Chapter 1

INTRODUCTION, REVIEW OF VOLTAMMETRY AND THEORETICAL CONSIDERATIONS
1.1. Introduction

Electron transfer plays a fundamental role in governing the pathway of chemical reactions. Measurement of speed of electron transfer process and the number of electrons involved were difficult in traditional experimental method like spectroscopy. Consequently our knowledge of the driving force for many reactions remains exclusive.

Electrochemistry is a branch of chemistry that studies chemical reactions which take place in a solution at the interface of an electron conductor (a metal or a semiconductor) and an ionic conductor (the electrolyte), and which involve electron transfer between the electrode and the electrolyte or species in solution. Reduction and oxidation (redox) reactions involve the transfer of electron density from one atom to another. Oxidation describes the loss of electrons or an increase in oxidation state by a molecule, atom or ion. Reduction describes the gain of electrons or a decrease in oxidation state by a molecule, atom or ion. Such reactions are carried out in a suitable electrolytic cell.

In all these electrochemical studies chemical reactions bonds are broken and new bonds are formed as with all types of organic reactions [1]. All types of organic reactions are possible by electrochemical methods such as substitutions, cleavages, eliminations, coupling, cyclizations, oxidations or reductions of functional group.

Electroanalytical technique is a powerful and sensitive tool used for both qualitative analysis and quantitative analysis over a wide range of concentrations. The utility of electrochemical methods stems not only from their sensitivity to trace amounts and the simplicity of the instrumentation, but also because these methods can be used for separation of ionic species in addition to detection. Numerous standard electrochemical methods exist that can be categorized into three general classes:

Potentiometry is based on the measurement of solution potential in the absence of appreciable current. These methods often employ ion selective electrodes for fast, simple measurements of certain ionic species in solution.
Coulometry measures the current passed through an indicator electrode while it is held at a fixed potential. By appropriate choice of potential for select species, quantitative determinations are achieved by simply integrating the current over time in order to calculate charge passed. The integrated current (charge passed) gives a direct measure of the number of ions that have been oxidized or reduced. Thus in certain cases, no reference solutions are needed to achieve quantitative results.

Voltammetry refers the methods in which the current in an electrochemical system is measured as the voltage of the system is changed.

1.2. History and Development of Voltammetry

The polarography in 1922 was invented by the Czechoslovakia chemist Jaroslav Heyrovsky and he received the Noble Prize in 1959. From his invention of polarography, the voltammetry was also emerged and now it becomes one of the branches in the field of electroanalysis. Electroanalysis can be defined as the application of electrochemistry to solve real-life analytical problems. It has another two branches namely, Conductometry and Potentiometry. The voltammetric technique become most important because of the measurement of current as a function of applied potential where in conductometry, one can measure only current and in potentiometry, only potential. In voltammetry, three electrodes are used (working electrode, reference electrode and counter/auxiliary electrode) to monitor both current and potential. Hence, most analytical chemists' routinely use voltammetric techniques for the quantitative determination of variety of dissolved organic and inorganic substances. Inorganic, physical and biological chemists widely use voltammetric techniques for a variety of purpose including fundamental studies of oxidation and reduction process in various media, kinetics of electron transfer process and thermodynamics properties of solvated species etc.

The common characteristic of all voltammetric techniques is that they involve the application of a potential ($E$) to an electrode and the monitoring of the resulting current ($i$) flowing through the electrochemical cell. In many cases the applied potential is varied or the current is monitored over a period of time ($t$). Thus, all voltammetric techniques can be described as some function of $E$, $i$, and $t$. They are considered active techniques (as opposed to passive techniques such as...
potentiometry) because the applied potential forces a change in the concentration of an electroactive species at the electrode surface by electrochemically reducing or oxidizing it.

The analytical advantages of the various voltammetric techniques include excellent sensitivity with a very large useful linear concentration range for both inorganic and organic species ($10^{-12}$ to $10^{-1}$ M), a large number of useful solvents and electrolytes, a wide range of temperatures, rapid analysis times (seconds), simultaneous determination of several analytes, the ability to determine kinetic and mechanistic parameters, a well-developed theory and thus the ability to reasonably estimate the values of unknown parameters, and the ease with which different potential waveforms can be generated and small currents measured.

Voltammetric techniques are routinely used by analytical chemists for the quantitative determination of a variety of dissolved inorganic and organic substances. Inorganic, physical, and biological chemists widely use voltammetric techniques for a variety of purposes, including fundamental studies of oxidation and reduction processes in various media, adsorption processes on surfaces, electron transfer and reaction mechanisms, kinetics of electron transfer processes and transport, speciation and thermodynamic properties of solvated species. Voltammetric methods are also applied to the determination of compounds of pharmaceutical interest and when coupled with HPLC, they are effective tools for the analysis of complex mixtures [2]. Polarography, which is still an important branch of voltammetry, differs from other types of voltammetry in the respect that the working electrode takes the form of a dropping mercury electrode (DME), which is invaluable tool of modern electroanalytical chemistry [3].

1.2.1. Voltammetric Techniques and Their Theoretical Aspects

The techniques used in the voltammetry were distinguished from the each other by the function of potential that is applied to the working electrode to drive the electrochemical reaction and by the material used as working electrode. Some of these are listed as follows.

- Linear Sweep Voltammetry (LSV)
- Staircase Voltammetry (SV)
Square Wave Voltammetry (SWV)
Anodic Stripping Voltammetry (ASV)
Cathodic Stripping Voltammetry (CSV)
Normal Pulse Voltammetry (NPV)
Differential Pulse Voltammetry (DPV)
Fast Scan Cyclic Voltammetry (FSCV)
Cyclic Voltammetry (CV)

**Linear Sweep Voltammetry** is a voltammetric method where the current at a working electrode is measured while the potential between the working electrode and a reference electrode is swept linearly in time. Oxidation or reduction of species is registered as a peak or trough in the current signal at the potential at which the species begins to be oxidized or reduced.

Linear sweep voltammetry involves applying a linear potential sweep to the working electrode (the electrode under study) while monitoring simultaneously the current flowing in the circuit. A signal generator produces a voltage sweep from \( E_i \) to \( E_f \) and a potentiostat applies this potential wave to the electrode under study. The scan direction can be positive or negative and in principle, the sweep rate can possess any constant value:

\[
\text{Sweep rate} = \frac{dE}{dt}
\]

This method of analysis is commonly employed in polarography whereby under well-defined conditions, the limiting current derived from a redox process in solution during LSV may be used to quantitatively determine the concentration of electroactive species in solution.

**Staircase Voltammetry** is a derivative of linear sweep voltammetry. In staircase voltammetry the potential sweep is a series of stair steps. The current is measured at the end of each potential change, right before the next, so that the contribution to the current signal from the capacitive charging current is minimized.

**Squarewave Voltammetry**, a squarewave is superimposed on the potential staircase sweep [4, 5]. Oxidation or reduction of species is registered as a peak or trough in the current signal at the potential at which the species begins to be oxidized or
reduced. In staircase voltammetry the potential sweep is a series of stair steps. The current is measured at the end of each potential change, right before the next, so that the contribution to the current signal from the capacitive charging current is minimized. The differential current is then plotted as a function of potential, and the reduction or oxidation of species is measured as a peak or trough. In this technique, the peak potential occurs at the \( E_{1/2} \) of the redox couple because the current is symmetrical around the potential \([6, 7]\). Due to the lesser contribution of capacitative charging current the detection limits for SWV are on the order of nanomolar concentrations. This technique was invented by Ramaley and Krause and developed extensively by Osteryoungs and their co-workers \([8]\).

**Anodic Stripping Voltammetry** is a voltammetric method for quantitative determination of specific ionic species. The analyte of interest is electroplated on the working electrode during a deposition step, and oxidized from the electrode during the stripping step. The current is measured during the stripping step. The oxidation of species is registered as a peak in the current signal at the potential at which the species begins to be oxidized. The stripping step can be either linear, staircase, square wave or pulse.

**Cathodic Stripping Voltammetry** is a voltammetric method for quantitative determination of specific ionic species. It is similar to the trace analysis method anodic stripping voltammetry, except that for the plating step, the potential is held at an oxidizing potential, and the oxidized species are stripped from the electrode by sweeping the potential positively. This technique is used for ionic species that form insoluble salts and will deposit on or near the anodic, working electrode during deposition. The stripping step can be either linear, staircase, square wave or pulse.

**Differential Pulse Voltammetry (Differential Pulse Polarography)** is often used to make electrochemical measurements. It can be considered as a derivative of linear sweep voltammetry or staircase voltammetry, with a series of regular voltage pulses superimposed on the potential linear sweep or stair steps. The current is measured immediately before each potential change, and the current difference is plotted as a
function of potential. By sampling the current just before the potential is changed, the effect of the charging current can be decreased.

By contrast, in *Normal Pulse Voltammetry* the current resulting from a series of ever larger potential pulses is compared with the current at a constant 'baseline' voltage. Another type of pulse voltammetry is squarewave voltammetry, which can be considered a special type of differential pulse voltammetry in which equal time is spent at the potential of the ramped baseline and potential of the superimposed pulse.

*Fast Scan Cyclic Voltammetry* is a linear sweep voltammetric technique in which the background subtracted voltammogram gives additional information about the electroanalyzed species. The current response over a range of potential is measured, making it a better technique to discern additional current contributions from other electroactive species. It is relatively fast technique with signal scans typically recorded every 100 ms, however, the fast scan rate decrease the signal to noise ratio.

*Cyclic Voltammetry* is generally used to study the electrochemical properties of an analyte in solution. It was first reported in 1938 and described theoretically by Randles [9]. It is most widely used technique for acquiring qualitative information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of the redox processes, on the kinetics of heterogeneous electron transfer process and on couple chemical reactions or adsorption process. Cyclic voltammetry is often first experimental approach performed in an electroanalytical study since it offers rapid location of redox potentials of the electroactive species and convenient evaluation of the effect of media upon the redox process [10 – 14].

The focus of the thesis is to use of different modified electrodes for the investigation of organic compounds to get excellent reproducible results by voltammetric techniques. The organic compounds were chosen for electrochemical investigation were dopamine, ascorbic acid, uric acid, serotonin and omeprazole. In the real sample these compounds were interfere each other during the investigation by overlapping their voltammetric responses [15-21]. Moreover, the traditional electrodes very often suffer from fouling effect due to the accumulation of oxidized
products on the electrode surface which results in rather poor selectivity and sensitivity [21-29].

1.3. Fundamentals of Cyclic Voltammetry

1.3.1. Circuit

Voltammetric analysis consists of two circuits: one of which is a polarizing circuit that applies the potential to the cell and the other is a measuring circuit that monitors the cell current. The working electrode is potentiostatically controlled. The potential is varied in some systematic manner and resulting current vs potential plot is known as voltammogram.

1.3.2. Scan Rate

A simple potential waveform that is used often in electrochemical experiments is the linear waveform i.e., the potential is continuously changed as a linear function of time. The rate of change of potential with time is called scan rate.

1.3.3. Switching Potentials and the Excitation Signal

Cyclic voltammetry (CV) involves the cycling of potential of an electrode between two designated values called the switching potentials in an unstirred solution and measuring the resulting current. The controlling potential applied across the working electrode (WE) and the reference electrode (RE) is called the excitation signal which is a linear potential scan with a triangular waveform as shown in Fig. 1.1. The excitation signal causes the potential to scan negatively from +0.8V to -0.2V vs SCE, at which point the scan direction is reversed causing a positive scan back to the original potential of +0.8V. Single or multiple cycles can be used.

1.3.4. Potential Control

The potential control of the external point is done using a potentiostat and a three electrode system in which the potential of the WE is controlled relative to the RE, saturated calomel electrode (SCE) or Silver-Silver chloride (Ag/AgCl) electrode. The current passes between WE and the auxiliary electrode (AE).
Because of its relative experimental simplicity, CV has became a very popular technique for electrochemical studies of new systems, and has proved as a sensitive tool for obtaining information about fairly complicated electrode reactions.

CV is a technique, where in a species that undergoes a reduction during a cathodic polarization of the WE in an unstirred solution is reoxidized by applying a reverse [i.e. anodic] scan. The correlation of the cathodic and the anodic peak currents and differences in cathodic and anodic potentials with the voltage scan rates has been studied mathematically for different electrochemical reaction [30-32]. The sweep rates in the CV can be about the same as in single sweep voltammetry.

1.3.5. CV- An Active Electrochemical Method

CV can describe as ‘active’ electrochemical method because the experiment drives an electrochemical reaction by incorporating the chemistry in to a circuit and then controlling the reaction by circuit parameter such as voltage.

1.3.6. Characteristic Parameters of A Cyclic Voltammogram

The parameters of a cyclic voltammogram are peak potential and peak current. There are two peaks associated with the redox reaction and accordingly we have the anodic peak potential (Epa) and cathodic peak potential (Epc) and the corresponding current associated are anodic peak current (ipa) and cathodic peak current (ipc) respectively. Fig. 1.2 depicts a typical voltammogram for a reversible process with current (vertical) vs potential. Since the potential varies linearly with time, the horizontal axis can also be thought of as a time axis. More positive potentials will speed up all oxidations and more negative potential will speed up all reductions.

1.4. Theory

Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical research. It is used in the study of electroactivity of compounds particularly biological molecules probe coupled chemical reactions particularly to determine mechanisms, rates of oxidation/reduction reactions and also study of electrode surfaces. It is used in all
fields of chemistry as a means of studying redox states. The electrode potential at which a drug, a metal ion or complex or some other compounds undergoes reduction (addition of electrons) or oxidation (removal of electrons) can be rapidly located by cyclic voltammetry. 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 cyclic voltammetry results from its ability considerable information on the thermodynamics of redox process and the kinetics of heterogeneous electron transfer reactions and on coupled chemical reactions or adsorption process. The correlation of the cathodic and anodic peak currents and difference in cathodic and anodic peak potentials with the voltage scan rate has been studied mathematically for different electrochemical reaction [30, 31]. The sweep rates in cyclic voltammetry can be about the same as in single sweep voltammetry.

Cyclic voltammetry makes possible the elucidation of the kinetics of electrochemical reactions taking place at the electrode surface [33, 34]. In a typical voltammogram, there can be several peaks. From the sweep-rate dependence of the possible to investigate the role of adsorption, diffusion and coupled homogeneous chemical reaction mechanism [35].

The important parameters of a cyclic voltammogram are the magnitudes of anodic peak current ($i_{pa}$), the cathodic peak current ($i_{pc}$), the anodic peak potential ($E_{pa}$) and cathodic peak potential ($E_{pc}$). The basic shape of the current verses potential response for a cyclic voltammetry experiment as shown (Fig. 1.2). At the start of the experiment, the bulk solution contains only the oxidized form of the redox couple so that at potenials lower than the redox potential, i.e. the initial potential, there is no net conversion of oxidized species (O) into reduced species (R) (point A). As redox potential is approached, there is net cathodic current which increases exponentially with potential. As O is converted to R, concentration gradients are set up for both O and R, and diffusion occurs down these concentration gradients. At the cathodic peak (point B), the redox potential is sufficiently negative that any O that reaches the electrode surface is instantaneously reduced to R. Therefore, the current now depends upon the rate of mass transfer to the electrode surface and so the time dependence is $qt$ resulting in an asymetric peak shape. Upon
reversal of the scan (point C), the current continuous to decay with \( q_t \) until the potential nears the redox potential. At this point, a net oxidation of \( R \) to \( O \) occurs which caused a cathodic current which eventually produces a peak shaped response (point D). If a redox system remains in equilibrium throughout the potential scan, the electrochemical reaction is said to be reversible. In other words, equilibrium requires that the surface concentrations of \( R \) and \( O \) are maintained at the values required by the Nernst Equation. Under these conditions, the following parameters characterize the cyclic voltammogram of the redox process. The peak potential separation \( (E_{pe} - E_{pa}) \) is equal to \( 57/n \) mV for all scan rates where \( n \) is the number of electron equivalents transferred during the redox process. The situation is very different when the redox reaction is not reversible, when chemical reactions are couple to the redox process or when adsorption of either reactants or products occurs. In fact, it is these non ideal situations which are usually of greatest chemical interest and for which the diagnostic properties of cyclic voltammetry are particularly suited.

Since the reference electrode has a constant makeup, its potential is fixed. Therefore any changes in the cell are ascribable to the working electrode. The control of potential of working electrode with respect to reference electrode, is equivalent of the controlling of energy of electrons within the working electrode. As shown in Fig. 1.3, scanning the potential in the negative direction makes the electrode a stronger reductant, whereas scanning the potential in the positive direction makes it a better oxidant.

1.5. Applications

Cyclic voltammetry (CV) is the most effective and versatile electro analytical technique available for the mechanistic study of redox systems [36-40]. It enables the electrode potential to be rapidly scanned in search of redox couples once located, a couple can be characterized from the potential of peaks on the cyclic voltammogram and from changes caused by variation of the scan rate. CV method have found to have extensive application for the evaluation of thermodynamic and kinetic parameters such as number of electron change \( (n) \), heterogeneous rate constant \( (k^3) \), entropy \( (S) \), Gibb's free energy \( (G) \) and diffusion coefficient \( (D_0) \) etc.,
of a number of redox reaction associated chemical reactions. These methods are especially useful in both oxidation and reduction process and to study the multiple electron transfer in an electrochemical reaction [41].

CV has become increasingly popular in all fields of chemistry as a means of studying redox states. The method enables a wide potential range to be rapidly scanned for reducible or oxidizable species. This capability together with its variable time scale and good sensitivity make this the most versatile electroanalytical technique. It must, however be emphasized that its merits are largely in the realm of qualitative or “diagnostic” experiments. CV has its ability to generate a species during one scan and then probe its fate with subsequent scans.

1.6. Solvent

A number of physicochemical properties must be considered while choosing a solvent for electrochemical work [42] like being in a liquid state at room temperature, capable of dissolving electro active species of interests, having a large potential window and having required acid-base properties. The dielectric constant is the most important parameter for a solvent.

The cheapest solvent is water, which possesses many physico-chemical properties. It can dissolve ionic components and form highly conducting solutions. Water, deionized and repeatedly distilled with alkaline KMnO₄, is usually considered as pure. The purity is checked by conductivity measurements. The volatile and organic impurities [43] are removed by passing the distilled water vapor through a column containing Pt catalyst at about 800°C over which oxygen also simultaneously passed.

Acetonitrile is perhaps a solvent with inert electrochemical properties. It has +3.0V (versus SCE) anodic and -3.0V cathodic limits. However, this solvent has very poor solubility for ionic species. Salts containing organic ions such as tetra-alkyl ammonium salts must be employed.

Dimethyl formamide (DMF) is one of the aprotic solvents, which has very good dissolving power of ionic species. It has a cathodic limit up to -3.0 V for anion radicals. Hence, this is the solvent of choice for studies on anion radicals and
dianinons. In the positive potential regions above +1.0V, the solvent itself decomposes. Cation radicals are less stable in this medium.

Dimethyl sulphoxide has electrochemical properties similar to DMF in the cathodic region. Since it is not as basic as DMF, cation radicals are somewhat stable in this medium.

Methylene chloride is the solvent of choice for organic oxidation studies. It is stable up to +3.0 V as acetonitrile. Cation radicals and dications are quite stable in this medium. Electrolytes are easily soluble in methylene chloride. However, at negative potentials of −1.0 V, the solvent decomposes. The anionic species are less stable in this medium.

Even totally non-polar solvents such as benzene and other hydrocarbons may be used to study the solution phase [44] as well as surface [45-49] processes. Water, deionized and repeatedly distilled with alkaline KmnO₄, is usually considered as pure. The purity is checked by conductivity measurements. The volatile and organic impurities [10] are removed by passing the distilled water vapor through a column containing Pt catalyst at about 800°C over which oxygen also simultaneously passed.

The main impurity present in non-aqueous solvents is water. Refluxing with anhydrous copper sulphate, alumina, aluminum chloride, P₂O₅ etc., and distilling under reduced pressure many times and collecting the proper fraction usually remove this. Vacuum lines are employed during purification, storage and dehydrating agent such as anhydrous alumina is added as an internal addition [50].

1.7. Supporting Electrolytes

All ionic salts or ionizable compounds in a solvent are defined as the supporting electrolytes. It is very important to realize that they can influence the electrochemical processes in a number of ways.

a) These electrolytes impart conductivity to the solvent and hence enable the continuous current flow in solution.
b) They must remain electro-inactive in the potential region of interest, if any useful Voltammetric study is to be conducted.

c) If the concentration of the supporting electrolyte should be very high, they can form a space charge near the surface and the space charge potential can influence the charge transfer kinetics.

d) If the ions of the supporting electrolyte are adsorbed on the surface, they can catalyze or inhibit other reactions.

e) Small cations may form ion pairs with the anion radicals formed in the electrode Process and the properties of the ion pairs can be very different from those of the free anion radical.

f) Some ions may form complexes with the reactants and products.

g) The supporting electrolyte generally controls the acidity of the ionic solution.

h) The liquid electrolyte melts and solid electrolyte acts as the medium for the ionic phase.

H₂SO₄, HClO₄ and HCl are normally employed for studies in acidic aqueous solutions and NaOH or KOH are employed for alkaline media. In neutral region, if buffering is important, acetate, citrate and phosphate buffers are usually employed. B-R buffer is used over a wide pH range. If the redox process does not involve acid-base reactions, no buffers are needed and any electrolyte may be used.

Even today a number of voltammetric results at very positive potentials in KCl media are interpreted without possible influence of Cl⁻ adsorption. Reductions in Li⁺ salt solutions are interpreted without consideration of ion pair effect. One must always consider all possible influence of supporting electrolytes if such pitfalls are to be avoided.

Solubility is the main consideration in selecting supporting electrolyte for aprotic solvent. A number of Tetra-Alkyl Ammonium (TAA) salts show good solubility in aprotic media. Tetra-ethyl ammonium (TEA) salts and more recently Tetra-n-Butyl Ammonium (TBA) salts are widely employed for this purpose.
Most of the inorganic acids, bases or salts are commercially available in the high purity grade. TAA salts are frequently available in the form of halides. The perchlorates or fluroborates may be easily obtained by double decomposition of these salts with the corresponding sodium salts. The precipitated \text{TAAClO}_4 or \text{TAABF}_4 may be recrystallized twice or thrice [51].

Some electrolytes may be dehydration may be done in an oven. Dehydrated samples should be stored in desiccators. Care must be exercised in handling explosives salts such as \text{NaClO}_4. They must neither be overheated nor ground in mortars with force and contact with organics should scrupulously be avoided.

1.8. Electrodes

The advent of modern electrochemistry created the need for new electrodes and electrode set-ups. The most common arrangement today is the electrochemical cell with three different electrodes.

- Working Electrode (WE)
- Reference Electrode (RE)
- Counter/Auxiliary Electrode (AE)

1.8.1. Working Electrode

The performance of the voltammetric procedure is strongly influenced by the material of the working electrode. Electrode is a metallic conductor immersed in an electrolyte solution through which charge is carried by electronic movement i.e. at the surface of the electrode dissolved electroactive ions change their charges by exchanging the electrons with the conductor and the electrode at which this charge transfer occurs is called the working (or indicator) electrode. These electrodes are generally encased in a rid of inert insulator made from Teflon, glass or epoxy with a disk exposed at one end. The working electrode should provide high signal-to-noise characteristics, as well as a reproducible response. Thus, its selection depends primarily on two factors: the redox behavior of the target analyte and the background current over the potential region required for the measurement. Other considerations include the potential window, electrical conductivity, surface
reproducibility, mechanical properties, cost, availability and toxicity. A range of materials have found application as working electrodes for electroanalysis. The most popular are those involving mercury, carbon (carbon paste electrode, glassy carbon electrode and pencil graphite electrode) or noble metals.

1.8.1.1. Mercury Electrodes

Mercury is a very attractive choice of electrode material because it has a high hydrogen overvoltage that greatly extends the cathodic potential window (compared to solid electrode materials) and possesses a highly reproducible, readily renewable and smooth surface. In electrochemical terms, its roughness factor equals unity (i.e., identical geometrical and actual surface areas). Disadvantages of the use of mercury are its limited anodic range (due to the oxidation of mercury) and its toxicity.

1.8.1.2. Solid Electrodes

The limited anodic potential range of mercury electrodes has precluded their utility for monitoring oxidizable compounds. Accordingly, solid electrodes with extended anodic potential windows have attracted considerable analytical interest. Of the many different solid materials that can be used as working electrodes, the most often used is carbon, platinum and gold. Silver, nickel and copper can also be used for specific applications. A monograph by Adams [52] is highly recommended for a detailed description of solid-electrode electrochemistry. An important factor in using solid electrodes is the dependence of the response on the surface state of the electrode. Accordingly, the use of such electrodes requires precise electrode pretreatment and polishing to obtain reproducible results. The nature of these pretreatment steps depends on the materials involved. Mechanical polishing (to a smooth finish) and potential cycling are commonly used for metal electrodes, while various chemical, electrochemical or thermal surface procedures are added for activating carbon-based electrodes. Unlike mercury electrodes, solid electrodes present a heterogeneous surface with respect to the electrochemical activity [53].
1.8.1.2a. Metal Electrodes

A wide choice of noble metals is available, platinum and gold are the most widely used metallic electrodes. Such electrodes offer very favorable electron-transfer kinetics and a large anodic potential range. In contrast, the low hydrogen overvoltage at these electrodes limits the cathodic potential window (to the -0.2 to -0.5V region, depending upon the pH). More problematic are the high background currents associated with the formation of surface-oxide or adsorbed hydrogen layers. Such films can also strongly alter the kinetics of the electrode reaction, leading to irreproducible data. These difficulties can be addressed with a pulse potential (cleaning/reactivation) cycle, as common in flow amperometry [54]. The surface layers problem is less severe in nonaqueous media where noble metals are often an ideal choice. Compared to platinum electrodes, gold ones are more inert, and hence are less prone to the formation of stable oxide films or surface contamination. Gold electrodes are also widely used as substrates for self-assembled organosulfur monolayers or for stripping measurements of trace metals. Other metals, such as copper, nickel or silver have been used as electrode materials in connection with specific applications, such as the detection of amino acids or carbohydrates in alkaline medium (copper and nickel) and of cyanide or sulfur compounds (silver). Unlike platinum or gold electrodes, the copper electrode offers a stable response for carbohydrates at constant potential.

1.8.1.2b. Carbon Electrodes

Solid electrodes based on carbon are currently in widespread use in electroanalysis, primarily because of their broad potential window, low background current, rich surface chemistry, low cost, chemical inertness and suitability for various sensing and detection applications. In contrast, electron transfer rates observed at carbon surfaces are often slower than those observed at metal electrodes. The electron-transfer reactivity is strongly affected by the origin and history of the carbon surface [55, 56]. While all common carbon electrode materials share the basic structure of a six-member aromatic ring and sp² bonding, they differ in the relative density of the edge and basal planes at their surfaces. The edge orientation is more reactive than the graphite basal plane toward electron transfer and adsorption.
Materials with different edge-to-basal plane ratios thus display different electron-transfer kinetics for a given redox analyte. The edge orientation also displays undesirably high background contributions. A variety of electrode pretreatment procedures have been proposed to increase the electron transfer rates. The type of carbon, as well as the pretreatment method, thus has a profound effect upon the analytical performance. The most popular carbon electrode materials are those involving glassy carbon, carbon paste, graphite pencil electrode, carbon fiber, screen printed carbon strips, carbon films, or other carbon composites (e.g., graphite epoxy, wax-impregnated graphite, Kelgraf).

1.8.2. Reference Electrode

A RE is an electrode which has a stable and well-known electrode potential. REs however are so called because the potential of a WE in voltammetry experiment is always controlled with respect to this. The high stability of the electrode potential is usually reached by employing a redox system with constant (buffered or saturated) concentrations each participants of the redox reaction [8] when the experiments are performed, their concentrated electrolytes should be well separated from the analyzed solutions in other words, everything should be done to prevent a leakage of the solution from the reference electrode to the cell and vice versa.

The potential of a working electrode in a voltammetry experiment is always controlled with respect to some standard and that standard is the reference electrode. While the thermodynamic scale of half-reaction potentials found in most textbooks measures electrode potentials against the "standard hydrogen" reference electrode (SHE), in actual practice the SHE is much too cumbersome to use. For this reason, a number of other reference electrodes have been developed. Experimental measurements of potential are made against these alternate reference electrodes, and then the potentials are "corrected" by simple addition or subtraction and reported against the SHE. One of the most generally available reference electrodes for work in aqueous solutions is the saturated calomel electrode (SCE). The half reaction that occurs inside of an SCE reference is given below.

\[
\text{Hg}_2\text{Cl}_2(\text{s}) + 2e^- \rightleftharpoons 2 \text{Hg} (\text{l}) + 2 \text{Cl}^- (\text{aq})
\]
At 25°C, the formal potential for the SCE half reaction lies 0.2415 volts more positive than the SHE reference electrode. A potential measured against using an SCE can be reported versus the SHE simply by adding 0.2415 volts to it. The SCE electrode must be constructed in an appropriate piece of glassware that can keep a small amount of mercury in direct contact with solid calomel (Hg₂Cl₂) paste while at the same time keeping the paste in contact with a saturated aqueous solution of potassium chloride. The short hand notation for the SCE half cell is as follows:

Pt(s) / Hg(l) / Hg₂Cl₂(s) / KCl (aq, sat’d) //

Electrical contact is made by immersing a platinum wire into the liquid mercury and the potassium chloride solution maintains ionic contact with the test solution in the electrochemical cell via a salt bridge or porous glass frit. Such electrodes can be “home made” or purchased from a variety of manufacturers. Other useful reference electrodes are based on half reactions involving a silver electrode. For work in aqueous systems, the “silver-silver chloride” or “Ag/AgCl” reference is quite popular. The half reaction for this reference electrode is as follows:

AgCl(s) + e⁻ <---------> Ag(s) + Cl⁻(aq)

The actual potential assumed by an Ag/AgCl reference depends only on the activity of the chloride anion. (The other two species appearing in the half reaction are solids which always have unit activity.). To serve as a reference, the chloride activity needs to be held constant. To accomplish this, a silver wire (coated with a layer of silver chloride) is immersed in an internal solution saturated with potassium chloride. The chloride ion concentration remains fixed at the saturation limit. The short hand notation for this reference electrode half cell is given below:

Ag(s) / AgCl(s) / KCl (aq, sat’d), AgNO₃ (aq) //

Electrical contact is made by direct connection to the silver wire, and the internal electrode solution is placed in ionic contact with the test solution via a salt bridge or porous glass frit.
1.8.3. Counter/Auxiliary Electrode

The flow of current through the reference electrode which alter the internal composition causing its potential to drift away from the expected standard value. For this and other reason the electrochemical measurements were made without current flowing through the reference electrode. Modern three electrode potentiostats use a feedback circuit to prevent this from happening, but this feedback circuit requires that an additional auxiliary electrode by introduced into the electrochemical cell. This electrode provides an alternative route for the current to follow, so that only a very small current flows through the reference electrode.

The auxiliary electrode can be made from just about any material using any desired electrode geometry. Design choices are usually based on finding a material that is chemically inert in the particular test solution being studied and it is generally a good idea for the auxiliary electrode to have a large surface area. In most cases, a coil of platinum wire is used but stainless steel, copper or aluminum wire may work in non-corrosive solutions where metal cation interference is not a concern. If the electrochemical cell is made of metal, then the cell itself might be used as the auxiliary. Because current flow at the auxiliary electrode, electrochemical process will also occur here. If the reduction occurs at working electrode, then at auxiliary electrode must oxidation occurs and vice versa. The products generated at the auxiliary, if allowed to diffuse to the working electrode, may interfere with the experimental measurement. When this is a problem, the auxiliary electrode is placed in a separate compartment containing an electrolyte solution that is in ionic contact with the main test solution via a glass frit. In most cases, however, the auxiliary can be placed right in the test solution along with the reference and working electrodes.

1.9. A Brief Literature Survey of Cyclic Voltammetric Investigation

Our research interests involve the study of different modified electrodes like modified carbon paste electrode, modified glassy carbon electrode, graphite pencil electrode and the behavior of electrode on the analyte that are taken in the system. The application of the different modified electrodes in electroanalysis offer several advantages due to their unique electrode surface properties. Therefore, there has
been an increasing interest in the creation of different modified electrode surfaces that differ from the corresponding bare surfaces.

*Lei Zhang, et. al.*, studied the separation of anodic peaks of ascorbic acid and dopamine at an α-alanine covalently modified glassy carbon electrode [57]. *Hong Zhao, et. al.*, determine the dopamine electrochemically using a poly (2-picolinic acid) modified glassy carbon electrode [58]. Selective determination of dopamine in the presence of ascorbic acid at an over-oxidized poly (N-acetylaniline) electrode was done by *Longzhen Zheng, et. al* [59]. Carbon nanotube-modified microelectrodes for simultaneous detection of dopamine and serotonin in vivo were carried out by *B. E. Kumara Swamy, et. al* [60]. *Xiaohua Jiang, et. al.*, immobilized the DNA on carbon fiber microelectrodes by using overoxidized polypyrrole template for selective detection of dopamine and epinephrine in the presence of high concentrations of ascorbic acid and uric acid [61]. *Michael L. A, et.al.*, detection the dopamine at overoxidised carbon-fiber microelectrodes [62]. Carbon nanotube-modified electrodes for the simultaneous determination of dopamine and ascorbic acid were done by *Zonghua Wang, et. al* [63]. *Levent Ozcan, et. al.*, carried out the electrochemical preparation of a molecularly imprinted polypyrrole-modified pencil graphite electrode for determination of ascorbic acid [64]. *Suely S. L, et.al.*, explored the electrooxidation and determination of dopamine using a nafion-cobalt hexacyanoferrate film modified electrode [65]. *Cheng Yin Wang, et. al.*, evaluated the voltammetric determination of dopamine in human serum with amphiphilic chitosan modified glassy carbon electrode [66]. *Nianhang Chen, et. al.*, studied the Voltammetric studies on mechanisms of dopamine efflux in the presence of substrates and cocaine from cells expressing human norepinephrine transporter [67]. *Hanwen Sun, et. al.*, performed the electrochemical behavior and determination of dopamine and ascorbic acid by cyclic voltammetry using an activated roughened glassy carbon electrode [68]. *Chuneya Li* [69] worked on voltammetric determination of tyrosine based on chemically electropolymerisation of L-serine. *Rui Zhang et al.*, [70] published work on poly (acid chrome blue K) modified glassy carbon electrode by electropolymerisation and achieved selective separation of dopamine, ascorbic acid and uric acid in real sample of human urine. *Yong Xin Li et al.*, [71] worked on simultaneous electro analysis of dopamine ascorbic acid by poly
(vinyl alcohol) modified. *Yuzhong Zhang et al.* [72] determined dopamine in presence of ascorbic acid by poly (amidosulfonic acid) modified glassy carbon electrode. *Xing-Yuan Liu et al.* [73] electropolymersied poly (carmine) on glassy carbon electrode for detection of parathion. *Tae-Hun et al.* [74] worked on electrochemical preparation of poly (p-phenyl vinylene) in aceto nitrile. *Ai-Min Yu et al.* [75] worked on catalytic oxidation of uric acid at poly (glycine) modified electrode and its trace determination. *Yuzhong Zhang et al.* [76] determined dopamine in presence of ascorbic acid using poly (acridine-red) on modified glassy carbon electrode. *Lei Zhang et al.* [77] studied for simultaneous determination of uric acid and ascorbic acid with modified poly (glutamic) acid. *T. Selvaraju et al.* [78] worked on simultaneous detection of dopamine and serotonin in presence of ascorbic acid and uric acid at poly (o-phenyldiamine) electrode. *Xiangqin Lin et al.* developed DNA/Poly(p-aminobenzensulfonic acid) composite bi-layer modified glassy carbon electrode for determination of dopamine and uric acid under coexistence of ascorbic acid was investigated using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and differential pulse voltammetry (DPV) [79]. *Hossnia S. Mohran et al.* worked on An Electrochemical Investigation of the Redox Properties of Murexide in Aqueous and Non-Aqueous Media has been studied [80]. *B.Jill Venton et al.* published Psychoanalytical electrochemistry: Dopamine and behavior was constructed [81]. *J.W. Mo et al.* reported simultaneous measurement of dopamine and ascorbate at their physiological levels using voltammetric microprobe based on over oxidized poly (1,2-phenylenediamine)-coated carbon fiber was found [82]. *Zahra Nasri et al.* [83] worked on Application of silica gel as an effective modifier for the voltammetric determination of dopamine in the presence of ascorbic acid and uric acid. Simultaneous determination of dopamine and serotonin on a glassy carbon electrode coated with a film of carbon nanotubes has been studied by *Kangbing Wu et al.* [84]. *Yanyi Sun et al.* [85] was analysed the simultaneous electrochemical determination of xanthine and uric acid at a nanoparticle film electrode. *Umesh Chandra et al.* was reported that determination of dopamine in presence of uric acid at poly (eriochrome black T) film modified graphite pencil electrode [86]. *E. Colin-Orozco et al.* [87] published work on the electrochemical oxidation of dopamine, ascorbic acid and uric acid onto a bare carbon paste electrode from a 0.1 M NaCl aqueous solution at pH 7. *Zihong
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Zhu et. al., was published electrochemical detection of dopamine on a Ni/Al layered double hydroxide modified carbon ionic liquid electrode was studied [88]. Electrochemical determination of dopamine using banana-MWCNTs modified carbon paste electrode has been reported by Jahan Bakhsh Raoof et. al [89]. S. Corona-Avendano et al., Influence of CTAB on the electrochemical behavior of dopamine and on its analytic determination in the presence of ascorbic acid was developed [90].

1.10. Faradaic and Non-Faradaic process

Two types of process occur at electrode. One kind comprises reactions involves the electron transfer across the metal-solution interface. Electron transfer causes oxidation or reduction to occur. Since the reactions are governed by Faraday’s law (i.e., the amount of chemical reaction caused by the flow of current is proportional to the amount of electricity passed), they are called Faradaic Process. Electrode at which faradaic processes occur are sometimes called charge transfer electrodes. Under some conditions, a given electrode-solution interface will show a range of potentials where no charge-transfer reaction occur because such reactions are thermodynamically of kinetically unfavorable. However, processes such as adsorption and desorption can occur and the structure of the electrode-solution interface can change with changing potential or solution composition. These processes are called Non-faradaic Processes. Although charge does not across the interface, external currents can flow (at least transiently) when the potential, electrode area or solution composition changes, both faradaic and non-faradaic process occurs when electrode reaction takes place. Although faradaic process are usually of primary interest in the investigation of an electrode reaction (except in studies of the nature of the electrode-solution interface itself), the effects of the non-faradaic processes must be taken into account in using electrochemical data to obtain information by discussing about the charge transfer and associated reactions.

1.11. Polarisable and Non-Polarisable Interface

All electrode-solution interfaces can be classified as polarisable or non-polarisable. An electrode for which an electron can pass easily across the interface is called non-polarisable. In this case, external application of a change of potential may
result in more electrons passing rapidly across the interface. Thus, there is a negligible build-up of excess charge in the electrode surface, i.e., the interface does not polarise. Platinum in contact with hydrochloric acid is a non-polarizable interface. In contrast when the transfer of electrons is difficult, a potential change from outside will induce a substantial build-up of excess charges at the interface, hence, the electrodes is termed polarisable. When a potential is applied externally to the electrode, the transfer of electrons through is negligible. That is, a small change in current flow causes a large change in electrode potential. An ideally polarisable interface is one which can allow the passage of current without causing a change in the potential difference across it. In addition, when the current associated with charging the electrode-electrolyte interface arises purely from capacitive effect, such an interface is termed an ideally polarisable electrode. While no real electrode behaves ideally over the entire potential range, some electrode-solution system, over limited potential ranges, can show behavior which is approximately, ideal for instance, a mercury electrode in contact with a de-aerated potassium chloride solution which behaves as an ideal polarisable electrode at potential in excess of 1.5V.

1.12. Electrodes Processes

The reaction taking place between the electrode surface and species within the solution can proceed through a series of steps that causes the conversion of the dissolved oxidised species (O) to reduced species (R) in solution (Fig. 1.4). The electrode reaction rate is governed by the reaction rates such as.

i. Mass transfer

ii. Electron transfer of non-adsorbing species.

iii. Chemical reactions preceding or following the electron transfer which could be homogeneous such as protonation or dimerization’ or heterogeneous ones like catalytic decompositions on the electrode surfaces.

iv. Other surface reactions such as adsorption, desorption, crystallisation etc.
The simplest reaction involves only mass transfer of reactant to the electrode, heterogeneous electron transfer involving non adsorbed species and the mass transfer of the product to the bulk solution. More complex reaction sequence involving a series of electron transfer, protonations, branching mechanisms, parallel paths or modifications of the electrode surfaces are quite common. When a steady state current is obtained, the rates of all reactions steps are the same. The magnitude of this current is often limited by the inherent sluggishness of one or more reactions called rate determining steps. The more facile reactions are then held back from maximum rates by the slowness with which such steps disposes of their products or create their participants [91, 92].

1.12.1. Mass Transfer Processes

Whenever an electrochemical charge transfer process takes place at the electrode surface, the electroactive material gets depleted and a concentration gradient is set up. Under such conditions the reactant diffuse towards the electrode surface and the corresponding product of the electrode reaction diffuses away from the electrode surface. Mass transfer in electrochemistry illustrates the movement of electroactive species from differences in electrical or chemical potential at the two locations. There are three forms of mass transport namely, convection, migration and diffusion which influence and electrolysis reaction (Fig. 1.5).

**Convection** is the process independently taking place by the discharge process, a solution is stirred or when in the solution is present a temperature or a density gradient. In this case the molecules of the solvent and the analyte move themselves with a more or less troublesome motion, but that become more laminar in the vicinity of the electrode surface. The layer of solution closer to the electrode surface is practically stationary.

**Migration** is the process of moving due to the attraction force of the electric field generated by the electrode toward every ion having opposite charge and also due to the contemporary repulsion force of every ion having the same charge of the electrode.
Diffusion is the spontaneous movement of those chemical compounds subjected to a concentration gradient that means a situation in which a zone of the solution is poorer than another with the process of diffusion the system tries to destabilize its homogeneity.

The diffusion speed is directly proportional to concentration gradient and then to the concentration of the electro active compound in the solution.

1.13. Electron Transfer or Charge Transfer Process

The electron transfer at the interface between the electrode and electrolyte is central to an electrode reaction. Electroactive species having moved from the bulk of the solution by either diffusion or under forced convection enters in the electrical double layer, which is under direct influence of the electrode. On entering the double layer the species undergoes a structural orientation so that it can gain or lose electrons from or to the electrode surface respectively with the leak activation energy when a suitable potential is applied and macroscopically, we observe current. This state of reactant species is known as transition state. Being unstable the species is in transit state converts itself to the final product by release of activation energy and gets reduced of oxidized. This final product after undergoing suitable re-orientation either gets deposited on the electrode surface or moves away from the electrode surface into the bulk solution. The transfer of an electrons to or from the substrate is an activated process. The electron transfer process can be

- Reversible electron transfer process
- Irreversible electron transfer process
- Quasi-reversible electron transfer process

1.13.1. Reversible Electron Transfer Process

For a reversible process, oxidation and reduction peak is observed as shown in Fig. 1.6. Reversibility can be defined as chemical or electrochemical. In an electrochemically reversible process the electron transfer is not rate limiting. For a chemically reversible process, both forms of redox couple (O for oxidized form and R for reduced form) are stable in the time scale of measurement. The rate of electron
transfer is fast compared to the rate of mass transport and does not control the overall rate. In this process the rate of reaction is fast enough to maintain equal concentration of the oxidized and reduced species at the surface of electrode. The concentration Cox and Cred of oxidized and reduced forms of the redox couple respectively follow the Nernst equation

\[ E = E^0 + \frac{RT}{nF} \ln \frac{C_{ox}}{C_{red}} \]

Where, \( n \) = no. of electrons transferred, \( F \) = Faraday constant, \( R \) = Gas constant and \( T \) = temperature. If the system is diffusion controlled then the Fick's law of diffusion holds for both oxidation and reduction. Under these conditions, peak current given by Randles Sevcik equation;

\[ i_p = (2.69 \times 10^5) n^{3/2} A D_0^{1/2} C_0^* v^{1/2} \]

where \( n \) is the stoichiometric number of electrons involved in the electrode reaction, \( A \) is the area of electrode in cm\(^2\), \( D_0 \) is the diffusion coefficient of the species O in cm\(^2\)s\(^{-1}\), \( C_0^* \) is the concentration of the species O in mol/cm\(^3\) and \( v \) is the scan rate in Vs\(^{-1}\).

**Diagnostic tests for cyclic voltammograms of reversible system at 25 °C**

i. \( \Delta E_p = E_{pa} - E_{pc} = 59/n \) mV, where \( n \) is number of electrons change

ii. \( i_{pc}/i_{pa} = 1 \)

iii. \( i_p \propto v^{1/2} \)

iv. \( E_p \) is independent of \( v \)

**1.13.2. Irreversible Electron Transfer Process**

For an irreversible process, only forward oxidation or reduction peak is observed but at times with a weak reverse peak (Fig. 1.7). This process is usually due to slow electron exchange or slow chemical reactions at the electrode surface [93]. In an irreversible electrode process, the mass transfer step is very fast as compared to the charge transfer step.

For an irreversible reaction, the peak current is given by [94]
\[ i_p = 2.99 \times 10^5 n (\alpha n)^{1/2} A D_0^{1/2} \nu^{1/2} C_0^* \]

\[(\alpha n_a) = 47.7/E_p - E_{p/2}\]

The value of \( E_p \), the difference between the cathodic and anodic peak is of the order of 59 mV/n is given by equation. The peak separation \( E_p \) is a factor determining the reversibility or irreversibility of an electrode reaction. The equation by Nicholson is normally used to calculate electron transfer rate constants.

**Diagnostic Tests for Cyclic Voltammograms of Irreversible System at 25°C**

i. no reverse peak

ii. \( i_p \propto \nu^{1/2} \)

iii. \( E_p \) shifts = \( 30/\alpha n_a \) mV, where \( \alpha \) is charge transfer coefficient

iv. \( [E_p-E_{p/2}] = 47.7/\alpha n_a \) mV

**1.13.3. Quasi Reversible Electron Transfer Process**

This is a class of electrode reactions in which the rates of charge transfer and mass transfer are comparable or competitive. Quasi-reversible process is intermediate between reversible and irreversible systems (Fig. 1.8). The current due to quasi-reversible processes is controlled by both mass transport and charge transfer kinetics. [95] The process occurs when the relative rate of electron transfer with respect to that of mass transport is insufficient to maintain Nernst equilibrium at the electrode surface. In the quasi-reversible region both forward and backward reactions make a contribution to the observed current.

**Diagnostic Tests for Cyclic Voltammograms of Quasi-Reversible System at 25°C**

i. \( i_p \) increases with scan rate, but is not proportional to scan rate.

ii. \( i_{pc}/i_{pa} = 1 \), provided \( \alpha_c = \alpha_a = 0.5 \)

iii. \( \Delta E_p \) is greater than 59/n mV and its increases with increasing scan rate
iv. $E_{pc}$ shifts negatively with increasing $v$

**Coupled chemical reaction**

In addition to charge transfer and mass transfer processes electrode process can be complicated by parallel homogeneous chemical reaction. The coupling of chemical reactions to the electron transfer reactions can lead to changes in the peak potentials and/or the peak currents and the effect of chemical reactions is often expressed in terms of changes in the peak current ratio and/or peak potentials. The most commonly occurring reaction mechanisms are given as:

**Proceeding chemical reactions (CE):** In this case, the electrode process is (E) preceded by a chemical reaction (C) whereby an electroactive substance undergoes a homogeneous chemical reaction to liberate an electroactive substance.

**Following chemical reaction (EC):** In this case, the product of the electron transfer undergoes a homogeneous chemical reaction.

### 1.14. Objectives and Scope of the Thesis

The focus of the work covered in this thesis is to controllably alter the properties of carbon surfaces by chemically grinding modification method, surfactant mobilization and immobilization method, Electropolymerization of monomer, pretreatment of carbon paste electrode, activation of glassy carbon electrode and graphite pencil electrode was used in cyclic voltammetric and differential voltammetric techniques leads to the surfaces are useful for desired sensor applications.

Alongside the primary goal, the research carried out promotes knowledge at many levels relevant to the interests of the academic community in the field of sensor fabrication and technology.

The present work is also aimed at investigating the electrochemical studies and elucidation of the sequence of electron transfer and chemical reactions that occur at or near the electrode surface. Research interests involve the study of reactive intermediates that are formed when compounds are reduced or oxidised electrochemically.
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The aspects investigated are reversible/irreversible or coupled nature of electron transfer, number of electrons involved, adsorption and diffusion-controlled processes, effect of concentration of electroactive species on the redox pathways, pH, nature of the intermediates formed, nature of the products formed etc.

More emphasis have been given not only to the electrochemical behavior of dopamine, ascorbic acid, uric acid, serotonin and omeprazole but also the versatility of use of carbon electrode (carbon paste electrode, glassy carbon electrode and graphite pencil electrode). The preparation and characterization of bare and chemically modified carbon paste electrode surface has been studied. The preparation and characterization of bare and chemically modified glassy carbon electrode surface has been studied. The preparation and characterization of graphite pencil electrode surface has been studied. Thorough characterization of different electrode has been studied.

The focus of the thesis is to use of chemically modified different electrodes for the electrochemical studies of organic compounds to get excellent reproducible results by voltammetric techniques. The organic compounds like dopamine, ascorbic acid, uric acid and serotonin, drug like Omeprazole were chosen for electrochemical studies. In the real sample some organic compounds were interfering each other during the investigation by overlapping their voltammetric responses. Moreover, the traditional electrodes very often suffer from fouling effect due to the accumulation of oxidized products on the electrode surface which results in rather poor selectivity and sensitivity.

In addition to analytical aspects, CV has been used to establish the electrochemical behavior of the given molecules through mechanistic studies. Electrochemical techniques are most suitable to investigate the redox properties of new drugs. Because the biological electrons transfer reactions are complicated, though they have many things in common. Both involves essentially heterogeneous electron transfer process, pH and temperature dependent and occur at electrode/electrolyte interface or membrane/solution interface. Hence, explanations based on electrochemistry have played an important role in interpreting and understanding the biological phenomena. Starting with simple carbon pastes,
improving their performances by chemical modification implies its versatility. Exploring the advantage of the modified, an attempt has been made to explore its applications to real life situations.

Because of the advantages like, high conductivity, wide potential window for analysis, chemically inert, relatively inexpensive, easy modification, easy preparation of paste with organic binder and easily renewal of electrode surface, the carbon paste electrode was chosen for the investigation. In addition graphite pencil electrode and glassy carbon electrode were chosen in the investigation of organic compounds by using voltammetric technique. This thesis also discusses on the different types of modifications used for the electroactive species. In this research work the bioactive organic compounds like dopamine, ascorbic acid, uric acid, serotonin and omeprazole were investigated at modified carbon paste electrode, graphite pencil electrode and glassy carbon electrode surface by using voltammetric techniques.
Fig. 1.1 - Typical excitation signal for CV – a triangular wave form with switching potentials at +0.8 and −0.2 vs SCE; F = forward scan, R = reverse scan.

Fig. 1.2 - Typical cyclic voltammogram: the quantities of interest and how to obtain them from the scan rate.
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Fig. 1.3 - Potential-Current axes for Cyclic Voltammetry.

Fig. 1.4 - General pathway of electrode-mediated processes of oxidized (O) and reduced (R) electroactive species.
Fig. 1.5 - Modes of mass transport.
Fig. 1.6 - Typical voltammogram for a reversible process.

Fig. 1.7 - Typical voltammogram for an irreversible process.
Fig. 1.8 - Typical voltammogram for a quasi-reversible process.
1.15. References


