The present thesis entitled “Design of plasmonic nanosensors for the detection of heavy metal ions in water” deals with the synthesis of various plasmonic nanoparticles for the detection of different heavy metal ions from aqueous media. The thesis comprises seven chapters. The first chapter deals with the problems associated with heavy metal ions exposure to environment and the need of their detection. It explains colorimetric nanosensors as the solution for the problem. This followed by the review of literature which deals with the recent trends in the field of colorimetric sensing. In the next chapter analytical techniques utilized for the characterization of nanosensor has been addressed. The next section describes the synthesis of various nanosensors i.e. C-SNSs, C-AuNPs, L-dopa-AgNPs, P-AgNPs, I2CA-AgNPs, C-AgNPs, MDA-AuNPs, and gelatin-AuNPs and their application in detection of many heavy metal ions in water.

7.1 Summary

The thesis consists of seven chapters, conclusions of which are described below.

Chapter first highlights the origin of heavy metal ions and their toxicological effect on environment and human health. Some of these heavy metal ions are desirable for human being but most of them pose a harsh effect on human health and environment. Some of the effects are discussed in the chapter. In general, they cause dermatitis to lung and kidney cancer damage of the nervous system, loss of memory, listlessness, and damage to brain, liver and the central nervous system. Chapter explains various conventional methods for detection of heavy metal ions and the various shortcomings associated with these methods. It briefs the advantages of colorimetric nanosensors over conventional methods. It gives a detail knowledge on basics of nanochemistry such as nanotechnology, nanoscience, and nanomaterials. A brief history, classification, and various methods of synthesizing nanoparticles with their advantages and disadvantages are discussed. A quick insight on green approach for the synthesis of nanoparticles with their benefits over chemical reduction method is also discussed. It provides an overview of the unique properties of plasmonic nanoparticles which make them popular over their bulk counterparts. Optical property i.e. SPR of the nanoparticles is explained in detail. Effect of various parameters such
as size, shape, aggregation of particles on the SPR of nanoparticles and the relation of SPR with the color of nanoparticles is described. The chapter also presents an overview on the science and technology behind the sensing of heavy metal ions by nanoparticles. As the stability of particles is a major parameter for a sensor a detailed explanation on the electrostatic and steric stability of nanoparticles is provided. At the end of the chapter scope of the thesis is outlined.

**Chapter two** represents the review of literature related to the plasmonic nanoparticles as nanosensor for the detection of heavy metal ions. Recent trends in synthesis of nanoparticles using aqueous as confined media with the objective to make them easily applicable in biological and environmental samples are discussed. Recent advancement in the synthesis of nanoparticles by utilizing various chemical moieties such as Schiff bases, ionic liquid etc is also presented. Based on the fact of high thiophilic affinity of nanoparticles and heavy metal ions, various nanosensor for the detection of these toxicants is discussed. Synthesis and application of various biocompatible sensor synthesized by utilizing various amino acids and protein is addressed in brief. An overview of the exciting and rapidly growing field of utilization of plant extract as GMA for the synthesis of nanoparticles has been highlighted through example of recent work of the several groups. It is intended to familiarize the reader with the basic assumption about problem solving that went into design of this research program and the interpretation of the results.

**Chapter three** serves as a general catalogue of various analytical technique used for the characterization of synthesized plasmonic nanoparticles. It includes UV-Vis spectroscopy, FTIR spectroscopy, SEM, HRTEM, DLS, and $\zeta$ analysis. Principle, instrumentation, and sample preparation for all these techniques are addressed in detail.

**Chapter four** is focused on detection of Cr$^{3+}$, Mn$^{2+}$, and Cr$^{6+}$ using different types of green synthesized Ag and AuNPs. These nanoparticles are synthesized by using various reducing agents such as clove seed extract, L-dopa, and potato extract which also act as stabilizing agent. C-AgNPs synthesized at pH 4.5 and 11.5 with spherical and square pyramidal geometry respectively. The synthesized nanosensor
simultaneously detects Cr\(^{3+}\) and Mn\(^{2+}\) with LODs of 0.20 μM. In the presence of Cr\(^{3+}\), C-SNSs at pH 4.5 showed a color change from light yellow to colorless. At pH 11.5, they showed rapid aggregation, not only with a colorimetric change from dark yellow to reddish brown, but also with an alteration in morphology of spheres to square pyramidal. Spherical C-AuNPs and P-AgNPs have been shown good sensitivity with high selectivity and rapid response for Cr\(^{3+}\) and Mn\(^{2+}\) ions respectively. L-dopa as a reducing and stabilizing agent results in the formation of flower shaped AgNPs. The synthesized AgNPs have been proved good candidate for the detection of Cr\(^{6+}\) with high selectivity and sensitivity. Aggregation of AgNPs in the presence of Cr\(^{6+}\) was also confirmed by SERS spectroscopy by using R6G as Raman enhancer. Performance of synthesized nanosensors is good or comparable with reported methods.

**Chapter fifth** explains the synthesis of AgNPs by I2CA and cinchona bark extract as reducing and capping agent at room temperature and at increased temperature. It compiles results of developed AgNPs for the detection of Al\(^{3+}\) ions. The synthesized particles were monodispersed, and very small in diameter (3 to 20 nm). Each nanosensor discussed for optimization of synthesis and sensing condition by varying pH, extract volume, temperature and reaction time. The probable mechanism of synthesis and sensing also explained on the basis of literature and experimental studies. The applicability of synthesized probes evaluated in real water samples and the result obtained are in good agreement with the AAS results. The effect of size and pH on the sensing of Al\(^{3+}\) also observed. In our knowledge it is the first time to synthesize AgNPs by I2CA and cinchona bark extract.

**Chapter six** is described the synthesis of MDA-AuNPs and gelatin-AuNPs. Thiophilic ability of both AuNPs and Hg\(^{2+}\) form the basis of aggregation based detection. The mechanism of sensing supported by DLS and ζ measurement and synthesis of biocompatible gelatin-AuNPs is also explained. They could not be used as nanosensor. The small charge on the surface may be the reason behind their disability.

Chapter seven summarizes the summary of all six chapters.
7.2 Outlook and future perspective

- Regeneration of nanoparticles which increase their viability.

- Development of nanoparticles with the ability to detect more than one heavy metal ion simultaneously.

- Development of nanoparticles with controllable shape and size and study of their effect on sensing is an appealing research application.

- The extension of applications to other types of matrix-rich samples, such as food, food additives, wastewater, sediment, soil, and biological samples, will be a matter of interest. Also, fabrication of gold-based nanomaterials loaded to solid supports (e.g., paper, membrane or glass slides) to give a more convenient, portable strip test would benefit users more.

- The field of phytosynthesis of plasmonic nanoparticles for the sensing purpose is yet not very popular thus the field requires special attention.