CHAPTER - II

Aim and Scope
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The scientific community is conscious of the fact that there is an incessant demand for reliable and economical technologies for efficient determination and monitoring of compounds of biological, environmental and clinical interest. In new millennium a major impact of science and technology is was improved by improvising new methods which have some of the advantages such as turnout time, cost, convenience, and user friendly methodology and to have major impact on science and technology in analysis. Over the years new trends and rapid improvements in electroanalytical techniques particularly in chemical sensor and biosensor have been reported.

The wide spread desire for reliable, inexpensive and repetitive chemical measurements and the need for continuous on-line monitoring have fuelled the explosive growth in the field of chemically modified electrode. The concept of chemically modified electrodes (CMEs) was in part borne out of the frustrated electrochemists desire to size direct control of the chemical nature of the electrode surface. By deliberately attaching chemical reagents to it, one hoped that the electrode surface would take on the chemical properties of the attached reagents. Electrochemical reaction is mainly depend on the mediators attached at the electrode surface, so the mediator should have some desirable properties for electron transfer process. This appealing concept in the design of modified electrode has introduced more research in the field of electrochemical sensor.

Although the idea of CMEs was first demonstrated only in 1970s this approach has assured a dominant position in modern electrochemistry. Chemically modified
electrode (CMEs) using different modifying reagent on the electrode surface is a modern approach of electrode system. Depending on the nature of the modifying reagent the modified electrodes were used for various analytical applications. Combining the intrinsic properties of the modifier, CMEs are emerging in the field of electroanalytical techniques because they meet the needs of analytical problem and they exhibits significant improvement with respect of conventional unmodified electrodes and forms a foundation for new electroanalytical applications and different sensing device [289]. Apart from the electrochemical application CEMs are used in other applications, such as energy conversion, molecular electronics, electrochromic displays, corrosion protection, and electro-organic syntheses [290]. Chemically modified electrode (CEMs) in combination with electroanalytical techniques have turned into a sensitive sensor which is simple, inexpensive and rapid for determination of trace concentration of biologically important analytes and environmental pollutants. The uses of CMEs in analytical application and improvements have been extensively reviewed [291, 292]. Electrocatalytic process at CMEs improves the stability, sensitivity, selectivity and kinetics of reaction. Therefore the electrochemical behaviour of CMEs propounds diverse advantages in comparing with other electrochemical methods.

The electron/ solution interface properties of modified solid electrode differ from those of the bare electrode. If PIGE is used as such for electrochemical applications, it causes some disadvantages such as low sensitivity, reproducibility, slow electron transfer, low stability and high over potential at which the electron transfer process occurs. Such drawbacks are overcome by attaching suitable mediators
to the surface. The role of the mediator in the electrocatalytic determination of substances is to facilitate the charge transfer between the substrate and the electrode.

Due to high sensitivity and selectivity of CMEs, various electrocatalytic applications have been reported by using CMEs, some of the notable applications are bio-sensing of Cobalt phthalocyanine-coated electrode for detection of thiols [293], electropolymerization of nickel (II)-prophyrinic based carbon fibre micro sensor for detection of nitric acid [294]. Ruthenium dioxide modified carbon paste electrode for determination of carbohydrates [295] and toluidine blue modified electrodes for detection of hydrogen peroxide [296].

CMEs applied to electrocatalysis have successfully employed mediators of all varieties, both organic and inorganic. Some of the mediators used for the modification of the electrode are metal oxides [297], zeolites [298], metal phthalocyanines [299], metal porphyrines [300], carbon based material such as graphene [301], carbon nanotubes [302], silica [303], quantum dots [304]. Among these, in recent years organic dyes have been widely used the construction of the modified electrode. The organic dyes show some of the interesting properties such as physical and chemical stabilities, shape, size, and high ion exchange capacity. The oxidation and reduction of their redox sites can proceed without dissolution of the compounds. By electropolymerization, adsorption and covalent attachment the above organic dyes are attached to the electrode surface for detection of several analytes and toxic metal ions.

Numerous analytical techniques have been reported for the analysis of heavy metal ions which include, UV-vis spectrometry [305], colorimetry [306], atomic absorption spectrometry (AAS) [307], Fluorescent spectroscopy [308], inductively
coupled plasma-mass spectrometry (ICP-MS) [309], surface-enhanced Raman spectroscopy (SERS) [310] and electroanalytical techniques [311]. Although these analytical methods have been used for determination of heavy metal ions, most of them required more time for sample analysis, tedious sample preparation, sophisticated instrumentation, high cost and use of more organic solvents which cause toxic effects to the environment. Electrochemical methods have been pronounced more prominently because of less operating time, simple sample preparation, flexibility in handling the instrument, high sensitivity and selectivity. Stripping voltammetry is the mostly used electroanalytical method for determination of heavy metal ions because the faradic current is measured effectively by reducing the non-faradic current [312]. Detection of ultra-trace metal ions even at ppb levels can be achieved by the stripping voltammetry method because it involves the pre-concentration of metal ions.

For anodic stripping analysis, the working electrode is usually made up of mercury film, dropping mercury electrode (DME) and hanging mercury drop electrode (HMDE). These electrodes have been widely used for the detection of heavy metal ions because of their extensive potential window [313]. But the mercury electrode has many limitations such as toxicity, difficulty in storage and disposal of mercury. To override these limitations, mercury free electrode was developed and used for detection of heavy metal ions.

Keeping in mind the above points, an attempt has been made to construct CMEs by means of electropolymerization of polymer film and adsorption of metal nanoparticles co-oriented organic ligand on to the PIGEs. The analytical applications
of the modified electrode have been studied by employing these electrodes for
electrocatalytic oxidation of some of the important compounds of biological, clinical
and environmental interest. These modified electrodes were also used for the
determination of heavy metal ions which are important environmental pollutants and
cause serious health issues to the mankind. Three different modified electrodes were
fabricated in the present investigation. The three electrodes are

1. Poly O-Cresophthalein complexone film (POCF) modified electrode
2. Poly O-Cresophthalein complexone film/ Multiwall carbon nanotubes (POCF-
   MWCNTs) modified electrode
3. Poly AmidoBlack-10B (PAB) modified electrode
4. 2, 4, 6-Trimercaptotriazine/gold nanoparticles (TMT/GNPs) modified electrode

The present work was studied by following process.

1. Fabrication of paraffin impregnated graphite electrode (PIGE).
2. Fabrication of POCF and PAB modified electrodes by electropolymerization method.
3. Characterization of POCF modified electrode by ATR-IR spectroscopy, Raman
   spectroscopy, XPS analysis, optical microscopy, FESEM and EDAX analysis.
4. Characterization of PAB modified electrode by AT-IR spectroscopy, Raman
   spectroscopy, optical microscopy, FESEM and EDAX.
5. Electrochemical characterization of POCF and PAB modified electrodes by cyclic
   voltammetry and electrochemical impedance spectroscopy.
6. Optimization of parameters such as pH and scan rates for POCF and PAB modified
   electrodes.
7. The POCF and PAB electrodes used for quantification and detection of that are bioanalytes, industrial pollutants and toxic metal ions.

8. Flow system analysis of POCF and PAB modified electrodes by hydrodynamic voltammetry.

9. Amperometric determination of analysts with the POCF and PAB modified electrodes by chronoamperometric techniques.

10. Differential pulse anodic stripping voltammetry (DPASV) for detection of toxic metal ions.

11. Studies on stability and reproducibility of POCF and PAB modified electrodes.

12. Determination of some of the analytes in real sample using POCF and PAB modified electrodes.

13. A comparison of the linear rage, detection limit and sensitivity of POCF and PAB modified electrodes towards various analytes under analysis.

With an intend of constructing nanomaterial based electrochemical sensor for heavy metal ions. An attempt was also made to fabricate modified electrodes using different nanomaterials like MWCNTs and gold nanoparticles (GNPs) with O-Cresophthalein complexone and 2, 4, 6-Trimercaptotriazine respectively as mediators.

The present work was done in following manner,

1. Preparation of MWCNTs/POCF modified electrode by electropolymerization method.

2. Preparation of GNPs by chemical reduction method.

3. Characterization of GNPs with UV, FESEM, HRTEM.

4. Fabrication of TMT/GNPs modified electrode by drop casting GNPs over PIGE followed by dipping the GNPs/PIGE in TMT ligand solution.
5. Characterization of MWCNTs/POCF modified electrode by DRS-UV, optical microscopy, FESEM and EDAX analysis.

6. Characterization of TMT/GNPs modified electrode by FESEM, EDAX and XPS

7. Electrochemical characterization of MWCNTs/POCF and TMT/GNPs modified electrode by cyclic voltammetry and electrochemical impedance spectroscopy.

8. Optimization of experimental variables such as electrolytes, pHs, pre-concentration time and deposition time for stripping analysis.

9. Applicability of MWCNTs/POCF and TMT/GNPs modified electrodes towards detection of toxic metal ions such as Lead, Cadmium, mercury, tin and Zinc (II) by Differential pulse anodic stripping voltammetry (DPASV).

10. Studies on stability and reproducibility of MWCNTs/POCF and TMT/GNPs modified electrodes.

11. Determination of some of the heavy metal ions in real samples using MWCNTs/POCF and TMT/GNPs modified electrodes.

12. A comparison of the linear range, detection limit and sensitivity of MWCNTs/POCF and TMT/GNPs modified electrodes towards toxic metal analysis.