Chapter 7

Summary and Conclusions
7.1 SUMMARY

This thesis documents the indepth information related to the research work carried out in the laboratory on certain biomolecules such as dopamine, ascorbic acid and uric acid using various modified carbon paste electrodes with CV and DPV techniques supplemented by SEM. It highlights the various modifiers used for the investigation in the present study and the advantages of these modifiers with respect to the sensitivity, selectivity, cost and ease of fabrication, detection and quantification limits, stability, reproducibility and availability over the ones used earlier for the similar investigations, as quoted in the literature. It focuses on the fact that as far as possible, cheap and easily available modifiers should be used to achieve the best results. The summary of the entire thesis in a nutshell is given below. The thesis is divided in to seven chapters.

7.1.1 Chapter 1: Introduction

This chapter briefly gives an overall view of chemical and structural characteristics of the neurotransmitter dopamine, a vitamin ascorbic acid (vitamin C) and uric acid. The dietary sources, absorption mechanism in the human body, metabolism, biological functions, role of each of the biomolecules in various body disorders and curative effects of each of them are comprehensively discussed. It also discusses the importance of these biomolecules for the survival of living organisms. The ill effects of abnormal concentrations of these biomolecules are also discussed in detail. Finally, it contains a brief review of various methods employed so far in the investigation of these biomolecules i.e. both cyclic voltammetric and nonelectroanalytical methods.

7.1.2 Chapter 2: Experimental details

In this chapter, basic principles behind CV, DPV and SEM analytical techniques are elaborately discussed. Instrumentation and basic equipment required for these techniques are diagrammatically explained. The description regarding various parts of the CV analyser instrument such as electroanalyser, recording device and three electrode electrochemical cell is given. The nature of input potential for CV and DPV, interpretation of cyclicvoltammetric and differential pulse voltammetric results are also described in great detail.
Chapter 3: Zirconia/Poly (oxalic acid) modified carbon paste electrode for the electrochemical investigation of uric acid in presence of dopamine and ascorbic acid

The experimental details and results of the investigation of uric acid in the presence of dopamine and ascorbic acid using CV, DPV at a carbon paste electrode modified with zirconia and oxalic acid are given in detail in this chapter. The modified electrode fabricated for this investigation is Zirconia/Poly (oxalic acid) modified carbon paste electrode. In short, it is denoted by ZrO2/POA/CPE. It is a double modified electrode, i.e. it is both bulk modified (with zirconia) and surface modified (with oxalic acid). The modified electrode could resolve well the anodic peaks of UA, DA and AA and also showed far better sensitivity for UA (two folds) compared to bare carbon paste electrode (BCPE). Scan rate studies indicated that the electrode process is both diffusion and adsorption controlled. The detection limit (LOD) and quantification limit (LOQ) of the modified electrode for UA were found to be 5.07×10−7 M and 1.69×10−6 M respectively. The recovery percentage of UA in human urine and human blood serum were found to be 92 and 97 respectively with ZrO2/POA/CPE in the real sample analysis. On the whole, the modified electrode was found to be very selective, sensitive, inexpensive and stable. Hence, it could be used in analytical chemistry and biochemical investigations in the field of medicine.

Chapter 4: Poly (benzoic acid) modified carbon paste electrode as an electrochemical sensor for the determination of uric acid in the presence of ascorbic acid and dopamine: A voltammetric study

Uric acid (UA) detection is quite important in humans as high blood concentrations of UA called Hyperuricemia can lead to Gout and is also associated with other medical conditions including diabetes and formation of kidney stones etc. In the present work, a sensitive and selective method is presented for the voltammetric determination of UA in the presence of ascorbic acid (AA) and dopamine (DA) using a carbon paste electrode (CPE) modified with benzoic acid in 0.1 M phosphate buffer solution (PBS) of pH 7 by the electropolymerisation in the potential window of -0.8 V to 1.2 V. The obtained poly (benzoic acid) modified carbon paste electrode
(PBA/CPE) showed an excellent electrocatalytic activity for the selective detection of UA in the presence of AA and DA and it also showed good reproducibility. Its sensitivity was increased 2.33 folds for the detection of UA compared to bare carbon paste electrode (BCPE). Effect of variation of scan rate on the peak current indicated that the electrode process is both diffusion controlled and adsorption controlled. The detection limit (LOD) and quantification limit (LOQ) of the present technique were found to be $3.33 \times 10^{-7}$ M (0.333 μM) and $1.11 \times 10^{-6}$ M (1.11 μM) respectively for UA. The pH effect suggested that equal number of protons and electrons were involved in the electrochemical oxidation of UA. The percentage of recovery of UA in the real sample analysis i.e. in human urine is quite good and was found to be 100.5% using PBA/CPE. Thus, the selectivity, reproducibility and sensitivity of the PBA/CPE provide a good possibility for applying the technique in the routine analysis of selected class of electroactive biomolecules.

7.1.5 Chapter 5: Simultaneous determination of dopamine, ascorbic acid and uric acid at poly (cinnamic acid) modified carbon paste electrode: An voltammetric investigation

This chapter discusses the details and results of investigation of dopamine (DA) in the presence of ascorbic acid (AA) and uric acid (UA) by poly (cinnamic acid) modified carbon paste electrode. In this study, a polymeric film of cinnamic acid was formed on the surface of a bare carbon paste electrode (BCPE) by the electropolymerisation of Cinnamic acid in pH 7 Phosphate buffer solution (PBS) by using cyclic Voltammetry (CV). This lead to the formation of poly (cinnamic acid) modified carbon paste electrode (PCA/CPE). CV was used to study the electrochemical properties of the polymer film on the modified carbon paste electrode (MCPE). The poly (cinnamic acid) MCPE was used for the simultaneous electrochemical detection of DA, AA and UA. The MCPE showed a very good electrocatalytic activity for the oxidation of DA, AA and UA. The favourable electrostatic interaction (i.e. electro static attraction) between negatively charged polymer film and cations of DA contributes to the oxidation potential of DA, at the same time the repulsion between negatively charged polymer film due to the carboxylate anions and anions of AA (ascorbate anions) negatively shifted the
oxidation potential of AA. Thus, the MCPE exhibited an excellent ability to separate DA from AA by means of CV and the separation of anodic peak potentials of DA and AA is by 0.259 V in pH 7 PBS containing 0.1 mM of DA and 2 mM of AA at the scan rate of 50 m V/S. The detection limit (LOD) and quantification limit (LOQ) of the present technique were found to be $3.52 \times 10^{-7}$ M and $1.16 \times 10^{-6}$ M respectively for DA. Compared to BCPE, the MCPE exhibited the enhanced peak currents for DA, AA & UA. Also, the MCPE showed good recoveries for DA in real sample analysis i.e. for both pharmaceutical formulations and blood serum. Hence, this modified electrode can be used for the selective determination of DA in the presence of higher concentrations of AA and UA in pharmaceuticals and medicine with greater sensitivity, selectivity and reproducibility.

7.1.6 Chapter 6: Resolution of ascorbic acid in presence of dopamine and uric acid by the Montmorillonite K10-clay/poly (glycine) modified carbon paste electrode

A detailed description of the investigation of ascorbic acid (AA) in the presence of dopamine (DA) and uric acid (UA) using Montmorillonite K10-clay/poly (glycine) modified carbon paste electrode is given in this chapter. AA alternatively called as vitamin C is a very important antioxidant. Its deficiency could lead to a disease called scurvy, which when not attended leads to death. It is useful in controlling common cold and cancer. Hence, its determination has become very important. It usually exists along with DA and UA in the extracellular fluids of mammalian brain. The major problem encountered in the electrochemical determination of AA, however is the serious interference caused by the coexisting compounds DA and UA. In the present work, a novel modified carbon paste electrode was fabricated, which was successful in overcoming the problem and resolved AA very well. Carbon paste was first bulk modified with Montmorillonite K10-clay followed by the surface modification using glycine, an amino acid by electropolymerisation in phosphate buffer solution (PBS) of pH 7 in the potential window of -0.4 to 1.0 volts. The resulting modified electrode is called Montmorillonite K10-clay/poly (glycine) modified carbon paste electrode (M-clay/Pgly/CPE). This modified electrode could resolve well the anodic peaks of AA.
UA and DA and showed far better sensitivity for AA (two folds) compared to bare carbon paste electrode. Scan rate studies indicated that the electrode process was both diffusion and adsorption controlled. The detection limit (LOD) and quantification limit (LOQ) of the modified electrode for AA were found to be $1.133 \times 10^{-7}$ M and $3.77 \times 10^{-6}$ M respectively. The recovery of AA in vitamin C tablet was found to be 96.5% with M-clay/Pgly/CPE in the real sample analysis. On the whole, the modified electrode was found to be very selective, sensitive, inexpensive, stable and provide a good possibility for applying the technique in the analysis of biomolecules in the medicine and analytical chemistry.

7.2 CONCLUSIONS

The thesis ends with the conclusions of the investigations made in the present research work.

1. Simple and cheap, organic and inorganic molecules/substances such as oxalic acid, zirconia, cinnamic acid, benzoic acid, glycine, Montmorillonite K10-clay were successfully used as modifiers for the simultaneous determination of DA, AA and UA.

2. Avoided the costly modifiers and cumbersome methods of electrode preparation etc.

3. Double modification i.e. both bulk modification and surface modification of the carbon paste electrode, as expected enormously improved the detection, quantification limits and also improved the rates of oxidation-reduction reactions of the biomolecules.

4. Equally good detection and quantification limits were obtained even with the low cost, easily available materials and very easy fabrication methods.

5. For each of the investigations optimum conditions of pH, number of cycles of polymerization and medium of the reaction were unambiguously established.

6. The fabricated electrodes in this study have the potential uses in real life situations in medicine and biochemical analysis.