_{596/424}$ values of nanospheres probe solution at 424 nm.

Varied concentrations of Cr^{3+} and Mn^{2+} ions were added into nanospheres solution for calculating limit of detection of prepared probe. On detecting colorimetrically, we found that if we increase Cr^{3+} ion conc. From 0.2 to 2.0 μM then we will observe color deviation from light yellow to colorless (Figure 6.2a). 0.2 μM is the limit of detection for Cr^{3+} ion. Although, Cr^{3+} ion has dissimilar reaction rates but the ultimate outcome was similar at varied conc. Due to continuation of reaction until complete accumulation of nanospheres. Figure 6.2b shows surface plasmon spectra of detection on collision with different concentration of Cr^{3+} at pH 4.5. On adding Cr^{3+} to detection system, a peak generates at 596 nm which later disappeared at ultimate concentration of 2.0 μM and along with this, it decreases the intensity

and cause red shifting of plasmon band. Figure 6.2c depicts that Al^{3+} too is responsible for color deviation of nanospheres. To quantitatively understand the sensitization of nanospheres, a graph depicting ratio of A596/424 against the concentration of Al^{3+} and Cr^{3+} metal ions was plotted which explains the sensitivity of nanospheres towards Al^{3+} and Cr^{3+} at pH 4.5. Figure 6.2c depicts that at low concentration, Cr^{3+} ion influence interparticle alliance of nanospheres causing deviation in spectra although, at high concentration Al^{3+} displayed a small deviation. That's why, nanospheres show high sensitivity for Cr^{3+} than Al^{3+} . Later it was applied for measuring Cr^{3+} in solution quantitatively (Figure 6.2d). The concentration of Cr^{3+} ions ranging from 0.4–2.0 μM were used to create calibration curve showing linearity ($R^2=0.9913$) up to 2.0 μM .

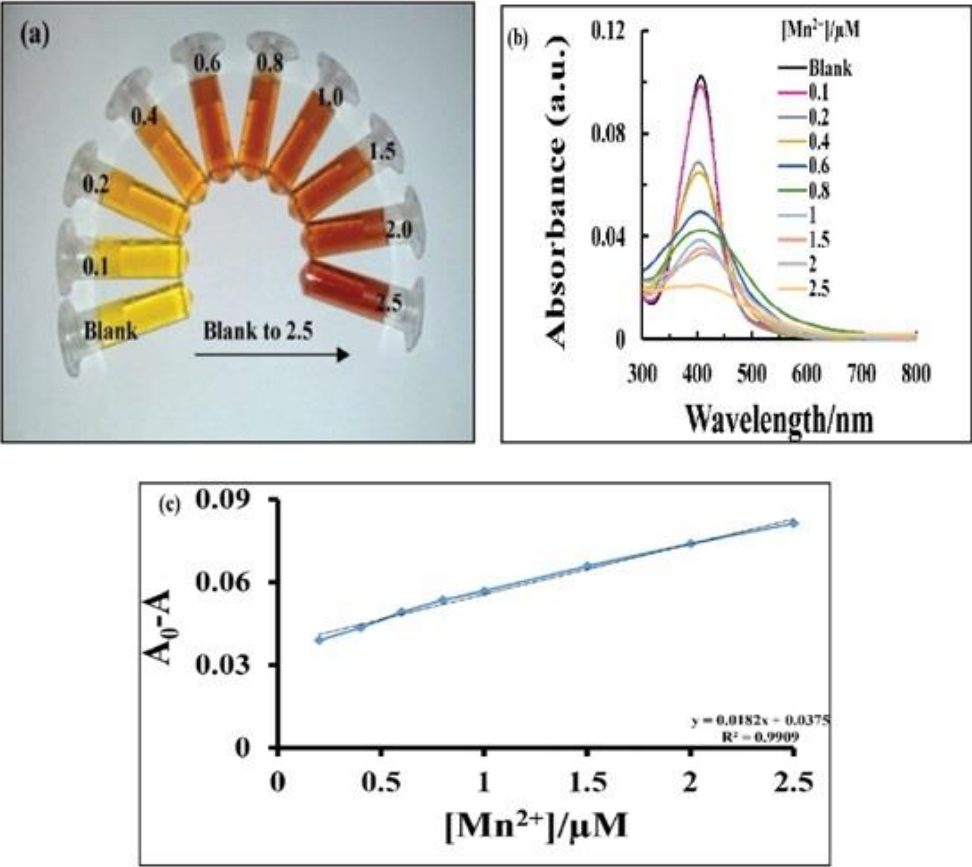


Figure 6.3: (a) Optical images of nanospheres. (b) Surface plasmon spectra of nanospheres based detection system in presence of different volumes of Mn^{2+} ranging from 0.1-2.5 at pH 11.5 (c) Plot of A_0-A against concentration of Mn^{2+} at pH 11.5.

With increase in concentration from 0.2-2.0 μM of Mn^{2+} , it showed color deviation from dark yellow to reddish brown (Figure 6.3a). The limit of determination for Mn^{2+} is 0.2 μM . Figure 6.3b reveals the spectra of the detection system at pH 11.5, when it interacts with vivid volumes of bivalent manganese ions. As the concentration of bivalent manganese increase, the intensity decrease with a progressive shift towards a broadened longer wavelength which lately disappeared at 2.5 μM concentration. Figure 6.3c depicts direct relation between absorption intensity and Mn^{2+} ion concentration ranging from 0.2–2.5 μM with 0.9909 correlation values.

Table-2: Comparison of the performance of various sensors for Cr^{3+} and Mn^{2+} .

Detection System	Metal Ion	LOD/ μM	Reference
C-SNSs	Cr^{3+} , Mn^{2+}	0.20	Current experiment
PMAA @ Au NPs	Cr^{3+}	40	149
$\text{Na}_4\text{P}_2\text{O}_3$ and HPMC SNSs	Mn^{2+}	0.50	153
Citrate- Au NPs	Cr^{3+} , Cr^{6+}	4.0	150
Dopa- Au NPs	Mn^{2+}	5.0	152
XT- Au NPs	Cr^{3+}	3.0	148
NTP @ Au NPs	Cr^{3+}	1.4	151

The efficiency of biologically acceptable nanospheres based detection system for Cr^{3+} and Mn^{2+} ions compared with indicated sensors (refer to aforementioned table). The efficiency of sensitization and fabrication of suggested detection system makes this system preferable over others.

Table-3: Detection of Mn^{2+} and Cr^{3+} in samples of tap water by our prepared Clove-SNS probe.

Sample	[M^{n+}]/ μM	Mn^{2+} and Cr^{3+} found (mean $\pm$ E, n=3)	Recovery (%)
Domestic tap water	Blank	0	-
Mn^{2+}	1.5	1.39 ± 0.02	92.66 ± 1.34
	2.0	2.2 ± 0.09	110 ± 4.5
Domestic tap water	Blank	0	-
Cr^{3+}	1.5	1.47 ± 0.10	98 ± 6.6
	2.0	1.92 ± 0.05	96 ± 2.5

The probe synthesized at pH 4.5 and 11.5 was checked on domestic tap water, to improve the efficiency of detecting. The contamination caused by Cr^{3+} and Mn^{2+} in domestic water was lower than limit of detection of prepared probe, so it needed to be contaminated with Cr^{3+} and Mn^{2+} and results were checked

colorimetrically. The probe shows an increase with increase in concentration of metal ion. The result was analogous for Millipore water as well as tap water which ensure the detection Cr^{3+} and Mn^{2+} without intervening contagions. At lower concentration, there is accuracy with R2 values of 0.9942 for Cr^{3+} and 0.9926 for Mn^{2+} . To further manifest the applications of nanospheres, a restoration test was done with Cr^{3+} and Mn^{2+} contagioned tap water (1.5-2.0 μM). The mean percent recovered for nanospheres range from 91.32 to 114.50, which ensures the usefulness of prepared nanospheres for detecting Cr^{3+} and Mn^{2+} ions in real water samples.

7. Conclusion

In this paper we deliberated the recent advancement in sensors and their classification. Out of which Plasmon based nanosensors are the most efficient one. Recent advancement in plasmon-based sensors has greatly overpower the disadvantages of optical sensors with respect to tenability, photo stability, sensitivity and in vivo applicability, by utilizing nanostructured materials. Plasmonic nanostructures can be implemented for detecting analytes biologically and chemically, and prominent ways to reform the sensitivity. Recent advancement in plasmonic nanosensors has signified modern and extraordinary options towards highly sensitive biological and chemical sensors, and in our perspective, plasmonic nanosensors has vivid scope. Further we have discussed about the fabrication of Au and Ag nanoparticles and their sensing operations.

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