Summary of the Thesis

Introduction

Analytical chemistry is an important branch of modern chemistry which deals with the separation and determination of the constituents present in the matter of interest. Analytical chemistry involves the application of a range of techniques to obtain and assess the qualitative, quantitative and structural information of the analyte. Qualitative analysis enables us to identify the species present in the sample, while quantitative analysis determines the absolute or relative amount of species present in the sample. Now a day’s analytical chemistry plays an important role in all the branches of science. The methodologies of the analytical chemistry was successfully employed and utilised in all manufacturing industries, biological studies, clinical diagnosis and monitoring as well as control of pollutants in environmental issues. Analytical measurements are carried out using various instrumental techniques to get high accuracy and precision in the result. The most common analytical techniques are gravimmetry, thermo-gravimetry, titrimmetry or volumetry, atomic and molecular spectroscopy, mass spectrometry, Mossbauer spectroscopy, auger spectroscopy, chromatography, electrophoresis, thermal analysis, electrochemical analysis and radiochemical analysis. The story behind the growth of analytical chemistry was tremendous and instrumental analysis revolutionized the field of analytical chemistry. Now, the applications of analytical chemistry are wide spread over all disciplines of science.

Electroanalytical chemistry

Electroanalysis forms a new branch of chemistry called “electroanalytical chemistry” which encompasses a group of quantitative analytical methods that are based upon the electrical properties of a solution of the analyte when it is made part of an electrochemical cell. The examination of electrical parameters such as potential (E), current (I), charge (Q) and resistance (R) are related to chemical parameters such as concentration (C) of the analyte. These types of electrochemical measurements for analytical purposes cover a wide range of applications in the field of biomedical analysis, environmental monitoring and industrial quality control.
In general atoms and molecules consist of a centrally situated positively charged heavy nucleus with electrons spinning around it. These electrons carry an electrical current creates a secondary magnetic field around the nucleus are called as “bar magnets” which plays a fundamental role in governing the pathway of chemical reactions and detection of this current is the basis of the measurement method. But the electron movement happens within an extremely short distance and measurement of speed of electron transfer process and calculation of the number of electrons involved are difficult in traditional experimental methods like spectroscopy and other techniques. Electrochemical methods are employed as an important tool in the study of chemical systems over chemical routs for a variety of reasons. Electrochemical reactions are often much cleaner with respect to possible pollutants than chemical reactions, economic concerns over chemical processes, high selectivity of desired product and mainly determination of low amounts of compounds etc.

Several organic and inorganic compounds of biological interest are either oxidizable or reducible by the way in which they give electrochemical response by applying potential and are therefore said to be “electroactive” .Since they contain lone pair of electrons or multiple bonds, different functional groups, ionized molecular groups, or electrically polarised biomolecules which are electrochemically active. Thus electrochemical techniques are most suitable to investigate the redox properties of organic compounds or drugs in pharmaceutical preparations or new drugs or in biological matrix. There is very wide range of molecules such as pharmaceuticals, neurotransmitters, hormones, vitamins, muscle relaxants, diuretics, antibiotics, analgesics, non-steroidal anti-inflammatory drugs, staining compounds and others.

Cyclic voltammetry (CV) is widely used technique to study biologically active organic compounds under interest. A very important aspect of cyclic voltammetry is its ability to generate a new redox species during the first potential scan and then probe the species fate on the second and subsequent scans. The power of CV results from its ability to rapidly provide information about redox potentials of the electroactive species present in new drugs, reaction mechanism, rate constants, number of electrons involved in each of the observed redox processes, transfer coefficients and diffusion coefficients of redox
processes and the kinetics of electron-transfer reactions and detection of chemical reactions coupled to electron transfer or adsorption processes etc.

**Organisation of the Thesis**

Carbon paste electrode (CPE) is one of the convenient conductive matrices to prepare a stable working electrode. It is a simple and homogeneous mixture of graphite powder and a liquid binder. Such as, paraffin oil, nujol mull, silicon oil, bromonaphthalene or tricresyl phosphate etc. In recent years the modification in the preparation of carbon paste electrode is of great significance in voltammetric analysis of electroactive molecules. Moreover, due to the low background current, wide potential range, easy preparation and convenient surface alteration CPEs are extensively used as an ideal working electrode for the voltammetric analysis. The carbon paste modified with different types of modifiers for the determination of various electro-active molecules has been reported. Still there is a need for the development of new working electrodes in the electrochemical sensor field.

The main focus of the research work covered in this thesis was to study the electrochemical properties of bioactive molecules such as Folic acid (FA), Dopamine (DA), Epinephrine (EP), Ascorbic acid (AA), Catechol (CC), Hydroquinone (HQ), Paracetamol (PA), 5-amino salicylic acid (5-ASA), Haematoxylin (HX) and Quercetin(QT) at bare carbon paste electrode (BCPE) and modified carbon paste electrode (MCPE). The voltammetric response at BCPE was poor in sensitivity and selectivity with slow electron transfer kinetics, making their individual identification very difficult and also requires high over potential due to fouling of the electrode surface due to the adsorption of oxidized products. Therefore, the modification of the BCPE by the different ways to get the modified carbon paste electrode followed by the electrochemical characterisation. Then it is employed for the electroanalysis of above mentioned bioactive molecules in the presence of probable existence of interfering substances. This thesis also includes the different type of methodologies adopted in the modification procedure. The aspects like number of electrons involved, heterogeneous electron transfer rate, reaction mechanism and nature of electrode process were observed.
The work carried out in this thesis is divided and described into seven chapters.

**Chapter-1**

**Introduction, Review of Voltammetry and Theoretical Considerations**

This chapter consists of introduction, voltammetry and voltammetric techniques and their theoretical aspects. Basic principles, theoretical considerations and applications of cyclic voltammetry, solvents, supporting electrolytes and electrodes have been covered. Brief literature survey of cyclic voltammetric investigations of folic acid, paracetamol, epinephrine, dopamine, ascorbic acid, catechol, hydroquinone, haematoxylin, 5-amino salicylic acid and quercetin has been reviewed. The electrode processes, objectives and scope of the present work is also included in this chapter.

**Chapter-2**

**Experimental**

This chapter describes the basic experimental setup of voltammetric techniques, the instrumentation and methodology adopted, basic equipment needed for electrochemical measurements such as a potentiostat, a recording device and an electrochemical cell comprised of three electrodes are explained. The working electrode system with special focus on the carbon paste electrodes used in the course of this research is explained in detail. The preparation and characterisation of carbon paste electrode and modified carbon paste electrodes and procedures used in the present work are detailed. In addition, an overview of the theories and related equations are described.

**Chapter-3**

**Voltammetric Determination of Folic acid in presence of Dopamine and Ascorbic Acid at Poly(Alanine) Modified Carbon Paste Electrode**

A sensitive, selective and reproducible electrochemical method was developed for the electroanalysis of folic acid (FA) using poly(alanine) modified carbon paste electrode. The modified electrode shows excellent electrocatalytic activity towards the oxidation of FA in acetate buffer solution (PBS) of pH 5.0, by cyclic voltammetric and differential
pulse voltammetric techniques. The limit of detection of FA was found to be 3.40\textsuperscript{M}. The interference studies showed that the modified electrode exhibits excellent selectivity in the presence of large excess of dopamine (DA) and ascorbic acid (AA). The oxidation peak potentials for FA, DA and AA were about 0.744 mV, 0.307 mV and 0.026 mV respectively. The differences in peak potentials were enough to determine FA, DA and AA individually and simultaneously. This work provides a simple and easy approach to selectively detect FA in the presence of DA and AA.

![Cyclic Voltammogram](image)

Cyclic Voltammogram obtained for the simultaneous determination of 1x10\textsuperscript{-6}DA, 1x10\textsuperscript{-4} AA and 1x10\textsuperscript{-4} FA in 0.2 M ABS solution of pH 5.0 at poly(alanine) MCPE at scan rate of 100 mVs\textsuperscript{-1}

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Chapter-4

This Chapter is divided into two sections.

Part-A : Voltammetric Resolution of Paracetamol in presence of Folic Acid at Poly(Alanine) Modified Carbon Paste Electrode

The Poly(alanine) film was prepared on the surface of carbon paste electrode by electrochemical method. The synthesized polymeric film coated electrode exhibits
excellent electrocatalytic activity towards the detection of paracetamol by cyclic voltammetry (CV) and DPV technique in phosphate buffer (PBS) solution of pH 7.0. The lower limit of detection of PA was found to be 1.63µM. The interference studies showed that the modified electrode exhibits good selectivity and sensitivity. A well defined oxidation peak potential obtained for of PA & FA at 0.433mV and 0.684mV respectively. This indicates that MCPE act as a good electrochemical sensor for the determination of PA & FA.

Cyclic voltammograms obtained for oxidation of 0.1 mM PA and 0.1 mM FA in 0.2 M PBS solution of pH 7.0 at Poly(alanine) MCPE (dotted line) at scan rate of 100 mVs⁻¹

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The electropolymerisation of DL-alanine was carried out at the surface of carbon paste electrode by cyclic voltammetric (CV) technique. The fabricated electrode was used for the electrocatalysis of adrenaline at neutral pH. The lower limit of detection was calculated to be 28.0 nM. Further, the poly(alanine) modified carbon paste electrode can be used for the selective determination of adrenaline in presence of acetaminophen. A
well-defined oxidation peaks observed at 0.174V and 0.367V for AD and AP respectively. The peak to peak separation was 0.193 V; this indicates that poly(alanine) MCPE act as a good electrochemical sensor for the determination of AD and AP present in the binary mixture. Overall, the fabricated electrode can be used as a promising analytical sensor in the determination of adrenaline in pharmaceutical and biological samples.

Electropolymerisation of Poly(alanine) modified carbon paste electrode

Cyclic voltammograms obtained for oxidation of 0.1 mM AD and 0.1 mM AP in 0.2 M PBS (pH 7.0) at BCPE (dashed line) and poly(alanine) MCPE (solid line) at scan rate of 50 mVs$^{-1}$

*Journal of Biosensors and Bioelectronics 7 (2016) 1-6*
Chapter-5

Electrochemical Sensor for the Simultaneous Determination of Catechol and Hydroquinone at Poly(alanine) Modified Carbon Paste Electrode: A Voltammetric Study

The poly(alanine) modified carbon paste electrode (MCPE) was fabricated for the determination of catechol (CC) and hydroquinone (HQ) by cyclic voltammetric and differential pulse voltammetric techniques. The poly(alanine) MCPE exhibits high sensitivity and selectivity in the determination of catechol and hydroquinone in in phosphate buffer solution (PBS) of pH 7.4. The lower limit of detection of CC was found to be 0.18μM and HQ was 0.42μM. The interference studies showed that the modified electrode exhibits good selectivity and sensitivity. The oxidation peak potentials for CC–HQ was about 0.106V and 0.116 V by CV and DPV techniques respectively. This peak differences were large enough for the electroanalysis of CC and HQ individually or simultaneously. This work provides a simple and easy approach for the modification of the bare carbon paste electrode.

Cyclic voltammograms for simultaneous determination of 0.05 mM CC and 0.05 mM HQ at bare CPE (dashed line) and poly(alanine) modified CPE (solid line) at scan rate of 0.05 Vs⁻¹

*Analytical and Bioanalytical Electrochemistry (Revised and submitted: 2018)*
Chapter- 6

An Electrochemical Sensor for the Determination of 5-amino Salicylic Acid at Poly(alanine) Modified Carbon Paste Electrode: A Cyclic Voltammetric Study

Poly(alanine) modified carbon paste electrode (CPE) was fabricated for the determination of 5-amino salicylic acid (5-ASA) in phosphate buffer solution pH 7.4 by cyclic voltammetric technique. The poly(alanine) modified CPE exhibited a high sensitivity towards the oxidation of 5-ASA. The effect of scan rate was found to be surface-controlled adsorption process. The limit of detection was found to be 0.23µM. At the bare CPE, 5-ASA oxidation peak was located at 0.219V (versus SCE). On the other hand, at poly(alanine) modified CPE a significant enhancement in the current signals was observed and oxidation peak was observed at 0.184V. Because of high sensitivity in the electro-oxidation, the fabricated poly(alanine) modified CPE can be used as a promising electrochemical sensor for the determination of 5-ASA in both commercial as well as in pharmaceutical samples.

Mechanism of oxidation of 5-Amino salicylic acid
Cyclic voltammograms obtained for the oxidation of 10.0µM 5-ASA at poly(alanine) MCPE (solid line) and BCPE (dashed line) in 0.2 M PBS (pH7.4) scan rate 50 mVs⁻¹

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Chapter-7

This chapter is divided into two sections.

Part-A : Electrochemical Oxidation of Haematoxylin at Poly(alanine) Modified Carbon Paste Electrode: A Cyclic Voltammetric Study

Electrochemical oxidation of haematoxylin (HX), a bioactive bis-catechol molecule was studied at poly(alanine) modified carbon paste electrode (CPE) in the phosphate buffer solution of pH 7.4, by using cyclic voltammetric technique followed by its electrochemical characterisation. The poly(alanine) modified CPE exhibited a high sensitivity towards the oxidation of HX. The limit of detection was found to be 0.102µM. At the bare CPE, haematoxylin oxidation peak was located at 0.068V. On the other hand, at poly(alanine) modified CPE a significant enhancement in the current signals was observed and oxidation peak was observed at 0.079V. The effect of concentration and scan rate reveals the electrode process was controlled by the adsorption of the analytes. Therefore, the result suggests poly(alanine) modified CPE catalyses the oxidation process
of HX. Because of the high sensitivity of the fabricated poly(alanine) modified CPE it can be used as a promising electrochemical sensor for the determination of HX.

Electrochemical interaction of haematoxylin at poly(alanine) modified carbon paste electrode

Cyclic voltammograms obtained for the oxidation of 0.05mM HX at poly(alanine) MCPE (solid line) and BCPE (dashed line) in 0.2 M PBS (pH7.4) scan rate 50 mVs$^{-1}$

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Part-B : Poly(alanine) Modified Carbon Paste Electrode Sensor for Quercetin: A Cyclic Voltammetric Study

The oxidation of flavonoids is of great interest because of their action as antioxidants with the ability to scavenge radicals by electron transfer processes. An poly(alanine) electrochemical sensor is fabricated for the determination of quercetin (QT), a bioactive flavonoid molecule through electropolymerization method by alanine at bare carbon paste electrode using cyclic voltammetric technique. The poly(alanine) modified CPE exhibited a high sensitivity towards the oxidation of QT. The limit of detection was found to be 0.154µM. The effect of scan rate was found to be adsorption-controlled. At the bare CPE, quercetin oxidation peak was located at 0.12V. On the other hand, at poly(alanine) modified CPE a significant enhancement in the current signals was observed and oxidation peak was observed at 0.17V. However at Poly(alanine)/SDS modified CPE further increase in the current signals and oxidation peak was observed at 0.18V. Therefore, the result suggests that poly(alanine) modified CPE catalyses the oxidation process of QT

Cyclic voltammograms obtained for the oxidation of 100.0µM QT at poly(alanine) MCPE (solid line, b) and BCPE (solid line, a) and at Poly(alanine)/SDS MCPE (Solid line, c) in 0.2 M PBS (pH 7.0) scan rate 100 mVs⁻¹

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