HEAVY METAL ADSORPTION ON MONTMORILLONITE AS A MODIFIER TO CARBON PASTE ELECTRODES
(CPE)

by

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Dissertation submitted in partial fulfilment of
the requirements for the
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CERTIFICATION OF APPROVAL

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CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

BAYRAM OVEZOV

ABSTRACT

Heavy metal pollutants in water samples cause severe health risks. A real-time, monitoring system is needed for instantaneous analysis of samples. Presently, CPEs represent one of the most frequent types of working electrodes. Carbon paste electrodes (CPEs) belong to promising electrochemical or bioelectrochemical sensors of wide applicability. Carbon paste electrodes have a wide range of anodic and cathodic utility and are inexpensive and easy to prepare and replace. These electrodes also have several drawbacks, such as a high cathodic residual current, a low resistance towards mechanical damage and electrochemical polymerization of analytes. Carbon Paste Electrodes can be modified simply to obtain quantitatively new sensors with desired, often predefined, properties. Electrode surfaces modified with clay offer the advantages of high chemical stability, known structural features and low cost. The electrochemistry of clay modified electrodes is a subject of considerable interest; recently, clay-modified electrodes have been used for studying transport in layered materials. Clays are able to adsorb an electroactive species for its direct determination. Objective of this project is to use clay as a modifier for carbon paste electrode and observe its performance after modification. The clay that will be used during project progress is Montmorillonite (MMT) because of its high cation exchange capacity and that its current market price is considered to be 20 times cheaper than that of activated carbon.

Project is consists of 2 stages: preparation of Na-MMT and Anodic Stripping Voltammetry analysis. First stage is done in order to obtain monoionic MMT with same properties in all structure of clay. Second stage is done to observe performance of clay modified carbon paste electrode in which Na-MMT obtained from first stage will be used as clay.

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Environmental monitoring of heavy metals is of great importance for ecological assessments as well as for understanding the dissemination of pollutants (Neuman et al., 1991). Contamination by metals is indeed widespread all over the world (Nriagu et al, 1998). Pollution with cadmium is a highly significant risk factor in predicting higher rates of crime, attention deficit disorder or hyperactivity, and learning disabilities. The major existing techniques for metal trace analyses are spectroscopic (in particular, graphite furnace atomic adsorption spectroscopy (GF-AAS) and inductively coupled plasmamass spectroscopy (ICP-MS)), voltammetric and chronoamperometric. Recently, it has been demonstrated that the chemically modified carbon-paste electrodes (CMCPEs) have received considerable attention due to their numerous advantages, such as easy manufacture, no poison, low price, wider operational window, renewable surface, stability in various solvents and longer life time (Kalcher et al, 2001).

The clay minerals are an important constituent of all soils and they play the role of a natural scavenger by filtering out pollutants from water through both ion exchange and adsorption mechanisms. Clays are hydrous alumino - silicates broadly defined as those minerals that dominantly make up the colloid fraction (<2 μm) of soils, sediments, rocks and water (Pinnavaia, 1983). The high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity, etc., have made the clays excellent adsorbent materials. Clay minerals can be used as a modifier to Carbon Paste Electrode (CPE).

Carbon paste electrodes have a wide range of anodic and cathodic utility and are inexpensive and easy to prepare and replace. These electrodes also have several drawbacks, such as a high cathodic residual current, a low resistance towards mechanical damage and electrochemical polymerization of analytes (Stulik et al, 1987). To retain their advantages and remove most of the drawbacks, modified carbon paste electrodes incorporating exchanger resins and clays have been studied. The montmorillonite exhibits similar properties to other clays. These materials are able to adsorb an electroactive species for its direct determination (Hernandez et al, 1988). Several groups have reported the use of clay film electrodes (Ghosh et al, 1983). Electrode surfaces modified with clay offer the advantages of high chemical stability, known structural features and low cost. The electrochemistry of clay-modified electrodes is a subject of considerable interest (Baker et al, 1994); recently, clay-modified electrodes have been used for studying transport in layered materials (Fitch et al, 1995).

In this paper, a montmorillonite - modified carbon paste electrode was used for the determination of cadmium in water solution and see how modified electrode functions when clay is used as modifier.

1.2 Problem Statement

Toxic metals at trace levels contamination of soil and potential fouling of groundwater is a complex and common problem, and it is well known that heavy metal pollution is a serious threat to the environment. Cd is one of the main trace elements that are of greatest concern.

Selectivity and determination of the amount of heavy metal ions present in water systems has been a troubling factor. Even though research has been going on to determine heavy metals in the system for more than a decade, there is still no sensor invented to overcome the problems (Ricco, 1997).

In order to prevent contamination of subsoil, groundwater and surface water by those elements, real time monitoring system is need to be developed. Carbon Paste Electrodes are first step towards inventing such kind of sensor. But it is important to modify it in order to make it more efficient.

Therefore this research is focused on using clay material as a modifier for Carbon Paste Electrodes in order to make them more effective to detect heavy metals.

1.3 Objective of Study

Upon completing the project, a few objectives need to be achieved. The objectives of study are as follows:

1. To develop a method of detecting trace heavy metals level using clay as a modifier or reaction media to Carbon Paste Electrode in Anodic-Stripping Voltammetry (ASV) analyses.
2. To study the characteristics of adsorption, the clay types and structures and their relations towards heavy metal adsorption.
3. To select the best type of clay for use as a modifier or reaction media.

The scope of this research would be the study on clay as the solvent, reaction media or electrolyte in order to develop a sensor using carbon paste electrode for trace heavy metals. This would include extensive research on clays properties and adsorption, types of clays and their structure, functions towards selectivity over heavy metals..

CHAPTER 2

LITERATURE REVIEW

Review for the study was taken abundantly from journals, the internet and Information Resource Centre of UTP. Basically, spot to be highlighted for the study consists of adsorption, clay types, adsorption isotherms and their use, and operating variables that may affect adsorption. Here are some notes taken for the study:

2.1 Environmental Pollutants

Any undesirable and toxic chemical commodity, organism, or other object present in the environment may be considered an environmental pollutant. The pollutant may be present in solid, liquid or gas form. In all forms, the presence of toxic pollutants is serious and harmful to human beings and other useful organisms. Broadly, environmental pollutants may be categorized into chemical and biological classes. Chemical pollutants are organic and inorganic compounds; biological contaminants are toxic microbes. The presence of inorganic pollutants, especially toxic metal ions, is a serious issue, as metal ions may often be carcinogenic in nature. The route of these toxic metal ions to the human body is through water and other foodstuffs. Therefore, the monitoring of the metal ions and elimination of them in water bodies and foodstuffs is essential and important.

2.1.1 Brief Description of Heavy Metals

"Heavy metals" is a term which is used to define metals with elemental densities above 5g/cm3. As many other metals they can be found in the Earth's shell. Human body also contains small amount of these substances. Mainly they get to organisms via food, drinking water and air. Some heavy metals (e.g. copper, selenium, zinc) are involved in the metabolism of the human body (so called "essential elements") but at very low concentrations. If the concentration of heavy metal in the environment and as a result in a body exceeds certain amount it can be toxic. The reason of heavy metal poisoning is e.g. metals contained water pipes – drinking water pollution, or air emissions from factories.

Danger of heavy metals is in their ability for bioaccumulation. Bioaccumulation is a deposition of a chemical substance in a biological organism with an increase of its concentration in the organism every time this substance is emitted to the environment independently from its amount. Accumulation of compounds in living things is faster than its decomposition and happens at any time they are exposed to the substance.

Environmental pollution from industry is main source of high amounts of heavy metals in the environment. Food poisoning is a consequence and the easiest way to enter human body.

Such an environmental pollution has the internationally known example which occurred in Japan between 1932-55. In 1932 "Chisso's chemicals" built a plant for sodium alkali production by amalgam process on Minimata Bay in Japan. Sewage of the plant contained mercury and were released into Minimata Bay. The mercury was consumed by sea creatures and especially by fish. In 1952, strange illness caused the death of dozens of people and animals. In total 500 victims were recorded. The reason was identified later. It appeared to be mercury poisoned fish which was consumed in great amounts by the population of Minimata Bay. Since then, all industrialized world and especially Japan has passed strict environmental laws and the illness has become known as the Minimata disease.

2.1.2 Source of Contamination

The contamination of our environment due to toxic metal ions is a very serious and challenging issue. It is essential to know the sources of the pollutions of metal ions to control and minimize pollution. Knowledge of pollution sources is also helpful in explaining the transportation behaviour of metal ions. The source of contamination can be classified into **point** and **nonpoint** categories. The point sources include the activities of industries and domestic survival (home lawns, ornaments, pests control etc.), while the nonpoint sources are of geological origin, from agriculture, forestry and related activities.

There are many types of industries that use metal ions as raw materials, consequently releasing some of them as their by-products. Moreover, metallurgical industries are the major sources of metal ion contamination. The major industries using and releasing metal ions are classified in Table 1.

Table 2.1: Major Industries Employing and Releasing Heavy Metals

	Industries	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Pb**	**Zn**
1	Pulp. papermill, building paper, board mills			**x**	**x**			**x**	**x**
2	Organic Chemicals, petrochemicals	**x**		**x**		**x**		**x**	**x**
3	Alkalis, chlorine, inorganic chemi..	**x**		**x**		**x**		**x**	**x**
4	Fertilizers	**x**		**x**	**x**	**x**	**x**	**x**	**x**
5	Petroleum refining	**x**		**x**	**x**	**x**		**x**	**x**
6	Steel works	**x**		**x**	**x**	**x**		**x**	**x**
7	Nonferrous metal works	**x**		**x**	**x**			**x**	**x**
8	Motor vehicle, aircraft plating	**x**		**x**	**x**				
9	Flat glass, cement, asbestos			**x**					
10	Textiles			**x**					
11	Leather tanning			**x**					
12	Steam generation			**x**					**x**

2.2 Cadmium

2.2.1 Notable Characteristics

Cadmium, Cd, is a chemical element of the II group of the periodic table that has atomic number 48, molecular weight 112.41, consists of the mixture of 8 stable isotopes. Cadmium is a bluish-white soft, malleable, easily melted metal with density 8.65g/cm^3 (this fact allows to count cadmium as heavy metal). It has two oxidation states +2 and +1. +2 is the most common. In its properties cadmium is similar to zinc.

2.2.2 Applications

- Batteries (especially Ni-Cd batteries)
- Alloys
- Color television picture tubes
- Pigments
- PVC as stabilizers
- Molecular Biology

2.2.3 Cadmium Poisoning

Cadmium enters human body mainly through food. Examples are liver, mushrooms, shellfish, cocoa powder and dried seafood. An exposure to high cadmium levels occur when people smoke. Tobacco smoke transports cadmium into the lungs. Blood transports it through the body where it can have toxic effects.

Other high exposures can occur with people who live near hazardous waste sites or factories that release cadmium into the air (heat-and-powder engineering) and people that work in the metal refinery industry. When people breath in cadmium it can damage the lungs. This may even cause the death.

Surface water pollution with cadmium may occur because of sewage waters from factories (e.g. batteries production), drainage waters from waste dump, precipitation polluted by gaseous emissions. Cd-containing wastes such as accumulators and batteries which are not treated are the sources of elevated levels of cadmium in water (Budnicov, 2004).

Cadmium is first transported to the liver through the blood. There, it is bond to proteins to form complexes that are transported to the kidneys. Cadmium accumulates in kidneys, where it damages filtering mechanisms. This causes the damages of essential proteins and sugars from the body and further kidney damage. It takes a very long time before cadmium that has accumulated in kidneys is extracted from human body.

Acute exposure to cadmium fumes may cause flu like symptoms including chills, fever, and muscle ache sometimes referred to as "the cadmium blues." Symptoms may resolve after a week if there is no respiratory damage. More severe exposures can cause tracheo-bronchitis, pneumonitis, and pulmonary edema. Symptoms of inflammation may start hours after the exposure and include cough, dryness and irritation of the nose and throat, headache, dizziness, weakness, fever, chills, and chest pain.

Inhaling cadmium-laden dust quickly leads to respiratory tract and kidney problems which can be fatal (often from renal failure). Ingestion of any significant amount of cadmium causes immediate poisoning and damage to the liver and the kidneys. Compounds containing cadmium are also carcinogenic.

The bones become soft (*osteomalacia*), lose bone mineral density (*osteoporosis*) and become weaker. This causes the pain in the joints and the back, and also increases the risk of fractures. In extreme cases of cadmium poisoning, mere body weight causes a fracture.

The kidneys lose their function to remove acids from the blood in *proximal renal tubular dysfunction*. The kidney damage inflicted by cadmium poisoning is irreversible and does not heal over time. The *proximal renal tubular dysfunction* creates low phosphate levels in the blood (*hypophosphatemia*), causing muscle weakness and sometimes coma. The dysfunction also causes gout, a form of arthritis due to the accumulation of uric acid crystals in the joints because of high acidity of the blood (*hyperuricemia*). Another side effect is increased levels of chloride in the blood (*hyperchloremia*). The kidneys can also shrink up to 30% (Jarup, 1998).

2.3 Carbon Paste Electrode (CPE)

Carbon paste electrodes (CPEs) belong to promising electrochemical or bioelectrochemical sensors of wide applicability. In 2008, it was exactly a half century since Ralph Norman Adams from the University of Kansas published a short one-page report (Adams, 1958) in which he introduced this kind of electrode, which was originally designed as an alternative to the dropping mercury electrode. Although the concept of a dynamic renewable electrode surface was not successful, it turned out that the material with paste-like consistency could be practically employed in voltammetric analysis. After the pioneering work of Kuwana, (Kuwana et al., 1964) who actually first modified a CPE by introducing an electrochemically active surface into the material and, after the first chemical modification of an electrode for electrosynthesis (Cheek et al., 1978), the modification was soon applied to carbon paste electrodes (Yao et al., 1979). Finally, Baldwin described a simple method of direct mixing of a solid modifier to the paste, (Kalcher, 1990) which was the commencement of explosive research activity in this field. Presently, CPEs represent one of the most frequent types of working electrodes. The overwhelming number of CPEs used worldwide belongs to pastes with insulating liquids (paraffin oil, silicon oil, bromonaphthalene, tricresyl phosphate and others). The basic requirements for a pasting liquid are its practical insolubility in the solution under measurement, a low vapour pressure to ensure both mechanical stability and long lifetime, and further, in the case of voltammetric and amperometric applications, its electrochemical inactivity in the potential window of interest. In contrast to the relatively complicated modifications of solid substrates, carbon pastes can be modified simply to obtain quantitatively new sensors with desired, often predefined, properties. Very recently, a review with 333 references was published in the form of a retrospective compilation presenting the field by means of various facts, notes, data, surveys, and summaries that illustrate individual achievements and milestones.

Carbon pastes undoubtedly represent one of the most convenient materials for the preparation of modified electrodes. A modifier can be dissolved in a binder or admixed mechanically to the paste during its homogenization. For example, a CPE modified with cobalt (II) phthalocyanine was used for voltammetric determination of ascorbic acid in foodstuffs (Nováková et al, 1997). *In situ* modification of the electrode paste surface is often used as well; examples may be given dealing with applications of an anionic surfactant for voltammetric determination of silver (I) at ultra trace levels (Švancara et al, 1996). Recently, some procedures utilizing cationic surfactants for *in situ* modifications of CPEs were reported for determinations of chromium (VI) (Švancara et al., 2004), osmium (IV) (Galík et al, 2006) and other platinum metals (Švancara et al, 2007), whereby negatively charged complex anions were formed.

2.4 Adsorption

The process of adsorption involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface of that phase is the adsorbate.

Adsorption at a surface or interface is largely the result of binding forces between the individual atoms, ions, or molecules of an adsorbate and the surface, all of these forces having their origin in electromagnetic interactions. Four principle types of adsorption – exchange, physical, chemical, and specific – may be distinguished.

Exchange adsorption, or ion exchange, involves electrostatic attachment of ionic species to sites of opposite charge at the surface of an adsorbent, with subsequent displacement of these species by other ionic adsorbates of greater electrostatic affinity. Physical adsorption results from the action of van der Waals forces, which are comprised of both London dispersion forces and classical electrostatic forces. Chemical adsorption involves a reaction between an adsorbate and an adsorbent resulting in a change in the chemical form of the adsorbate. The resulting chemisorptive bond is usually stronger than that derived from the physical van der Waals forces. Attachment of adsorbate molecules at functional groups on adsorbent surfaces can also result from specific interactions which do not result in adsorbate transformation. Those interactions designated “specific adsorptions”, exhibit a range of binding energies ranging from values commonly associated with physical adsorption to the higher energies involved in chemisorptions. The net dispersion, electrostatic, chemisorptive, and functional – group interactions broadly define the affinity of an adsorbent for specific adsorbate.

Adsorption is one of the most important physicochemical processes that occur at the solid-liquid and solid-gas interfaces. Adsorption has become a preferred method for removal, recovery and recycling of toxic heavy metals from wastewater. Different conventional and non-conventional type of adsorbents have been tried for removal of various metal ions like red mud, activated carbon, tree fern, coconut coirpith, sewage sludge, sawdust, silica, bone char, rice husk, polymetallic sea nodule, modified zeolite, etc.

2.5 Adsorbent

For the adsorbent the most important determinants of equilibrium capacity and rate of approach to this capacity include surface area, the physicochemical nature of the surface, the availability of that surface to adsorb molecules and/or ions, and the physical size and form of the adsorbent particles. System parameters such as temperature and pH can also markedly influence adsorption to the extent that they effect changes in any one or more of the aforementioned parameters.

A large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitable gives rise to large numbers of small sized pores between adsorption surfaces. The size of micropore determines the accessibility of adsorbate molecules to the adsorption surface so the pore size distribution of micropore is another important property for characterizing adsorptivity of adsorbents.

Also some adsorbents have larger pores in addition to micropores which result from granulation of fine powders or fine crystals into pellets or originate in the texture of raw materials. These pores called macropores are several micrometers in size. Macropores function as diffusion paths of adsorbate molecules from outside the granule to the micropores in the fine powders and crystals. Adsorbents containing macropores and micropores are often said to have “bi-dispersed” pore structure.

Surface polarity corresponds to affinity with polar substances such as water. Polar adsorbents are thus called “hydrophilic” and aluminosilicates such as zeolites, porous alumina, silica gel or silica-alumina are examples of adsorbents of this type.

On the other hand, nonpolar adsorbents are generally “hydrophobic.” Carbonaceous adsorbents, polymer adsorbents and silicalite are typical nonpolar adsorbents. These adsorbents have more affinity with oil than water.

Since its first introduction for heavy metal removal, activated carbon has undoubtedly been the most popular and widely used adsorbent in wastewater treatment applications throughout the world. In spite of its prolific use, activated carbon remains an expensive material since higher the quality of activated carbon, the greater its cost. Activated carbon also requires complexing agents to improve its removal performance for inorganic matters. Therefore, this situation makes it no longer attractive to be widely used in small-scale industries because of cost inefficiency.

Due to the problems mentioned previously, research interest into the production of alternative adsorbents to replace the costly activated carbon has intensified in recent years. Attention has been focused on the various adsorbents, which have metal-binding capacities and are able to remove unwanted heavy metals from contaminated water at low cost. Because of their low cost and local availability, natural materials such as chitosan, zeolites, clay, or certain waste products from industrial operations such as fly ash, coal, and oxides are classified as low-cost adsorbents.

2.6 Theory of adsorption isotherms

2.6.1 Langmuir isotherm

The Langmuir isotherm has been used extensively by many authors for the sorption of heavy metal ions in clay, metal oxides, soils, etc. The Langmuir isotherm is a valid monolayer sorption on a surface containing a finite number of binding sites. It assumes uniform energies of sorption on the surface and no transmigration of sorbate in the plane of the surface. The Langmuir equation may be written as:

$$q_e = \frac{q_m b C_e}{1 + b C_e} \qquad (\textit{non-linear form})$$

$$\frac{C_e}{q_e} = \frac{1}{q_m b} + \frac{C_e}{q_m} \qquad (\textit{linear form})$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e, the equilibrium concentration of solute in the bulk solution (mg/l), q_m, the monolayer adsorption capacity (mg/g) and b is the constant related to the energy of adsorption. It is the value reciprocal of the concentration at which half the saturation of the adsorbent is attained.

The effect of isotherm shape can be used to predict whether a sorption system is "favourable" or "unfavourable" both in fixed bed systems (Weber et al., 1974) as well as in batch processes (Poots et al., 1978). According to Hall et al. [33] the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter K_R, which is defined by the following relationship:

$$K_R = \frac{1}{1 + K_a C_o}$$

where K_R is a dimensionless separation factor, C_0, the initial metal ion concentration (mg/L) and K_a is Langmuir constant (L/mg). The parameter K_R indicates the shape of the isotherm accordingly:

Table 2.2: Indication of K_R term for isotherm shape

Values of K_R	*Type of Isotherm*
$K_R>1$	Unfavourable
$K_R=1$	Linear
$0<K_R<1$	Favourable
$K_R=0$	Irreversible

2.6.2 Freundlich isotherm

The Freundlich isotherm theory says that the ratio of the amount of solute adsorbed onto a given mass of sorbent to the concentration of the solute in the solution is not constant at different concentrations. The Freundlich equation may be written as:

$$q_e = K_F C_e^{1/n} \qquad \textit{(non-linear form)}$$

$$\log q_e = \log K_F + 1/n \log C_e \qquad \textit{(linear form)}$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent (mg/g), C_e, the equilibrium concentration of solute in the bulk solution (mg/l), K_F, the constant indicative of the relative adsorption capacity of the adsorbent (mg/g) and $1/n$ is the constant indicative of the intensity of the adsorption.

2.6.3 Toth isotherm

This is Langmuir-based isotherm. It belongs to the left handed widened Gaussian energy distribution and assumes a continuous distribution of site affinities (Altin et al., 1998):
The equation may be written as:

$$q_e = KC_e q_m /(1+(KC_e)^n)^{1/n}$$

where q_e, K, C_e, q^m and $1/n$ are same as those in Langmuir and Freundlich isotherms.

2.6.4 Langmuir–Freundlich isotherm

That is an isotherm that fuses both Langmuir and Freundlich isotherms together. It is expected to describe heterogeneous surfaces much better. The equation can be written as:

$$q_e = (KC_e)^n q_m / 1 + (KC_e)^n$$

where q_e, K, C_e, q^m and $1/n$ are same as those in Langmuir and Freundlich isotherms.

2.7 Clay

2.7.1 General Structure Features

Clays are hydrous aluminosilicates broadly defined as those minerals that make up the colloid fraction of soils, sediments, rocks and water and may be composed of mixtures of fine grained clay minerals and clay-sized crystals of other minerals such as quartz, carbonate and metal oxides. Usually the term clay is used for materials that become plastic when mixed with a small amount of water. Clays play an important role in the environment by acting as a natural scavenger of pollutants by taking up cations and anions either through ion exchange or adsorption or both. Thus, clays invariably contain exchangeable cations and anions held to the surface. The prominent cations and anions found on clay surface are Ca^{2+}, Mg^{2+}, H^+, K^+, NH^{4+}, Na^+, and SO_4^{2-}, Cl^-, PO_4^{3-}, NO^{3-}. These ions can be exchanged with other ions relatively easily without affecting the clay mineral structure.

There are two major types of clay minerals found in soils: 1:1 and 2:1. When scientists talk about 1:1 ("one to one") or 2:1 clays, they refer to the ratio of silica tetrahedron sheets to aluminum octahedron sheets. 1:1 clay has one of each sheet; 2:1 clays have two tetrahedral sheets on either side of an aluminum octahedron sheet. These tetrahedral and octahedral sheets are variously arranged and modified during mineral formation to create several types of clay minerals. The 2:1 type is typical for clays montmorillonite and illite. The unit cell here is built from two silica tetrahedral layers, (Si_2O_5), surrounding an aluminium octahedral layer, $Al_2O_4(OH)_2$. Only weak van der Waals forces exist between two units so that water, nutrients, chemicals can readily enter the interlayer regions and react with the inner surface, often being immobilised. This also causes the ability to expand montmorillonite or illite when in contact with water. The water content in montmorillonite can vary so that its chemical formula can be written $Al_2(OH)_2(Si_2O_5)_2 \bullet nH_2O$ (Dobrzanski et al., 1993). The 1:1 type is typical for clay kaolinite. A unit cell of kaolinite is composed of one silica tetrahedral layer bonded to an aluminium octahedral sheet. The unit cells in 1:1 type are hydrogen bonded together providing no interlayer regions. Thus water and chemicals cannot enter between cells so the distance between them remains constant opposite to montmorillonite. The chemical formula of kaolinite is $Al_2(OH)_4(Si_2O_5)$.

The major difference between expandable, type 2:1, and nonexpanding clays is in the surface area. The 2:1 type of clays have much higher total surface area than the 1:1 type has because of the existence of the internal surface area (Weber et al., 1991). The expandable clay minerals have also a much greater cation exchange capacity (C.E.C.) than the nonexpanding types and thus have a much greater propensity for immobilizing chemicals such as metal ions. The basic characteristics of some clays are listed in Table 3 and Figure 1 shows how the clay structures are arranged.

Table 2.3: Characteristics of typical clays

Characteristics	Montmorillonite	Illite	Kaolinite
Type of layering	2:1	2:1	1:1
Layer charge	0.25-0.6	0.6-0.9	1.0
C.E.C. cmol(+)/kg	80-120	20-50	1-10
Surface area ($x10^3$ m^2 kg^{-1})	600-800	70-120	10-20
pH dependent charge	minor	medium	extensive
Shrink/swell potential	highly expansive	expansive	non-expansive
Interlayer space	very large		none (very small)

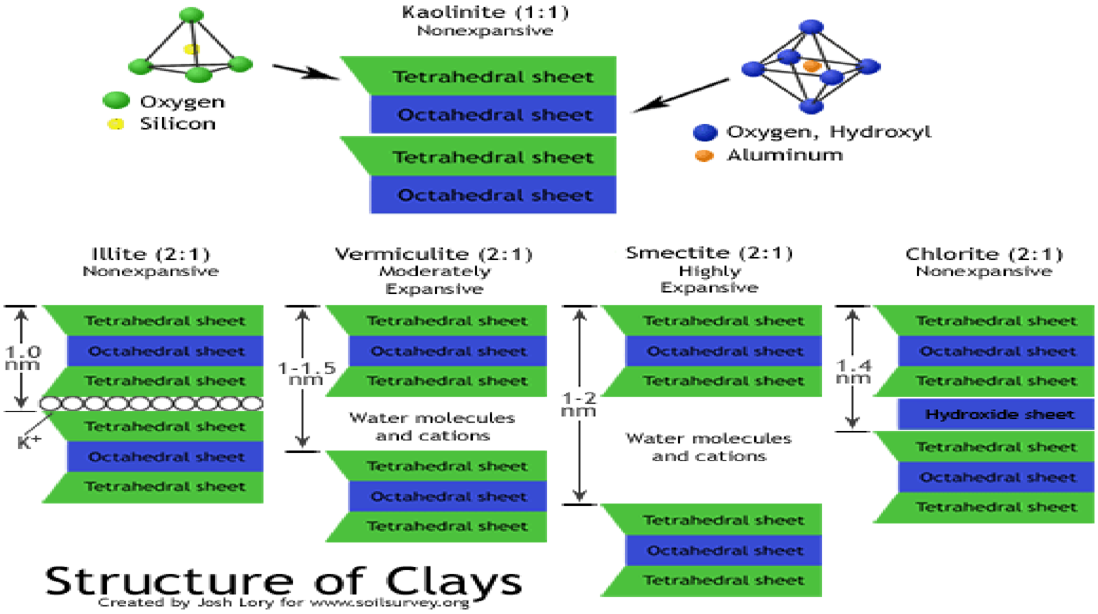


Figure 2.1: Structure of Clays

Kaolinite is one of the 1:1 clay minerals (Barak et al., 2003). It does not shrink when dry or swell when wet, which makes it well-suited for uses such as construction of roads and buildings, for septic adsorption fields, and pottery. X-ray diffraction analysis has shown that sheets of kaolinite are arranged like pages in a book; this affects the amount of surface area available for holding water or cations like Ca^{2+} or K^{+}. Imagine a closed book with many pages; each page has surface area on the front and back, which might be a lot of surface area. But if the book is closed the pages are so tightly packed the surface area is not available. The only practical surface for water or cations to attach (or "adsorb") to would be the edges of the book, plus the front and back covers. Because of this arrangement, kaolinite has less external surface area than other clay minerals, no internal surface area, and less capacity for holding water and cations.

The 2:1 clay minerals look much different. Using X-ray diffraction analysis, montmorillonite (one of the smectite clay minerals) looks like a sponge (Barak et al.,, 2003). Observe in the figure above the differences in spacing between the 2:1 sheets. The larger interlayer spaces have the capacity to hold water molecules and a variety of cations (some of which, like Na^+, cause the clay to disperse) with important consequences for plant growth. Also, with larger interlayer spaces comes a greater tendency for shrink/swell behavior (not all 2:1 clays are expanding). If a clay swells when wet, it is poorly suited for building site development or for septic leach fields. However, these clays are excellent for sewage lagoons or wildlife ponds; if they remain wet they "seal" and hold water.

Clay's sorption capabilities come from their high surface area and exchange capacities. The negative charge on the structure of clay minerals gives clay the capability to attract metal ions. This is a very important factor influencing sorption properties of the clay. There are at least two major possibilities as to how these charges are formed (Loughnan, 1969). Firstly the hydroxyl groups which exist on the edges and on the outer layers oxygen probably covalently, not very tight. This is a pH-dependent process and the ability to split the hydrogen atom decreases when pH decreases. When pH is above 6 hydrogen may easily by replaced by other ions like Ca^{2+}, Al^{3+}, Pb^{2+}, Cd^{2+}. The second process of creating negative charges is connected to the isomorphous ion replacement in the minerals. In the silica tetrahedral Al^{3+} can replace the silicon ion Si^{4+} because these two have a similar ionic radius, whereas Mg^{2+} Fe^{2+} can exist in the octahedral layers instead of Al^{3+}. The negative charge, which appears as a result of isomorphous ion replacement, is pH independent and therefore quite persistent. The ability to create negative charges is the highest for 2:1 type of clays (Dobrzanski et al., 1993).

The high specific surface area, chemical and mechanical stability, layered structure, high cation exchange capacity (CEC), and tendency to hold water in the interlayer sites have made the clays excellent adsorbent materials.

2.7.2 Classifications

Based on the layer types (1:1 or 2:1), layer charge or charge per formula unit, and octahedral types (dioctahedral or trioctahedral), clay minerals can be divided into different groups and subgroups. Each subgroup in turn is divided into mineral species. Such a classification criterion is shown in Table 2.4 and Figure 2.2.

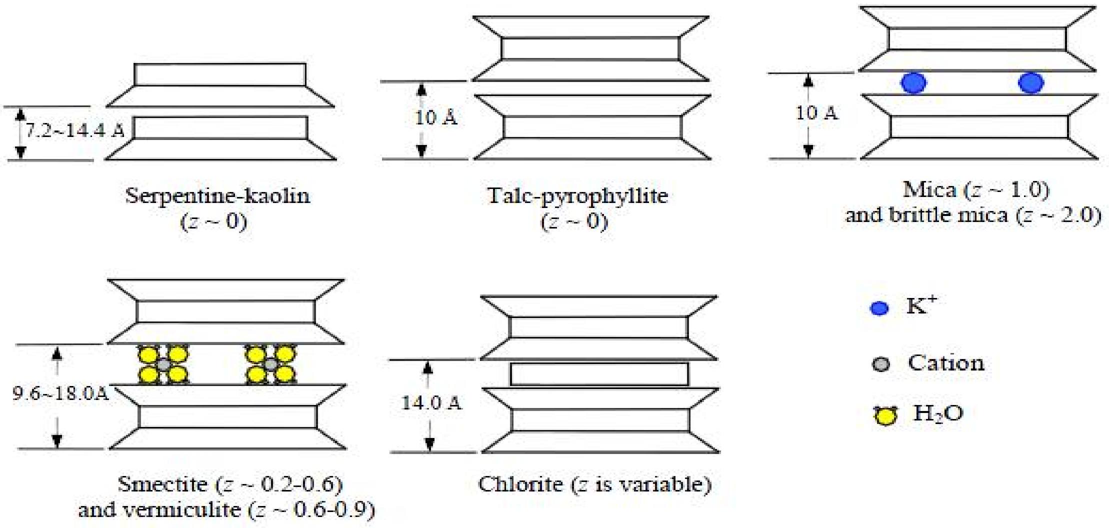


Figure 2.2: Schematic illustration of the crystal structures of major clay minerals. *z is the negative charge per formula unit layer,* $O_5 (OH)_4$ *for 1:1 layer minerals and* $O_{10} (OH)_2$ *for 2:1 layer minerals* (Bailey, 1980; Brown, 1984; Moore and Reynolds, 1997, Mitchell and Soga, 2005).

Table 2.4: Classification of clay minerals and related phyllosilicates (Lambe et al., 1979; Brindley, 1981; Bailey, 1980; Brown, 1984; Moore and Reynolds, 1997; Mitchell and Soga, 2005)

Layer Type	Interlayer Material	Group	Subgroup	Basal spacing (00l)	Species
1:1	None or H_2O only (*z* ~ 0)	Serpentine-Kaolinite	Serpentine (Tr)	7.2~14.4 Å	Chrysotile, antigorite, lizardite, berthierine, odinite
			Kaolins (Di)		Kaolinite, dickite, nacrite, halloysite
2:1	None (*z* ~ 0)	Talc-pyrophyllite	Talc (Tr)	10 Å	
			Pyrophyllite(Di)		
	Hydrated exchangeable cations (*z* ~ 0.2-0.6)	Smectite	Tr smectite	9.6 Å~18 Å	Saponite, hectorite
			Di smectite		Montmorillonite, beidellite, nontronite
	Hydrated exchangeable cations (*z* ~ 0.6-0.9)	Vermiculite	Tr vermiculite	10.5~14Å	
			Di vermiculite		
	Non-hydrated monovalent cations (0.6 <*z* < 0.9)	Illite	Tri illite		Illite, glauconite
			Di illite		

	Non-hydrated monovalent cations (z ~ 0.6-1.0)	Mica	Tr micas	10 Å	Biotite, phlogopite, lepidolite
			Di micas		Muscovite, paragonite
	Non-hydrated divalent cations (z ~ 1.8-2.0)	Brittle Mica	Di brittle micas	10 Å	Margarite
	Hydroxide sheet (z ~ variable)	Chlorite	Tr,Tr chlorites	14 Å	
			Di,Di chlorites		Donbassite
			Di, Tr chlorites		Sudoite, cookeite (Li)
			Tr, Di chlorites		
2:1	Regularly interstratified (z ~ variable)	variable		variable	

Note: Tr = trioctahedral; Di = dioctahedral; z = charge per formula unit.

2.7.3 Exchange of Ionic Species

A very important property of clay surfaces is their chemical activity and their interaction with ions in aqueous solutions. The charged ions or molecular species can be attracted by charged surface and *adsorbed* onto the surface. In some species of the clays the activity of the surface (surface charge) is increased by a sort of internal surface into which charged ions or molecules can find their way. These ions are *absorbed* by the clay into internal crystallographic sites. The absorbed ions are normally accompanied by water molecules, expanding the clay, when in aqueous solution. In this way the chemical action of the surface area in increased greatly, by factor of 25 or more.

The property of adsorbing and absorbing ionic species in solution is called *cation exchange capacity (CEC)*. This capacity is measured in terms of the total number of charged ions which can be fixed onto the surfaces of clays. This capacity is measured in terms of the total number of charged ions which can be fixed onto the surfaces of clays. The values are expressed in milli-equivalents of charge (moles)/100g. Often the CEC is expressed in meq (milli-equivalents) without any reference to the other units of measure.

2.8 Montmorillonite (MMT)

It is widely known that there are three basic species of clay: smectites (such as montmorillonite), kaolinite, and micas; out of which montmorillonite has the highest cation exchange capacity and that its current market price is considered to be 20 times cheaper than that of activated carbon. Therefore, a number of studies have been conducted using clays, mainly montmorillonite, to show their effectiveness for removing metal ions such as Zn^{2+}, Pb^{2+}, and Al^{3+} from aqueous solutions.

Montmorillonite is a very soft phyllosilicate group of minerals that typically form in microscopic crystals, forming clay. It is named after Montmorillon in France. Montmorillonite, a member of the smectite family, is 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately one micrometre. Members of this group include saponite.

The formula for montmorillonite is $(Si_{7.8}Al_{0.2})^{IV}(Al_{3.4}Mg_{0.6})^{VI}O_{20}(OH)_4$ and the theoretical composition without the interlayer material is SiO_2, 66.7%, Al_2O_3, 28.3%, H_2O, 5%. The above formula indicates that there is substitution of Si^{4+} byAl^{3+} in the tetrahedral layer and of Al^{3+} by Mg^{2+} in the octahedral layer.

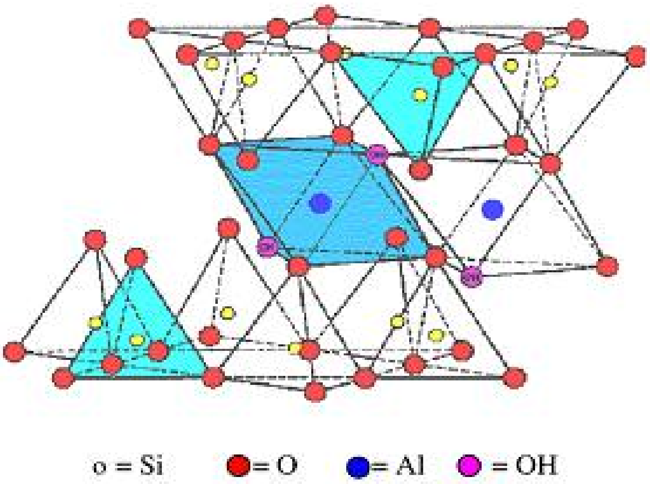


Figure 2.3: Structure of Montmorillonite

Thus, the net layer charge of montmorillonite is: [7.8 (+4)]+[0.2 (+3)]+[3.4 (+3)]+[0.6 (+2)]+[20 (−2)]+[4 (−1)]=−0.8 charge/ unit cell. The resulting negative net charge is balanced by exchangeable cations adsorbed between the unit layers and around their edges. Montmorillonite is a clay mineral with substantial isomorphic substitution. Exchangeable cations in the 2:1 layers balance the negative charges generated by isomorphic substitution. The uptake kinetics of cation exchange is fast and the cations such as Na^+ and Ca^{2+} form outer-sphere surface complexes, which are easily exchanged with solute ions by varying the cationic composition of the solution. In addition to cation exchange there is a pH-dependent uptake of metals on montmorillonite. In this adsorption process, adsorbate ions are bound to the clay surface by sharing one or several ligands (generally oxygen) with adsorbent cations as isolated complexes. With increasing pH or adorbate cation concentration, metal precipitation can occur. In the montmorillonite structure, interlayer swelling occurs when it is exposed to water. The swelling procedure depends on valences and atomic radii of the exchangeable cations. Al and Si atoms exposed to the crystallite edges are partially hydrolyzed to silanol (SiOH) and aluminol (AlOH) groups. These unsaturated edge sites are much more reactive than the saturated basal sites. In montmorillonite, adsorption can occur both at the edge sites, which leads to inner-sphere metal complexes, and at the planar (internal) sites of the clay mineral, which results in outersphere metal complexes.

2.9 Effect of Some Variables on Adsorption of Heavy Metals on Clays

Kayode O. Adebowale et al., presented on his research paper effect of some operating variables on adsorption of lead and cadmium on kaolonite clay. We can say for most of the clays the effect would be the same. This section presents some effects of the operating variables that should be taken into consideration.

2.9.1 Amount of adsorbent

As the weight of the clay increases there should be a corresponding increase in the amount of heavy metal ion adsorbed. This could be due to increase in surface negative charge as well as a decrease in the electrostatic potential near the solid surface.

2.9.2 pH

Increasing pH should enhance the uptake of the metal ions. This may be as a result of increased overall negative charge. In addition, increasing pH decreases the concentration of H^+ therefore reducing the competition between metal ions and protons for adsorption sites on the particle surface. Another factor that could also contribute to enhancing metal ion adsorption is the increasing pH which encourages metal ion precipitation from the solution in the form of hydroxides.

2.9.3 Heavy Metal Ion Concentration

With increasing metal ion concentration, there should be increase in the amount of metal ion adsorbed due to increasing driving force of the metal ions towards the active sites on adsorbent.

2.10 Anodic Stripping Voltammetry (ASV)

ASV is one of the most sensitive, convenient, and cost effective analytical methods for detection of metal ions contaminants, such as cadmium, in water whether from rivers, lakes, process streams or drinking sources. With ASV, it is possible to analyze simultaneously very low levels of several metals such as Pb, Cu, Cd and Zn. ASV can detect levels in the range of part-per-millions (ppm) or even part-per-billion (ppb).

ASV involves a deposition step (often called pre-concentration) at an applied negative potential for a specified period of time. The metals, as ions in solution, are concentrated by plating them onto the electrode in their metallic form. Then the electrode is scanned linearly toward positive potentials so that the metals, one at a time, is stripped from the electrode and re-oxidized at a potential characteristic of each metal. The resulting current-voltage peaks can be compared with those in a calibration done with standard solution of known quantities of metal ions. Besides determining which metal are present, the quantity of each metal can be correlated to the peak height of the current or the integrated charge under the peak. Thus, this method is ideal to be used for detecting cadmium particles using the carbon paste electrodes that were to be developed.

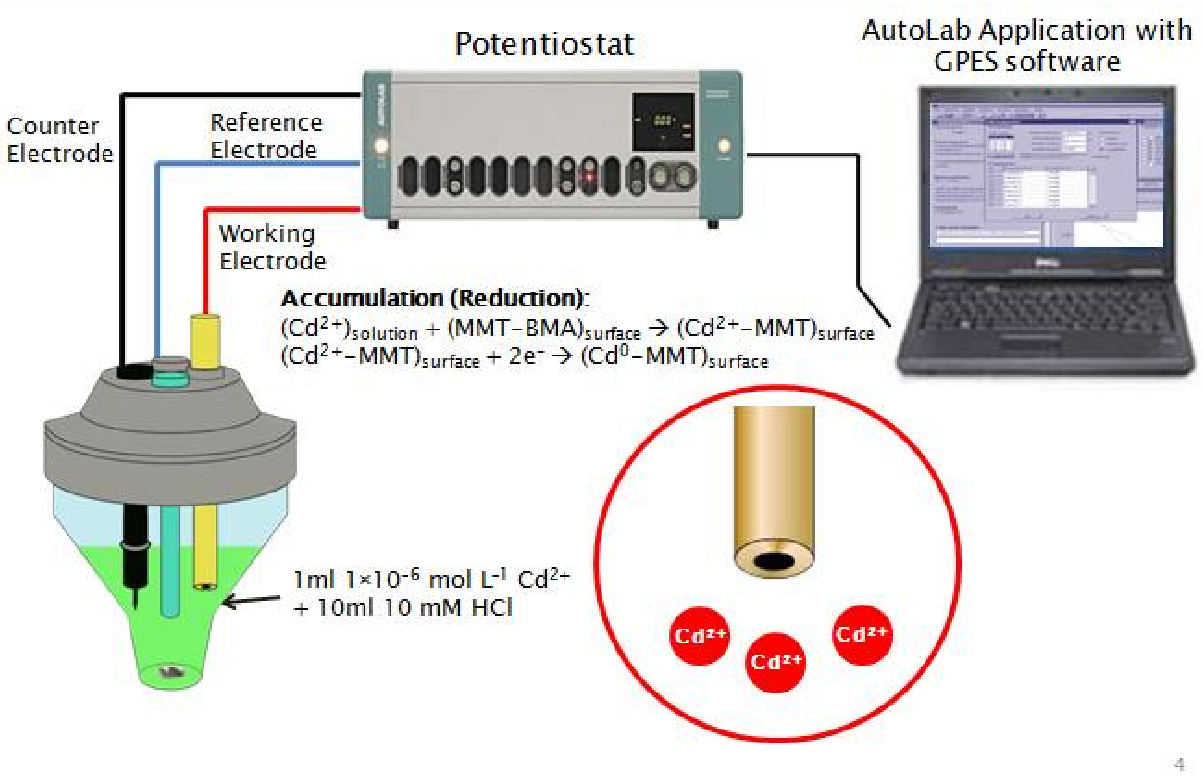


Figure 2.4: Anodic Stripping Voltammetry Design

2.10.1 Working Electrode

- Makes contact with the analyte, facilitate the transfer of electrons to and from the analyte.
- Apply the desired potential in a controlled way.

- Modified carbon paste electrode used as working electrode.

2.10.2 Counter Electrode

- Passes all the current needed to balance the current observed at the working electrode.
- Graphite electrode used as Counter electrode.

2.10.3 Reference Electrode

- Half cell with a known reduction potential.
- Act as reference in measuring and controlling the working electrodes potential.
- Silver/Silver Chloride (Ag/AgCl) used as reference electrode.

The output of the test would be a current versus potential plot. There are normally four notable regions in the graph (Protti, 2001).

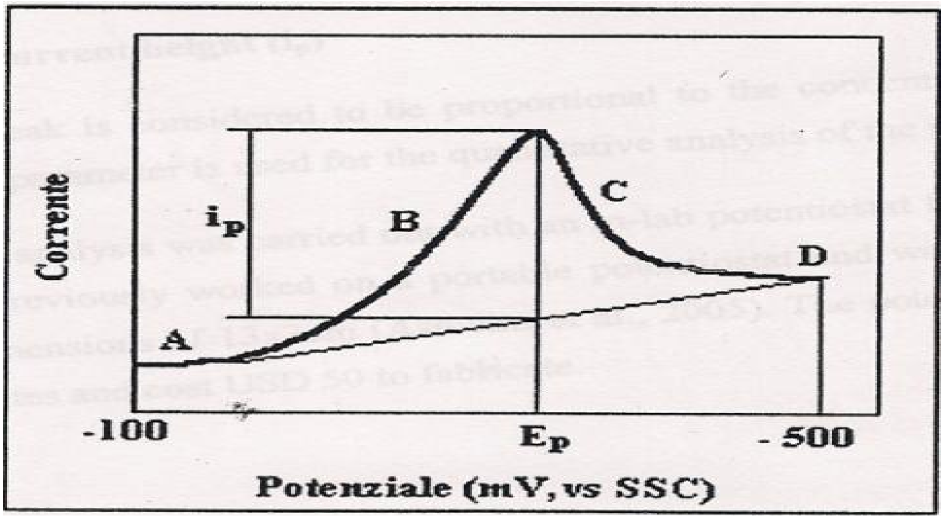


Figure 2.5: Current versus potential plot

2.10.4 Background Current (Part A in Figure 4)

At this stage, the potential supplied by the potentiostat is not sufficient enough to discharge any pre-deposited metal ions on the surface of the working electrode. The measured background current can be due to initial resistance of the cell, discharge of oxygen in the solution, the capacitive current, electronic noise of the potentiostat and etc.

2.10.5 Ascending part of the peak (Part B in Figure 4)

The measured current through the working electrode will go up if it is nearing the discharge potential (a point where the ions are discharged from the electrode surface). The lead ions are discharged into the bulk solution and more ions will try to deposit back at the surface.

2.10.6 Descending part of the peak (Part C in the Figure 4)

The concentration of cadmium ions near the electrode surface nears zero. The current starts to decrease as the cadmium ions will not be able to reach the electrode surface. At this moment, all cadmium ions are reduced almost instantaneously before they even have the chance to near the electrode surface. The current trends then diminish as seen in part D in Figure 4.

2.10.7 Peak potential (E_P)

The highest point of the graph is denoted at the E_P. This point peak is than becomes the analytical parameter for qualitative analysis for the cadmium ions.

2.10.8 Peak current height (i_P)

The peak is considered to be proportional to the concentration of the metal ions in the sample. This parameter is used for the quantitative analysis of the metal ions present.

CHAPTER 3

METHODOLOGY

Before proceeding with the experiment itself, steps are needed to be identified. Below are the steps and explanation on the experiment expansion.

3.1 Tools and Chemicals

3.1.1 Tools

- An analog or computer-controlled potentiostat with appropriate data acquisition equipment
- Electrochemical sell and electrode
- Graphite powder
- Paraffin oil or silicon oil
- Na-MMT-Carbon Paste Electrode
- Pt/Graphite bar auxiliary electrode
- Ag/AgCl reference electrode
- Sand paper
- A magnetic stirrer and a small bar inside the cell
- 1000ml, 500ml and 250 ml flask

3.1.2 Chemicals

- $1.00\text{x}10^{-4}$ M $Cd(NO_3)_2$ in 10mM HCl
- 10mM HCl – supporting electrolyte
- Montmorillonite (MMT)
- 1.00M NaCl

3.2 Preparation of Na- Montmorillonite (Na-MMT)

To convert natural MMT into sodium MMT (Na-MMT), 20g of MMT is mixed with 1L of 1M of NaCl solution, and continuously stirred for 12 hours. Then, the liquid is discarded and the solid is taken. Again, the solid sample was contacted with fresh 1L of 1M NaCl solution and stirred for another 12 hour. This was performed to ensure complete conversion of the clay into its homoionic form.

To remove the excess NaCl and Cl^- ion (that could impregnated in the solid phase), the solid is filtered and washed several times with distilled water until a negative test for Cl^- is achieved (absence of Cl^- as detected by titrating the filtrate with $AgNO_3$). Finally, the pH of the dispersion was around 8 and Na^+-exchanged MMT particles are obtained. The material is then dried at room temperature for 24 hour or oven dried at 60°C.

3.3 Anodic Striping Voltammetry (ASV)

3.3.1 Preparation of Modified Carbon Paste Electrode

Preparation of Na-MMT modified CME is similar to that of the blank CME. Appropriate amount of Na-MMT and graphite powder is mixed thoroughly in a mortar to form a homogeneous carbon paste by addition of paraffin oil. A portion of this paste is filled into one end of a plastic tube and a copper wire is inserted through the opposite end to establish an electrical contact. Prior to use, the surface of the well prepared CME is smoothed with a sand paper.

3.3.2 Anodic Stripping Analysis

At this stage electrode is used in and Anodic Stripping Voltammetry (ASV). First, a stock solution of Cd^{+2} 10^{-2} M is prepared. Few drops of 1M HNO_3 are added to preserve stock.
Electrolytic solution (0.1 M KCl) is added in cell followed by addition of analyte using a pipette. Smaller concentration of Cd^{+2} solution would be prepared fresh daily. Anodic

stripping analysis (ASV) under the following conditions to be performed using a potentiostat:

Table 3.1: Anodic Stripping Voltammetry test procedure

Voltammetric analysis	
Deaeration step (bubbling N_2)	t = 120s
Preconcentration step (Deposition)	E = -800mV t = 60s
Rest step (Equilibration)	t = 15s
Anodic dissolution step:	potential scan = from -800mV to 200mV step duration = 0.1s step amplitude = 5mV pulse amplitude = 25mV
Stirring rate	200 rpm

Process is to be repeated several times for reproducibility. The average and the standard deviation would also be carried out. Effect of process parameters would also be evaluated i.e. deposition time, potential, pH, Stirring rate and modifier dosage.

3.3.3 Calibration Curve

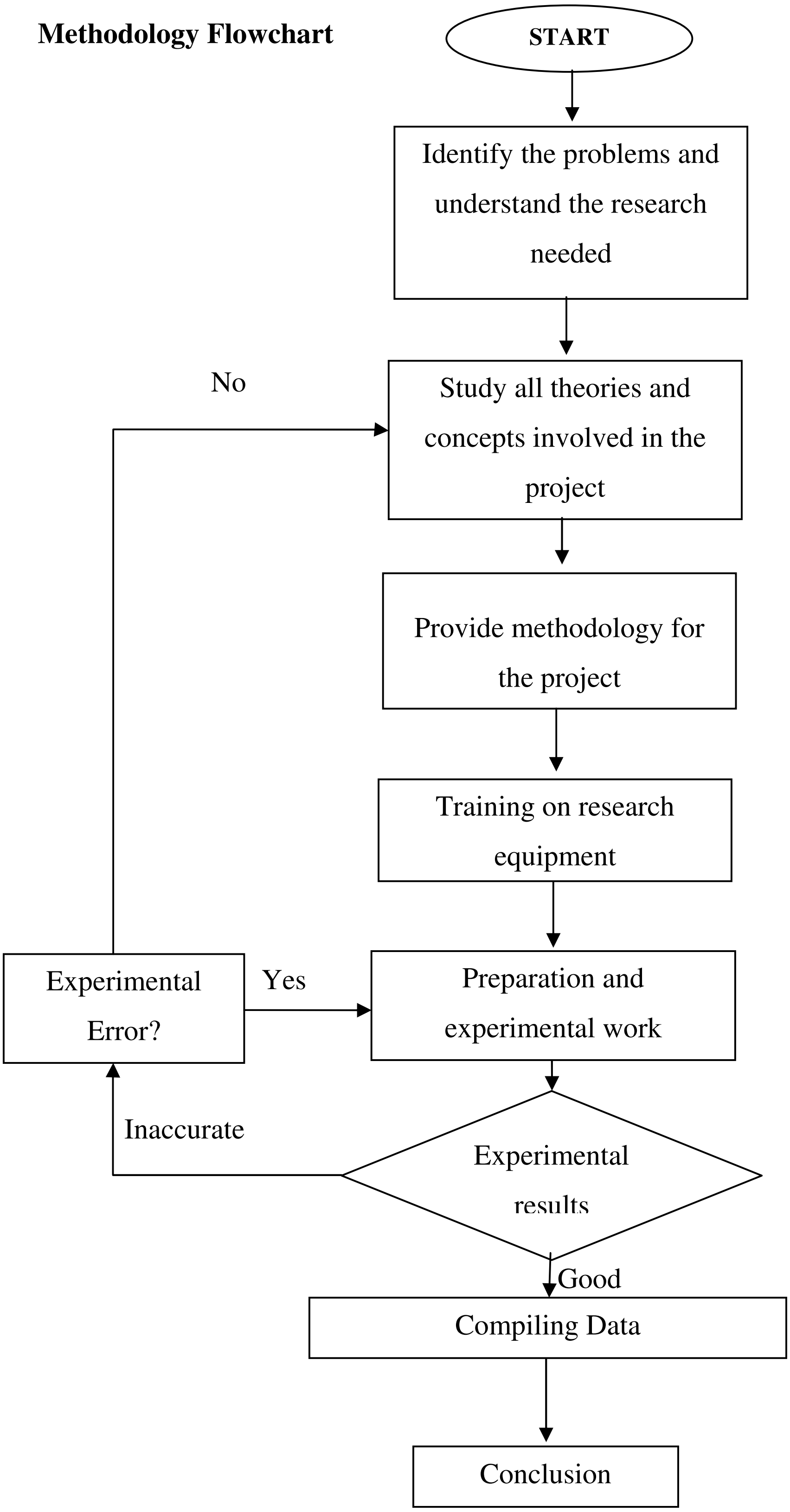
A calibration curve for the analyzed metal is constructed for two reasons:

To enable rough estimation of the concentration of the metal in the unknowns by comparing peak heights, and

To test if, linearity between analytical signal and concentration is obtained in the concentration range of interest.

First, 5 ml of the 10mM is added into the electrochemical cell. Then, a stripping curve of the blank is recorded. The experiment is repeated with 5 subsequent additions of 0.05 ml of the 10^{-4} M Cd^{+2} solution. Finally, the calibration curve is plotted using the values obtained.

3.4 Methodology Flowchart



CHAPTER 4

RESULTS AND DISCUSSION

Experimental part is divided into two parts: **Preparation of Na-MMT and ASV (Anodic Striping Voltammetry) analyses**.

The first part is done in order to make clay monoionic and replace other ions with Na ions with which clay will have same properties in all structure.

In the second part of project stage, ASV analysis was done to observe functionality of Na-MMT modified Carbon Paste Electrode. Some results that were taken from this analysis are shown below.

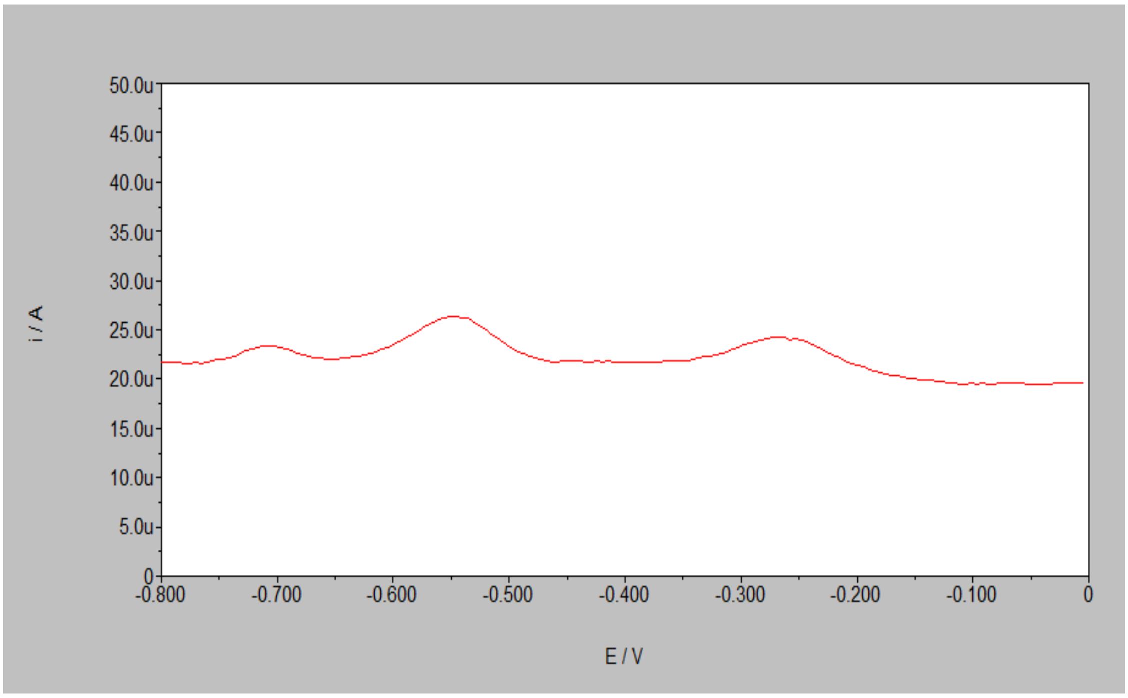


Figure 4.1: Voltammogram for Na-MMT modified CPE with Square wave voltammetry for 0.1M KCL and 240sec deposition time.

In Figure 4.1, heavy metal solution, Cd^{2+}, was not used in order to get reference graph for analytes that are present before adding heavy metal ion solution. With help of it we could compare later results and clearly see the peak that is related to heavy metal detection.

Trial 1:

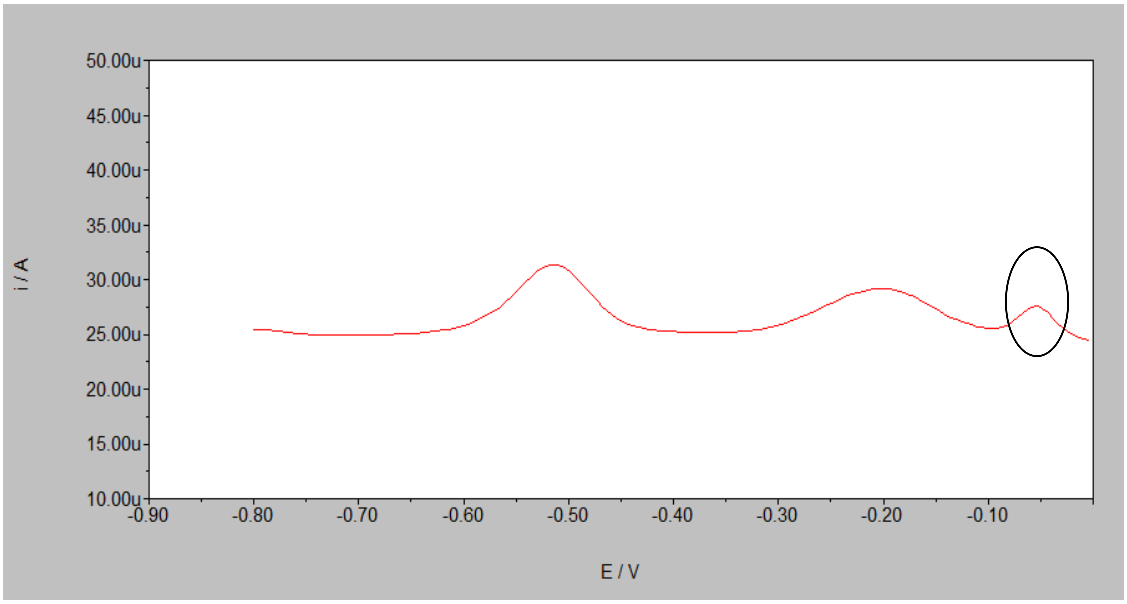


Figure 4.2: Voltammogram for Na-MMT modified CPE with Square wave voltammetry for Cd(II) 1x 10^{-7}M, 0.1M KCL and 240sec deposition time.

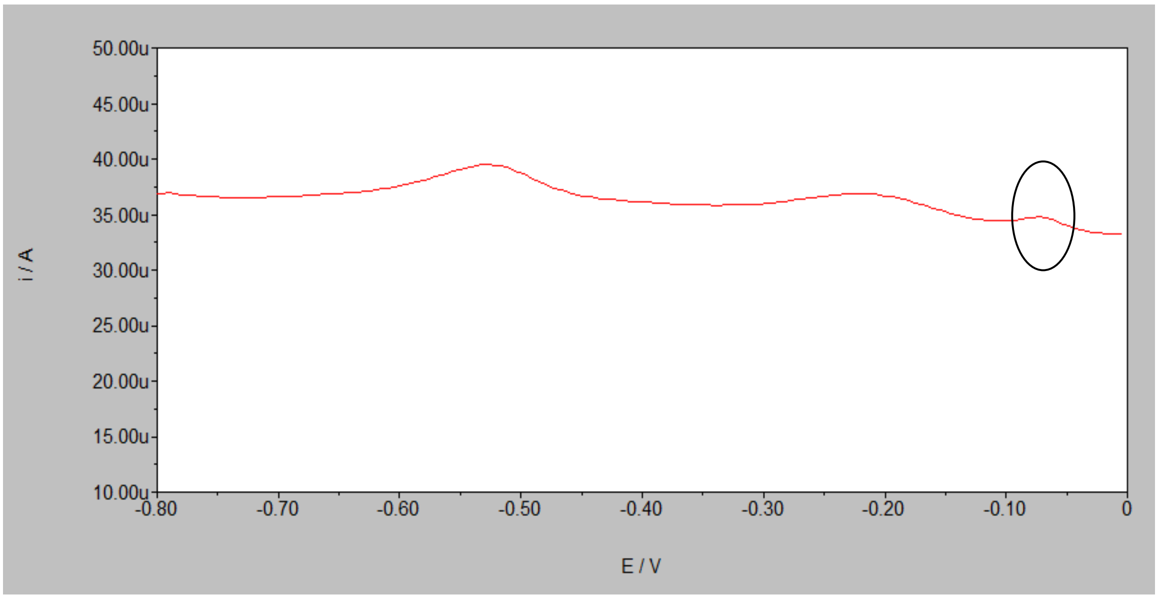


Figure 4.3: Voltammogram for Na-MMT modified CPE with Square wave voltammetry for Cd(II) 1x 10^{-8}M, 0.1M KCL and 240sec deposition time.

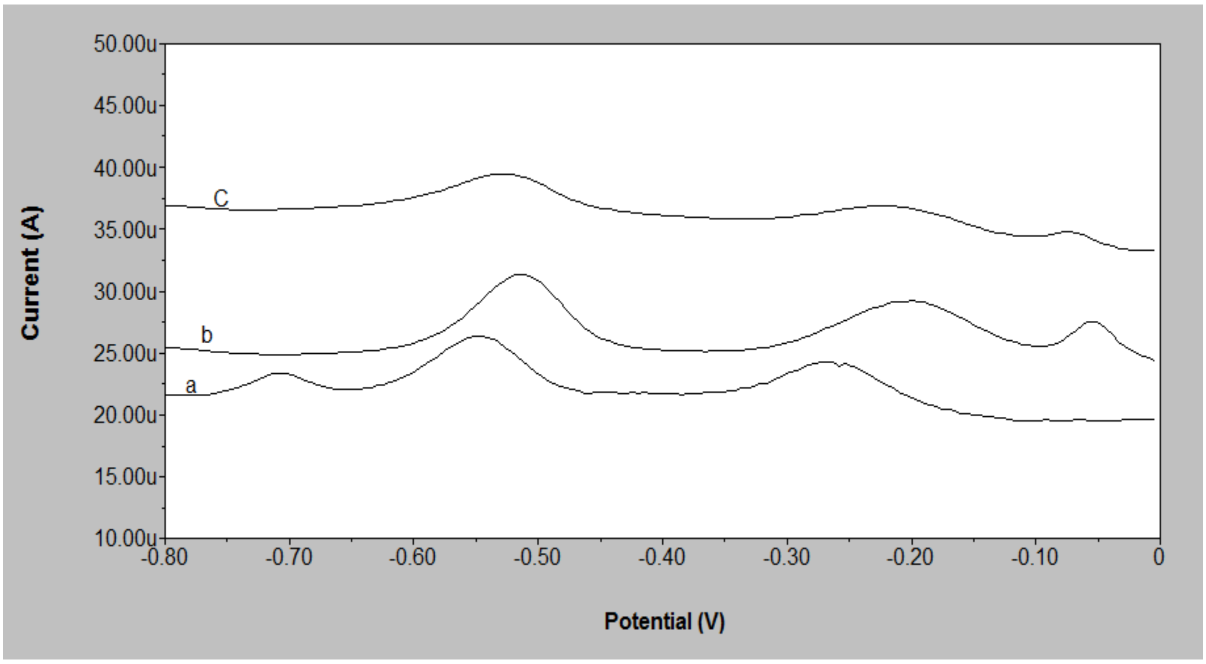


Figure 4.4: Voltammogram for Na-MMT modified CPE with Square wave voltammetry for (a) 0.1 KCl, b) Cd(II) 1x 10^{-7}M and c) Cd(II) 1x 10^{-8}M with electrolyte 0.1M KCL and 240sec deposition time.

Trial 2:

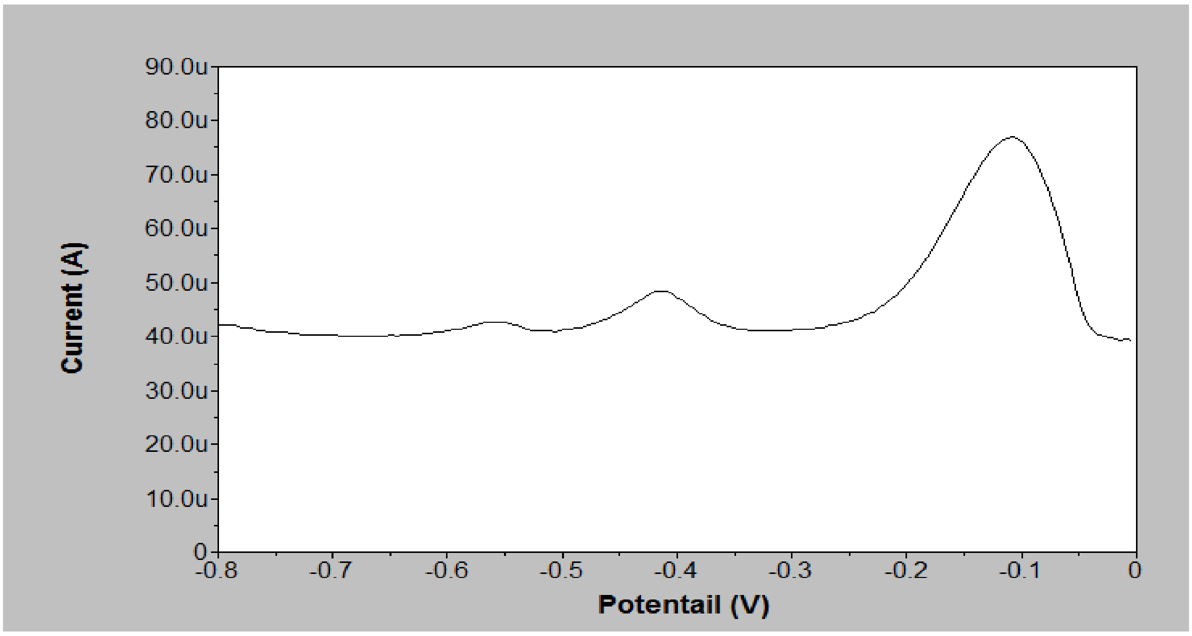


Figure 4.5: Voltammogram for Na-MMT modfied CME with Square wave voltammetry for Cd (II) 1 x 10^{-8} M, with electrolyte 0.1M KCL and 240sec deposition time.

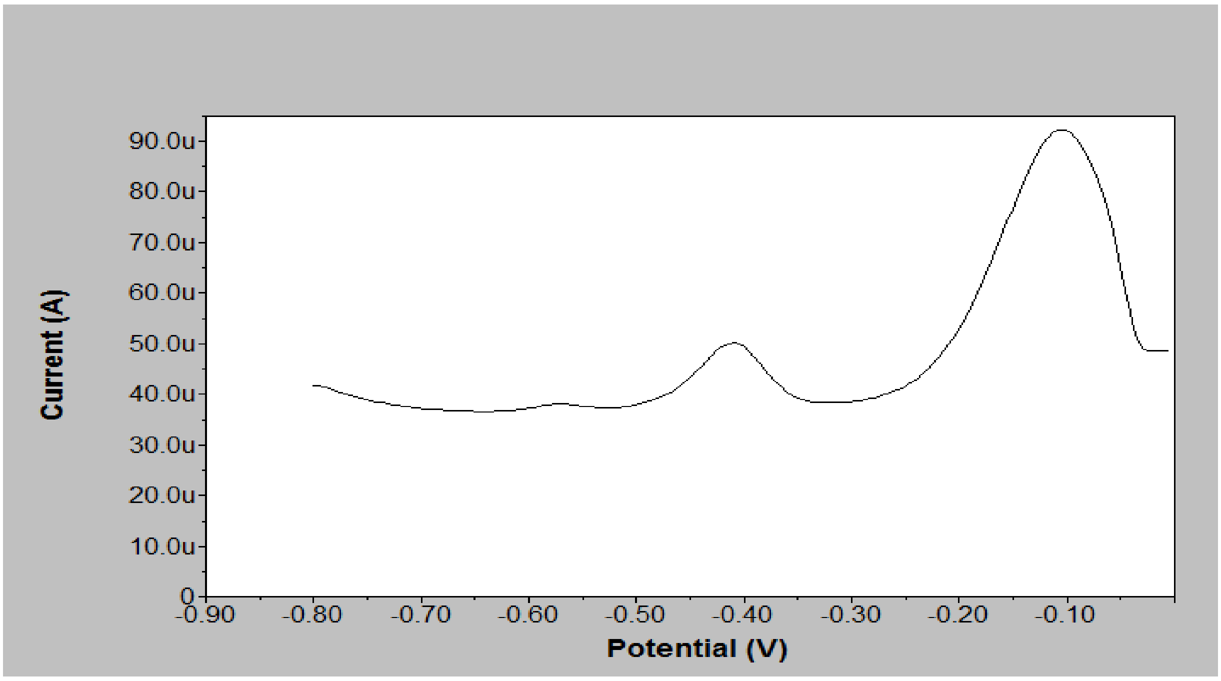


Figure 4.6: Voltammogram for Na-MMT modfied CME with Square wave voltammetry for Cd (II) 1 x 10^{-7} M, with electrolyte 0.1M KCL and 240sec deposition time.

First of all we need to do at least 2 trails in order to make sure that Na-MMT-CPE is working, even with change in the concentration of Cd ion in the solution. As we can see from graphs in Trial 1, Figure 4.2 and Figure 4.3, and Trial 2, Figure 4.5 and Figure 4.6, with different concentrations of Cd ions, $1x10^{-7}$ and $1x10^{-8}$ M, the height of peak is different and it gives higher peak when the concentration is higher and lower height when concentration of heavy metal ion is lower which means that Na-MMT modified CPE is sensitive to change in concentration of metal ions and it is working. It gives great opportunity to analyze the amount of heavy metal ions, Cd ions for our case, present in the solution.

In the figure 4.2 and 4.3, the Cd^{2+} solution is added with amount of $1x10^{-7}$ and $1x10^{-8}$ M respectively. As can be seen from the graph in Figure 4.2 and 4.3, the third peak, represented with circle in each graph, is representing detection of heavy metal inside the solution. In Figure 4.4, where all three graphs are compared with each other, when the concentration of Cd^{+2} solution is increased the height of the peak is also increased which shows that even if the amount of Cd^{+2} ions is increased detection of those ions still improves and gives better results. Meaning that, Na-MMT modified CPE can be used for detection of Cd^{+2} ions even with small amounts which is very important because for heavy metals even concentration with part per million (ppm) or part per billion (ppb) can be toxic.

For Trial 2 the peak for Cd ions were detected at position -0.107V for both concentrations of $1x10^{-7}$ and $1x10^{-8}$ M. From Figure 4.5 the height of the peak for concentration of $1x10^{-8}$ M of Cd ions is 3.66E-05 A and area below the peak is 4.07E-06. For the Figure 4.6 where the concentration of the Cd ions is $1x10^{-7}$ M the height of the peak is 4.63E-05 A and area under peak is 5.33E-06. Table 4.1 presents all information for the peaks registered for graphs in Figure 4.5 and 4.6. The difference between them can be clearly seen. So we can conclude that Na-MMT modified CPE are sensitive to detection of Cd ions and can be used for detection of Cd ions in the water solution.

Table 4.1: Data of peak search analysis for Na-MMT-CPE

Cd Concentration (M)	Position (V)	Peak height (A)	Area
1 x 10-7	-1.07E-01	4.63E-05	5.33E-06
1 x 10-8	-1.07E-01	3.66E-05	4.07E-06

The reason for good detection of Cd ions by Na-MMT modified Carbon Paste Electrodes is may be the adsorption process that happens on the surface of electrode by Na-MMT. With adsorption process Cd ions are attached or adsorbed on clay surface and during scanning of those ions by ASV detection will be improved. When the concentration of Cd ions is increased adsorbed amount on clay also increases which results in height and area increase under peak in the graph. So later on with further research and experimental work new kind of sensor could be developed that could detect amount of heavy metal ions.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

4.1 Conclusion

Montmorillonite was chosen for this research because of its good adsorption properties like high surface area and high Cation Exchange Capacity compare other types of clays. This study had shown that Monmorillonite can be used as modifiers to carbon paste electrodes for cadmium detection. With increasing metal ion concentration, there is an increase in the amount of metal ion adsorbed due to increasing metal ion species for active sites on adsorbent and improved detection via ASV, which can be seen from the height and area of peaks. Carbon Paste Electrode (CPE) modified with clays have great potential to be developed as a part of methodologies for real-time, in-situ monitoring and control of the contamination of heavy metals in the environment especially in groundwater.

4.2 Recommendation

Few recommendations that can be applied for this research is:

- Research should be continued in order to develop real-time monitoring sensor for detection of heavy metal ions. This research project is just first step towards that.
- MMT-Carbon Paste Electrodes should be tested with different clay/graphite ratio to test effectives and effect of different mass ratios.
- Carbon Paste electrodes also should be tested with other clays as a modifier.
- Clay modified CPE should be tested with mixed concentration different heavy metals in order to see effect of more than one heavy metal in the solution.
- New Anodic Stripping Voltammetry should be bought by UTP and proper manual for use should be made.

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