CHAPTER 1

INTRODUCTION

1.1 Environmental Monitoring

Environmental monitoring for the detection of pollutants is becoming increasingly important to regulatory agencies, the regulated community and the general public. This is true for compounds that pose a potential human health risk or risk to the environment. Especially, environmental contamination by harmful chemicals including explosives, heavy metals, and inorganic, organic and organometallic species is a serious problem due to the possible health threat these contaminants pose to public [1-2]. In recent years, increased concerns with the toxic effects of chemicals in the environment have led to the necessity of monitoring pollutant levels at various points in industrial processes and recycling processes, in effluents and wastewaters, and at industrial, agricultural, and urban sites. Additionally, continuous monitoring of environmental pollution in the field requires portable fast-response sensors that are robust and with sufficient sensitivity and long lifetime. However, the high cost and slow turnaround times typically associated with the measurements of regulated pollutants clearly indicate a need for analytical technologies that are fast, portable and cost effective. To meet this need, a variety of analytical methods have been introduced. Although a very small number of these methods are commercially available, many are under research and development.

1.2 Monitoring of Heavy Metals

Heavy metals are natural constituents of the Earth's crust and are present in varying concentrations in all ecosystems. Human activity has drastically changed the biogeochemical cycles and balance of some heavy metals. Heavy metals are stable and persistent environmental contaminants since they cannot be degraded or destroyed. As trace elements, some heavy metals, e.g. Cu, Se and Zn, are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination, high ambient air concentrations near emission sources, or intake via the food chain. Excessive levels of metals in the marine environment can affect marine biota and pose risk to human consumers of seafood. Heavy metals are also known to have adverse effects on the environment and human health [3].

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemicals concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater.

Environmental monitoring of heavy metals is of great importance for ecological assessments as well as for understanding the dissemination of pollutants [4]. Contamination by these metals is indeed widespread all over the world. Due to their toxicity, even at low concentrations, Cr, U, Pb, Cd, As, Hg, Al, are key elements, while Cu, Zn, Ni, Co, Se, Bi are important because they may play a vital or a toxic role, depending on their concentrations and the nature of the considered organisms. Their biogeochemical role also strongly depends on their physico-chemical forms, which include particulate (>1 μm), colloidal (1 nm-1 μm) and dissolved (< 1 nm) species. The latter include free-metal ions, simple inorganic complexes and complexes with anthropogenic and natural organic ligands. Thus, measurements of total metal concentrations alone do not yield sufficient information on the ecotoxicological impact and fate of trace elements. The measurement of specific species or groups of homologous species, denoted as speciation, is therefore essential [5].

1.3 Electrochemical Sensor

Electroanalytical chemistry can play a very important role in the protection of our environment. In particular, electrochemical sensors and detectors are very attractive for on-site monitoring of priority pollutants, as well as for addressing other environmental needs. Such devices satisfy many of the requirements for on-site environmental analysis. They are inherently sensitive and selective towards electroactive species, fast and accurate, compact, portable and inexpensive.

The purpose of an electrochemical sensor is to provide real-time dependable information about the chemical composition of its surrounding environment. Ideally, the sensor is capable of responding continuously and reversibly and does not agitate the sample. Such devices consist of a transduction element covered with a biological or chemical recognition layer. In the case of electrochemical sensors, they are concerned with the interplay between electricity and chemistry, namely the measurements of electrical quantities, such as current, potential or charge and their relationship to chemical parameters. The analytical information is obtained from the electrical signal that results from the interaction of the target analyte and the recognition layer. Different electrochemical devices can be used for the task of environmental monitoring depending on the nature of the analyte, the character of the sample matrix, and sensitivity or selectivity requirements.

Some of the criteria to be considered for the selection of electrochemical sensors for environmental monitoring are shown in Figure 1.1 [6]. The contribution of electrochemical sensors and electroanalysis can make to this strategy. In general, most of the electrochemical devices used for environmental monitoring fall within three major categories, amperometry and voltammetry, potentiometry and conductimetry.

Amperometry and Voltammetry: The use of a potential applied between a reference and a working electrode causing the oxidation or reduction of an electroactive species. The applied potential thus serves as the driving force for the electron-transfer reaction. The resulting current is a direct measure of the rate of the electron transfer reaction and proportional to the target analyte concentration. The most common example is the oxygen Clark electrode that has been routinely used for monitoring the level of oxygen in water column and sediment pore water.

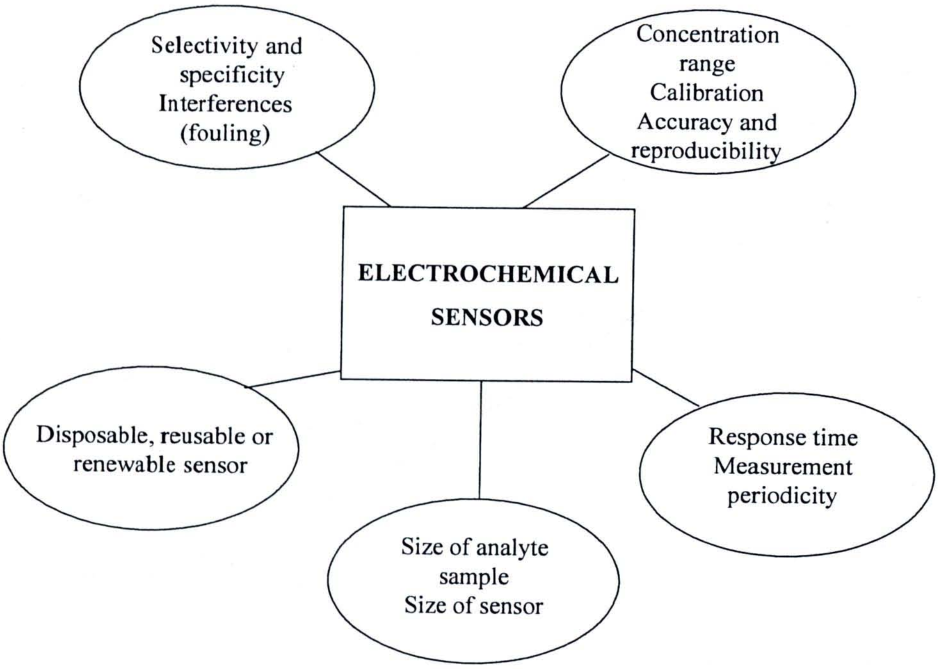

Figure 1.1 Important aspects for choosing electrochemical sensors for environmental monitoring.

Potentiometry: In potentiometric sensors (primarily ion-selective electrodes), the analytical information is obtained by converting an ion-recognition event into a potential signal. A local equilibrium is established across the recognition membrane, leading to a change in the membrane potential. The analytical information is obtained from the potential difference between the ionselective electrode and a reference electrode. Potentials are a function of species activity, not concentration. Typical examples are potentiometric devices for in situ monitoring of pH, pCO_2 or pS.

Conductimetry: Conceptually the simplest of the electroanalytical techniques but inherently non-specific. The concentration of the charge is obtained through measurement of solution resistance and is therefore not species-selective. Conductimetric detectors can, however, be useful in situations where it is necessary to ascertain, for example, whether the total ion concentration is below a certain permissible maximum level or for use as an on-line detector after separation of a mixture of ions by ion chromatography. Such situations can arise in electroremediation.

1.4 Electroanalytical Methods

1.4.1 Electrode Reaction

The goal of an electroanalytical measurement is to acquire a response, e.g. current, potential, or charge, which is related to analyte concentration in the bulk solution. Voltammetry, potentiometry and amperometry are the three major techniques that are commonly used. The three techniques are based on similar electrochemical reactions that occur at the electrode surface. These reactions can be illustrated, in general, as follows:

$$O + ne^- \rightleftharpoons R \qquad [1.1]$$

Where O and R are the oxidized and reduced forms, respectively, of the redox couple.

The overall electrode reaction can be considered as composed of a series of steps that cause the conversion of the dissolved oxidized species, O, to a reduced form, R, also in solution. Some of the simple reactions involve mass transport of the electroactive species to the electrode surface, the electron transfer across the interface and the transport of the product back to the bulk solution. In general, the net rate of the reaction and thus the current is mainly governed either by mass transport of the reactant from the bulk solution to the electrode surface or by the rate of electron transfer at the electrode surface. The slower rate of these two processes controls the overall rate. Furthermore, the two processes are determined by the analyte and various experimental conditions such as media, electrode material, operating potential, time scale, mode of mass transport, etc.

Thus, if the overall rate is controlled by the electron transfer kinetics, the limiting current, i_l, is given by Buttler-Volmer equation [7]:

$$i_l = nFAk^0[C_O(0, t)e^{-\alpha nf(E-E0)} - C_R(0, t)e^{(1-\alpha)nf(E-E0)} \qquad [1.2]$$

and

$$f = F/RT \qquad [1.3]$$

where n is the number of electrons per molecule oxidized or reduced, F is the Faraday constant, A is the area of the working electrode, $C_O(0, t)$ and $C_R(0, t)$ are the concentrations of the oxidized and reduced species at the electrode surface at time 0 or t. k^0 is the standard constant, α is the transfer coefficient, R is the gas constant, T is the temperature, E^0 is the formal potential of the redox couple and E is the potential of the working electrode expressed by the Nernst equation [7]:

$$E = E^0 + RT/nF \ln C_O/C_R \qquad [1.4]$$

Since the kinetics of all electron transfer in most electrode reactions are very rapid compared to those of mass transfer processes, in most cases, the limiting current is mass transfer dependent.

Reactions which are controlled solely by mass transport are called nernstian or reversible, because they obey thermodynamic relationships. The phenomenon of mass transport may occur via three routes: diffusion, convection and migration. While diffusion looks into movement under concentration gradient, i.e. from regions of high concentrations to regions of lower ones, convection deals with gross physical movement to the electrode surface and is minimized via solution (stirring, flowing, sonicating) of electrode (rotating, vibrating). Migration on the other hand deals with movement of charged particle along an electric field, i.e., an electric field is set up at the electrode-solution interface whenever a potential is supplied to a solution, and results in a potential drop across the phase boundary. Such effects are minimized by employing background electrolyte consisting of an electrolytically inert substance (usually an alkali metal salt such as KCl or $NaNO_3$ in aqueous solution). Provided the background electrolyte is concentrated enough (usually 0.1- 1.0 M) the abundance of conducting ions at the electrode interface will effectively prevent the build up of a localized electric field and hence eliminate the contribution of migration to the overall mass transport. Thus, under such diffusion controlled conditions, the limiting current passed through the electrochemical cell and electrode at the time t, $i_l(t)$, can be expressed by the Cottrel equation [7]:

$$i_l(t) \;=\; nFA\pi^{-1/2}t^{-1/2}D_i^{1/2}C_i^{*} \qquad [1.5]$$

Where D_i is the diffusion coefficient and C_i^* is the bulk concentration of species i. Several electroanalytical methods quantitative behavior is based on this equation.

1.4.2 Voltammetry

Voltammetry is a controlled-potential technique which involves measurement of current at a working electrode as an applied potential runs through a limited range which depends on the electrode material, supporting electrolyte and the reference electrode. In other words, the current is measured as a function of a potential waveform applied to the electrode. The current is proportional to the analyte concentration in the bulk solution. The basic difference between these voltammetric techniques are in their potential-time waveforms. In this thesis, cyclic, linear scan, differential pulse and square wave voltammetry associated with stripping analysis were used.

1.4.2.1 Cyclic Voltammetry (CV)

CV is usually the first experiment performed in an electroanalytical study and the most widely used technique for acquiring qualitative information about electrochemical reactions. The power of CV results from its ability to rapidly provide considerable information on the thermodynamics of redox processes, on the kinetics of heterogeneous electron-transfer reactions and on coupled chemical reactions or adsorption processes. Particularly, CV offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect of media upon the redox process [7].

CV thus involves monitoring the current at the working electrode when it is linearly scanned between E_1 to E_2 using a triangular potential waveform at a given scan rate (ν), as shown by the potential-time profile in Figure 1.2. Upon reaching potential E_2 the scan direction is reversed and is often terminated at the start potential, E_1. The gradient of this potential-time plot defines the scan rate, which can vary from a few millivolts per second to millions of volts per second.

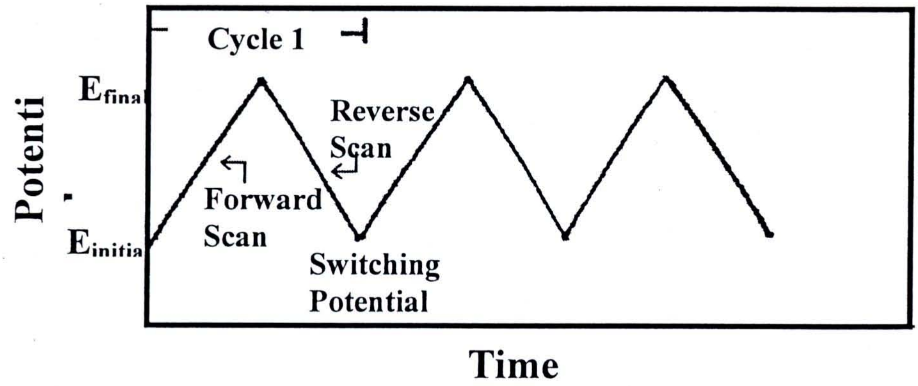

Figure 1.2 A typical potential-time excitation signal in CV.

For an oxidation process, the initial scan direction is positive. There are three main types of electrode process: reversible, irreversible and quasi-reversible. Reversible system (as shown in Figure 1.3) requires fast electrode kinetics compared to the rate of mass transport. An example of this type of process is the oxidation of ferrocene (Fc) to the ferricenium cation (Fc^+) in acetonitrile with 0.1 M $(C_4H_9)_4NClO_4$ as supporting electrolyte [8]. At the initial potential E_1 no current is passed as the magnitude of potential is insufficient to drive electron transfer. As the potential sweeps from E_1 to the oxidizing potential, a current is produced as Fc is converted to Fc^+. The concentration of Fc at the electrode surface ($[Fc]_{x=0}$) decreases as it is converted into Fc^+. This result is an increase in the concentration gradient of Fc at the surface of the electrode and thus the diffusional flux of Fc to the electrode increases. Beyond the formal potential of the redox couple depletion of the reduced species Fc at the electrode surface occurs and more Fc is required

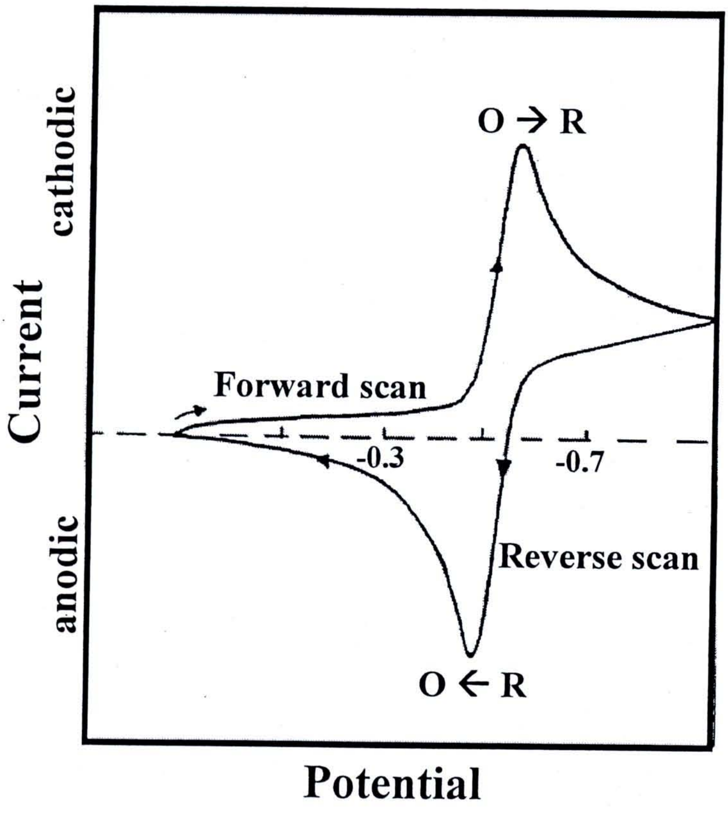

Figure 1.3 A typical cyclic voltammogram showing reversible redox process.

to diffuse in from the bulk. This cause a current maximum (E_p^{ox}) and the subsequent drop in current is controlled by the rate at which a fresh solution can diffuse to the electrode surface.

The magnitude of the peak current, i_p, is predicted by the following equation

$$i_p = (2.69 \times 10^5)\, n^{3/2} A C D^{1/2} \mathrm{V}^{1/2} \qquad [1.6]$$

Where n is the number of electrons transferred, A is the electrode area (in cm^2), C is the species concentration (in mol cm^{-3}), D is the diffusion coefficient (in cm^2 s^{-1}), and V is the scan rate (in V s^{-1}). It should be noted that as the scan rate is increased the value of i_p increases because the diffusion layer becomes thinner and the flux will be greater leading to an enhanced peak current.

At potential E_2 the scan direction is reversed. On this scan an analogous sequence of events occurs. However, in this instance the main reaction is the reductive conversion of Fc^+ back to Fc. A current peak arises at the reduction potential (E_p^{red}). This is where the concentration of Fc^+ has been depleted at the surface and the current depends on the rate of diffusion to the electrode from the bulk. Through scrutinizing the position of the peak potentials and peak heights the reversibility of the redox couple can be assessed.

In these types of processes, the oxidative and reductive peak heights are identical and are separated by a potential of 59 mV (at 25°C), which is independent of scan rate and hence characteristic of an electrochemically reversible couple. If n electrons are transferred in such a system the peak separation is given by [7]:

$$\Delta E_p = E_p^{ox} - E_p^{red} = 0.059/n \qquad [1.7]$$

It should also be noted that the position of the peak on the potential axis (E_p) is related to the formal potential, which is centered between E_p^{ox} and E_p^{red}.

$$E^o = (E_p^{ox} + E_p^{red})/2 \qquad [1.8]$$

Irreversible systems have slow electrode kinetics compared to the mass transport. The increase in the potential E_p^{ox} is due to the over potential required to push the reaction to completion and the loss of a significant reduction peak is because the electrode process does not occur at a measurable rate at potentials close to the formal potential. Unlike the reversible case the peak potentials depend on scan rate. Quasi-reversible systems are intermediate between the two extremes discussed above.

1.4.2.2 Stripping Voltammetry (SV)

SV is a two-step technique, i.e., preconcentration and stripping steps. In the first step, the species of interest is electrolytically or non-electrolytically accumulated into or onto the working electrode under conditions of forced convection. Stirring the solution increases the efficiency of this process. The concentration of the analyte on or in the electrode is much higher than the concentration in the solution (up to 1000-fold increase). Following a period of inactivity allows homogeneous distribution of the analyte and restoration of quiescent solution conditions. The analyte is electrolytically removed in the stripping step. The preconcentrated species is then stripped back to the solution, under a quiescent condition. The current at a working electrode is measured as a function of a potential waveform applied to the electrode. The response due to a given analyte in the stripping step is proportional to the concentration of that analyte in the solution. The conversion of the response to a concentration can be achieved using a calibration curve, but the method of standard additions is generally used. The dynamic range limits depends on the type of electrode material, the electrolyte solution, and the reference electrode. The detection limit of this technique depends on the length of the preconcentration time.

Based on the excitation potential-time waveforms, the three techniques, linear sweep stripping voltammetry (LSSV), differential pulse stripping voltammetry (DPSV), and square wave stripping voltammetry (SWSV) are commonly used in stripping voltammetry. The stripping peak current is directly proportional to the concentration of the analyte in solution. Determination of the analyte in real samples can be performed by calibration or by standard addition methods. In standard addition, a known amount of the analyte is added to the solution and the experiment is repeated. For each sample, two or more standard additions are often made.

SV techniques differ in their methods of accumulation, electrolytic vs. adsorptive. In general, SV includes three kinds of methods such as Anodic Stripping Voltammetry (ASV), Cathodic Stripping Voltammetry (CSV) and Adsorptive Stripping Voltammetry (AdSV). The basic principles of these methods are explained briefly in the following sections.

1.4.2.2.1 Anodic Stripping Voltammetry (ASV)

ASV is carried out in two steps. Firstly, the deposition step involves the electrolytic reduction of metal ions M^{n+} to their elemental state at a constant potential into/onto the surface of an electrode. During the deposition step analyte is brought to the electrode surface by diffusion and/or convection. Secondly, the stripping step consists of the application of a potential waveform to the electrode which causes dissolution of the deposit, the element state metal stripped off into solution followed by a positive-going (anodic) potential scan and obtained a peak shape voltammogram. The peak potential in this scan is used for identification of the metal, and the peak current is proportional to the concentration. The process can be described as follows (e.g., Hg electrode):

Deposition step: $M^{n+} + ne^- \longrightarrow M(Hg)$ [1.9]

Stripping step: $M(Hg) \longrightarrow M^{n+} + ne^-$ [1.10]

with a positive-going potential scan

ASV is the oldest and best established stripping technique. For most applications, the measuring cell is very simple, and many commercial instruments are available, at relatively low cost, which allow the application of different excitation signals. Procedures using linear sweep anodic stripping voltammetry (LSASV), differential pulse anodic stripping voltammetry (DPASV), or square wave anodic stripping voltammetry (SWASV) at a hanging mercury drop electrode (HMDE), a thin mercury film electrode (TMFE), or a solid microelectrode (SME) show very good performance for many applications. The technique has been widely used in the determinations of trace metals such as Pb, Cu Cd, Zn, Bi, Tl, Sn, Sb, In, Ag, Hg, *etc.*, in varies media.

1.4.2.2.2 Cathodic Stripping Voltammetry (CSV)

CSV has been used in the determination of species which can form insoluble derivatives during the pre-electrolysis step. An important group of CSV procedures is devoted to anions, and is based on the formation of sparingly soluble Hg(I) compounds. Like ASV, there are two steps. The first step is the accumulation in which the species is adsorbed on the electrode surface by forming an insoluble salt. Following the preconcentration step, the adsorbed analyte is then stripped off from the electrode by a negative-going (cathodic) potential scan. The mechanism can be simply described as following:

Accumulation step: $[\mathrm{MO_x}]^{m-} - ne^- \rightarrow [\mathrm{MO_x}]^{(m-n)-}$ [1.11]

Stripping step: $[\mathrm{MO_x}]^{(m-n)-} \rightarrow [\mathrm{MO_x}]^{m-} - ne^-$ [1.12]

with a negative-going potential scan

CSV has been used for the determination of inorganic anions such as halides, selenide, and sulfide, and oxyanions such as $\mathrm{AsO_3^{3-}}$, $\mathrm{SeO_3^{2-}}$, $\mathrm{TeO_3^{2-}}$, $\mathrm{MoO_4^{2-}}$, $\mathrm{CrO_4^{2-}}$, $\mathrm{WO_4^{2-}}$, $\mathrm{VO_3^{2-}}$ and some organic compounds.

1.4.2.2.3 Adsorptive Stripping Voltammetry (AdSV)

In adsorptive stripping analysis, a spontaneous adsorption process is purposely utilized as a preconcentration step for trace measurements of important species that cannot be accumulated by electrolysis. For instance, trace and ultratrace metals such as Cr, U, Al, Ni, Co, Mo, W, Ti, V, Fe, are impossible, or at least very difficult, to be determined by ASV or CSV. Adsorption generally means the attachment of molecules or ions to the surface of electrodes. The relatively new strategy involves the formation, adsorptive accumulation, and reduction of a surface active complex of the metal. Adsorptive stripping analysis enhances the scope of stripping measurements for numerous trace elements. The voltammetric stripping schemes, with a negative potential scan can be employed for measuring the adsorbed complex. Short adsorptive time (0.5-5.0 min) results in a very effective interfacial accumulation. The resulting voltammetric response of the adsorbed species is significantly larger than that of the solution alone. Hence, the detection limits are improved by several orders of magnitude as compared to the corresponding solution phase voltammetric response. The surface-active characteristics of numerous organic analytes can be exploited for obtaining effective adsorptive accumulation. Low levels of reducible and oxidizable compounds can thus be determined at mercury-based electrodes. The application of adsorptive stripping analysis for measuring organic analytes in various environmental samples is restricted due to the interference and relative poor selectivity.

Alternative preconcentration schemes based on adsorptive accumulation greatly extend the scope of stripping voltammetry towards numerous metals as well as organic molecules of environmental and biological interest. Adsorption processes of surfactant-active compounds onto the electrode surface involve many mechanisms including electrostatic and hydrophobic interactions as well as $\pi-\pi$ electron interactions and chemisorption. The relationship between the surface and bulk concentrations of an adsorbate is given by the adsorption isotherm. One of the simplest models, the Langmuir isotherm, assumes that there is (a) no interaction between the adsorbed species on the electrode surface, (b) no heterogeneity of the surface, and (c) a saturation coverage at high bulk concentration. The coverage of the electrode surface by species i, Γ_i, according to the Langmuir isotherm, is given by the following equation [9]:

$$\Gamma_i = \Gamma_s \alpha_i C_i/(1+\alpha_i C_i) \qquad [1.13]$$

Where Γ_s is the saturation coverage concentration and α_i is the adsorption coefficient of species i. Therefore, in an electrode electrochemical process during which an adsorption action is involved, the relationship between the quantity of electricity Q and the adsorption quantity Γ_i can be described as follows,

$$Q = nFA\Gamma_i \qquad [1.14]$$

Where A is the surface area of the electrode, F, Faraday constant. Thus, the relationship between the measured response i and the analyte concentration Ci can be given,

$$i = dQ/dt = nFA(\Gamma_s \alpha_i C_i)/(1+\alpha_i C_i) \qquad [1.15]$$

Therefore, the basis of the quantitative analysis using the adsorptive stripping technique can be described as follows [9]:

$$i = k' t_{acc} C_i \qquad [1.16]$$

Where t_{acc} is accumulation time, and k', a constant. A linear relationship between the stripping current and the bulk concentration is expected when the saturation coverage is avoided. This can be achieved by choosing an appropriate accumulation period. For instance, shorter or longer adsorption time is suggested for higher or lower concentration, respectively. However, AdSV is done under conditions of optimum adsorption based on the Langmuir assumptions, and the adsorptive stripping responses, thus, corresponds to the surface coverage which is proportional to the bulk concentration according to equation [1.16].

There are two main advantages related to adsorptive accumulation. The first one is that any oxidation state can be collected rather than only the metallic state. This aspect of AdSV has opened up the technique of electrolysis to any element with a reduction potential falling within the stability range of mercury and hydrogen. The second advantage is that the material is collected as a monomolecular layer on the electrode surface, so almost all the adsorbed species are instantaneously accessible to deduction. Therefore, the reduction current is independent of diffusion of the reactive species and a very fast potential scanning technique can be employed producing larger currents. In addition, the stripping step in AdSV can be anodic or cathodic, so the direction of the potential scan should be specified. A typical electrode reaction based on the adsorption stripping technique can be described in Figure 1.5.

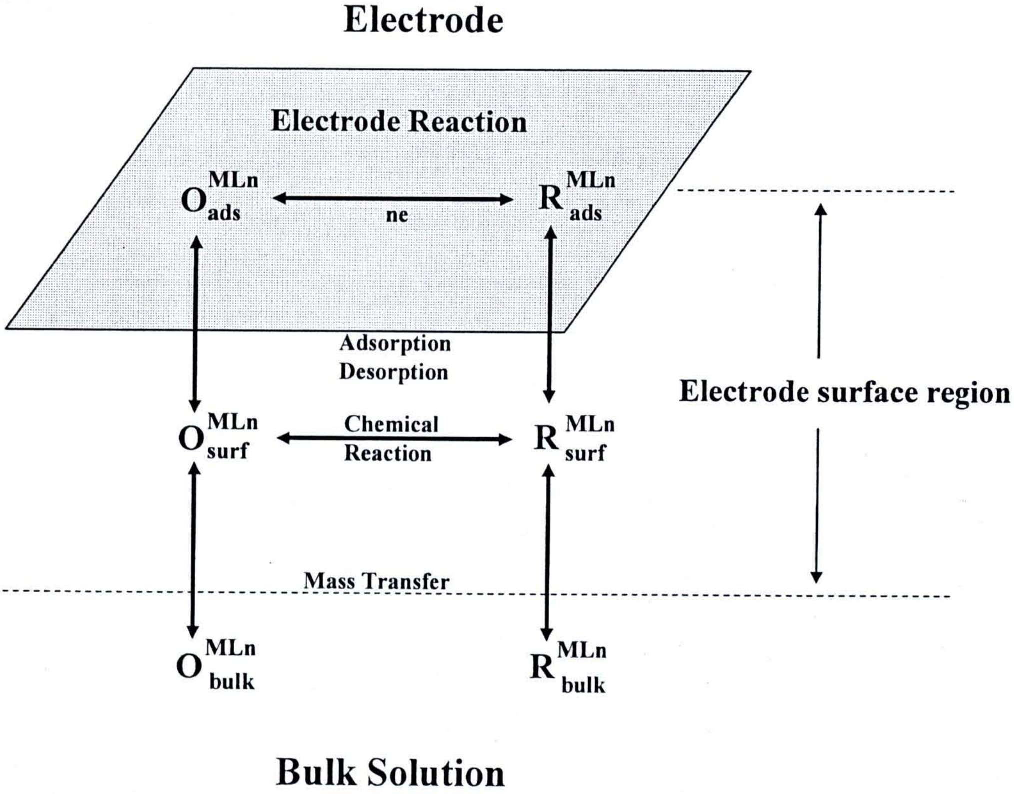

Figure 1.4 A pathway for a typical electrode reaction related to an adsorption reaction.

AdSV has attracted considerable attention for the determination of trace and ultratrace concentration of the metals described above [23, 24, 28-33]. The basis of determination of trace metals by AdSV differs essentially from that of conventional ASV or CSV. The difference is focused on the preconcentration mechanism; according to this mechanism, the metal complex formed, after the addition of the suitable ligand, is accumulated by adsorption on the surface of an electrode. The adsorbed species is subsequently reduced as the potential is scanned to more negative values according to two main mechanisms:

(1) reduction of the elemental species in the adsorbed complex,

Complex step: $M^{n+} + nL \rightarrow ML_n$ [1.17]

Adsorption step: $ML_n \rightarrow [ML_n]_{ads}$ [1.18]

Stripping step: $[ML_n]_{ads} + ne^- \rightarrow M + nL$ [1.19]

(2) reduction of the ligand in the adsorbed complex.

$$M^{n+} + nL \rightarrow ML_n \quad [1.20]$$

$$ML_n \rightarrow [ML_n]_{ads} \quad [1.21]$$

$$[ML_n^{O}]_{ads} + me^- \rightarrow [ML_n^{R}]_{ads} \quad [1.22]$$

In AdSV, the surface-active complex that has been collected can be quantified by reduction of metal or ligand in the complex. However, reduction of metal is preferable to ligand reduction as the reduction peak potential is specific to the metal which minimizes interferences by other metals [32]. In addition, the sensitivity of methods employing ligand reduction tends to be lowered by adsorption and reduction of free ligand in addition to that of the chelate. However, reduction of the ligand is convenient if the metal is reduced only at very negative potentials such as Al, Ca, Sr, and some of the rare earths.

1.4.2.2.4 Catalytic Adsorptive Stripping Voltammetry (CAdSV)

Catalytic and adsorptive processes have greatly enhanced the sensitivity of voltammetric procedures. It has been shown that the coupling of catalytic and adsorptive processes, via controlled adsorptive accumulation of a catalyst, yields remarkable sensitivity and detectability down to the picomolar (ppt) level. In general, the main mechanisms in the ultra-sensitive catalytic adsorptive stripping are based on these steps involving complex information, adsorptive accumulation, complex reduction and oxidant regeneration. More important one is that the products of the electrochemical reduction of the adsorbed species are chemically re-oxidized and reenter the electrochemical reduction cycle.

For instance, a very sensitive procedure for the determination of trace iron by catalytic adsorptive stripping voltammetry of an iron-benzohydroxamic acid-hydrogen peroxide (Fe-HBA-H_2O_2) system has been developed. Figure 1.5 shows the cyclic voltammograms for 0 (a) and 20 (A, b), 2 (B, b) μg/L Fe(III), in the absence (A) and presence of 5×10^{-4} M hydrogen peroxide (B), obtained after 120 s stirring at -0.3 V (B, dotted, without preconcentration). The catalytic character of the Fe-BHA-H_2O_2 redox system is indicated in Figure 1.6, which displays differential pulse voltammograms for 5 μg/L iron in the absence (A) and presence (B) of hydrogen peroxide. The addition of hydrogen peroxide results in significant (~20 fold) enhancement of the complex peak. Overall, very large signals and favorable signification effect associated with the coupling of the catalytic process and the adsorptive accumulation. The main mechanisms in this catalytic-adsorptive stripping system can be described as follows,

Complexion $Fe(III) + BHA \rightarrow Fe(III) - BHA$ [1.23]

Adsorption $Fe(III) - BHA + Hg \rightarrow [Fe(III) - BHA]_{ads}(Hg)$ [1.24]

Reduction $$\begin{tikzcd} {[Fe(III) - BHA]_{ads}(Hg) + e^-} \arrow[r] & {[Fe(II) - BHA]_{ads}(Hg)} \arrow[l, bend left, "H_2O_2"] \end{tikzcd}$$ [1.25]

Oxidation

Such use of catalytic adsorption greatly amplifies the response of the accumulated complex, hence permitting convenient quantitation of ng/L (ppt) concentration. Many procedures for the determinations of trace and ultratrace metals by using AdSV and ultra-sensitive CAdSV have been established. It is possible to determine about 40 elements in a great variety of samples [2]. Due to their excellent sensitivity, accuracy, precision, and low cost of instrumentation, the techniques have been successfully and widely used in environmental sample analysis.

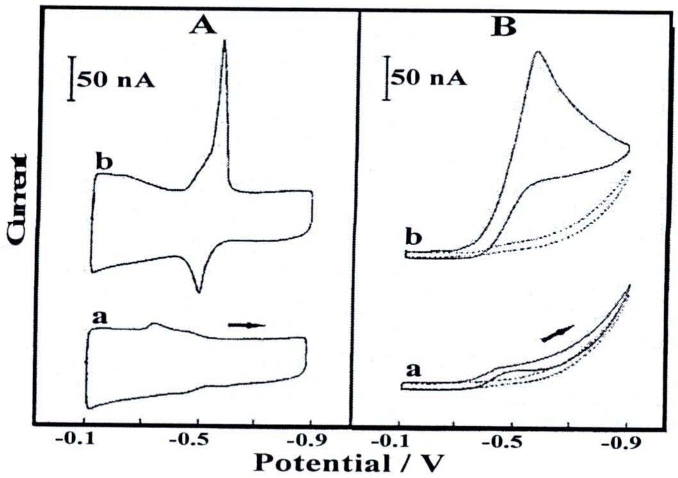

Figure 1.5 Cyclic voltammograms of the Fe-BHA complex. Cyclic voltammograms for 0 (a) and 20 µg/L (A, b), 2 µg/L (B, b) iron(III) in the absence (A) and presence (B) of $5x10^{-4}$ M hydrogen peroxide, in the presence of $5x10^{-4}$ M BHA and 1 mM HEPES buffer (pH 8.0), obtained after 120 s accumulation at -0.3 V (B, dotted, no preconcentration). Differential pulse scan at 10 mV/s with a 25 mV amplitude.

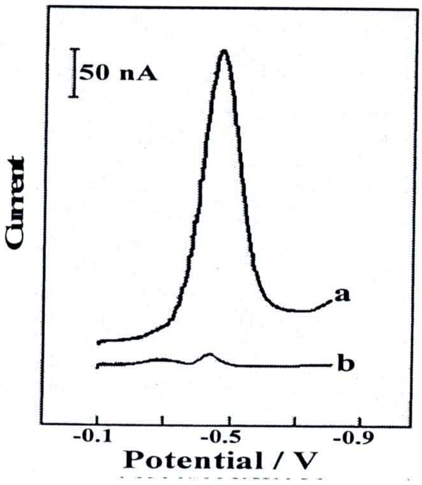

Figure 1.6 Effect of hydrogen peroxide on the Fe-BHA complex adsorptive voltammetry. Stripping voltammograms for 5 µg/L iron(III) in the presence of $5x10^{-4}$ M BHA, and in (A) the absence and (B) presence of $8x10^{-4}$M hydrogen peroxide. Accumulation for 2 min at -0.1 V. Differential pulse scan at 10 mV/s with a 25 mV amplitude. Electrolyte, 1 mM HEPES buffer (pH 8.0).

1.5 Research objectives

This research seeks the development and characterization of new electrochemical sensors for on-site monitoring priority inorganic contaminants natural waters. Unfortunately, the technique has traditionally relied on the use of toxic mercury electrodes. Despite of intensive research efforts and growing concerns on the use of mercury, a 'non-mercury' stripping electrode, truly competitive to mercury ones, has not emerged. The proposed research aims at gaining such insights into the behavior of the new non-mercury stripping electrodes, and for using the new knowledge for optimizing the preparation and operation the non-mercury based metal-sensing devices. We will thus critically assess the analytical 'figures of merit' of the 'mercury-free' stripping sensors. We will also develop an easy-to-use hand-held analyzer, compatible with the new disposable non-mercury electrodes, and will extensively test the integrated microsystem with relevant water samples. The effort would thus lead to the emergence of reliable alternative ('non-mercury') sensing electrodes that would have a major impact upon the monitoring of inorganic contaminants in drinking and natural waters and upon the management of water supplies, in general.