# DECLARATION

I, SANI MOHAMMED HASKE, hereby declare that this thesis was done solely by me under the supervision of Dr Duncan F. Aloko of the Department of Chemical Engineering, Federal University of Technology, Minna and have never been presented anywhere for any degree.

…………………………

21st/may/08

Signature & Date

## CERTIFICATION PAGE

This thesis titled, 'OPTIMIZATION OF THE ADSORPTION OF SOME CATIONS ON MANGANESE DIOXIDE USED IN LECLANCHE' DRY CELL', by SANI MOHAMMED HASKE (M.ENG/SEET/2005/1119) meets the regulations governing the award of the degree of M.ENG of the Federal University of Technology, Minna and is approved for its contribution to scientific knowledge and literary presentation.

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# DEDICATION

This work is dedicated to my children

**Ibrahim and A'isha**

who Almighty GOD 'ALLAH' blessed me with while on the programme, with the prayer that may

**ALLAH** bless all my children,

Amin.

# ACKNOWLEDGEMENT

Praise be to Allah. I reserve my profound gratitude to GOD for the opportunity and blessings given to me to accomplish this work. Next, my sincere appreciation and gratitude go to Engr (DR) D.F. Aloko my supervisor whose immeasurable advice, guidance, assistance and criticisms throughout the period of this work had made this task fruitful. Sincere appreciations to my HOD - DR E.O Edoga, Professors K.R Onifade, J.O Odigure and F. Agberuagba, others are Mr Akpan, Mr Agbajelola, Mr Olutoye and Mr M. Alhassan, all members of the Department of Chemical Engineering FUT Minna.. Other staff of the Department whose names are not listed here are overwhelmingly acknowledged. My appreciation also goes to my classmates especially Rasheed Babalola, Ken Kenneth Adama, including Jim, Moshood, Adija, and Abdullahi Mohammed to mention a few. The computer software package was obtained from Engr Hassan Akande Funsho of Inovative Technology, his assistance had contributed immensely, thank you. The assistance obtained from the officers and staff of the Departments of Chemical Engineering and Applied Science of Kaduna Polytechnic, are hereby appreciated. Mohammed Lawal Danbaba among others offered immeasurable assistance in the cause of the programme and experimental work. Importantly, my Manager; Engr Mathew Edogun, my Superintendent; Mr Thedius Tsavnande and colleagues; Abubakar Audu, Sabo Maiyaki, Olorunfemi D J, Anderson Sako, Abdul Anako, Sani Sabo, John Tachio, Maigamu Mangachu, Benjamin Brown, Samuel Olatoyegun, Bala Abdullahi, Abubakar Danbala, and Adewole to mention a few, were very supportive, 'Nagode' .Others whose names were not listed was not because they were not important or their support was not recognized but because space and time did not permit: God bless you all. Finally, I must mention my wives Samira and Sa'adiyya and the entire members of my family for their patience, encouragement, endurance and understanding, GOD bless, Amin.

## ABSTRACT

The adsorption of somecations on $MnO_2$ is to improve the life span of the leclanche' cell which is only 300 seconds on a non-stop operation of an appliance using Leclanche cell as battery. The effect of concentration and temperature of nitrate solutions of sodium, calcium, lead and magnesium ions on manganese dioxide ($MnO_2$) was investigated by potentiometric titration method such that when used on battery the life span of Leclanche cell (battery) was increased. Therefore, quadratic models describing the adsorption process of these cations on $MnO_2$, were developed by factorial analysis and further optimized using Minitab standard software. Previous works were based on linear model and could not be optimized. The concentrations of these solutions were varied from 1M to 0.001M at two different temperatures; 30 and 50 °C. The experiments were performed based on the factorial design techniques in order to enhance determination of the surface response analysis of the relationship between the surface charge ($E_v$) of manganese dioxide ($MnO_2$), and two factors; concentration ($X_1$) and temperature ($X_2$). Line response (pH – volume) plots of the cations solutions were made to calculate the change in volume ($\Delta V$) at different pH using the Kokarev formula of adsorption. The $\Delta V$ was used to calculate the electric surface charge which serves as input for factorial analysis.

Furthermore, the test for significance of individual cations shows Sodium, Calcium and Magnesium ions data were significant and Lead was not. The second order model equations describing the process were developed, further reduced, then fitted for optimization. Optimization using Minitab software showed that the highest surface charge with the adsorption of sodium, calcium and magnesium ions were obtained when the electrolyte concentration is set to 0.75M at 30°C, 0.85M at 40°C and 0.5M at 47°C respectively. These gave corresponding surface charge, electric current density and potentials of 1.25 $C/m^2$, 1.50 $C/m^2$ and 1.80 $C/m^2$, 4.5$A/m^2$, 5.4$A/m^2$, 6.5$A/m^2$ and 2400mV, 2180mV, 2300mV respectively. The lifespan of conventional Leclanche' cell free of adsorbed cations is 300seconds. The result gives 480s, 575s, and 690s corresponding to 60%, 92% and 130% increase in life span for cells incorporating sodium, calcium and magnesium ions respectively.

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# CHAPTER 1

## 1.0 INTRODUCTION

As human activities extend beyond the span between sun rise and sun set, the needs to provide lighting in dark areas and at night or even for provision of handy power sources are achieved in electric cells commercially known as batteries. Millions of batteries are made annually for use in torch lights, bicycle lambs, clocks, walkie - talkie, radio receiver sets e.t.c. One of the simple cells earlier produced and in use today is the leclanche' dry cell. It consists of a zinc negative pole, a carbon positive pole and a depolarizer of manganese dioxide ($MnO_2$) powder (in mixed form with powdered carbon) a good conductor, to lower the internal resistance of the cell, and a solution of Sal ammoniac or ammonium chloride, $NH_4Cl$.

This work is therefore geared towards finding the optimum condition for the successful adsorption of some cations on manganese dioxide. Therefore some cations of alkaline group, transition group and alkaline earth are selected for the study. These are Sodium, Calcium, Lead and Magnesium. Theoretically, factors such as concentration of the elements, temperature of reaction, degree of agitation, contact time of reactants as well as the mass of the adsorbents are believed to influence the reaction.

Therefore this experiment selected concentration and temperature as factors to be varied while keeping the others constant in a potentiometric titration experiment. The data obtained are then used to generate model equations of the adsorption process by factorial analysis method for second order equation. The data obtained are optimized by the use of Minitab computer software.

## 1.1 Background

The modern dry cell is based primarily on the one invented by GEORGES LECLANCHE' in 1886. Leclanche' cells are in declining use today. Although cheap to manufacture and purchase, they suffer from a number of limitations:

- They are not suitable for high-drain applications (such as driven electrical motors) as they readily polarize and the available capacity falls sharply with increased charged rate.
- Their shelf life is not especially long
- The optimum temperature range of operation is 20 - $50^0C$ (outside of this temperature range the performance deteriorates markedly)

Leclanche' cells are best suited to low drain intermittent use, with rest periods for recuperation (depolarization) to take place, and for use within 1-2 years. When used non-stop the life expires in 300 seconds. A good example is domestic flash-lamb battery. They may also be used in low-drain applications, such as door-chime or as smoke detectors, but then their relatively short operational life becomes a nuisance as they require periodic replacement.

Previous works had successfully adsorbed a number of ions on $MnO_2$ to improve the life span of the leclanche' cell but these attempts could not be optimized because of the linear models used, three dimensional plots, obtained were flat. Hence, this project is designed to adsorb some cations and selected from the studies a quadratic model since linear model could not be optimized. This work is intended to investigate the possible means of improving the usage Life of the primary cell, by carrying out optimization of the selected quadratic model equations of the adsorption process.

## 1.2 Aim

This project work is directed towards improving the efficiency of the cell (battery) by increasing its' usage period. This will enhance the technology, increase the consumers' economy and above all reduce disposal of spent battery which litters the environment.

## 3 Objectives

This work is set objectively to investigate the possibility of improving the service life of leclanche' dry cell by

Adsorbing some cations on Manganese dioxide ($MnO_2$) by potentiometric analysis; uni-factor approach.

Calculating the electric surface charge of Manganese dioxide (depolarizer) as a function of adsorption and number of ions.

Using statistical method (Factorial analysis) to formulate a suitable model equation based on the empirical data obtained; factorial interaction or randomized experiments.

Using suitable computer software to solve the models and further optimize them.

Compare the electric surface obtained at the optimum conditions to the normal life rating of the cell to estimate the change in charge time.

## Justification

As the electric surface charge ($E_v$) of the depolarizer ($MnO_2$), measured in coulombs, is a function of the adsorption (θ) and the number of ions (n). Potentiometric method was used to determine PH values of variable concentrations of cations on manganese dioxide ($MnO_2$).Thereafter, the variations in volume of titrant and PH values were plotted to find change in volume(Δv). Adsorption (θ) was then obtained as a function of the change in volume, concentration(C) of sodium nitrate ($NaNO_3$) and surface area(S) using equation 1.2 above. The Electronic surface charge ($E_v$) was then calculated from equation 1.1 where n is the number of ions and F represents the Faraday constant; 96500 coulombs.(Stephen, K.L, 2004) The data obtained from the potentiometric titration served as the input for the calculation of the surface charge.

These are then fitted for optimization. Optimization using Minitab software showed that the highest surface charge with the adsorption of sodium, calcium and magnesium ions are obtained when the electrolyte concentration is set to 0.75M at $40^oC$, 0.85M at $40^oC$ and 0.5M at $47^oC$ respectively. These gave corresponding surface charge, electric current density and potentials of 1.25 $C/m^2$, 1.50 $C/m^2$ and 1.80 $C/m^2$, $4.5A/m^2$, $5.4A/m^2$, $6.48A/m^2$ and 4500mV, 5400mV, 6480mV respectively.

A simple comparison of the usage life of conventional leclanche' cell free of adsorbed cations of 300seconds to the leclanche' cell with adsorbed cations gives, 480sec., 560sec., and 400sec respectively, thus higher life span.

# CHAPTER 2

## 2.0 LITERATURE SURVEY

### 2.1 Battery/ Primary Cell

One of the oldest and most important applications of electrochemistry is the storage and conversion of energy. Galvanic cell converts chemical energy to work. Similarly, electrolytic cell converts electrical energy into chemical free energy. Devices that carry out these conversions are called Batteries. In ordinary batteries the chemical components are contained within the device itself*. If the reactants are supplied from an external source as they are consumed, the device is called fuel cell.

The term battery derives from the older use of this word to describe physical attack or beating. Benjamin Franklin, a prominent American scientist of 18th century, first applied the term to the electrical shocks that could be produced by an array of charged glass plates. In common usage, the term 'cell' is often used in place of battery. (Stephen K.L, 2004)

Over the past 50 years the applications for small batteries in the home (consumer batteries) have expanded phenomenally. Today small primary or rechargeable batteries are employed in huge number of appliances. With these applications which have developed over the past few decades, the market for consumer batteries has grown correspondingly. Many batteries are in used today because of advance design and construction, giving greatly improved performance as a result of developments in material science and technology.

### Consumer Batteries

Most primary cells are of the leclanche' type in which the zinc negative electrode was in the form of a metal can which acted as the container for the other cell components. There is a central carbon rod that is surrounded by a mixture of crude manganese dioxide ($MnO_2$) (often the mineral pyrolusite) and carbon powders, intimately mixed together. The function of the carbon powder is to increase conductivity of the positive active mass and so to reduce the internal resistance of the cell. The electrolyte, an aqueous solution of ammonium chloride and zinc chloride, is absorbed into the pores of a paste type separator (eg. Starch) and the manganese dioxide ($MnO_2$)/ carbon mixture, and for this reason those cells became known as 'dry cells'. The cells had a seal and vent at their upper and a non-conducting board cap which served to insulate the positive carbon rod from the negative zinc can. Finally, the zinc can was surrounded by a cardboard jacket, on which the manufacturers name and information were printed. Some improvements have been made over the years in the design and materials of construction of leclanche' cell. The metallurgy of the can has been improved through alloying additions to facility deep drawing. Bother designs of seals have been developed. The use of mercury to increase the over potential for hydrogen evolution at the zinc electrode has been largely phased out for environmental reasons. The card-board jacket is now replaced by a steel container coated with polymer and a polyester film label. This steel outer case is insulated from the zinc can. The insulating cell cap is made of a hard polymer rather than board. There improvements greatly reduce the tendency of the cells to leak electrolyte when fully discharged which used to be a serious problem. (R.M.Dell, 2000)

## 3 Electrolysis & Electrolytic Dissociation in Batteries

The study of current electricity began in 1790, when GALVANI noticed the twitching of a frog's leg as it lay between two metals. He mentioned the observations to his friend, VOLTA, who made many experiments on the phenomenon, which he recognized as an electric one, he succeeded in making the first battery, a device which can maintain two points at difference of potential for a considerable time. This opened up an entirely new advance in the study of electricity, and enable scientists at the beginning of the nineteenth century to begin investigations into the continuous flow of electricity thorough metals and liquids.

In 1834 Faraday began to investigate this behavior of liquid conductors, such as acids and salts solution, the study of the flow of electricity through liquids in called electrolysis, and the liquids are called electrolyte. Some liquids do not conduct an electric current but when an acid, a base, or a salt is dissolved in water, the solution is usually a good conductor. The two materials which lead the current into and out of the liquid are known as electrodes. The electrode through which the conventional current leaves the solutions is known as the cathode, while the electrodes in which the current enters the solution in known as the Anode. And the system consisting of the electrodes and electrolyte is known as voltmeter.

In 1887 ARRHENIUS suggested that the molecules of electrolytes were dissociated into particles each carrying a charge, which he called ions, and all the experimental evidence available agree with the theory, which was therefore accepted.

A molecule of sulphuric acid ($H_2 SO_4$) in solution dissociates into 2 hydrogen ions (made up of 2 atoms of hydrogen H, each carrying a positive charge numerically equal to the charge on an election e), and a sulphate ion (made up of one atom of sulphur-5 and four atoms of oxygen, ie, $SO_4$, carrying a negative charge equal to double that on an electron). The total charge on the two ions is thus zero, and hence no electrical shocks are experienced on dipping one's finger into dilute sulphuric acid solution.

$H_2SO_4 = 2H^+ + SO_4^{2-}$ ..........2.1

Similarly, capper sulphate molecule dissociates in solution into a copper ion carrying a positive charge double that as a hydrogen ion, and a sulphate ion carrying an equal negative charge.

$CuSO_4 = Cu^{++} + SO_4^{2-}$ ..........2.2

Water also dissociates, but to a slight degree, and hydrogen and hydroxyl ions are obtained in dilute sulphuric acid or copper sulphate solutions. Thus,

$H_2O = H^+ + OH^-$ ...........2.3

The ions is electrolyte are moving about haphazardly is the solution and making frequent collisions; on the whole, there is no general movement of the ions in any one direction. When, however, a battery is connected to the electrodes, a potential difference is set up across the electrolyte, and as we have seen with electrons in the case of metals, the ions with a negative charge begin to drift across the liquid towards the anode. At the some time, the ions with a positive charge drift in the opposite direction towards the cathode. If the battery is disconnected the drift of electricity between the plates ceases, the ions once again have a completely random motion.

Electrons are the particles which carry the electric current through metals, and are a very small fraction of the total weight of the atoms. (Stephen K.L, 2004)

## Polarization, Resistance Effect and local Action of Battery

When a cell/battery electrodes are joined with a wire or conductor current flows. But after a short time the current in the simple cell/battery almost ceases. Experiment showed that this is primarily due to the hydrogen ($H_2$) produced at the cupper plate. Hydrogen and zinc are dissimilar elements, and they produce an e.m.f. in the acid which is opposite to that set up between the copper (Cu) and zinc (Zn) plates, with the result that the net charge inside the cell soon becomes very small. This phenomena is termed 'polarization. Besides the effect of polarization, the current maintained by a simple cell drops to a low value because the layer of hydrogen gas ($H_2$) on the cupper plate acts as an insulator, and causes a fairly large increase in the resistance between the plates of the cell. Another disadvantage of the cell arises from the impurities, such as iron (Fe) present in commercial zinc. These forms tiny cells with the zinc (Zn) and cause it to be used up even when no circuit is completed between the copper and the zinc plates. This phenomena is known as Local Action. It is eliminated by rubbing the zinc with mercury (Hg), which covers the impurities and prevent them from making contact with the zinc and Acid, however, with pure zinc there is no chemical action when no circuit is completed between the plates.

## 5 The Leclanche' Cell

### 5.1 Leclanche' wet type battery

The wet leclanche' cell is shown in Figure 2.1. It consist of

a zinc negative pole

a carbon positive pole

a Depolarizer of manganese dioxide ($MnO_2$) powder (mixed with powdered carbon, which is a good conductor, to lower the internal resistance of the cells)

a solution of sal ammoniac, or ammonium chloride ($NH^4CL$).

The zinc rod is deeped inside the solution of sal ammoniac or ammonium chloride, which is contained in a glass vessel, and the depolarizer, $MnO_{2,}$ is packed round the carbon rod in a porous pot. (see figure below).

When the carbon and zinc are joined by wire, electrons flow in the wire from the zinc to the carbon. Inside the cell, therefore, the negative chloride ions of the ammonium chloride, $NH_4$ CL, solution move towards the zinc, and from zinc chloride which goes into solution. The ammonium ions ($NH_4{}^+$) drift toward carbon pole through the porous pot, and hydrogen is formed at this pole. The net chemical reaction can be represented by the equation.

$Zn + 2NH_4 CL = Zn (NH_3)_2CL_2 + H_2$ ..........2.4

The manganese dioxide then attacks the hydrogen, oxidizing it to water

$H_2 + 2MnO_2 = H_2O + Mn_2O_3$ ............2.5

A harmless substance, $MnO_{3,}$ is thus produced at the carbon pole by the chemical action, but after a short time the hydrogen is produced too fast for the manganese dioxide, $MnO_{2,}$ to cope with it, and the cell then polarizes.

This is the defect of leclanche' cell. Nevertheless, it is used in house hold devices and in other cases where a current is required only intermittently. The e.m.f of leclanche cell is originally about 1.5 volts, and the internal resistance is originally of the order of 10 ohms or more.

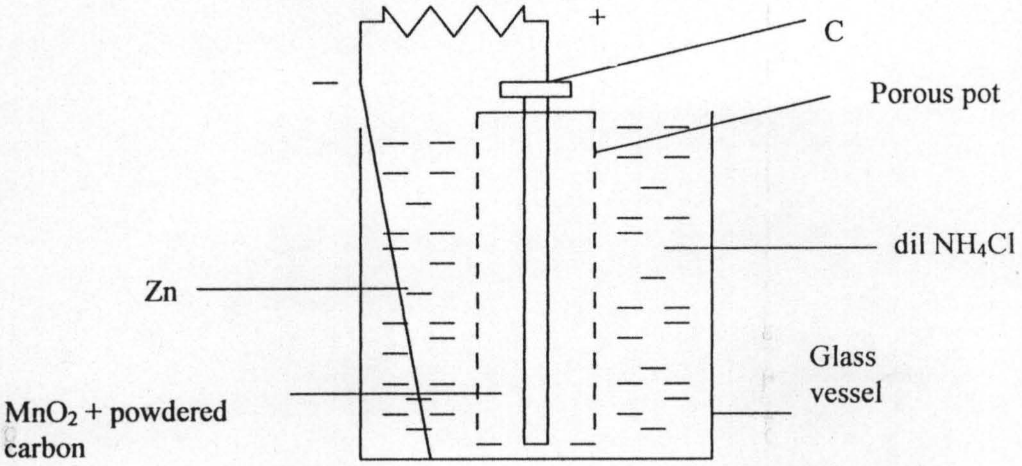


Figure 2.1: The leclanche' cell (wet type)(Kenneth, 1956)

### .2 Leclanche' dry type battery

The leclanche' wet cell is inconvenient to carry about owing to the solution of ammonium chloride used. This disadvantage is overcomed by making a paste of ammonium chloride, flour, and gum. Figure 2.2 illustrates the comparatively 'Dry Cell' manufactured commercially for use in torches and as high tension and grid bias batteries.

In a high tension battery of 120 volts there are 80 cells connected together to assist each other, in series, each having an e.m.f. of about 1.5 volts.

The dry cell has a zinc container with ammonium chloride paste inside it. The carbon rod and manganese dioxide with powdered carbon are contained in a muslin bag separated from the zinc by cardboard. The cell has a lower internal resistance than the wet type owing to the closer spacing of the electrodes, but the e.m.f is exactly the same as the wet type as this depends only on the nature of the chemicals used.

When the battery is used in a torch, the positive (carbon) pole is in electrical contact with the lower end of the bulb, to which one end of the Bulb is connected. The other end of the filament is connected to the metal casing of the bulb. The negative (Zinc) pole of the battery is in contact with bottom of the metal torch case, and when the switch is pressed, contact is made between the case and the metal casing of the bulb, thus causing the filament to light up. The depolarizing action in the dry cell is batter than in the wet cell; a cycle-lamb, for example, will burn for two hours with a dry battery supplying the current. (Brant V, 1976)

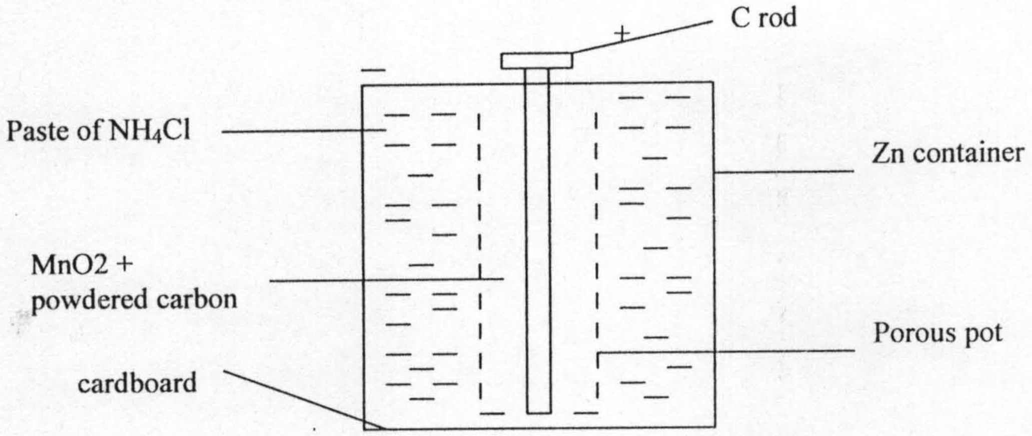


Figure 2.2: The laclanche' cell (Dry type)(Kenneth, 1956)

## 2.5 Physical Limitation of a Leclanche' Cell Performance

The most important of these are

i. Effective surface area of the electrode:- A 1cm$^2$ sheet of polished metal presents far less active surface than does one that contains numerous surface projections or pores. All useful batteries and fuel cell employ highly porous electrodes.

ii. Current density of electrode surface:- Expressed in amperes/ M$^{-2}$ this is essentially a measure of the catalytic ability of the electrode, that is, ability to reduce the activation energy of the electron transfer process.

iii. Rate at which electro-active components can be delivered or depart from active election surface.

These processes are controlled by thermal diffusion and are inhibited by the way narrow pores that are needed to produce the large active surface.

iv. Side reactions and irreversible processes.

The products of the discharge reactions may tend to react with the charge – storing components. Thermal diffusion can also cause self-discharge, limiting the staff-life of the battery. Recharging of some storage batteries may lead to formation of less active modifications of solid phases, thus reducing the number of the charge/discharge cycles possible. Clearly, these are all primarily kinetic and mechanistic factors which require great deal of experimentations to understand and optimize from a region of higher concentration to one of lower concentration. The diving force for this process is the free energy change DG associated with the concentration gradient ($C_2$-$C_1$), sometimes known as the free energy of dilution

$AG$ dilution = $RT$ in $(C^2/C^1)$ ..........2.6

Note, however, that $Cu^{2+}$ ions need not physically move between the two compartments; electron flow through the external circuit creates a virtual flow, as copper ions are created in the low concentration side and discharged at the opposite electrode.(Stephen K.L, 2004)

## 2.7 Thermodynamics of Leclanche' Cells.

The free-energy charge for a process represents the maximum amount of non-PV work that can be extracted from it. In the case of an electrochemical cell, this work is due to the flow of elections through the potential difference between the two electrodes. Note, however, when that the rate of electron flow (i.e the current) increases, the potential difference unit decreases, then full amount of work can be realized only if the cell operates at an infinitesimal rate. The total amount of energy a reaction can supply under-standard conditions at constant pressure and temperature is give by $\Delta H^o$. If the reaction takes place by combing the reactants directly (no cell) or in a short –circuited cell, no work is done and the heat released is diminished by the amount of electrical work done.

In the limit of reversible operation, the heat released becomes.

$\Delta H = \Delta G^o + T\Delta S$ ...........2.7

## 8 Analytical Application of the Nernst Equation

A very large part of chemistry is concerned, either directly or indirectly, with determining the concentrations of ions in solution. Any method that can accomplish such measurements using relatively simple physical techniques is bound to be widely exploited. Cell potentials are fairly easy to measure, and although the Nernst equation relates them to ionic activities rather than to concentrations, the difference between them becomes negligible in solution where the total ionic concentration in less than about $10^{-3}$ M.

## 9 Potentiometric Titrations

Potentiometric titrations provide accurate determination of ions concentrations in which direct measurement is impossible. It is often possible to determine the ion indirectly by titration with some other ion. For example, the initial concentration of an ion such as $Fe^{2+}$ can be found by titrating with a strong oxidizing agent such as $Ce^{2+}$. The titration is carried out in one side of the cell whose other half is a reference electrode:

$Pt(s) \mid Fe^{2+},\ Fe^{2+} \parallel$ reference electrode ...........2.8

Initially the left cell contains only $Fe^{2+}$. As the titrant is added, the ferrous ion

is oxidized to $Fe^{3+}$ in a reaction that is virtually complete;

$Fe^{2+} + Ce^{4+}$ --- 2+ $Fe^{3+} + Ce^{3+}$ ...........2.9

The cell potential is followed as the $Fe^{2+}$ is added in small increments. Once the first drop of titrant has been added, the potential of the left cell is controlled by the ratio of oxidized and reduced iron [Fe] according to the Nernst equation.

$E = 0.68 - 0.059 \log \{Fe^{3+}/Fe^{2+}\}$ ............2.10

When the equivalence point is reached, the $Fe^{2+}$ will have been totally consumed (the large equilibrium constant ensures that this will be so), and the potential will then be controlled by the concentration ratio of $Ce^{3+}/ Ce^{4+}$. The idea is that both the species of a redox couple must be present in reasonable concentration for a concentration to control the potential of this kind. (Stephen K.L, 2004).

## 2.10 Development Models for Optimization

Optimization is being defined as the use of specific methods to determine the most cost-effective and efficient solution to a problem or design for a process. It is a technique used as a major quantitative tool in industrial decision making. Because the solution of optimization problem involves features of mathematics, the formation of an optimization problem must use mathematical expressions.

Such expressions do not necessarily need to be very complex. To organize the problem, we must consider

(a) the model representing the process and

(b) choose a suitable objective criterium to guide the decision making.

Every optimization problem contains three essential categories

i- At least one objective function (profit, cost etc.)

ii- Equality constraints (equations)

iii- Inequality constraints (inequalities)

where ii ant iii constitute the model of the process or equipment, whereas category (i) is sometimes called the economic model. So, the feasible solution of an optimization problem is a set of variables that satisfy categories ii and iii to the desired degree of precision. The problem process model is underdetermine if there are more process variables whose values are unknown ($N_F$ >0) in category ii than there are independent equations i.e the model has an infinite number of feasible solutions, so at least one variable can be optimized. (Degree of freedom = $N_F$)

### 2.10.1 Classification of models

Models are classified into two general categories

i- Those based on physical theory

ii- Those based on strictly empirical descriptions(so called black box models)

Models based on physical and chemical laws are frequently employed in optimization applications because such models can be developed even before the system is constructed. But empirical models are attractive when a physical model cannot be developed due to limited time or resources. Input-output data are necessary in order to fit unknown coefficient in either type of model. In addition to classifying model as theoretically or empirically based, we can generally group models according to the following types

i- linear versus non-linear

ii- steady state versus unsteady state

iii- lumped parameter versus distributed parameter

iv- continuous versus discrete variables

### 2.10.2 Factorial experimental design

This model of experimental design forces the data to be orthogonal and avoids the problems encountered by methods such as the least square method where the estimates of the values of the coefficients in the model have considerable associated uncertainty. Factorial method allows one to determine the relative importance of each input variable and thus to develop a parsimonious model, one that includes only the most important variables and effects. Factorial experiment also represents efficient experimentation. It is a systematically planned experiment in which all of the variables are changed simultaneously rather than one at a time, thereby reducing the number of experiments needed.(Edgar, et al, 2001) of reactions take place at the cathode: manganese dioxide is reduced to $Mn^{2+}$ as the primary cathodic reaction. And the product $Mn^{2+}$ is then oxidized by the remaining $MnO_2$ to form $MnO(OH)$ and $ZnO.Mn_2O_3$ at the cathode. These reactions can be summarized as

$MnO_2 + 4H^+ + 2e \quad = \quad Mn^{2+} + 2H_2O$ ........2.11

$Mn^{2+} + MnO_2 + 2OH^- \quad = \quad 2MnO\,(OH)$ .........2.12

$Mn^{2+} + Zn^{2+} + MnO_2 + 4OH^- \quad = \quad ZnO.Mn_2O_3 + 2H_2O$ ..........2.13

The formation of $Mn^{2+}$ and the lower oxidations state manganese dioxide which can be found in the Leclanche' type of electrolytes and in the electrodes from the cathodic reduction of manganese dioxide has been observed by other investigators, Vosburgh and co-workers (Encylo. 1973, 35,120 – 126) thoroughly investigated the characteristics of manganese dioxide electrodes. The presence of manganese ion in the electrolyte as a reduction product of manganese dioxide electrode was observed. However, the analyses of the electrolyte at different stages of discharge revealed that the formation of $Mn^{2+}$ ions occurred only during the later stages of discharge.

In fact, the initial product of the cathodic reaction at the manganese dioxide was MnO(OH). Very little manganese II entered the solution during the first third of discharge in ammonium chloride solution at pH 7. However, if appeared in increasing amounts thereafter $Mn^{2+}$ ions were detected much earlier much in solutions with pH values of less than 5. These observations led Vosburgh and Workers to conclude.

i- The initial product of the cathodic reaction is MnO(OH):

$MnO_2 + H + e \quad = \quad MnO\,(OH)$ ...........2.14

ii- In acidic electrolytes MnO (OH) can react with the electrolyte to form $Mn^{2+}$ and $MnO_2$:

$2MnO\,(OH) + 2H^+ \quad = \quad MnO_2 + Mn^{2+} + 2H_2O$ ...........2.15

iii- In neutral electrolyte the MnO (OH) accumulated on the surface of the electrode can be further reduced to $Mn(OH)_2$ which dissolves in the electrolyte as $Mn^{2+}$:

$MnO(OH) + H^+ + e^- \quad = \quad Mn(OH)_2$ ..........2.16

$Mn(OH)_2 + 2H^+ \quad = \quad Mn^{2+} + 2H_2O$ .........2.17

Furthermore, the diffusion of protons and electrons in the $MnO_2$ lattice is considered to be involved in the formation of MnO(OH). When current is applied, electrons from the electrolyte meet at the surface of $MnO_2$ exposed to the electrolyte and also beneath the surface as protons penetrate the $MnO_2$ crystal lattice. The electronsare retained by $Mn^{4+}$ to form $Mn^{3+}$ and protons are attached to $O^{2-}$ ions to form $OH^-$ ions.

The manganese dioxide crystal structure has a profound effect on the discharge behaviour of the electrode. Under similar discharge conditions in an electrolyte of pH 7.5, Vosburgh and Lan (Encyclo. 1973, 39) found that the over potential of a $\gamma$ - manganese dioxide electrode is substantially less than that of an $\alpha$ - manganese dioxide electrode with identical capacity and physical dimensions. From their analytical results these authors also found that the $\alpha$ - manganese dioxide electrode produces substantially larger amounts of $Mn^{2+}$ in the electrolyte than $\gamma$ - manganese dioxide electrode during discharge. Furthermore, the oxide composition at the end of discharge was found to be $MnO_{1.57}$ for the $\gamma$ - electrode and $MnO_{1.66}$ for the $\alpha$ - electrode. These differences between the two electrodes are consistent with the theory that the diffusion of protons in the lattice is involved in the discharge process and that $\alpha$ - $MnO_2$ is less penetrable for protons than $\gamma$ - $MnO_2$.

The mechanism proposed by Vosburgh's school on the cathodic process of manganese dioxide has been generally confirmed by recent studies. Vether and Jaegar (24,32) have shown through thermodynamic studies the wide range of homogeneity of $\gamma$ - $MnO_2$ and the ability of $\gamma$ - $MnO_2$ to form solid solutions with lower manganese oxides. Bode and Schmier (Encyclo. 1973, 34, 127-129) found that the reduction of $\gamma$ - $MnO_2$ proceeds in a homogeneous phase to $MnO_{1.5}$, $\alpha$ - $MnO_2$ in a homogeneous phase to $Mn_{1.86 \pm 0.01}$. on the other hand, the reduction of $\beta$ - $MnO_2$ takes place heterogeneously as early as the composition of manganese dioxide reached $MnO_{1.97}$. These results again point out the fact that the capability of $\gamma$ - $MnO_2$ in forming solid solution with lower manganese oxides and that the diffusion of protons takes place more readily in the lattice of $\gamma$ - $MnO_2$ than that of $\alpha$ or $\beta$ - $MnO_2$.

The diffusion of protons and electrons in the lattice of manganese dioxide was proposed by Brenet years ago. Gosh and Brenet (Encylo. 1973, 131, 132) studied the reaction products at various discharge stages of $\gamma$ - $MnO_2$ by means of x – ray and electron diffraction, electron microscopy, differential thermal analysis, thermogravimetry, and magnetic susceptibility. They concluded that during the initial stages of discharge the manganese dioxide lattice is dilated by proton addition. This conclusion is in agreement with that related by Vosburgh. However, there is a difference between the Brenet theory and the Vosburgh theory. Brenet considered that the initial discharge process involved the random reduction of $Mn^{4+}$ to $Mn^{2+}$ in the lattice whereas Vosburgh considered the electrochemical process to produce MnO(OH). In the case of $\gamma$ - $MnO_2$ it is material whether the reduction of $MnO_2$ proceeds through manganese III or manganese II oxides since it is recognized that $\gamma$ - $MnO_2$ possesses a wide range of homogeneity and the formation of the manganese oxides proceeds homogeneously in the lattice, resulting in a continuous change of the Stoichiometry of "manganese dioxide". In fact, Gabano, Morignot, and Laurant (Encyclo. 1973, 133, 134), using the theory of homogeneity of Vetter and Jaeger, proposed a general equation for the reduction of $\gamma$-manganese dioxide.

$MnO_{2n-2}(OH)_{4-2n} + ZdnII^{+} = Zdne^{-} + MnO_{2n-2+2nd}(OH)_{4-2n+2nd}$ ..........2.18

Where n is the degree of oxidation having any value between 1.5 to 2.0. This equation presents a good concept of continuity existing between the two infinitesimally dose states of reduction.

Nevertheless, since MnO(OH) has been identified analytically as the electrochemically reducing product from $MnO_2$, the Vosburgh equation

$MnO_2 + H^{+} + e^{-} = MnO(OH)$ ..........2.19

is more acceptable as a special case for the general expression shown above.

From the discussion, one can conclude that the reduction of manganese dioxide (at least for the gamma variety) proceeds through the diffusion of protons and electrons in the lattice.

Johnson and Vosburgh, found that the potential of $MnO_2/MnO(OH)$ electrode is a function of the mole ratio R of $MnO_2$ and MnO(OH) in the solid solution. At 25°C it can be expressed as:

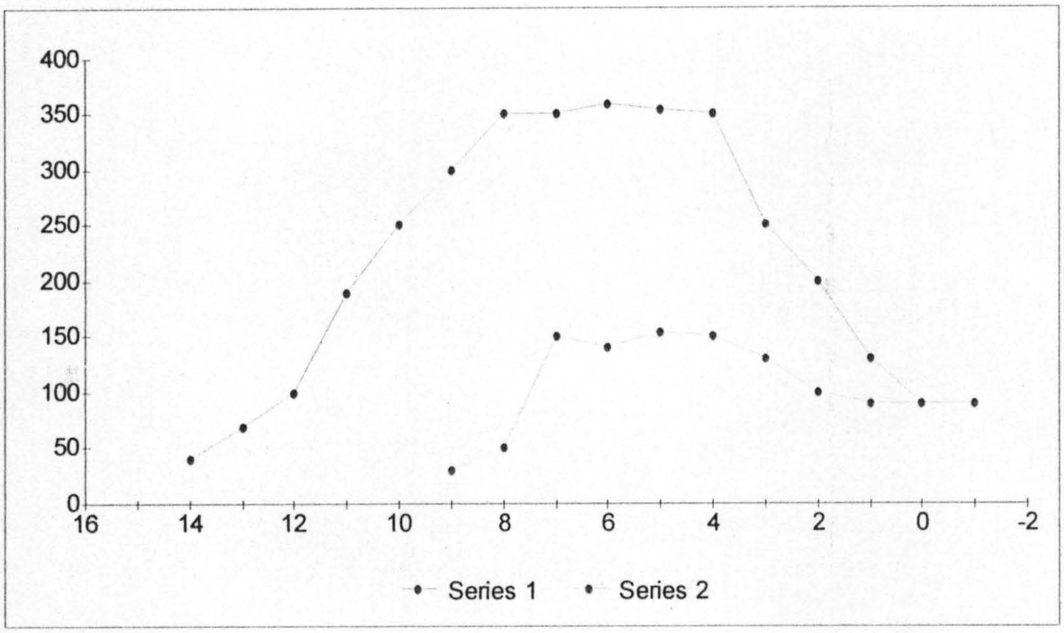
$E = E + 0.073 \log R$ ..........2.20

Where E is the potential of the $MnO_2/MnO(OH)$ electrode; $E_o$ has an guage value of 0.416V vs the saturated calored electrode at pH 7.5.

The difference between the value of the constant 0.073 and the expected value of 0.05g is attributed to the fact that R is the mole ration rather than the activity ratio of $MnO_2$ and MnO(OH) in the electrode. Benson, Price and Type (Encylo.1973, 135) examined the equilibra involved in a manganese dioxide electrode and concluded that in the absence of $Mn^{2+}$ ion in the electrolyte the potential is determined by the surface condition of the electrode in the event the surface is not equilibrium with the bulk of the electrode. Based on these findings and conclusions, an examination can be made for the detailed mechanism of the polarization and the open circuit potential recuperation processes. Upon discharge of the $MnO_2$ electrode, MnO(OH) is formed on the surface of the electrode, Causing a decrease in the electrode potential. At the same time the removal of MnO(OH) from the electrode surface will also take place either by diffusion towards the interior of the electrode (involving protons and electrons) or by disproportionation. In acidic electrolytes the removal of the reduction product is primarily through the reaction.

$2MnO(OH) + 2H^{+} = MnO_2 + Mn^{2+} + 2H_2O$ .........2.21

The rate of reaction is higher than of the diffusion of protons. As a result, the over potential of the manganese dioxide electrode in an acidic electrolyte is considerably lower than that in a neutral electrolyte where the removal of MnO(OH) is increasingly dependent on the lower process of proton and electron diffusion.



(series 1 = 3M KCl, series 2 = 1.5M $NH_4^+$)

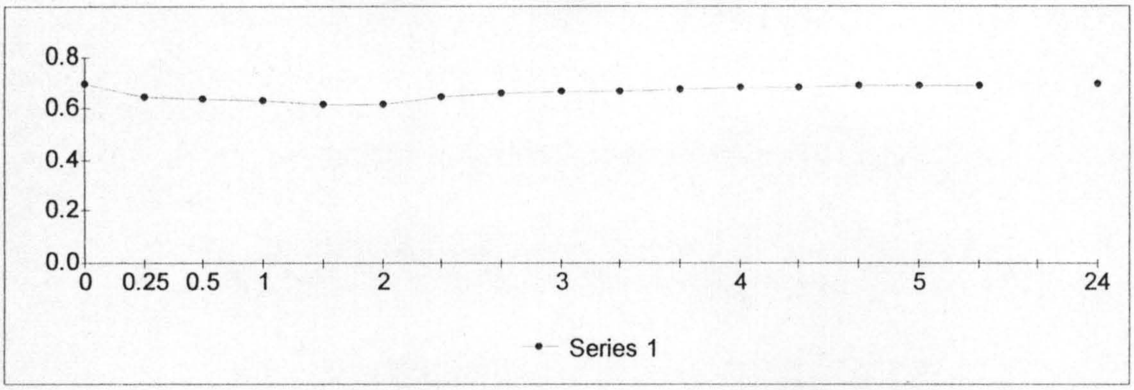
(pH = x axis, Over potential, mV = y axis)

Figure 2.3: Effect of pH and ($NH_4^+$) on the over-potential of $\gamma$ -manganese dioxide electrode.(Takehara and Yoshizawa, 1973)

The above figure shows the discharge over potential of a $\gamma$ -$MnO_2$ electrode as a function of the pH value of the electrolyte as reported by $E_m$, Takehara, and Yoshizawa (Encycl, 1973, 136). It is noted from the above figure that under a similar discharge current of 0.1mA/cm$^2$, the over potential of the $\gamma$ -$MnO_2$ electrode is less than 100mV in 3 N $H_2SO_4$ but more than 300mV in 3MKCL. It is also noted that in electrolytes of similar pH value, the over potential is much lower in the presence of $NH_4^+$ ions. Indeed, the $NH^+_4$ ion is assumed to act as a proton – donor to MnO(OH).

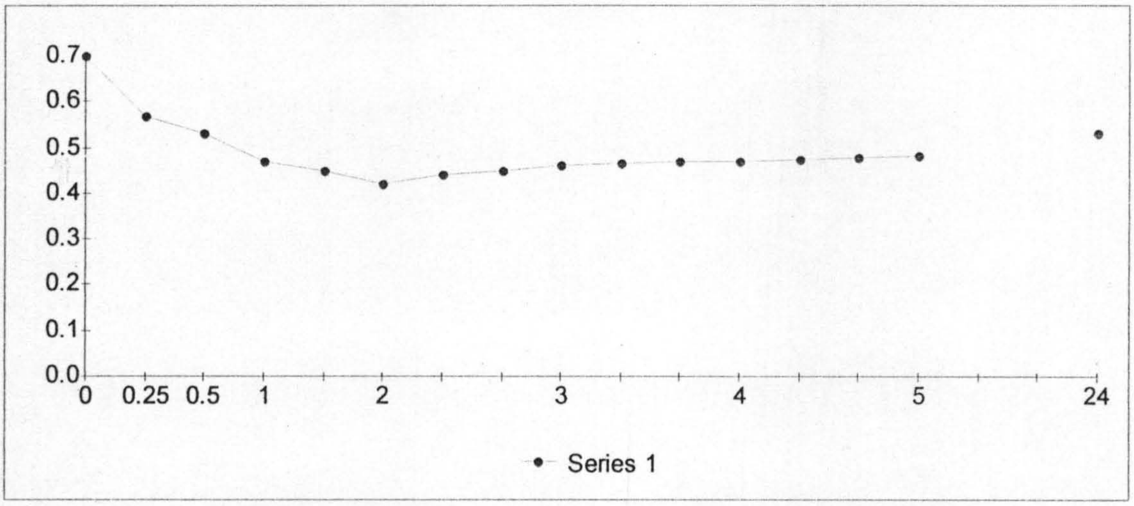
$2MnO(OH) + 2NH_4^+ MnO_2 \ - Mn^{2+} + 2NH_3 + 2H_2O$ ...........2.22

Furthermore, in the electrolytes containing $NH_4^+$ ions, $NH_3$ can complex metal ions such as $Zn^{2+}$, $N^{2+}$, or $Mn^{2+}$ and lower the potential as predicted by the above equation. The effect of $NH^+_4$ on the discharge over potential of the manganese dioxide electrode was also shown by Chreitzberg and Vosburgh (122).



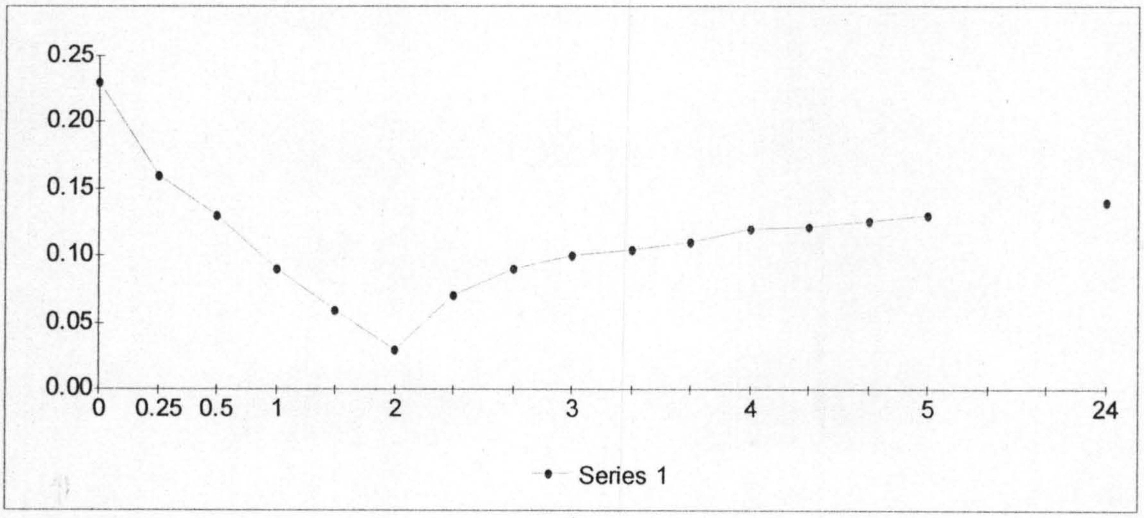
a

(Time, hr = x axis vs $Hg/Hg_2SO_4/3N\ H_2SO_4$ = y axis: 1.5M $H_2SO_4$)



b

(Time ,hr = x axis vs Potential,V vs sce = y axis: 3M $NH_4Cl$)



c

(Time, hr = x axis vs Hg/HgO; 3N KOH )

Figure 2.4: Comparative growth of polarization and recovery of open circuit potential of $MnO_2$ electrode in various electrolytes.(Chreitzberg and Vosburgh, Encycl., 1973).

The above figure also is a profound effect of the pH value of the electrolytes on the open circuit potential recuperation. In 3 N $H_2SO_4$ the rate of recuperation is relatively high. Furthermore, the open circuit potential of the electrode approximates the original value, indicating that the MnO(OH) is removed completely by the disproportion. Indeed, the products of the disproportion are $Mn^{2+}$ and $MnO_2$. $Mn^{2+}$ dissolves in the electrolytes and only $MnO_2$ remains in the electrode, and the original open circuit potential of the electrode is restored. On the other hand, in 3N $NH_4CL$ the rate of recuperation is lower than in 3N $H_2SO_4$ and the final open circuit potential is lower than that of the signal electrode. The diffusion of protons and electrons in manganese dioxide has been examined quantitatively.

SCOH considered a one dimensional semi-infinite solid manganese dioxide electrode and obtained the following equations for the diffusion of protons in the manganese

$$C_{(t,o)} = \frac{2F_o}{(Dn)^{1/2}} \{t^{1/2} - (t - T)^{1/2}\} \qquad \text{.......2.23}$$

$$C(t, x) = \frac{2F_o}{D^{1/2}} \left[ t^{1/2} (ierfc \frac{x}{2(Dt)^{1/2}}) - (t-T)^{1/2} (ierfc \frac{x}{2D^{1/2}(t-T)^{1/2}}) \right] \qquad \text{.........2.24}$$

Where C(t,o) = concentration of MnO(OH) on the surface of the electrode (x = o), C(t,x) = concentration of MnO(OH) in the interior, (x>o), Fo = equivalents of MnO(OH) produce per unit area per unit time during discharge at a constant current density, D = diffusion coefficient of proton (accompanied by electron) in the solid, t = time following the start of discharge, and T = time at which discharge stops and recuperation begins. For t < T the term involving (t – T) is to tbe taken as zero. By substituting the concentration – time relation on the surface of the electrode into the Johnson – Vosburgh equation and taking account of the fact that the sum of the concentration of $MnO_2$ and that of MnO(OH) is constant, the general potential time relation can be computed.

$$E = E_o + K \log \left[ \frac{(\pi D)^{1/2}}{2F_o t^{1/2} - (t-T)^{1/2}} - 1 \right] \qquad \text{........2.25}$$

The polarization and recuperation behaviour of the manganese dioxide electrode in the $NH_4CL$ –

Discharge duration - 2 hours

On the other hand, in 3M NH$_4$CL under te same discharge condition the over potential increased from 201.5 mV for the original $\gamma$ - MnO$_2$ to 285.0mV for the heat – treated $\gamma$ - MnO$_2$. The over potential increased from 78.7 to 145mV after the heat treatment when the electrodes were discharged in 3 N KOH under the same conditions. In acid solution the removal of the discharge product does not depend upon proton diffusion and the over potential is not affected by the water content in the lattice. As the pH of the electrolyte increase, the proton diffusion becomes more important for the removal of MnO(OH). Therefore, the amount of water in the lattice which facilitates the process has a profound effect on the over potential, especially in alkaline solutions where the removal of MnO(OH) depends solely on the proton diffusion process.

.2 Manganese dioxide in alkaline solution

The cathodic reduction of electrolytic manganese dioxide was studied by Cahoon and Korver in 7.6 N KOH using Zn(Hg) on the conten electrode. Based on analysis of the products at various stages of discharge, the authors postulated the formation of Mn(OH)$_2$ from the initial stage of the discharge and also suggested the formation of a hypothetical oxide Mn$_4$O$_7$. However, the formation of Mn(OH)$_2$ at the beginning of the of discharge has not been confirmed by later investigators.

It is conceivable that the Mn(OH)$_2$ formation observed by Cahoon and Korver was due to the high current density (approximately 15mA/cm$^2$ or 60mA) used in the reduction process, and under these conditions reduction to Mn(OH)$_2$ may have take place on the surface of the electrode. Further, Cahoon and Korver used 500cc of NH$_4$CL solution to extract the manganese ion from, the discharged electrode. Although, the pH value of the suspension adjusted to 5.4 wherein Mn$_2$O$_3$ or MnO(OH) may be stated, the presence of Nh$_4^+$ and Zn$^{2+}$ ions may cause the disprotionation of Mn$_2$O$_3$ according to

$$2MnO(OH) + 2NH_4^+ = Mn^{2+} + MnO_2 + 2H_2O + 2NH_3 \qquad ..........2.26$$

$$Zn^{2+} + {}_nNH_3 = Zn(NH_3)_n^{2+} \qquad .........2.27$$

Bell and Hubber investigated the cathodic reduction of both $\gamma$ and $\beta$ manganese dioxide in electrolytes containing 40 not % KOH and 7.5 not % ZnO. At low rates (0.5mA/g) and intermittent discharge (100hr/week), the $\gamma$ - MnO$_2$ electrode exhibits a three – step discharge curve. The electrode potential decreases gradually until the manganese oxide reaches the composition MnO$_{1.7}$. Between MnO$_{1.7}$ and MnO$_{1.625}$ the electrode potential shows a rather rapid decrease. From MnO$_{1.625}$ to MnO$_{1.47}$ and the potential is approximately constant. Between MnO$_{1.47}$ and MnO$_{1.43}$ the electrode potential shows another rapid decrease and remains constant

$NH_4OH$ electrolyte (pH = 7.5) was investigated experimentally by Kormeil, and compared with the results calculated from above equation. The agreement was good. However, deviations occurred at the start of the polarization and after relatively extended periods of potential recuperation. The derivation at the beginning of the discharge can be attributed to the assumption of zero MnO(OH) concentration making E infinite, $\infty$. The derivation during the latter part of the recuperation is due to the fact that the conditions for semi - infinite diffusion are no longer realized. Although the potential – time relation is derived from the surface conditions of the electrode, it is important to realize that as equilibrium approached during recuperation, the concentration ratio of manganese dioxide and the lower manganese oxides in the entire electrode determines the electrode potential.

The water in the manganese dioxide lattice plays an important role in the electrochemical process. It has been suggested that the presence of water in the lattice promotes the diffusion of protons and that the water molecule in the manganese dioxide lattice can be present as $H_2O$, $H_3^+O$, and $OH^-$. Johnson and Bosburgh used the formula $H_2MnO.\ X\ MnO_2$ to designate the hydrated manganese dioxide. Vether and Jacger (Encyclo. 1973, 24) used the general formula of $MnO_{2n-2}(OH)_{4-2n}$ or $MnO_n(2-n)\ H_2O$ to show the homogeneity and the presence of $H_2O$ in the lattice of $\gamma$ - manganese dioxide. Benet and Co-workers proposed the formula $MnO_x\ (OH)_{4-2x}$ and latter another formula $MnO_{n-z}(OH)_{2z}\cdot{}_{m}H_2O$ to show the action acidic OH group. The presence of water in manganese dioxide has been well established. Trarusko (Enclo.1973, 138) reviewed briefly the findings in this respect. Furthermore, he also found from analyses of a wide variety of manganese dioxide samples that the total water content (both in the lattice and adsorbed) variety from 1% for a highly crystalline $\beta$ - $MnO_2$ to 20% for synthetic, hydrous $MnO_2$ when equilibrated in an atmosphere of 75% relative humidity. The effect of the water in the lattice on the diffusion of proton during discharge was clearly shown by Era, Takehara, and Yoshizawa (Encycl., 136). Manganese dioxide of the gamma variety was heated at 200°C for 3 hours to remove part of the crystalline water while maintaining the gamma structure. The polarization behaviours of the heat – treated $\gamma$ - $MnO_2$ was compared with that of the original $\gamma$ - $MnO_2$. In 3 $\underline{N}$ $H_2SO_4$ no significant change was observed in the over potential under the following discharge conditions:

Electrode - disk type (0.5g $MnO_2$,0.2g acetylene black)

Geometric area - 2cm$^2$

Discharge current - 10mA

Temperature - 25°C

## .11 Electrochemistry of Manganese Dioxide

Manganese dioxide is one of the most studied compounds in the field of electrochemistry. Since 1866, when Leclanche' invented the Zn – $MnO_2$ cell, manganese dioxide has been an important battery reactant.

Manganese dioxide is usually classified according o crystal structure into etc. varieties. They are more or less different substances of the approximate composition $MnO_2$ with or without other elements.

In a recent review of solid state properties of manganese dioxide ($MnO_2$), milati (116) discussed the different crystal structures, the non-stoichiometry, the electrical and magnetic properties, and the general compositions of various types of manganese dioxide. The electrochemistry properties also vary with the types of manganese dioxide, example of a stable standard potential of the $MnO_2/Mn^{2+}$ electrode can be measured with $\beta$ - $MnO_2$, but it is difficult to do this with $\gamma$ - $MnO_2$ because of its ability to form solid solutions with lower manganese oxides over a wide range of compositions. In view of the fact that $\gamma$ - $MnO_2$ can be discharged more efficiently than other types of $MnO_2$, it is widely used in batteries as the cathode material. (Encyclo. Electrochem., 1973)

### .11.1 Cathodic reactions of manganese dioxide in neutral or acidic solutions

The determination of the mechanism of the manganese dioxide electrode has been approached from three perspectives/ways viz:

i- Analyses of the reaction products by both physical and chemical methods

ii- Analyses of the pH – potential relationship

iii- Analyses of the discharge characteristics

Cahon and co-workers (Encylo, 1973, 117 – 119) investigated the manganese dioxide electrode in $NH_4CL$ or $NH_4CL + ZnCL_2$ solutions with various pH values. The findings were:

\- The slope of the potential pH plot was 60mv/pH

i- $Mn^{2+}$ was found in the electrolyte and

iii- MnO(OH) and in the presence of zinc, $ZnO.MnO_2O_3$ were identified by x – ray diffraction measurements as solid products as the cathode.

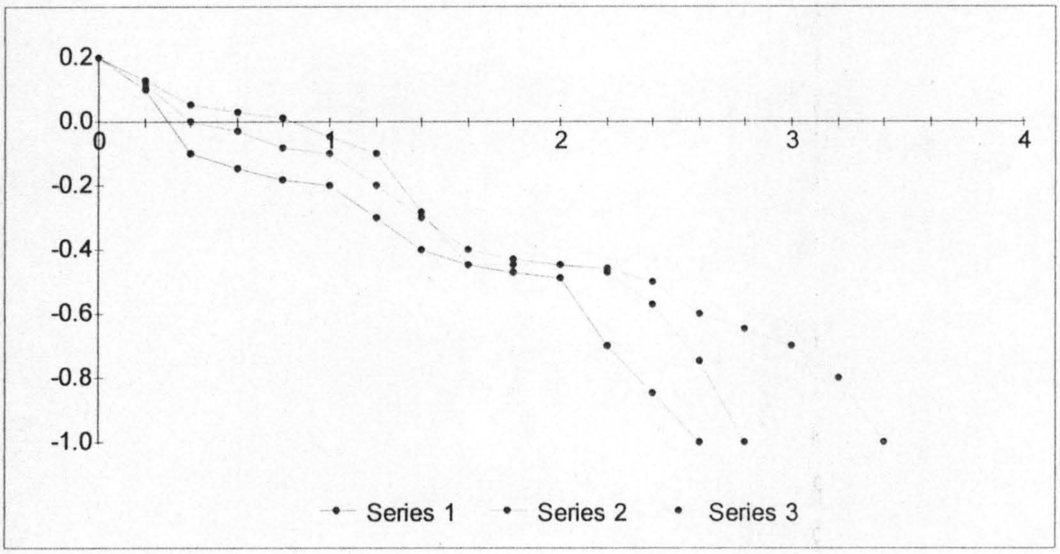
From these findings, Cahoon, Johnson, and Korver (Encycl. 1973, 118) concluded that two types beyond $MnO_{1.43}$.

Furthermore, the rest potentials of the electrodes at various stages of discharge exhibit similar behavior as the potential under load, viz, an initial continuous decrease as the oxidation state of the manganese decreases and remains constant after the composition reaches $MnO_{1.625}$ and $MnO_{1.47}$, respectively. Based on these results, Huber and Bell concluded that for the $\gamma$ - $MnO_2$ electrode the reduction proceeds in three steps.

i. $MnO_2 - MnO_{1.7}$ homogeneous phase reduction

ii. $MnO_{1.7} - MnO_{1.47}$ heterogeneous system

iii. Below $MnO_{1.47}$ heterogeneous system



(series 1= 0.11mA, series 2 = 0.33mA, series 3 = 3.0mA)

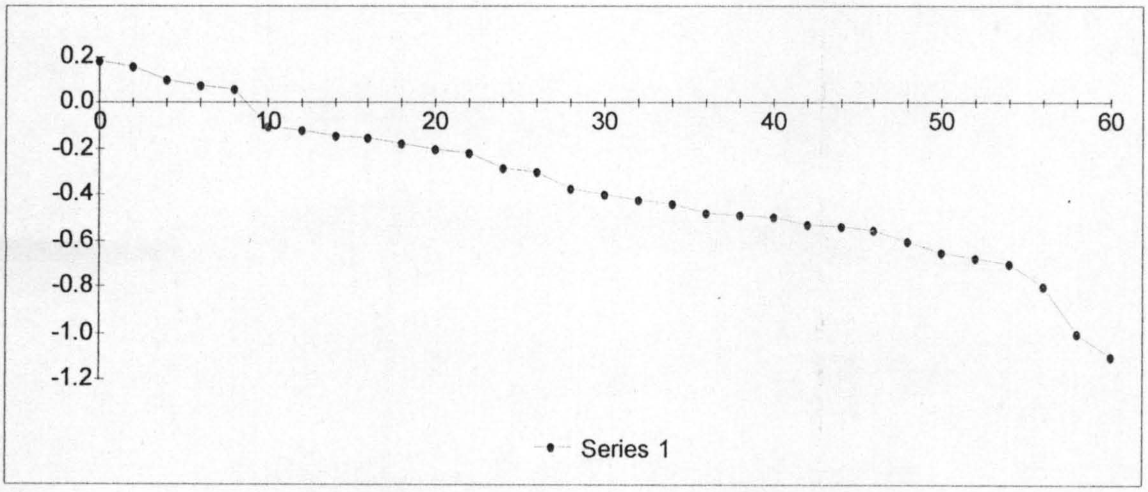
(Current, MA-HOUR = x axis, Potential vs Hg/HgO(9M KOH) at 28°C)

5: Discharge curves of the $\gamma$ - manganese dioxide electrode in 9 M KOH solution. (Huber and Bell, Encyclo. 1973)

During the reduction in the homogenous phase, lattice dilation has been observed by x-ray diffraction. It should be pointed out that under the low current density and intermittent discharge condition, re-crystallization of the lower manganese oxides may occur. Indeed, when the discharge stage reached $MnO_{1.625}$, Bell and Huber observed cementation of the electrode and $\gamma$ - $MnO_2$ electrode is distinctly different from that of the $\gamma$ - $MnO_2$ electrode. According to Bell and Buber, the following steps are involved in the reduction of $\beta$ - $MnO_2$ electrode.

| | | |
|---|---|---|
| i. | $MnO_2 - MnO_{1.96}$ | Homogeneous phase reduction |
| ii. | $MnO_{1.96} - MnO_{1.8}$ | heterogeneous system |
| iii. | $MnO_{1.8} - MnO_{1.6}$ | homogeneous phase reduction |
| iv. | $MnO_{1.6} - MnO_{1.48}$ | heterogeneous system |
| v. | Below $MnO_{1.48}$ | heterogeneous system |

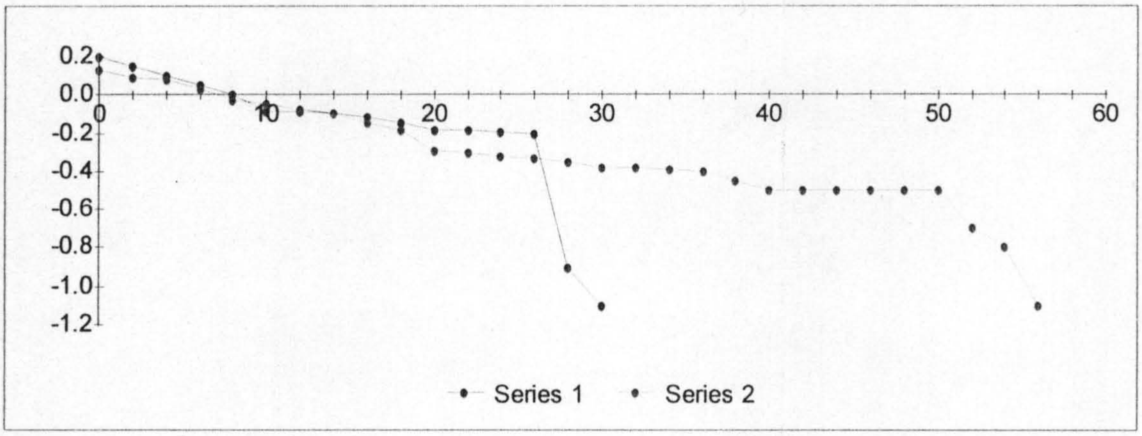
Recently, Kozawa, Yeager and powers conducted detailed investigations on the $\gamma$ - $MnO_2$ electrode in alkaline electrolytes. In order to eliminate any possible complications in interpreting the data, the authors avoided the use of zinc anodes and zinc oxide in her electrolyte. The discharge behaviour of the $\gamma$ - $MnO_2$ electrode depends upon the $OH^-$ ion concentration of the electrolyte. In concentrated alkaline solutions such as 9 M, KOH, two distinct discharge steps are shown in the discharge steps. In the first step $MnO_2$ is reduced to $MnO_{1.5}$ and the potential decreases continuously to about -0.4V vs the Hg/HgO (9M KOH) reference electrode. In the second step $MnO_{1.5}$ is reduced to $MnO_{1.0}$ and the potential remains practically constant especially under low current densities. On the other hand, in dilute KOH solutions such as 0.1 or 1.0 M KOH, the second step discharge is absent and the potential drops rapidly to a value lower than -1.0V vs Hg/HgO as the electrode reaches $MnO_{1.5}$ as shown by curves B and C in the figure below. Furthermore, in the dilute KOH solutions, the addition of tri-ethanol amine, which is a complexity agent for $Mn^{2+}$ and $Mn^{3+}$, can restore the second discharge step as shown below



(Discharge Time,MIN = x axis, y axis = Potential vs Hg/HgO in 9M KOH,V,Plot)

Figure 2.6: Effect of KOH concentration on the discharge behavior of the $\gamma$ - manganese dioxide electrode in 9M KOH solution.(Encyclo., 1973)

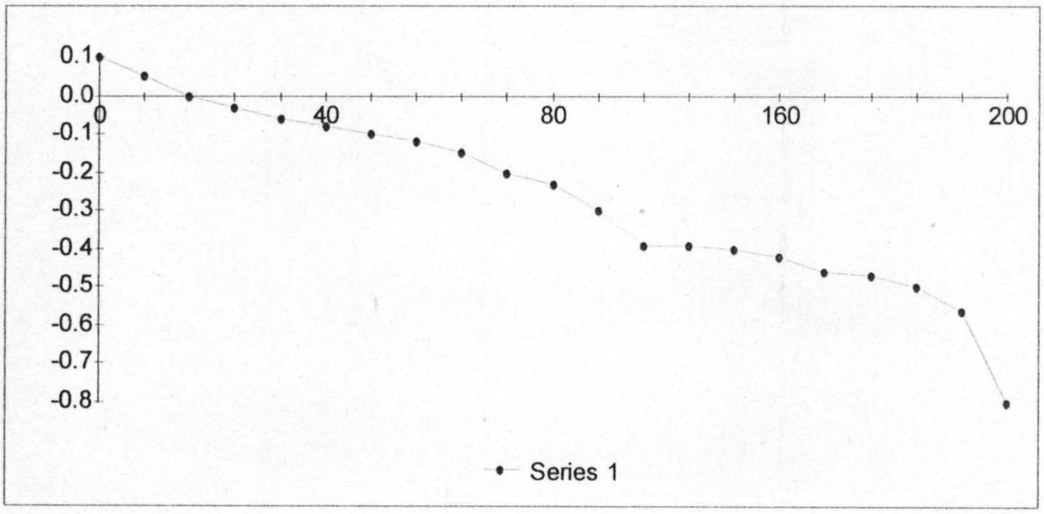
The open circuit equilibrium potential of the electrode also decreases with the oxidation state of the electrode in the first stage of discharge, however, it remains unchanged in the second step of discharge as shown in figure 2.8 below.



(series 1 = 1M KOH, series 2 = 1M KOH + 20% by volume triethanolamine)

(Discharge Time, MIN = x axis, y axis = Potential, V vs Hg/HgO( 1M KOH at 23°C)

Figure 2.7: Effect of tri-ethanol amine on the discharge behavior of the $\gamma$ - $MnO_2$ electrode in 1M KOH.(Encyclo.,1973)



(Discharge Time, MIN = x axis, Potential, V vs Hg/HgO )1M KOH)

Figure 2.8: Discharge curve and open circuit potential recovery of the $MnO_2$ electrode in 9 M

KOH (Encyclo., 1973)

a = discharge curve

b = open circuit equilibrium potential

c,d,e = recovery curve

These observations led Kozawa and Co-workers to the following conclusions:

i- In concentrated alkaline solutions the reduction of the $MnO_2$ electrode involves two distinct steps.

ii- The first step, reduction of $MnO_2$ to $MnO_{1.5}$, involves a homogenous process. As shown in figure 8 below

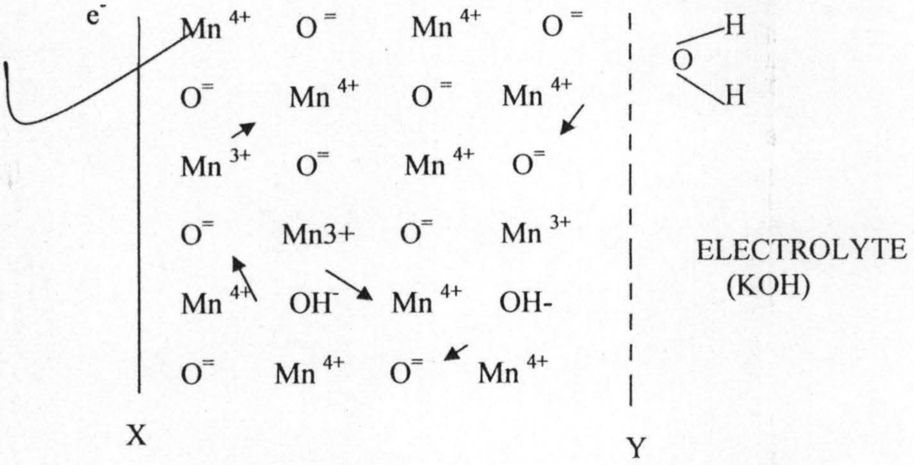


Figure 2.9: Diffusion of protons and electrons in manganese dioxide lattice during discharge. + ions shows electron movement, - ions shows proton movement,X = interface of Mno2 and electronic conductor, Y = interface of MnO2 and electrolyte.(Encycl.,electrochemical reactions, 1973)

Electrons are introduced into the $MnO_2$ lattice and $Mn^{4+}$ is reduced to $Mn^{3+}$. As a result of electron exchange between $Mn^{4+}$ and $Mn^{3+}$ in the lattice, the position of $Mn^{3+}$ moves around in the entire lattice. At the same time, $H_2O$ decomposes at the electrolyte – electrode interface and protons are introduced into the lattice to form $OH^-$. $OH^-$ also moves around in the entire lattice by means of proton jumping from one $O^{2-}$ site to another. The cathodic reduction of the first step may be expressed as:

$Mn_2 + H_2O + e = MnO(OH) + OH^-$ ..........2.28

It may be pointed out, however, that this is a simplified picture of the first discharge step. In fact, Kozawa and Powers (Enclo.1973, 47), in discussing the detains of the discharge mechanism, suggested that while the reduction of $MnO_2$ to $Mn_{1.5}$ proceeds in a homogenous phase, at this layer of $Mn_2O_3$ or $MnO(OH)$ may begins to form in a separate phase at the later stage of discharge.

The second step, reduction of $MnO_{1.5}$ to $MnO_{1.0}$, occurs heterogeneously. Due to the formation of complex ions

$Mn(OH)_4^-$ and $Mn(OH)_4^{2-}$g manganese III oxide manganese II oxides are quite soluble in concentrated KOH solutions. The electrochemical reduction of $MnO_{1.5}$ to $MnO_{1.0}$ takes place in the solution phase. These processes can be expressed as

$MnO(OH)_{(s)}$ = Mn(III)(insolution) ......2.29

Mn (III) + e = Mn (II) (electrochemical reduction) .......2.30

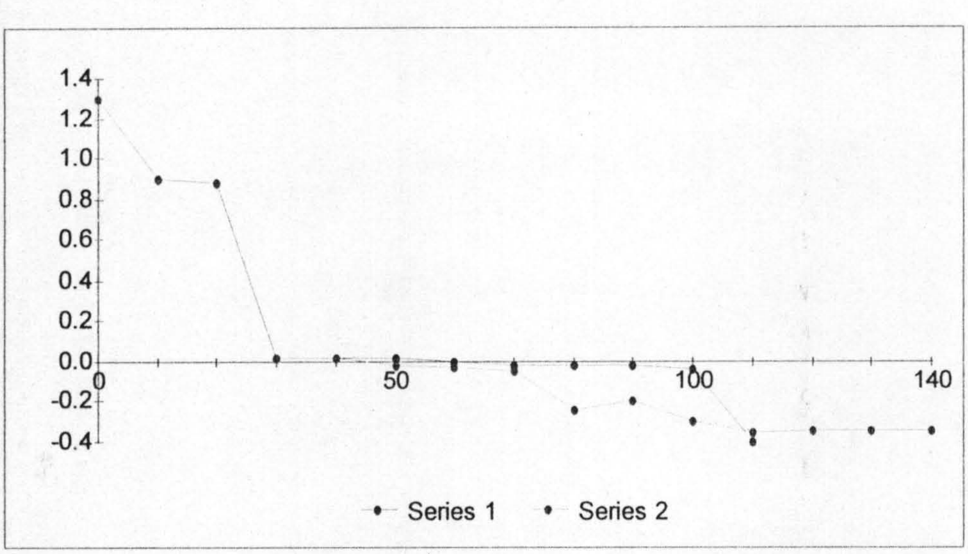
Mn(II)(insolution) = Mn .......2.31

Our discussion of the manganese dioxide electrode indicates repeatedly that the electrochemical reduction of manganese dioxide proceeds homogenously both in neutral and alkaline electrolytes via the proton and electron diffusion until the lattice becomes so strained it recrystalizes to another structure. Kozawa and Powers considered the potential – generating mechanism of the homogeneous $Mn^{3+}$ - $Mn^{4+}$ - $O^{2-}$ - $OH^-$ phase in contact with the KOH electrolyte analogous to an aqueous reduction system.

Therefore, the open circuit potential of the electrode at any stage of discharge between $MnO_2$ and $MnO_{1.5}$ may be expressed by the equation below with the concentration of $OH^-$ and $H_2O$ assumed constant, and ($Mn^{3+}$) and ($Mn^{4+}$) being the concentration of $Mn^{3+}$ and $Mn^{4+}$, respectively, in the solid electrode.

$$E = E^o - \frac{RT}{F} In \frac{[Mn^{3+}]}{[Mn^{3+}]} \qquad .........2.32$$

R, mole Ration $\{Mn^{3+}\}/\{Mn^{4+}\}$ in solid



( series 1 = CALCULATED, series 2 = EXPERIMENTAL)

(Discharge Time, MIN = x axis, y axis = Potential, V vs Hg/HgO)

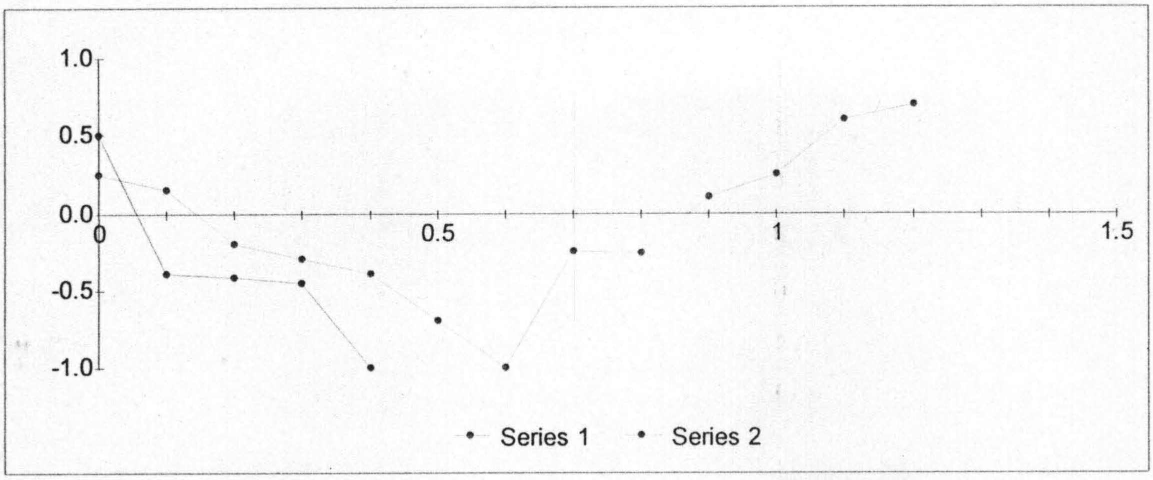
Figure 2.10: Equilibrium potential of manganese dioxide electrode in 9M KOH as a function of $\{Mn^{3+}\}/\{Mn^{4+}\}$ in the electrode.(Kozawa and Powers, Encyclo., 1973)

Figure 9 above shows a comparison between the calculated potential vs log $\{Mn^{3+}\}/\{Mn^{4+}\}$ relation from the above equation, and experimental results. A good agreement is noted in the first part of the curve. However, disagreement between the calculated and the experimental curve occurs at the latter stage. According to Kozawa and Powers, this is due to the formation of MnO(OH) or $Mn_2O_3$ in a new phase on the surface of the $Mn^{4+}$ - $Mn^{3+}$ - $O^{-2}$ – $OH^-$ system at the later discharge stages, an the electrode potential is controlled by the lower manganese dioxide on the surface.

General agreement exists among various investigators in regard to the initial homogenous process involved in the cathodic reduction of $\gamma$ -$MnO_2$. nonetheless, Kozawa and co-workers (Enclo. 1973, 14,16,146) were the first to study the effect of the $OH^-$ ion concentration on the cathodic reduction of manganese dioxide. They found that the further reduction of manganese (III) dioxide depends on the solubility of manganese (III) in the electrolyte. In low concentration KOH solution where the solubilities of both manganese (III) oxide and manganese (II) oxides are extremely low, no further reduction of manganese (III) oxide can take place unless a complex agent such as triethanlamine is added to increase the solubility of manganese (III) ions. On the other hand, in highly concentrated KOH solutions where the solubilities of manganese (III) and manganese (III) oxides are relatively large due to the complex ions of $Mn(OH)_4^-$ and $Mn(OH)_4^{2-}$ (e.g. in 9M KOH the solubilities of $Mn^{3+}$ and $Mn^{2+}$ are 4.4. x $10^{-3}$ and 0.4 x $10^{-3}$ M, respectively), the reduction of manganese (III) oxides to $Mn(OH)_2$ takes place and the electrode potential is dependent of the depth of discharge, which characterizes the heterogeneous system. Furthermore, they found that the limiting current for the reduction at this stage depends upon the apparent surface area rather than the true surface area of the manganese dioxides. In other words, the rate of dissolution of manganese (III) ions into the KOH solution controls the rate of reduction. Consequently the charge transfer step in the reduction of manganese (III) oxides to $Mn(OH)_2$ must be taking place in the solution phase. .(Encyclo. Electrochem., 1973)

## 1.2 The electrochemical characteristics of $\gamma$ – $MnO_2$ in alkaline electrolytes

In alkaline electrolytes the electrochemical characteristics of $\gamma$–$MnO_2$ were investigated by Liang and Co-workers, and the results of the cathodic reduction of the $\gamma$–$MnO_2$ electrode are in excellent agreement with those obtained by Kozawa and Co-workers. Furthermore, investigations were conducted on the anodic oxidation of the discharged manganese dioxide electrodes in alkaline electrolytes (149, 150). The results of thee investigations indicate that the state of discharge determines the recharge-ability of the electrode. That when the $\gamma$–$MnO_2$ electrode is reduced to -0.4V Hg/HgO in both 10 and 1M KOH solutions or -1.0V vs Hg/HgO in 1m KOH solutions, the product is manganese (III) oxide. This reduced electrolyte can be re-oxidized efficiently as shown by the similarity of the discharge behaviours of the re-oxidized electrode and that of the original manganese dioxide electrode as show in figure 10 and 11.0 below.



(series 1 = 1st discharge and charge, series 2 = 2nd discharge)

(Time, h = x axis, vs y axis = Potential, V vs. Hg/HgO( *10M* KOH))

Figure 2.11: Discharge curves of the manganese dioxide electrode. Electrode: 6mg $MnO_2$ electrodeposited on a 5cm$^2$ graphite rod current density: 1mA/cm$^2$. Temperature: 25°C (Kozawa and Co-workers, Encyclo. Electrochem.,1973)

However, when the $\gamma$–$MnO_2$, which can be accomplished by reducing the electrode to -1.0V vs Hg/HgO in high concentration KOH solutions, the electrode cannot be reoxidized efficiently and the reoxidized electrode behaves differently from the original manganese dioxide electrode fig 10a. in view of the fact that the reduction of manganese (III) oxide to $Mn(OH)_2$ occurs primarily in the solution phase and that the solubility of manganese (III) ions increases with the concentration of KOH, it is evident that the efficiency of manganese (III) oxide reduction decreases with the KOH concentration when the manganese dioxide is cathodized to -1.0V vs Hg/HgO. Accordingly, the recharge ability of manganese dioxide electrode which has been cathodized to -1.0V vs Hg/HgO increases as the KOH concentration decreases.

From the analytical results it is obvious that Mn $(OH)_2$ can be oxidized anodic ally to Manganese (III) oxide. However, further oxidation of this manganese (III) oxide to manganese (II) oxide dose not occurs. It has been suggested that the manganese (iii) oxide produced from the cathodic reaction of the $MnO_2$ electrode is different from that produced from the electrochemically active, while the latter is electrochemically in active$\gamma$-$Mn_2O_3$. Consequently, the electrochemical redox cycle of the $\gamma$-$MnO_2$ electrode in highly concentrated KOH solution is postulated to be

$\gamma$-$MnO_2$

$\alpha$ - $MnO(OH)$ Mn(III) (in solution) $\gamma$ - $Mn_2O_3$

Mn(II) (is solution) $Mn(OH)_2$

The first step oxidation of $Mn(OH)_2$ to manganese (III) oxide, may involve the dissolution of manganese (II), its solution oxidation to manganese (III), followed by the precipitation of manganese (III). The precipitated form of manganese (III) is thought to be $\gamma$ - $MnO_3$ which is in active to further oxidation. When the discharge process of $\gamma$ - $MnO_2$ is stopped at the end of the step, the re-oxidation of the product manganese (III) oxide, which is $\alpha$ - $MnO(OH)$, is efficient. Also, once manganese (III) is dissolved in KOH solution, re-precipitation to $\alpha$ - $MnO(OH)$ seems to be inhibited.

The effect of the discharge depth on the re-chargeability of the manganese dioxide electrode was also observed by Boden, Venuto, Wister, and Wyle who studied the discharge and charge behavior in 7 M KOH by x – ray diffraction and charge discharge curves. However, these authors concluded that the formation of $Mn_3O_4$ upon deep discharge hinders the rechargeability whereas Kang and Lian concluded that $\gamma$ - $Mn_2O_3$ cannot be anodized to $MnO_2$ efficiently. It should be pointed out that the distinction between $Mn_3O_4$ and $\gamma$ - $Mn_2O_3$ is difficult based on the x – ray diffraction patterns. Therefore, Boden, Venuto, Wisler, and Wylie did not rule out the existence of $\gamma$ - $Mn_2O_3$ in the products of discharge although they gave more weight to $Mn_3O_4$ based on the observation of a $Mn_3O_4$ line of $d = 1.57A^o$ in the x – ray diffraction pattern.

Ambrose and Briggs (Encyclo.1973, 152) studied the anodic oxidation of $Mn(OH)_2$ and the subsequent reduction of the anodized electrode in 1M KOH solutions. The electrode was a cathodically formed $Mn(OH)_2$ layer on a platinum electrode in a manganese nitrade solution. The electrochemical behaviour of the thin film $Mn(OH)_2$ electrode observed by Ambrose and Briggs is similar to that of the completely discharged manganese dioxide electrode observed by Kang and Liang (150). During the anodic process, the electrode potential exhibits two current at about -0.2 and +0.2V vs the Hg/HgO reference electrode before the oxygen evolution potential. During the cathodic process, the potential of the oxidized thin film electrode drops rapidly o a relatively constant value of about -0.35V vs Hg/HgO where the manganese (III) to manganese (II) process takes place.

It is interesting to note, however, that the reduction process was carried out in 1M KOH solution by Ambrose and Briggs where the solubilities of manganese (III) and manganese (II) are small (estimated at $10^{-5}$ M (15) and cannot sustain relatively high rate of discharge for the manganese

(III), to manganese (II) process according to the mechanism proposed by Kozawa and Yeager, (Encyclo. 1973, 14, 47, 146). Indeed, Ambrose and Briggs here found that during the cathodic process of the oxidized $Mn(OH)_2$ electrode, the potential only shows a long current at about -0.35V vs Hg/HgO when the current density is as low as 30 μA/cm$^2$. When the current density is 0.2mA/cm$^2$, the electrode polarizes to -1.0V vs Hg/HgO rather rapidly. Although the electrochemical behaviour of the $Mn(()H)_2$ thin film electrode observed by Ambrose and Briggs is in good agreement with that observed by Liang and Kang, they concluded that the oxygen to manganese ratio of the oxidation product is 1.85 ± 0.05 whereas the analytical results by Kang and Liang here shown that $MnO_{1.65 \pm 0.05}$ is the product when Mn(OH) is oxidized to 0.55 to0.60V vs Hg/HgO. These differences may be attributed to the fact that Ambrose and Briggs anodized the $Mn(OH)_2$ thin film electrode to aid held at 0.65V vsHg/HgO for several minutes. That the adsorbed oxygen on the electrode caused a higher ratio of O/Mn is indeed a possibility. .(Encyclo. Electrochem., 1973)

# OPTIMIZATION OF THE ADSORPTION OF SOME CATIONS ON MANGANESE DIOXIDE USED IN LECLANCHE' DRY CELL

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**(M.ENG/SEET/2005/1119)**

THESIS FOR THE AWARD OF

MASTERS DEGREE (M.ENG) IN CHEMICAL ENGINEERING

SUBMITTED TO

THE DEPARTMENT OF CHEMICAL ENGINEERING

SCHOOL OF ENGINEERING AND ENGINEERING TECHNOLOGY

FEDERAL UNIVERSITY OF TECHNOLOGY (FUT), MINNA

NIGER STATE

APRIL 2008

# CHAPTER 3

# METHODOLOGY

## 1 Introduction

This chapter deals with the method adopted to investigate and develop the optimum ondition for the adsorption of some selected cations on manganese dioxide ($MnO_2$) used in batteries known s Leclanche' dry cells. The experiment employed potentiometric (a volumetric analysis) titration method that rovides accurate determination of ion concentration in which direct measurement of cell potential is npossible, whereas it is often possible to determine the ion indirectly by titration with some other ion. The H potentiometric titration method is used in this work to determine the adsorption factors. The factorial xperiment was carried out to determine the second order (quadratic) model equation and finally the model quations were optimized.

## List of Chemicals and Equipment

The chemicals and equipment used in these experiments are given in Tables 3.1 and 3.2 below. The chemicals were obtained by purchase from the registered laboratory chemicals vendors at kaduna, Nigeria while the equipment used were those in used at the chemical engineering laboratory of City University Kaduna (.formerly known as kaduna Polytechnic).

### 1 Chemicals used

The chemicals used in this work are listed in Table 3.1below.

### 2 Equipment used

The equipment used in this work are listed in Table 3.2 below.

## Experimental Set up of Equipment

The set-up of the equipment for the experiment is shown in Figure 3.1

## 4 Potentiometric Titration Procedure

### .1 Preparation of 500ml of 0.1M sodium hydroxide (NaOH) solution

40g of sodium hydroxide, NaOH, was dissolved in 1000ml of distilled water in a 1000ml capacity beaker and stirred thoroughly. That gave 1.0M solution. Then 500ml of the solution was collected in a volumetric flask.

Table 3.1: List of Chemicals Used

| S/N | Chemicals | Producer | Comment |
|---|---|---|---|
| 1 | Distilled water | | Laboratorytype,99% water |
| 2 | Sodium Hydroxide | Dr. HESSE &CIE, Frankfurt $NaOH$ M.W 40.0 min. assay 98% | 500g, sodium hydroxide pellets, laboratory type |
| 3 | Sodium Nitrate | SEARLE, ANALAR &WILLIAMS $NaNO_3$ MW 84.99 min. assay 99.5% (CHADWELL HEATH) | 500g, sodium nitrate pellet laboratory type |
| 4 | Calcium Nitrate | BDH laboratory supplies, Poole, England. $(c(NO_3)_2.4H_2O$ MW 236.15 min.assay 98% | 500g, calcium nitrate 4 – hydrate |
| 5 | Potassium Nitrate | J.T Baler Chemicals Co. Phillipsburg. $KNO_3$ F.W 101.11 min. assay 99.4 | 500g, potassium nitrate crystals |
| 6 | Zinc nitrate | BDH chemical Ltd, Poole, England $(Zn(NO_3)$ 26.$H_2O$ M.W | 500g biochemical zinc nitrate |
| 7 | Magnesium Nitrate | Hopkin & Williams Ltd Essex, $Mg(NO_3)_2.6H_2O$ MW 256.4 min. assay 97% | 250g, magnesium nitrate crystal. |
| 8 | Lead Nitrate | Griffin & George, middlesex, England. $Pb(NO_3)_2$ MW 331.21 min assay 99% | 500g, lead nit crystals,laboratory chemic |
| 9 | Manganese dioxide | BDH Chemical Ltd, Poole England. $MnO_2$ (iodometric) 70% impurities limitChloride (CL) 0.04%Iron (Fe) 0.02Sulphate ($SO_4$) 0.01%MW. | 500g,laboratory chemical $MnO_2$ precipitated |

The experimental set up shown below was made up of a beaker containing the nitrate solution placed on top of a magnetic stirrer. The electrodes of the pH meter are immersed inside the solution in the beaker while the terminals were connected to the pH meter. The titrate solution is contained in the burette clipped to the retort-stand. Beside is a weigh balance to measure adequate amount of the materials needed.

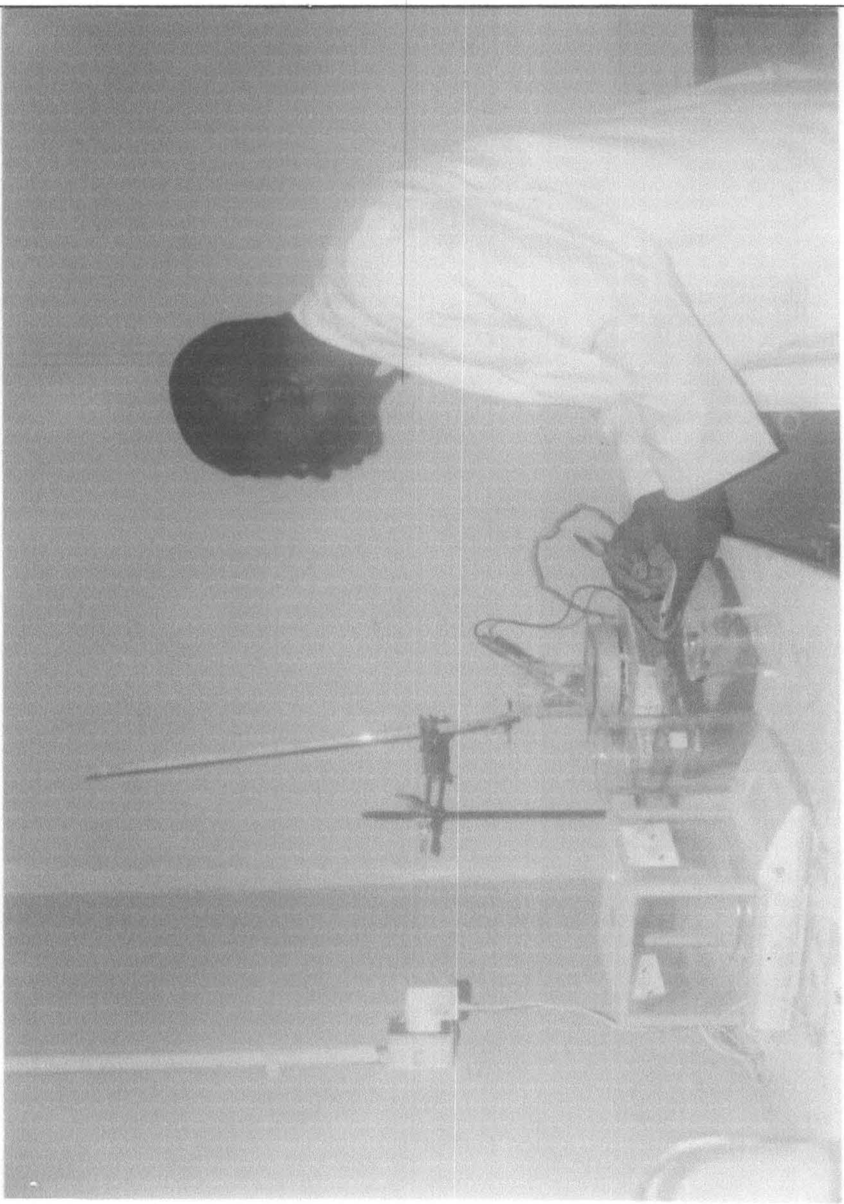

Figure 3.1: Diagram of experimental set-up

Table 3.2: List of equipment Used

| S/N | EQUIPMENT | PRODUCER | COMMENT |
|---|---|---|---|
| 1 | HEATER | ELECTROTHERMAL,CAT.model.221 Volt-200/250,wat-2500,England | Laboratory type |
| 2 | Magnetic Stirrer | GALLENKAMP, Magnetic Stirrer, Regulator Hot-Plate | Laboratory Type |
| 3 | PH METER | Hanna Inst. Model 209, PH meter | Laboratory size |
| 4 | WEIGHING BALANCE | College weigh balance | |
| 5 | POTENTIOMETER | Hanna Inst. PH meter,Model 209 | |
| 6 | RETORT STAND | | Laboratory Inst |
| 7 | THERMOMETER | | Laboratory Inst |
| 8 | BURETTE | | Laboratory type |
| 9 | PIPPETTE | | Laboratory type |

### 3.4.2 Preparation of 500ml of different concentrations of sodium nitrate ($NaNO_3$), calcium nitrate $Ca(NO_3)_2$, zinc nitrate $Zn(NO_3)_2$, potassium nitrate $KNO_3$, magnesium nitrate $Mg(NO_3)_2$, lead nitrate $Pb(NO_3)_2$ solution each.

#### 3.4.2.1 Solution preparation (Sodiun nitrate ($NaNO_3$))

85g of $NaNO_3$ was dissolved in 1000ml of distilled water in a 1000ml capacity beaker to give 1.0M solution of Sodiun nitrate ($NaNO_3$). This is further diluted to get 0.1M, 0.01M, 0.001M by adding distilled water and collected in different beakers.

The above prcedure is followed for 82g of $Ca(NO_3)_2$, 74g of $Mg(NO_3)_2$, and 82.75g of $Pb(NO_3)_2$.

### 3.4.3 Potentiometric titration experiments

#### 3.4.3.1 Titration of 50ml of 1.0M sodium nitrate ($NaNO_3$) solution with 50ml of 0.1M NaOH solution.

50ml of the titrant (NaOH) was collected with a pipette from the beaker containing it and transferred into the burette connected to the titration apparatus. The neat electrolyte was collected in a beaker and placed on top of the magnetic stirrer just under the burette. The stirrer was plugged onto the power mains supply and switched on. The temperature of the electrolyte was raised to 30 and later 50°C by setting the stirrer temperature. After the pH meter was initialized with a buffer tablet the electrodes of the pH meter was inserted into the electroyte. (The pH meter measures the pH, temperature and potential). The titration began by discharging drops of the titrant into the electrolyte and recording the volume of titrant, pH value and the potential. The experiment was repeated for solutions of 0.1M, 0.01M and 0.001M of $NaNO_3$. This same set of experiments were again repeated with 1g of $MnO_2$ dissolved in the neat electrolyte.The data obtained were tabulated. The above experiments were carried out for the other cations electrolyte $Ca(NO_3)_2$, $Mg(NO_3)_2$, $Pb(NO_3)_2$.

### .5 Factorial Experiment Procedure

The experimental data from the potentiometric titration serve as the input for the factorial experiment. The factors for the experimental design were first selected and used as the codes for the factorial analysis table as shown in Tables 3.3 and 3.4.

### 3.5.1 Selection of factors that affects the rate of adsorption

The rate of adsorption of the cations (adsorbents) on manganese dioxide (adsorbant) is affected by

i. Concentration of the solutions of the cations

ii. Temperature

iii. Time of contact or adsorption

iv. Degree of agitation or mixing

v. Mass of the adsorbant

In this experiment the concentration of solutions of the cations and the temperature of the solutions are varied whereas the other factors mass of adsorbant, time of contact and degree of agitation are fixed. The selected factors viz; concentration and the temperature, are represented by $x_1$ and $x_2$ respectively in Tables 3.4.

### 3.5.2 Development of factorial analysis tables for the surface response

The surface response is developed by factorial method as shown in tables 3.3 and 3.4 below. A $3^2$ quadratic equation gives 9 run experiments for the two factors; Concentration(X1) and Temperature(X2). $X_0$ is base factor selected. The sign + represents maximum value, – represents minimum value and 0 represents the average value or interval of the surface response. In this experiment, a two- variable, three level factorial design was used. The factors and the code levels are shown in Table 3.3. The calculation matrix, which includes the run-by-run experimental design, is shown in Table 3.4. Following the column of plus (+), labeled $x_o$, the next 2 columns (under the headings $x_1$and $x_2$) define the experimental design in standard order. Thus for Run 1, all 2 variables were set to vary form their heighest experimental levels. In the actual conduct of the experiment, the run order would generally be randomized.

Table 3.3: Factors and their coded levels for the cations

| Level of factors | Code | Independent Variables | |
|---|---|---|---|
| | | $x_1$(conc.) | $x_2$(temperature) |
| Base Level | $X_0$ | 0 | 0 |
| Interval or average | $\Delta x_i$ | 0.4995 | 40 |
| High Level | +1 | 1.0 | 50 |
| Low Level | -1 | 0.001 | 30 |

$$\Delta x_i = \frac{Xmax-Xmin}{2}$$

Table 3.4: Calculation Matrix and the Surface charge (Y) for $3^2$ Factorial design.

| Run | $x_0$ | $X_1$ | $X_2$ | $X_{11}$ | $X_{12}$ | $X_{22}$ | Y | Y | Y | Y |
|---|---|---|---|---|---|---|---|---|---|---|
| No | $a_0$ | $a_1$ | $a_2$ | $a_{11}$ | $a_{12}$ | $a_{22}$ | $Na^{++}$ | $Ca^{++}$ | $Pb^{++}$ | $Mg^{++}$ |
| 1 | + | + | + | + | + | + | | | | |
| 2 | + | 0 | + | 0 | 0 | + | | | | |
| 3 | + | - | + | + | - | + | | | | |
| 4 | + | + | 0 | + | 0 | 0 | | | | |
| 5 | + | 0 | 0 | 0 | 0 | 0 | | | | |
| 6 | + | _ | 0 | + | 0 | 0 | | | | |
| 7 | + | + | - | + | - | + | | | | |
| 8 | + | 0 | - | 0 | 0 | + | | | | |
| 9 | + | + | - | + | - | + | | | | |

That is, with two variables coded as $x_1$ and $x_2$, a 9-run experiment permits unique solutions for the coefficients (parameters) of equation 3.4

A 2-variable, 3-level factorial arrangement provided the framework for designing the experiment. The $3^2$ arrangement, when applied to only 2 variables, permits uncorrelated, low variance estimates of the 6 coefficients indicated in Equation (3.4). The numerical solution of Equation 3 is readily obtained using a computer or desk calculator (Douglas, 1991; Das, et.al, 1979; Guttman, et.al, 1982 and Betz, 1973).

Table 4.2; 50ml 0f 0.1M NaOH with 50ml 1.0M $NaNO_3$ soln at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 8.43 | 2 | - |
| 2 | 9.47 | 4 | -172 |
| 3 | 10.22 | 6 | -202 |
| 4 | 10.27 | 8 | -202 |
| 5 | 10.49 | 10 | -203 |
| 6 | 10.78 | 11 | -204 |
| 7 | 10.98 | 12 | -204 |
| 8 | 11.01 | 13 | -219 |
| 9 | 11.03 | 14 | -210 |
| 10 | 11.03 | 15 | -210 |
| 11 | 11.05 | 16 | -210 |
| 12 | 11.16 | 17 | -210 |
| 13 | 11.26 | 19 | -211 |
| 14 | 11.27 | 20 | -213 |
| 15 | 11.27 | 21 | -213 |
| 16 | 11.29 | 21.5 | -215 |
| 17 | 11.31 | 22 | -218 |
| 18 | 11.31 | 22.5 | -217 |
| 19 | 11.31 | 23 | -217 |
| 20 | 11.31 | 24.5 | -218 |
| 21 | 11.32 | 26 | -219 |
| 22 | 11.38 | 28.5 | -221 |
| 23 | 11.48 | 30.5 | -220 |
| 24 | 12.03 | 32.6 | -221 |
| 25 | 12.11 | 34 | -221 |
| 26 | 12.13 | 36.4 | -222 |

### Determination of Adsorption of Cations

Potentiometric titration was used to determine the adsorption of the cations (i.e $Na^+$, $Ca^{++}$, $Pb^{++}$, $Mg^{++}$) as adsorbent electrolyte with and without the adsorbant ($MnO_2$). 50ml solution of 0.1M sodium Hydroxide solution (NaOH) was titrated first with 50ml solution of each neat electrolyte at 30°C and 50°C and secondly titrated with neat electrolyte plus 1g $MnO_2$. The pH Meter was used to read the corresponding pH as the titration proceeded. The pH versus the volume of the titrant obtained was plotted for both the neat electrolyte and neat electrolyte with 1g $MnO_2$ on the same graph. At a given pH, the difference in volume ($\Delta V$) between the two graphs was used to calculate adsorption. The value of adsorption ($\theta$) is calculated using Kokarev's formula (Kokarev, et.al, 1988):

$$\theta = \frac{\Delta v.c}{s.1000} \text{Mole/cm}^2 \qquad \text{.........3.1}$$

where c = concentration of NaOH in mole/litre and s = surface area ($m^2/g$).

The electric surface charge of $MnO_2$, $E_v$, in coulomb/$cm^2$ is given by:

$$E_v = nF\theta \qquad \text{.........3.2}$$

n = absolute number of ionic charge and F = Faraday's constant.

### Determination of the Model Equation of Adsorption

### 1 Selection of model equation

A second order model equation of the form.

$$y = f(x_1, x_2) \qquad \text{.....3.3}$$

$$y = a_0 + a_1x_1 + a_2x_2 + a_{11}x_1^2 + a_{22}x_2^2 + a_{12}x_1x_2 \qquad \text{.....3.4}$$

($3^2$ quadratic factorial equation is selected)

where ai is the coefficient of regression and $x_{12}$ ($x_1x_2$) is the interaction effect.

# CHAPTER 4

# PRESENTATION OF RESULTS

## Table of Potentiometric Titration Results

This chapter presents the results obtained from the analytical experiments.

Table 4.1; 50ml 0f 0.1M NaOH with 50ml 1.0M $NaNO_3$ soln at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 6.77 | 2 | -212 |
| 2 | 9.37 | 4 | -219 |
| 3 | 10.11 | 6 | -220 |
| 4 | 10.16 | 7.2 | -223 |
| 5 | 10.36 | 9.0 | -225 |
| 6 | 10.59 | 10.5 | -230 |
| 7 | 10.67 | 12.0 | -233 |
| 8 | 10.79 | 14.0 | -238 |
| 9 | 10.85 | 16.0 | -240 |
| 10 | 10.96 | 18.0 | -240 |
| 11 | 11.02 | 20.0 | -245 |
| 12 | 11.06 | 22.2 | -247 |
| 13 | 11.13 | 23.4 | -249 |
| 14 | 11.18 | 25.2 | -251 |
| 15 | 11.21 | 26.5 | -252 |
| 16 | 11.23 | 28.0 | -253 |
| 17 | 11.23 | 29.5 | -255 |
| 18 | 11.23 | 31.0 | -256 |
| 19 | 11.24 | 32.0 | -256 |
| 20 | 11.25 | 33.4 | -257 |

Table 4.3; 50ml of 0.1M NaOH with 0.1M $NaNO_3$ solution at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 9.33 | 6 | - |
| 2 | 9.79 | 10 | -210 |
| 3 | 9.89 | 14 | -221 |
| 4 | 10.67 | 22 | -231 |
| 5 | 11.02 | 23 | -234 |
| 6 | 11.05 | 24 | -236 |
| 7 | 11.20 | 28 | -246 |
| 8 | 11.25 | 28.5 | -248 |
| 9 | 11.31 | 29 | -251 |
| 10 | 11.33 | 29.5 | -258 |
| 11 | 11.33 | 32 | -261 |
| 12 | 11.36 | 34 | -267 |
| 13 | 11.39 | 36 | -269 |
| 14 | 11.41 | 37 | -271 |
| 15 | 11.43 | 42 | -272 |
| 16 | 11.43 | 42.5 | -272 |
| 17 | 11.43 | 43.5 | -273 |
| 18 | 11.44 | 44.5 | -273 |
| 19 | 11.46 | 46 | -273 |
| 20 | 11.47 | 47 | -274 |
| 21 | 11.48 | 48 | -274 |
| 22 | 11.49 | 49 | -274 |

Table 4.4; 50ml of 0.1M NaOH with 0.1M $NaNO_3$ solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 6.72 | - | - |
| 2 | 7.05 | 1 | - |
| 3 | 7.95 | 2 | -80 |
| 4 | 8.38 | 3 | -108 |
| 5 | 8.64 | 4 | -124 |
| 6 | 9.84 | 5 | -138 |
| 7 | 10.86 | 6 | -154 |
| 8 | 10.58 | 6.5 | -187 |
| 9 | 10.47 | 6.8 | -193 |
| 10 | 10.60 | 7.2 | -201 |
| 11 | 10.72 | 7.8 | -209 |
| 12 | 10.85 | 9.5 | -211 |
| 13 | 10.87 | 10.5 | -212 |
| 14 | 11.02 | 11.5 | -234 |
| 15 | 11.05 | 12.2 | -223 |
| 16 | 11.09 | 13.5 | -228 |
| 17 | 11.11 | 14.5 | -229 |
| 18 | 11.13 | 15 | -231 |
| 19 | 11.13 | 18.5 | -232 |
| 20 | 11.13 | 19.5 | -236 |
| 21 | 11.23 | 26 | -238 |
| 22 | 11.41 | 31 | -239 |
| 23 | 11.46 | 33 | -241 |
| 24 | 11.47 | 34.5 | -242 |
| 25 | 11.48 | 35.5 | -247 |

Table 4.5; 50ml of 0.1M NaOH with 0.01M $NaNO_3$ solution at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 8 | 1 | - |
| 2 | 10.22 | 2 | -156 |
| 3 | 10.49 | 6 | -196 |
| 4 | 10.51 | 8 | -199 |
| 5 | 10.77 | 10 | 203 |
| 6 | 10.79 | 11.5 | -208 |
| 7 | 10.80 | 12.5 | -211 |
| 8 | 10.89 | 14 | -213 |
| 9 | 10.94 | 14.5 | -214 |
| 10 | 11.00 | 16 | -215 |
| 11 | 11.01 | 18 | -219 |
| 12 | 11.07 | 20 | -220 |
| 13 | 11.04 | 23 | -221 |
| 14 | 11.06 | 25 | -224 |
| 15 | 11.09 | 26 | -221 |
| 16 | 11.12 | 28 | -224 |
| 17 | 11.17 | 30 | -227 |
| 18 | 11.19 | 32 | -230 |
| 19 | 11.20 | 34 | -231 |
| 20 | 11.37 | 36 | -240 |
| 21 | 11.30 | 38 | -242 |
| 22 | 11.23 | 40 | -234 |
| 23 | 11.23 | 42 | -234 |
| 24 | 11.23 | 44 | -234 |

Table 4.6; 50ml of 0.1M NaOH with 0.01M $NaNO_3$ solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 6.77 | - | - |
| 2 | 7.56 | 2 | -120 |
| 3 | 8.89 | 4 | -147 |
| 4 | 9.47 | 6 | -165 |
| 5 | 9.9 | 8 | - |
| 6 | 10 | 10 | -216 |
| 7 | 10.83 | 12.5 | -221 |
| 8 | 11.01 | 13.5 | -223 |
| 9 | 11.07 | 14.5 | -227 |
| 10 | 11.12 | 16 | -228 |
| 11 | 11.16 | 17 | -229 |
| 12 | 11.17 | 18 | -231 |
| 13 | 11.17 | 19.5 | -231 |
| 14 | 11.17 | 20 | -231 |
| 15 | 11.18 | 21.5 | -232 |
| 16 | 11.21 | 23 | -234 |
| 17 | 11.26 | 25 | -236 |
| 18 | 11.29 | 27 | -238 |
| 19 | 11.35 | 28.5 | -244 |
| 20 | 11.41 | 32 | -244 |
| 21 | 11.41 | 33 | -242 |
| 22 | 11.40 | 34 | -246 |
| 23 | 11.41 | 37 | -2245 |

Table 4.7; 50ml of 0.1M NaOH with 0.001M $NaNO_3$ solution at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 6.77 | - | - |
| 2 | 8.67 | 1 | - |
| 3 | 8.79 | 1.5 | -075 |
| 4 | 8.93 | 2 | -084 |
| 5 | 9.02 | 3 | -095 |
| 6 | 9.08 | 4 | -102 |
| 7 | 9.12 | 6 | -103 |
| 8 | 9.18 | 8 | -103 |
| 9 | 9.24 | 10 | -105 |
| 10 | 9.34 | 12 | -106 |
| 11 | 9.36 | 14 | -106 |
| 12 | 9.45 | 16 | -108 |
| 13 | 9.56 | 18 | -117 |
| 14 | 9.67 | 20 | -112 |
| 15 | 9.81 | 22 | -115 |
| 16 | 9.95 | 24 | -126 |
| 17 | 10.03 | 26 | -126 |
| 18 | 10.23 | 28 | -125 |
| 19 | 10.24 | 30 | -123 |
| 20 | 10.31 | 32 | -126 |
| 21 | 10.38 | 34 | -127 |
| 22 | 10.42 | 36 | -131 |
| 23 | 10.54 | 38 | -131 |
| 24 | 10.55 | 40 | -132 |

Table 4.8; 50ml of 0.1M NaOH with 0.001M $NaNO_3$ solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.22 | - | - |
| 2 | 8.56 | 2 | - |
| 3 | 9.23 | 3.5 | -070 |
| 4 | 9.25 | 4 | -072 |
| 5 | 9.32 | 4.5 | -073 |
| 6 | 9.41 | 5 | -098 |
| 7 | 9.44 | 5.5 | -102 |
| 8 | 9.54 | 6 | -109 |
| 9 | 9.68 | 8 | -112 |
| 10 | 9.75 | 12 | -113 |
| 11 | 9.98 | 14 | -115 |
| 12 | 10.12 | 16 | -117 |
| 13 | 10.19 | 18 | -118 |
| 14 | 10.27 | 20 | -122 |
| 15 | 10.38 | 24 | -125 |
| 16 | 10.54 | 25 | -126 |
| 17 | 10.77 | 26 | -127 |
| 18 | 10.93 | 27 | -128 |
| 19 | 11.02 | 28 | -132 |
| 20 | 11.02 | 30 | -141 |
| 21 | 11.02 | 34 | -144 |
| 22 | 11.03 | 38 | -145 |
| 23 | 11.16 | 42 | -167 |
| 24 | 11.22 | 46 | -183 |

Table 4.9; 50ml of 0.1M NaOH with 1.0 M $NaNO_3$ + 1g $MnO_2$ solution at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 6.49 | 2 | - |
| 2 | 8.49 | 4 | - |
| 3 | 8.59 | 6 | - |
| 4 | 8.90 | 8 | -204 |
| 5 | 9.67 | 9 | -209 |
| 6 | 10.00 | 10 | -210 |
| 7 | 10.34 | 12.5 | -214 |
| 8 | 10.40 | 14 | -218 |
| 9 | 10.44 | 15 | -220 |
| 10 | 10.55 | 16.5 | -221 |
| 11 | 10.66 | 20 | -225 |
| 12 | 10.96 | 22 | -229 |
| 13 | 11.11 | 24 | -230 |
| 14 | 11.11 | 28 | -231 |
| 15 | 11.11 | 34 | -232 |
| 16 | 11.19 | 36 | -240 |
| 17 | 11.20 | 36.8 | -240 |
| 18 | 11.22 | 37.8 | -245 |
| 19 | 11.23 | 38 | -250 |
| 20 | 11.25 | 39 | -252 |
| 21 | 11.28 | 40 | -256 |
| 22 | 11.28 | 41 | -257 |
| 23 | 11.30 | 42 | -257 |
| 24 | 11.31 | 43 | -259 |

Table 4.10; 50ml of 0.1M NaOH with 1.0M $NaNO_3$ +1g $MnO_2$ solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 8.03 | 4 | -148 |
| 2 | 8.61 | 6 | -201 |
| 3 | 10.03 | 8 | -211 |
| 4 | 10.20 | 10 | -211 |
| 5 | 10.41 | 12 | -212 |
| 6 | 10.72 | 14 | -214 |
| 7 | 10.94 | 16 | -214 |
| 8 | 11.02 | 18 | -215 |
| 9 | 10.94 | 23 | -215 |
| 10 | 10.93 | 25 | -215 |
| 11 | 10.93 | 27 | -219 |
| 12 | 10.93 | 28 | -221 |
| 13 | 10.94 | 30 | -221 |
| 14 | 10.94 | 33 | -222 |
| 15 | 10.96 | 34 | -219 |
| 16 | 10.98 | 36 | -221 |
| 17 | 10.98 | 38 | -222 |
| 18 | 10.99 | 41.4 | -224 |
| 19 | 11.02 | 42 | -229 |
| 20 | 10.99 | 42.5 | -229 |
| 21 | 10.99 | 43.2 | -231 |
| 22 | 10.99 | 43.5 | -231 |

Table 4.11; 50ml of 0.1M NaOH with 0.1M $NaNO_3$ + 1g $MnO_2$ solution at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.16 | 2 | -205 |
| 2 | 8.2 | 4 | -209 |
| 3 | 8.42 | 6 | -211 |
| 4 | 8.85 | 11.5 | -218 |
| 5 | 8.72 | 11.8 | -220 |
| 6 | 9.09 | 14.8 | -228 |
| 7 | 9.67 | 15.5 | -230 |
| 8 | 9.72 | 16.2 | -231 |
| 9 | 10.13 | 17.5 | -231 |
| 10 | 10.14 | 18 | -234 |
| 11 | 10.62 | 18.5 | -235 |
| 12 | 10.82 | 19.0 | -236 |
| 13 | 10.83 | 22 | -238 |
| 14 | 10.87 | 25.5 | -238 |
| 15 | 10.87 | 26.8 | -239 |
| 16 | 10.93 | 28 | -241 |
| 17 | 10.94 | 30.5 | -225 |
| 18 | 10.96 | 31.5 | -249 |
| 19 | 11.05 | 37.2 | -250 |
| 20 | 11.18 | 40 | -257 |
| 21 | 11.27 | 41 | -258 |
| 22 | 11.29 | 42 | -261 |
| 23 | 11.34 | 43.5 | -267 |
| 24 | 11.38 | 44 | -274 |

Table 4.12; 50ml of 0.1M NaOH with 0.1M $NaNO_3$ + 1g $MnO_2$ solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 6.75 | 4 | -202 |
| 2 | 8.39 | 6 | -202 |
| 3 | 8.49 | 7 | -203 |
| 4 | 8.79 | 9 | -205 |
| 5 | 10.17 | 11.2 | -206 |
| 6 | 10.18 | 12.5 | -207 |
| 7 | 10.26 | 15 | -206 |
| 8 | 10.34 | 16.5 | -207 |
| 9 | 10.38 | 19 | -208 |
| 10 | 10.49 | 20 | -209 |
| 11 | 10.52 | 22 | -210 |
| 12 | 10.59 | 23 | -210 |
| 13 | 10.60 | 24 | -211 |
| 14 | 10.69 | 25 | -212 |
| 15 | 10.80 | 26 | -216 |
| 16 | 10.92 | 28 | - |
| 17 | 10.92 | 30.1 | -216 |
| 18 | 10.94 | 32.5 | -222 |
| 19 | 10.96 | 35.5 | -222 |
| 20 | 10.98 | 38 | -222 |
| 21 | 10.95 | 40 | -220 |

Table 4.13; 50ml of 0.1M NaOH with 0.01M $NaNO_3$ + 1g $MnO_2$ solution at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 6.45 | - | - |
| 2 | 7.88 | 1 | - |
| 3 | 9.45 | 2 | 201 |
| 4 | 9.54 | 4 | 202 |
| 5 | 9.76 | 6 | - |
| 6 | 9.78 | 8 | - |
| 7 | 9.90 | 10 | -206 |
| 8 | 10.09 | 12 | -08 |
| 9 | 10.40 | 14 | -208 |
| 10 | 10.67 | 16 | - |
| 11 | 10.71 | 18 | - |
| 12 | 10.79 | 20 | -210 |
| 13 | 11.09 | 22 | -210 |
| 14 | 11.12 | 23 | - |
| 15 | 11.16 | 23.5 | - |
| 16 | 11.19 | 24 | -212 |
| 17 | 11.21 | 24.5 | -211 |
| 18 | 11.23 | 25 | -213 |
| 19 | 11.28 | 25.5 | -- |
| 20 | 11.33 | 26 | -215 |
| 21 | 11.43 | 26.5 | -217 |
| 22 | 11.55 | 27 | -227 |
| 23 | 11.56 | 27.5 | -229 |
| 24 | 11.67 | 28 | -231 |

Table 4.14; 50ml of 0.1M NaOH with 0.01M $NaNO_3$ + 1g $MnO_2$ solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.67 | 2 | -201 |
| 2 | 9.01 | 4 | -203 |
| 3 | 9.87 | 6 | -211 |
| 4 | 10.17 | 8 | -221 |
| 5 | 10.83 | 10 | -232 |
| 6 | 11.03 | 12 | -234 |
| 7 | 11.11 | 14 | -242 |
| 8 | 11.37 | 14.5 | -247 |
| 9 | 11.47 | 15 | -251 |
| 10 | 11.48 | 17 | -248 |
| 11 | 11.50 | 19 | -249 |
| 12 | 11.52 | 20 | -250 |
| 13 | 11.56 | 24 | -250 |
| 14 | 11.55 | 28 | -251 |
| 15 | 11.56 | 30 | -251 |
| 16 | 11.56 | 34 | -252 |
| 17 | 11.59 | 36 | -253 |
| 18 | 11.59 | 39 | -254 |
| 19 | 11.60 | 41 | -255 |
| 20 | 11.61 | 42 | -255 |
| 21 | 11.62 | 44 | -255 |
| 22 | 11.64 | 45 | -255 |
| 23 | 11.64 | 46 | -256 |
| 24 | 11.66 | 47 | -256 |
| 25 | 11.66 | 48 | -256 |

Table 4.15; 50ml of 0.1M NaOH with 0.001M $NaNO_3$ + 1g $MnO_2$ solution at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.33 | 1 | - |
| 3 | 8.42 | 2 | - |
| 4 | 8.54 | 4 | -087 |
| 5 | 8.61 | 6 | -093 |
| 6 | 8.78 | 8 | -098 |
| 7 | 9.04 | 10 | -112 |
| 8 | 9.12 | 12 | -14 |
| 9 | 9.34 | 14 | -117 |
| 10 | 9.46 | 15.5 | -120 |
| 11 | 9.55 | 16 | -121 |
| 12 | 9.67 | 17.5 | -122 |
| 13 | 9.71 | 17 | -125 |
| 14 | 9.86 | 18.5 | -126 |
| 15 | 9.89 | 19 | -126 |
| 16 | 9.94 | 19.5 | -127 |
| 17 | 9.98 | 20 | -130 |
| 18 | 10.02 | 24 | -138 |
| 19 | 10.11 | 26 | -145 |
| 20 | 10.17 | 28 | -158 |
| 21 | 10.17 | 32 | -158 |
| 22 | 10.18 | 34 | -162 |
| 23 | 10.18 | 36 | -165 |
| 24 | 10.18 | 38 | -167 |
| 25 | 10.34 | 42 | -176 |

Table 4.16; 50ml of 0.1M NaOH with 0.001M $NaNO_3$ + 1g $MnO_2$ solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.32 | 1 | - |
| 2 | 9.10 | 2 | - |
| 3 | 9.18 | 4 | -067 |
| 4 | 9.21 | 6 | -072 |
| 5 | 9.22 | 8 | -084 |
| 6 | 9.26 | 10 | -198 |
| 7 | 9.28 | 12 | -101 |
| 8 | 9.33 | 14 | -103 |
| 9 | 9.36 | 14.5 | -112 |
| 10 | 9.38 | 15 | -112 |
| 11 | 9.45 | 16 | -117 |
| 12 | 9.52 | 16.5 | -122 |
| 13 | 9.54 | 17 | -122 |
| 14 | 9.71 | 17.5 | -123 |
| 15 | 9.87 | 18 | -134 |
| 16 | 10.01 | 18.5 | -134 |
| 17 | 10.08 | 21 | -137 |
| 18 | 10.10 | 24 | -143 |
| 19 | 10.11 | 26 | -144 |
| 20 | 10.11 | 28 | -148 |
| 21 | 10.11 | 32 | -154 |
| 22 | 10.11 | 36 | -155 |
| 23 | 10.14 | 38 | -165 |
| 24 | 10.16 | 42 | -169 |
| 25 | 10.17 | 44 | -171 |

Table 4.17; 50ml of 0.1M NaOH with 1.0M $Ca(NO_3)_2$solution at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 6.78 | - | - |
| 2 | 9.34 | 1.0 | -111 |
| 3 | 9.13 | 1.5 | -119 |
| 4 | 9.15 | 2 | -122 |
| 5 | 9.18 | 4 | -127 |
| 6 | 9.21 | 6 | -128 |
| 7 | 9.22 | 8 | -130 |
| 8 | 9.24 | 10 | -132 |
| 9 | 9.24 | 12 | -139 |
| 10 | 9.26 | 14 | -148 |
| 11 | 9.27 | 16 | -149 |
| 12 | 9.27 | 18 | -153 |
| 13 | 9.30 | 20 | -154 |
| 14 | 9.33 | 22 | -167 |
| 15 | 9.34 | 24 | -176 |
| 16 | 9.35 | 26 | -180 |
| 17 | 9.35 | 28 | -180 |
| 18 | 9.35 | 20 | -180 |
| 19 | 9.35 | 30 | -181 |
| 20 | 9.36 | 32 | -196 |
| 21 | 9.45 | 34 | -198 |

Table 4.18; 50ml of 0.1M NaOH with 1.0M $Ca(NO_3)_2$solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.12 | - | - |
| 2 | 7.91 | 1 | -042 |
| 3 | 8.25 | 2 | -058 |
| 4 | 8.30 | 4 | -065 |
| 5 | 8.79 | 5 | -070 |
| 6 | 8.86 | 6 | -075 |
| 7 | 8.90 | 7 | -083 |
| 8 | 9.27 | 8 | -098 |
| 9 | 9.43 | 9 | -103 |
| 10 | 9.64 | 10 | -110 |
| 11 | 9.52 | 12 | -117 |
| 12 | 9.72 | 13 | -120 |
| 13 | 9.66 | 15 | -127 |
| 14 | 9.69 | 17 | -138 |
| 15 | 9.77 | 19 | -142 |
| 16 | 9.82 | 20 | -142 |
| 17 | 10.02 | 21 | -156 |
| 18 | 10.05 | 23 | -172 |
| 19 | 10.20 | 27 | -183 |
| 20 | 10.37 | 29 | -184 |
| 21 | 10.47 | 31 | -188 |
| 22 | 10.55 | 33 | -193 |
| 23 | 10.72 | 35 | -195 |
| 24 | 10.68 | 38 | -196 |

Table 4.19; 50ml of 0.1M NaOH with 0.1M $Ca(NO_3)_2$solution at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | - | 2 | - |
| 2 | 8.37 | 4 | -123 |
| 3 | 9.11 | 6 | -161 |
| 4 | 9.15 | 8 | -161 |
| 5 | 9.23 | 10 | -162 |
| 6 | 9.31 | 12 | -162 |
| 7 | 9.38 | 14 | -164 |
| 8 | 9.41 | 16 | -168 |
| 9 | 9.48 | 18 | -170 |
| 10 | 9.49 | 19 | -171 |
| 11 | 9.49 | 20 | -172 |
| 12 | 9.52 | 22 | -172 |
| 13 | 9.58 | 24 | -173 |
| 14 | 9.67 | 26 | -173 |
| 15 | 9.81 | 28 | -175 |
| 16 | 9.92 | 30 | -177 |
| 17 | 10.03 | 33 | -180 |
| 18 | 10.03 | 35 | -183 |
| 19 | 10.03 | 37 | -185 |
| 20 | 10.41 | 38 | -188 |
| 21 | 10.53 | 39 | -197 |
| 22 | 10.81 | 40 | -197 |
| 23 | 11.01 | 42 | -198 |

Table 4.20; 50ml of 0.1M NaOH with 0.1M $Ca(NO_3)_2$solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | 2 | -101 |
| 2 | 7.23 | 4 | -103 |
| 3 | 9.37 | 6 | -109 |
| 4 | 9.57 | 7 | -117 |
| 5 | 9.77 | 8 | -121 |
| 6 | 9.98 | 9 | -123 |
| 7 | 10.09 | 10 | -31 |
| 8 | 10.11 | 11 | -158 |
| 9 | 10.18 | 12 | -158 |
| 10 | 10.23 | 15 | -158 |
| 11 | 10.30 | 18 | -159 |
| 12 | 10.34 | 22 | -160 |
| 13 | 10.38 | 24 | -164 |
| 14 | 10.38 | 26 | -167 |
| 15 | 10.39 | 27 | -169 |
| 16 | 10.51 | 28 | -171 |
| 17 | 10.54 | 30 | -178 |
| 18 | 10.57 | 32 | -181 |
| 19 | 10.58 | 33 | -181 |
| 20 | 10.58 | 34 | -182 |
| 21 | 10.58 | 35 | -182 |
| 22 | 10.58 | 36 | -183 |
| 23 | 10.59 | 37 | -185 |
| 24 | 11.01 | 38 | -188 |

Table 4.21; 50ml of 0.1M NaOH with 0.01M $Ca(NO_3)_2$solution at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.43 | 4 | - |
| 2 | 9.02 | 8 | -065 |
| 3 | 9.03 | 10 | -066 |
| 4 | 9.04 | 15 | -068 |
| 5 | 9.06 | 18 | -070 |
| 6 | 9.08 | 18.5 | -080 |
| 7 | 9.10 | 20 | -098 |
| 8 | 9.11 | 22 | -101 |
| 9 | 9.15 | 23 | -109 |
| 10 | 9.16 | 23.5 | -109 |
| 11 | 9.19 | 24 | -109 |
| 12 | 9.30 | 25 | -109 |
| 13 | 9.32 | 25.5 | -111 |
| 14 | 9.72 | 26 | -117 |
| 15 | 9.90 | 27 | -119 |
| 16 | 10.00 | 27.5 | -127 |
| 17 | 10.02 | 28 | -141 |
| 18 | 10.11 | 28.5 | -152 |
| 19 | 10.19 | 30 | -177 |
| 20 | 10.27 | 32 | -178 |
| 21 | 10.31 | 33 | -183 |
| 22 | 10.40 | 34 | -189 |
| 23 | 10.40 | 36 | -190 |
| 24 | 10.40 | 38 | -193 |
| 25 | 10.48 | 39 | -193 |

Table 4.22; 50ml of 0.1M NaOH with 0.01M $Ca(NO_3)_2$solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 6.74 | 2 | -103 |
| 2 | 7.21 | 4 | -121 |
| 3 | 7.45 | 6 | -131 |
| 4 | 8.78 | 8 | -135 |
| 5 | 9.09 | 10 | -138 |
| 6 | 9.23 | 12 | -141 |
| 7 | 9.37 | 14 | -145 |
| 8 | 9.41 | 16 | -148 |
| 9 | 9.43 | 18 | -151 |
| 10 | 9.48 | 20 | -159 |
| 11 | 9.51 | 21 | -166 |
| 12 | 10.02 | 21.5 | -169 |
| 13 | 10.23 | 22 | -170 |
| 14 | 10.33 | 22.5 | -173 |
| 15 | 10.41 | 23 | -175 |
| 16 | 10.56 | 23.4 | -179 |
| 17 | 10.81 | 24 | -183 |
| 18 | 11.02 | 24.5 | -194 |
| 19 | 11.09 | 26 | -201 |
| 20 | 11.11 | 27 | -202 |
| 21 | 11.12 | 29 | -204 |
| 22 | 11.29 | 31 | -206 |
| 23 | 11.30 | 33 | -211 |
| 24 | 11.30 | 35 | -217 |
| 25 | 11.30 | 38 | -219 |

Table 4.23; 50ml of 0.1M NaOH with 0.001M $Ca(NO_3)_2$solution at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 9.23 | 1 | -094 |
| 3 | 9.34 | 2 | -101 |
| 4 | 9.54 | 4 | -111 |
| 5 | 9.73 | 6 | -113 |
| 6 | 9.82 | 8 | -118 |
| 7 | 10.08 | 10 | -123 |
| 8 | 10.11 | 12 | -127 |
| 9 | 10.15 | 14 | -132 |
| 10 | 10.19 | 16 | -143 |
| 11 | 10.22 | 18 | -165 |
| 12 | 10.25 | 20 | -169 |
| 13 | 10.26 | 22 | -183 |
| 14 | 10.26 | 24 | -189 |
| 15 | 10.26 | 26 | -188 |
| 16 | 10.31 | 28 | -189 |
| 17 | 10.39 | 30 | -189 |
| 18 | 10.56 | 32 | -190 |
| 19 | 10.81 | 34 | -194 |
| 20 | 10.81 | 36 | -197 |
| 21 | 11.08 | 38 | -197 |
| 22 | 11.23 | 42 | -198 |
| 23 | 11.49 | 46 | -199 |
| 24 | 11.49 | 50 | -201 |

Table 4.24- 50ml of 0.1M NaOH with 0.001M $Ca(NO_3)_2$solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.54 | 1 | -092 |
| 3 | 9.12 | 4 | -109 |
| 4 | 9.33 | 6 | -110 |
| 5 | 9.38 | 8 | -111 |
| 6 | 9.94 | 10 | -127 |
| 7 | 10.04 | 14 | -127 |
| 8 | 10.09 | 16 | -132 |
| 9 | 10.18 | 18 | -134 |
| 10 | 10.32 | 20 | -138 |
| 11 | 10.34 | 24 | -154 |
| 12 | 10.34 | 28 | -155 |
| 13 | 10.34 | 30 | -154 |
| 14 | 10.38 | 34 | 166 |
| 15 | 10.67 | 36 | -167 |
| 16 | 11.00 | 40 | -167 |
| 17 | 11.03 | 42 | -174 |
| 18 | 11.14 | 44 | -177 |
| 19 | 11.21 | 45 | -182 |
| 20 | 11.22 | 46 | -187 |
| 21 | 11.23 | 47 | -188 |
| 22 | 11.31 | 48 | -188 |
| 23 | 11.30 | 49 | -188 |
| 24 | 11.30 | 50 | -189 |

Table 4.25; 50ml of 0.1M NaOH with 1.0M $Ca(NO_3)_2$+ 1g $MnO_2$ soln at 30°C

| S/N | PH | VOL.(ml)7 | E(mV) |
|---|---|---|---|
| 1 | 7.21 | 4 | - |
| 2 | 7.42 | 8 | - |
| 3 | 9.41 | 12 | -101 |
| 4 | 9.97 | 16 | -148 |
| 5 | 10.05 | 18 | -177 |
| 6 | 10.15 | 20 | -193 |
| 7 | 10.23 | 22 | -201 |
| 8 | 10.41 | 24 | -216 |
| 9 | 10.61 | 26 | -216 |
| 10 | 10.83 | 28 | -217 |
| 11 | 10.94 | 30 | -217 |
| 12 | 11.03 | 32 | -218 |
| 13 | 11.21 | 35 | -218 |
| 14 | 11.23 | 37 | -219 |
| 15 | 11.23 | 39 | -219 |
| 16 | 11.23 | 42 | -220 |
| 17 | 11.32 | 45 | -221 |
| 18 | 11.34 | 46 | -221 |
| 19 | 11.59 | 47 | -220 |
| 20 | 11.60 | 48 | -221 |
| 21 | 11.61 | 49 | -221 |
| 22 | 11.63 | 50 | -223 |

Table 4.26; 50ml of 0.1M NaOH with 1.0M $Ca(NO_3)_2$ + 1g $MnO_2$ at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 8.47 | 1 | - |
| 2 | 8.73 | 2 | -051 |
| 3 | 9.03 | 3 | -087 |
| 4 | 9.41 | 4 | -101 |
| 5 | 10.41 | 5 | -152 |
| 6 | 10.76 | 7 | -178 |
| 7 | 10.87 | 8 | -188 |
| 8 | 10.97 | 10 | -196 |
| 9 | 11.02 | 12 | -198 |
| 10 | 11.05 | 14 | -198 |
| 11 | 11.06 | 16 | -200 |
| 12 | 11.07 | 18 | -210 |
| 13 | 11.08 | 20 | -210 |
| 14 | 11.07 | 22 | -211 |
| 15 | 11.08 | 24 | -210 |
| 16 | 11.08 | 26 | -211 |
| 17 | 11.09 | 28 | -212 |
| 18 | 11.09 | 30 | -212 |
| 19 | 11.09 | 32 | -217 |
| 20 | 11.10 | 34 | -218 |
| 21 | 11.10 | 36 | -219 |
| 22 | 11.11 | 40 | -219 |
| 23 | 11.12 | 44 | -221 |
| 24 | 11.14 | 45 | -222 |
| 25 | 11.14 | 47 | -222 |

Table 4.27; 50ml of 0.1M NaOH with 0.1M $Ca(NO_3)_2$+ 1g $MnO_2$ soln at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.23 | - | - |
| 2 | 4.6 | 4 | 122 |
| 3 | 4.52 | 6 | 122 |
| 4 | 4.55 | 10 | 130 |
| 5 | 4.44 | 15 | 134 |
| 6 | 4.33 | 20 | 140 |
| 7 | 4.31 | 25 | 141 |
| 8 | 4.25 | 30 | 144 |
| 9 | 4.21 | 33 | 145 |
| 10 | 4.23 | 40 | 145 |
| 11 | 4.20 | 45 | 146 |
| 12 | 4.20 | 50 | 146 |

Table 4.29; 50ml of 0.1M NaOH with 0.01M $Ca(NO_3)_2$+ 1g MnO2 solution at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | 2 | - |
| 2 | 8.37 | 4 | 109 |
| 3 | 9.11 | 6 | 122 |
| 4 | 9.23 | 8 | 122 |
| 5 | 9.31 | 10 | 131 |
| 6 | 9.44 | 12 | 131 |
| 7 | 9.43 | 14 | 132 |
| 8 | 9.51 | 17 | 130 |
| 9 | 9.61 | 18 | 133 |
| 10 | 9.78 | 19 | 135 |
| 11 | 10.21 | 21 | 134 |
| 12 | 10.22 | 22 | 134 |
| 13 | 10.31 | 22.5 | 136 |
| 14 | 10.34 | 23 | 139 |
| 15 | 10.36 | 24 | 139 |
| 16 | 10.37 | 26 | 140 |
| 17 | 10.37 | 27 | 140 |
| 18 | 10.38 | 28 | 140 |
| 19 | 10.38 | 30 | 143 |
| 20 | 10.38 | 32 | 144 |
| 21 | 10.38 | 34 | 145 |
| 22 | 10.41 | 36 | 145 |
| 23 | 10.42 | 38 | 145 |
| 24 | 10.46 | 40 | 146 |

Table 4.30; 50ml of 0.1M NaOH with 0.01M $Ca(NO_3)_2$ +1g $MnO_2$ solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.61 | 2 | - |
| 3 | 9.01 | 4 | -101 |
| 4 | 9.03 | 6 | -118 |
| 5 | 9.03 | 8 | -121 |
| 6 | 9.17 | 10 | -134 |
| 7 | 9.19 | 12 | -142 |
| 8 | 9.17 | 14 | -143 |
| 9 | 9.17 | 16 | -143 |
| 10 | 9.18 | 20 | -147 |
| 11 | 9.20 | 24 | -150 |
| 12 | 9.26 | 24.5 | -153 |
| 13 | 9.27 | 25 | -154 |
| 14 | 9.31 | 25.5 | -157 |
| 15 | 9.41 | 26 | -158 |
| 16 | 10.01 | 26.5 | -159 |
| 17 | 10.02 | 27 | -161 |
| 18 | 10.12 | 27.5 | -161 |
| 19 | 10.20 | 28 | -171 |
| 20 | 10.21 | 29 | -171 |
| 21 | 10.41 | 31 | -177 |
| 22 | 10.68 | 32 | -181 |
| 23 | 10.73 | 34 | -187 |
| 24 | 10.73 | 36 | -187 |
| 25 | 10.73 | 38 | -190 |

Table 4.31; 50ml of 0.1M NaOH with 0.001M $Ca(NO_3)_2$ 1g $MnO_2$ solution at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.31 | 1 | -091 |
| 3 | 9.02 | 2 | -093 |
| 4 | 9.03 | 4 | -102 |
| 5 | 9.09 | 6 | -111 |
| 6 | 9.08 | 8 | -118 |
| 7 | 9.09 | 10 | -121 |
| 8 | 9.09 | 14 | -122 |
| 9 | 9.09 | 16 | --128 |
| 10 | 9.11 | 20 | -133 |
| 11 | 9.12 | 22 | -152 |
| 12 | 9.13 | 24 | -171 |
| 13 | 9.17 | 26 | -177 |
| 14 | 9.19 | 28 | -183 |
| 15 | 9.20 | 30 | -183 |
| 16 | 9.21 | 32 | --189 |
| 17 | 9.22 | 34 | -198 |
| 18 | 9.22 | 36 | -200 |
| 19 | 9.22 | 37 | -200 |
| 20 | 9.32 | 38 | -202 |
| 21 | 9.33 | 39 | -202 |
| 22 | 9.33 | 40 | -202 |
| 23 | 9.34 | 42 | -203 |
| 24 | 9.34 | 44 | -203 |
| 25 | 9.36 | 46 | -203 |

Table 4.32; 50ml of 0.1M NaOH with 0.001M $Ca(NO_3)_2$s+1g $MnO_2$ solution at 50$^o$C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | 1 | -078 |
| 2 | 9.23 | 2 | -102 |
| 3 | 9.29 | 4 | -118 |
| 4 | 9.33 | 6 | -119 |
| 5 | 9.45 | 7 | -119 |
| 6 | 9.48 | 8 | -121 |
| 7 | 9.67 | 9 | -121 |
| 8 | 9.87 | 10 | -122 |
| 9 | 9.92 | 14 | -123 |
| 10 | 10.03 | 18 | -125 |
| 11 | 10.11 | 22 | -125 |
| 12 | 10.12 | 24 | -125 |
| 13 | 10.12 | 26 | -133 |
| 14 | 10.13 | 28 | -134 |
| 15 | 10.15 | 30 | -134 |
| 16 | 10.16 | 34 | -135 |
| 17 | 10.17 | 36 | -135 |
| 18 | 10.17 | 37 | -134 |
| 19 | 10.19 | 38 | -139 |
| 20 | 10.20 | 40 | -141 |
| 21 | 10.21 | 42 | -167 |
| 22 | 10.22 | 44 | -144 |
| 23 | 10.22 | 46 | -167 |
| 24 | 10.22 | 48 | -178 |
| 25 | 10.23 | 50 | -188 |

Table 4.33; 50ml of 0.1M NaOH with 1.0M $Pb(NO_3)_2$ solution at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | 2 | - |
| 2 | 8.34 | 4 | -083 |
| 3 | 8.44 | 8 | -094 |
| 4 | 9.54 | 12 | -101 |
| 5 | 9.55 | 14 | -104 |
| 6 | 9.67 | 18 | -111 |
| 7 | 9.69 | 20 | -118 |
| 8 | 9.74 | 24 | -121 |
| 9 | 9.87 | 26 | -123 |
| 10 | 9.88 | 28 | -133 |
| 11 | 9.93 | 30 | -140 |
| 12 | 10.07 | 32 | -142 |
| 13 | 10.22 | 34 | -143 |
| 14 | 10.22 | 38 | -154 |
| 15 | 10.21 | 40 | -156 |
| 16 | 10.22 | 42 | -166 |
| 17 | 10.28 | 44 | -173 |
| 18 | 10.33 | 48 | -177 |
| 19 | 10.34 | 50 | -188 |

Table 4.34; 50ml of 0.1M NaOH with 1.0M $Pb(NO_3)_2$ solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.23 | 2 | -105 |
| 3 | 8.53 | 4 | -106 |
| 4 | 8.67 | 6 | -109 |
| 5 | 9.21 | 8 | -110 |
| 6 | 9.22 | 10 | -110 |
| 7 | 9.23 | 14 | -111 |
| 8 | 9.34 | 16 | -112 |
| 9 | 9.45 | 18 | -115 |
| 10 | 9.65 | 20 | -117 |
| 11 | 9.77 | 24 | -121 |
| 12 | 9.78 | 26 | -122 |
| 13 | 10.00 | 28 | -122 |
| 14 | 10.09 | 30 | -123 |
| 15 | 10.12 | 32 | -138 |
| 16 | 10.17 | 34 | -148 |
| 17 | 10.22 | 36 | -152 |
| 18 | 10.32 | 38 | -154 |
| 19 | 10.54 | 40 | -165 |
| 20 | 10.55 | 42 | -172 |
| 21 | 10.55 | 44 | -171 |
| 22 | 10.87 | 46 | -177 |
| 23 | 10.89 | 50 | -187 |

Table 4.35; 50ml of 0.1M NaOH with 0.1M $Pb(NO_3)_2$ soln at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.36 | 4 | 180 |
| 3 | 8.88 | 6 | 179 |
| 4 | 9.04 | 8 | 178 |
| 5 | 9.22 | 12 | 171 |
| 6 | 9.24 | 14 | 172 |
| 7 | 9.45 | 18 | 172 |
| 8 | 9.51 | 20 | 173 |
| 9 | 9.55 | 24 | 163 |
| 10 | 9.67 | 28 | 164 |
| 11 | 9.69 | 30 | 142 |
| 12 | 9.73 | 32 | 147 |
| 13 | 9.77 | 34 | 153 |
| 14 | 9.80 | 36 | 153 |
| 15 | 10.03 | 38 | 154 |
| 16 | 10.13 | 42 | 166 |
| 17 | 10.13 | 44 | 167 |
| 18 | 10.23 | 46 | 168 |
| 19 | 10.24 | 48 | 166 |
| 20 | 10.26 | 50 | 166 |

Table 4.36; 50ml of 0.1M NaOH with 0.1M $Pb(NO_3)_2$ soln at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.22 | 2 | -091 |
| 3 | 8.43 | 4 | -110 |
| 4 | 8.78 | 6 | -111 |
| 5 | 9.03 | 8 | -117 |
| 6 | 9.05 | 10 | -121 |
| 7 | 9.11 | 12 | -122 |
| 8 | 9.16 | 14 | -123 |
| 9 | 9.21 | 16 | -123 |
| 10 | 9.23 | 18 | -125 |
| 11 | 9.33 | 20 | -132 |
| 12 | 9.42 | 22 | -132 |
| 13 | 9.45 | 24 | -143 |
| 14 | 9.76 | 26 | -144 |
| 15 | 9.94 | 28 | -156 |
| 16 | 10.03 | 30 | -163 |
| 17 | 10.09 | 33 | -166 |
| 18 | 10.1 | 35 | -172 |
| 19 | 10.21 | 36 | -177 |
| 20 | 10.21 | 38 | -178 |
| 21 | 10.21 | 40 | -189 |
| 22 | 10.33 | 42 | -188 |
| 23 | 10.37 | 44 | -189 |
| 24 | 10.44 | 46 | -189 |
| 25 | 10.56 | 50 | -199 |

Table 4.37; 50ml of 0.1M NaOH with 0.01M $Pb(NO_3)_2$ soln at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | 1 | -091 |
| 2 | 8.53 | 2 | -110 |
| 3 | 8.87 | 4 | -111 |
| 4 | 9.07 | 6 | -111 |
| 5 | 9.11 | 8 | -112 |
| 6 | 9.12 | 10 | -117 |
| 7 | 9.22 | 12 | -122 |
| 8 | 9.27 | 14 | -123 |
| 9 | 9.32 | 16 | -135 |
| 10 | 9.44 | 18 | -133 |
| 11 | 9.56 | 20 | -136 |
| 12 | 9.61 | 22 | -137 |
| 13 | 9.72 | 24 | -143 |
| 14 | 10.02 | 26 | -144 |
| 15 | 10.09 | 28 | -144 |
| 16 | 10.18 | 30 | -154 |
| 17 | 10.19 | 32 | -154 |
| 18 | 10.22 | 34 | -161 |
| 19 | 10.28 | 38 | -163 |
| 20 | 10.33 | 40 | -174 |
| 21 | 10.37 | 42 | -174 |
| 22 | 10.40 | 44 | -175 |
| 23 | 10.41 | 46 | -187 |
| 24 | 10.55 | 48 | -188 |
| 25 | 10.63 | 50 | -189 |

Table 4.38; 50ml of 0.1M NaOH with 0.01M $Pb(NO_3)_2$+ solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.43 | 1 | -112 |
| 3 | 8.42 | 2 | -123 |
| 4 | 8.44 | 4 | -126 |
| 5 | 9.23 | 6 | -131 |
| 6 | 9.45 | 8 | -133 |
| 7 | 9.46 | 10 | -134 |
| 8 | 9.58 | 12 | -135 |
| 9 | 9.61 | 14 | -147 |
| 10 | 9.71 | 16 | -152 |
| 11 | 9.85 | 18 | -155 |
| 12 | 9.89 | 20 | -159 |
| 13 | 10.21 | 22 | -162 |
| 14 | 10.25 | 24 | -171 |
| 15 | 10.25 | 25 | -177 |
| 16 | 10.34 | 28 | -184 |
| 17 | 10.34 | 32 | -186 |
| 18 | 10.35 | 34 | -197 |
| 19 | 10.44 | 36 | -199 |
| 20 | 10.52 | 38 | -199 |
| 21 | 10.55 | 42 | -201 |
| 22 | 10.67 | 44 | -201 |
| 23 | 10.73 | 46 | -212 |
| 24 | 10.74 | 48 | -221 |
| 25 | 10.78 | 50 | -222 |

Table 4.39; 50ml of 0.1M NaOH with 0.001M $Pb(NO_3)_2$ soln at $30^oC$

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 9.23 | 2 | -110 |
| 3 | 9.25 | 4 | -110 |
| 4 | 9.52 | 6 | -112 |
| 5 | 9.66 | 8 | -111 |
| 6 | 9.73 | 10 | 112 |
| 7 | 9.75 | 11 | -121 |
| 8 | 9.82 | 12 | -127 |
| 9 | 9.94 | 14 | -132 |
| 10 | 10.03 | 16 | -133 |
| 11 | 10.10 | 18 | -134 |
| 12 | 10.17 | 20 | -142 |
| 13 | 10.21 | 22 | -147 |
| 14 | 10.22 | 24 | -153 |
| 15 | 10.22 | 26 | -159 |
| 16 | 10.21 | 28 | -162 |
| 17 | 10.22 | 30 | -164 |
| 18 | 10.52 | 32 | -177 |
| 19 | 10.74 | 34 | -194 |
| 20 | 10.95 | 36 | -196 |
| 21 | 10.98 | 38 | -198 |
| 22 | 11.07 | 40 | -198 |
| 23 | 11.18 | 44 | -201 |
| 24 | 11.19 | 46 | -201 |
| 25 | 11.22 | 48 | -211 |

Table 4.40; 50ml of 0.1M NaOH with 0.001M $Pb(NO_3)_2$ soln at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.12 | 2 | -098 |
| 3 | 8.38 | 4 | -101 |
| 4 | 8.41 | 6 | -101 |
| 5 | 8.44 | 8 | -100 |
| 6 | 8.54 | 10 | -110 |
| 7 | 8.67 | 16 | -110 |
| 8 | 8.72 | 18 | -111 |
| 9 | 9.03 | 22 | -112 |
| 10 | 9.12 | 24 | -122 |
| 11 | 9.23 | 26 | -132 |
| 12 | 9.28 | 27 | -134 |
| 13 | 9.32 | 28 | -137 |
| 14 | 9.39 | 30 | -142 |
| 15 | 9.56 | 32 | -144 |
| 16 | 9.67 | 34 | -154 |
| 17 | 10.02 | 38 | -165 |
| 18 | 10.12 | 40 | -166 |
| 19 | 10.12 | 42 | -172 |
| 20 | 10.12 | 44 | -175 |
| 21 | 10.24 | 46 | -187 |
| 22 | 10.34 | 48 | -195 |
| 23 | 10.31 | 50 | -201 |

Table 4.41; 50ml of 0.1M NaOH with 1.0M $Pb(NO_3)_2$+ 1g $MnO_2$ soln at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.11 | 2 | -094 |
| 3 | 8.37 | 4 | -109 |
| 4 | 8.44 | 6 | -110 |
| 5 | 9.04 | 8 | -112 |
| 6 | 9.23 | 10 | -122 |
| 7 | 9.45 | 11 | -128 |
| 8 | 9.68 | 14 | -132 |
| 9 | 9.78 | 16 | -13 |
| 10 | 10.23 | 18 | -143 |
| 11 | 10.26 | 22 | -134 |
| 12 | 10.26 | 26 | --142 |
| 13 | 10.26 | 30 | -142 |
| 14 | 10.32 | 32 | -144 |
| 15 | 10.32 | 34 | -154 |
| 16 | 10.38 | 38 | 1744 |
| 17 | 10.46 | 40 | -175 |
| 18 | 10.55 | 41 | -175 |
| 19 | 10.67 | 42 | -176 |
| 20 | 10.78 | 44 | -186 |
| 21 | 11.02 | 45 | -187 |
| 22 | 11.09 | 48 | -191 |
| 23 | 11.23 | 50 | -211 |

Table 4.42; 50ml of 0.1M NaOH with 1.0M $Pb(NO_3)_2$+ 1g $MnO_2$ soln at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.23 | 2 | -095 |
| 3 | 8.67 | 4 | -103 |
| 4 | 9.17 | 6 | -110 |
| 5 | 9.2 | 8 | -111 |
| 6 | 9.21 | 10 | -109 |
| 7 | 9.22 | 12 | -119 |
| 8 | 9.45 | 14 | -121 |
| 9 | 9.61 | 16 | -121 |
| 10 | 9.67 | 18 | -127 |
| 11 | 9.77 | 20 | -133 |
| 12 | 9.78 | 22 | -133 |
| 13 | 9.87 | 24 | -134 |
| 14 | 9.89 | 26 | -154 |
| 15 | 10.09 | 28 | -154 |
| 16 | 10.18 | 30 | -155 |
| 17 | 10.18 | 32 | -160 |
| 18 | 10.18 | 34 | -175 |
| 19 | 10.18 | 36 | -176 |
| 20 | 10.20 | 38 | -187 |
| 21 | 10.21 | 40 | -187 |
| 22 | 10.33 | 42 | -191 |
| 23 | 10.39 | 44 | -211 |
| 24 | 10.42 | 46 | -211 |
| 25 | 10.45 | 48 | -212 |

Table 4.43; 50ml of 0.1M NaOH with 0.1 M $Pb(NO_3)_2$+ 1g $MnO_2$ soln at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | 2 | - |
| 2 | 3.45 | 4 | - |
| 3 | 3.66 | 6 | -088 |
| 4 | 3.67 | 8 | -091 |
| 5 | 3.68 | 9 | -101 |
| 6 | 3.77 | 10 | -102 |
| 7 | 3.88 | 12 | -114 |
| 8 | 3.89 | 14 | -121 |
| 9 | 3.88 | 16 | -122 |
| 10 | 3.87 | 18 | -128 |
| 11 | 3.87 | 20 | -133 |
| 12 | 3.87 | 22 | -139 |
| 13 | 3.86 | 24 | -141 |
| 14 | 3.87 | 26 | -144 |
| 15 | 3.85 | 28 | -144 |
| 16 | 3.78 | 30 | -148 |
| 17 | 3.75 | 34 | -153 |
| 18 | 3.73 | 38 | -154 |
| 19 | 3.72 | 44 | -155 |
| 20 | 3.80 | 50 | -155 |

Table 4.44; 50ml of 0.1M NaOH with 0.1M $Pb(NO_3)_2$ + 1g $MnO_2$ solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.23 | 2 | - |
| 3 | 8.44 | 4 | - |
| 4 | 8.56 | 6 | -088 |
| 5 | 8.77 | 8 | -089 |
| 6 | 9.07 | 10 | -090 |
| 7 | 9.19 | 11 | -091 |
| 8 | 9.23 | 12 | -109 |
| 9 | 9.34 | 13 | -119 |
| 10 | 9.65 | 14 | -121 |
| 11 | 9.73 | 16 | -122 |
| 12 | 9.89 | 18 | -122 |
| 13 | 10.02 | 20 | -123 |
| 14 | 10.09 | 22 | -143 |
| 15 | 10.22 | 24 | -152 |
| 16 | 10.28 | 26 | -154 |
| 17 | 10.31 | 28 | -155 |
| 18 | 10.34 | 30 | -165 |
| 19 | 10.45 | 32 | -165 |
| 20 | 10.55 | 34 | -166 |
| 21 | 10.56 | 36 | -166 |
| 22 | 10.66 | 38 | -170 |
| 23 | 10.78 | 40 | -172 |
| 24 | 10.89 | 42 | -172 |

Table 4.45; 50ml of 0.1M NaOH with 0.01M $Pb(NO_3)_2$+ 1g $MnO_2$ soln at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 8.44 | 2 | - |
| 2 | 8.54 | 4 | -089 |
| 3 | 8.57 | 8 | -101 |
| 4 | 9.33 | 10 | -104 |
| 5 | 9.34 | 12 | -112 |
| 6 | 9.55 | 14 | -124 |
| 7 | 9.57 | 16 | -125 |
| 8 | 9.63 | 18 | -131 |
| 9 | 9.62 | 20 | -133 |
| 10 | 9.66 | 22 | -143 |
| 11 | 9.71 | 24 | -149 |
| 12 | 9.79 | 26 | -152 |
| 13 | 10.04 | 27 | -157 |
| 14 | 10.11 | 28 | -164 |
| 15 | 10.12 | 29 | -165 |
| 16 | 10.12 | 30 | -165 |
| 17 | 10.12 | 32 | -169 |
| 18 | 10.24 | 34 | -173 |
| 19 | 10.41 | 36 | -183 |
| 20 | 10.44 | 38 | 188 |
| 21 | 10.56 | 40 | -188 |
| 22 | 10.57 | 42 | -187 |
| 23 | 10.59 | 44 | -189 |
| 24 | 10.68 | 46 | -199 |
| 25 | 11.14 | 48 | 202 |

Table 4.46; 50ml of 0.1M NaOH with 0.01M $Pb(NO_3)_2$+ 1g $MnO_2$ soln at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.09 | 2 | -079 |
| 3 | 8.11 | 4 | -111 |
| 4 | 8.22 | 6 | -113 |
| 5 | 8.27 | 8 | -117 |
| 6 | 8.32 | 10 | -121 |
| 7 | 8.43 | 1 | -122 |
| 8 | 8.67 | 12 | -127 |
| 9 | 9.34 | 14 | -131 |
| 10 | 9.56 | 16 | -133 |
| 11 | 9.67 | 18 | -138 |
| 12 | 9.71 | 19 | -138 |
| 13 | 9.76 | 20 | -143 |
| 14 | 9.89 | 22 | -142 |
| 15 | 10.01 | 24 | -147 |
| 16 | 10.12 | 26 | -148 |
| 17 | 10.19 | 28 | -153 |
| 18 | 10.19 | 30 | -155 |
| 19 | 10.19 | 32 | -154 |
| 20 | 10.22 | 34 | -154 |
| 21 | 10.25 | 36 | -174 |
| 22 | 10.44 | 42 | -188 |
| 23 | 10.48 | 44 | -198 |
| 24 | 10.55 | 46 | -202 |
| 25 | 10.56 | 50 | -221 |

Table 4.47; 50ml of 0.1M NaOH with 0.001M $Pb(NO_3)_2$+ 1g $MnO_2$ soln at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.34 | 4 | -101 |
| 3 | 9.03 | 6 | -112 |
| 4 | 9.23 | 8 | -117 |
| 5 | 9.25 | 10 | -125 |
| 6 | 9.44 | 12 | -125 |
| 7 | 9.57 | 14 | -127 |
| 8 | 9.86 | 16 | --127 |
| 9 | 9.34 | 18 | -132 |
| 10 | 9.45 | 19 | -134 |
| 11 | 9.89 | 20 | -134 |
| 12 | 9.92 | 22 | -137 |
| 13 | 10.03 | 24 | -144 |
| 14 | 10.33 | 26 | -145 |
| 15 | 10.33 | 28 | -148 |
| 16 | 10.43 | 30 | -153 |
| 17 | 10.54 | 32 | -176 |
| 18 | 10.54 | 34 | -181 |
| 19 | 10.54 | 36 | -183 |
| 20 | 10.56 | 37 | -188 |
| 21 | 10.56 | 38 | -200 |
| 22 | 10.73 | 40 | -102 |
| 23 | 10.77 | 42 | -212 |
| 24 | 10.92 | 44 | -218 |
| 25 | 10.98 | 46 | -222 |

Table 4.48; 50ml of 0.1M NaOH with 0.001M $Pb(NO_3)_2$+ 1g $MnO_2$ soln at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 7.29 | 2 | -099 |
| 3 | 8.32 | 4 | -103 |
| 4 | 8.44 | 6 | -112 |
| 5 | 8.67 | 8 | -123 |
| 6 | 9.19 | 10 | -124 |
| 7 | 9.22 | 12 | -124 |
| 8 | 9.23 | 14 | -127 |
| 9 | 9.38 | 16 | -134 |
| 10 | 9.73 | 18 | -138 |
| 11 | 9.78 | 19 | -144 |
| 12 | 10.00 | 18 | -146 |
| 13 | 10.11 | 20 | -153 |
| 14 | 10.21 | 26 | -155 |
| 15 | 10.22 | 28 | -169 |
| 16 | 10.22 | 30 | -171 |
| 17 | 10.22 | 33 | -178 |
| 18 | 10.23 | 34 | -179 |
| 19 | 10.34 | 35 | -185 |
| 20 | 10.34 | 36 | -188 |
| 21 | 10.42 | 38 | -188 |
| 22 | 10.52 | 40 | -189 |
| 23 | 10.54 | 42 | -190 |
| 24 | 10.55 | 44 | -198 |
| 25 | 10.56 | 46 | -202 |
| 26 | 10.67 | 47 | -203 |

Table 4.49; 50ml of 0.1M NaOH with 1.0M $Mg(NO_3)_2$ soln at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.22 | - | - |
| 2 | 9.02 | 1 | -089 |
| 3 | 9.21 | 2 | -091 |
| 4 | 9.22 | 4 | -100 |
| 5 | 9.23 | 6 | -100 |
| 6 | 9.34 | 8 | -101 |
| 7 | 9.67 | 10 | -101 |
| 8 | 9.71 | 12 | -107 |
| 9 | 9.78 | 14 | -112 |
| 10 | 10.00 | 16 | -112 |
| 11 | 10.01 | 18 | -118 |
| 12 | 10.03 | 20 | -121 |
| 13 | 10.11 | 22 | -122 |
| 14 | 10.24 | 24 | -127123 |
| 15 | 10.24 | 26 | -131 |
| 16 | 10.24 | 28 | -132 |
| 17 | 10.25 | 30 | -132 |
| 18 | 10.32 | 31 | -144 |
| 19 | 10.33 | 32 | -148 |
| 20 | 10.36 | 34 | -165 |
| 21 | 10.41 | 36 | -165 |
| 22 | 10.44 | 38 | -169 |
| 23 | 10.47 | 38 | -170 |
| 24 | 10.50 | 40 | -172 |
| 25 | 10.55 | 42 | -172 |

Table 4.50; 50ml of 0.1M NaOH with 1.0M $Mg(NO_3)_2$ solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 9.11 | 1 | - |
| 3 | 9.17 | 2 | -111 |
| 4 | 9.16 | 4 | -112 |
| 5 | 9.21 | 6 | -117 |
| 6 | 9.23 | 8 | -121 |
| 7 | 9.25 | 10 | -122 |
| 8 | 9.26 | 12 | -122 |
| 9 | 9.27 | 14 | -133 |
| 10 | 9.33 | 16 | -134 |
| 11 | 9.78 | 28 | -142 |
| 12 | 9.93 | 20 | -148 |
| 13 | 10.02 | 22 | -151 |
| 14 | 10.12 | 24 | -153 |
| 15 | 10.17 | 26 | -152 |
| 16 | 10.17 | 28 | -154 |
| 17 | 10.16 | 30 | -159 |
| 18 | 10.17 | 32 | -162 |
| 19 | 10.42 | 34 | -164 |
| 20 | 10.54 | 36 | -166 |
| 21 | 10.57 | 38 | -174 |
| 22 | 10.89 | 40 | -177 |
| 23 | 11.00 | 44 | -179 |
| 24 | 11.04 | 48 | -188 |
| 25 | 11.11 | 50 | -188 |

Table 4.51; 50ml of 0.1M NaOH with 0.1M $Mg(NO_3)_2$ solution at 30°C

| S/N | PH | VOL.(ml) | (mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.44 | 1 | - |
| 3 | 9.36 | 2 | 112 |
| 4 | 9.38 | 4 | 126 |
| 5 | 9.54 | 6 | 126 |
| 6 | 9.78 | 8 | 128 |
| 7 | 9.79 | 10 | 133 |
| 8 | 9.86 | 12 | 138 |
| 9 | 9.89 | 14 | 154 |
| 10 | 10.09 | 16 | 155 |
| 11 | 10.18 | 18 | 156 |
| 12 | 10.26 | 20 | 162 |
| 13 | 10.29 | 22 | 162 |
| 14 | 10.29 | 24 | 170 |
| 15 | 10.63 | 26 | 172 |
| 16 | 10.71 | 28 | 184 |
| 17 | 10.77 | 30 | 188 |
| 18 | 10.78 | 32 | 198 |
| 19 | 10.78 | 34 | 09 |
| 20 | 10.78 | 36 | 212 |
| 21 | 10.88 | 40 | 221 |
| 22 | 10.89 | 45 | 221 |
| 23 | 10.92 | 47 | 222 |
| 24 | 10.97 | 50 | 222 |

Table 4.52; 50ml of 0.1M NaOH with 0.1M $Mg(NO_3)_2$ soln at $50^oC$

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.16 | 1 | - |
| 3 | 8.78 | 2 | - |
| 4 | 9.10 | 4 | - |
| 5 | 9.11 | 6 | - |
| 6 | 9.21 | 8 | -084 |
| 7 | 9.26 | 10 | -096 |
| 8 | 9.27 | 12 | -109 |
| 9 | 9.31 | 14 | -115 |
| 10 | 9.34 | 16 | -117 |
| 11 | 9.36 | 28 | -123 |
| 12 | 9.49 | 20 | -126 |
| 13 | 9.54 | 22 | -127 |
| 14 | 9.97 | 24 | -133 |
| 15 | 10.09 | 26 | -134 |
| 16 | 10.11 | 28 | -148 |
| 17 | 10.27 | 30 | -162 |
| 18 | 10.27 | 32 | -163 |
| 19 | 10.27 | 34 | -1741 |
| 20 | 10.33 | 36 | -175 |
| 21 | 10.41 | 37 | -175 |
| 22 | 10.45 | 38 | -187 |
| 23 | 10.67 | 40 | -197 |
| 24 | 10.87 | 42 | -198 |
| 25 | 10.99 | 44 | -198 |

Table 4.53; 50ml of 0.1M NaOH with 0.01M $Mg(NO_3)_2$ soln at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.34 | 2 | -110 |
| 3 | 9.17 | 4 | -112 |
| 4 | 9.21 | 6 | -112 |
| 5 | 9.47 | 8 | -123 |
| 6 | 9.49 | 10 | -125 |
| 7 | 9.52 | 12 | -125 |
| 8 | 9.57 | 14 | -127 |
| 9 | 9.75 | 16 | -131 |
| 10 | 9.77 | 18 | -144 |
| 11 | 10.11 | 20 | -151 |
| 12 | 10.18 | 21 | -152 |
| 13 | 10.21 | 22 | -153 |
| 14 | 10.30 | 23 | -162 |
| 15 | 10.33 | 24 | -168 |
| 16 | 10.33 | 26 | -169 |
| 17 | 10.33 | 28 | -177 |
| 18 | 10.33 | 30 | -178 |
| 19 | 10.51 | 32 | -178 |
| 20 | 10.55 | 34 | -188 |
| 21 | 10.56 | 36 | -187 |
| 22 | 10.66 | 38 | -188 |
| 23 | 10.69 | 40 | -198 |
| 24 | 10.77 | 44 | -208 |
| 25 | 10.78 | 46 | -211 |

Table 4.54; 50ml of 0.1M NaOH with 0.01M $Mg(NO_3)_2$ soln at 50°C

| S/N | PH | V2OL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 6.73 | 1 | - |
| 2 | 7.32 | 2 | -095 |
| 3 | 7.89 | 4 | -110 |
| 4 | 9.23 | 8 | -116 |
| 5 | 9.45 | 10 | -121 |
| 6 | 9.47 | 12 | -122 |
| 7 | 9.55 | 14 | -121 |
| 8 | 9.76 | 18 | -126 |
| 9 | 9.82 | 22 | -133 |
| 10 | 9.89 | 24 | -137 |
| 11 | 10.05 | 26 | -137 |
| 12 | 10.09 | 28 | -139 |
| 13 | 10.23 | 30 | -153 |
| 14 | 10.24 | 32 | -153 |
| 15 | 10.24 | 34 | -155 |
| 16 | 10.24 | 36 | -164 |
| 17 | 10.33 | 38 | -165 |
| 18 | 10.47 | 40 | -176 |
| 19 | 11.06 | 42 | -182 |
| 20 | 11.13 | 44 | -188 |
| 21 | 11.22 | 48 | -188 |
| 22 | 11.32 | 50 | -219 |

Table 4.55; 50ml of 0.1M NaOH with 0.001M $Mg(NO_3)_2$ soln at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.11 | 1 | - |
| 3 | 8.32 | 2 | - |
| 4 | 8.45 | 4 | - |
| 5 | 8.64 | 6 | -111 |
| 6 | 8.87 | 8 | -112 |
| 7 | 9.01 | 10 | -123 |
| 8 | 9.10 | 12 | -124 |
| 9 | 9.17 | 14 | -124 |
| 10 | 9.19 | 16 | -134 |
| 11 | 9.21 | 18 | -137 |
| 12 | 9.42 | 20 | -135 |
| 13 | 9.46 | 22 | -144 |
| 14 | 9.53 | 24 | -145 |
| 15 | 9.65 | 26 | -151 |
| 16 | 9.72 | 28 | -153 |
| 17 | 9.74 | 30 | -158 |
| 18 | 9.77 | 32 | -162 |
| 19 | 9.82 | 34 | -162 |
| 20 | 9.85 | 36 | -163 |
| 21 | 10.00 | 38 | -166 |
| 22 | 10.08 | 40 | -165 |
| 23 | 10.29 | 42 | -179 |
| 24 | 10.44 | 44 | -180 |
| 25 | 10.54 | 46 | -177 |

Table 4.56; 50ml of 0.1M NaOH with 0.001M $Mg(NO_3)_2$ soln at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 7.45 | 1 | - |
| 3 | 8.23 | 2 | -096 |
| 4 | 8.33 | 4 | -110 |
| 5 | 8.42 | 6 | -112 |
| 6 | 8.75 | 8 | -113 |
| 7 | 9.12 | 10 | -115 |
| 8 | 9.27 | 12 | -117 |
| 9 | 9.43 | 14 | -118 |
| 10 | 9.58 | 16 | -121 |
| 11 | 9.71 | 18 | -123 |
| 12 | 9.80 | 20 | -125 |
| 13 | 9.89 | 22 | -141 |
| 14 | 10.00 | 24 | -148 |
| 15 | 10.03 | 26 | -153 |
| 16 | 10.08 | 30 | -157 |
| 17 | 10.11 | 32 | -163 |
| 18 | 10.12 | 34 | -166 |
| 19 | 10.22 | 36 | -165 |
| 20 | 10.22 | 38 | -173 |
| 21 | 10.22 | 40 | -176 |
| 22 | 10.22 | 42 | -178 |
| 23 | 10.31 | 44 | -188 |
| 24 | 10.33 | 46 | -189 |
| 25 | 10.34 | 50 | -189 |

Table 4.57; 50ml of 0.1M NaOH with 1.0M $Mg(NO_3)_2$+ 1g $MnO_2$ soln at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.22 | 1 | - |
| 3 | 8.27 | 2 | - |
| 4 | 8.31 | 4 | -112 |
| 5 | 8.33 | 6 | -115 |
| 6 | 8.34 | 8 | -121 |
| 7 | 8.46 | 10 | -122 |
| 8 | 9.42 | 12 | -112 |
| 9 | 9.54 | 14 | -112 |
| 10 | 9.61 | 16 | -145 |
| 11 | 9.73 | 18 | -148 |
| 12 | 9.78 | 20 | -171 |
| 13 | 10.00 | 22 | -177 |
| 14 | 10.02 | 24 | -176 |
| 15 | 10.08 | 26 | -177 |
| 16 | 10.11 | 28 | -179 |
| 17 | 10.13 | 30 | -188 |
| 18 | 10.36 | 32 | -188 |
| 19 | 10.36 | 34 | -189 |
| 20 | 10.54 | 36 | -196 |
| 21 | 10.55 | 38 | -196 |
| 22 | 10.55 | 40 | -197 |
| 23 | 10.69 | 44 | -199 |
| 24 | 10.81 | 46 | -198 |
| 25 | 10.96 | 48 | -200 |

Table 4.58; 50ml of 0.1M NaOH with 1.0M $Mg(NO_3)_2$+ 1g $MnO_2$ soln at $50^0C$

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | 2 | - |
| 2 | 8.36 | 6 | - |
| 3 | 8.57 | 8 | -102 |
| 4 | 9.23 | 10 | -111 |
| 5 | 9.27 | 12 | -123 |
| 6 | 9.36 | 14 | -123 |
| 7 | 9.54 | 16 | -122 |
| 8 | 9.55 | 18 | -132 |
| 9 | 9.69 | 20 | -133 |
| 10 | 9.99 | 22 | -134 |
| 11 | 10.02 | 24 | -134 |
| 12 | 10.22 | 28 | -134 |
| 13 | 10.23 | 30 | -137 |
| 14 | 10.24 | 32 | -142 |
| 15 | 10.24 | 34 | -144 |
| 16 | 10.24 | 36 | -145 |
| 17 | 10.24 | 38 | -145 |
| 18 | 10.27 | 40 | -148 |
| 19 | 10.47 | 42 | -156 |
| 20 | 11.14 | 46 | -156 |
| 21 | 11.21 | 46 | -173 |
| 22 | 11.25 | 48 | -187 |
| 23 | 11.35 | 50 | -188 |

Table 4.59; 50ml of 0.1M NaOH with 0.1M $Mg(NO_3)_2$+ 1g $MnO_2$ solution 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 5.08 | 4 | - |
| 3 | 5.32 | 6 | - |
| 4 | 5.33 | 8 | -112 |
| 5 | 5.45 | 10 | -112 |
| 6 | 5.50 | 12 | -115 |
| 7 | 5.51 | 14 | -123 |
| 8 | 5.65 | 16 | -123 |
| 9 | 5.60 | 18 | -122 |
| 10 | 5.54 | 20 | -134 |
| 11 | 5.50 | 22 | -134 |
| 12 | 5.49 | 24 | -136 |
| 13 | 5.42 | 26 | -138 |
| 14 | 5.30 | 28 | -145 |
| 15 | 5.29 | 30 | -145 |
| 16 | 5.18 | 34 | -145 |
| 17 | 5.15 | 36 | -148 |
| 18 | 5.13 | 38 | -148 |
| 19 | 5.33 | 40 | -154 |
| 20 | 5.34 | 42 | -155 |
| 21 | 5.27 | 44 | -155 |
| 22 | 5.17 | 46 | -165 |
| 23 | 5.13 | 48 | -178 |
| 24 | 5.11 | 50 | -192 |

Table 4.60; 50ml of 0.1M NaOH with 0.1M $Mg(NO_3)_2$+ 1g $MnO_2$ solution at 50°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 6.75 | - | - |
| 2 | 7.27 | 2 | -099 |
| 3 | 8.33 | 4 | -101 |
| 4 | 8.37 | 6 | -106 |
| 5 | 8.53 | 8 | -111 |
| 6 | 9.09 | 9 | -112 |
| 7 | 9.18 | 10 | -117 |
| 8 | 9.52 | 12 | -122 |
| 9 | 9.59 | 14 | -123 |
| 10 | 9.69 | 18 | -123 |
| 11 | 9.71 | 19 | -124 |
| 12 | 9.82 | 20 | -124 |
| 13 | 9.91 | 21 | -138 |
| 14 | 10.06 | 22 | -142 |
| 15 | 10.23 | 24 | -144 |
| 16 | 10.33 | 26 | -145 |
| 17 | 10.33 | 28 | -145 |
| 18 | 10.33 | 30 | -155 |
| 19 | 10.34 | 34 | -163 |
| 20 | 10.55 | 36 | -165 |
| 21 | 10.78 | 38 | -167 |
| 22 | 11.12 | 40 | -167 |
| 23 | 11.28 | 42 | -169 |
| 24 | 11.38 | 44 | -175 |
| 25 | 11.38 | 45 | -179 |

Table 4.61; 50ml of 0.1M NaOH with 0.01M $Mg(NO_3)_2$+ 1g $MnO_2$ soln at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | 1 | - |
| 2 | 8.56 | 2 | - |
| 3 | 9.07 | 4 | - |
| 4 | 9.07 | 6 | - |
| 5 | 9.11 | 8 | - |
| 6 | 9.12 | 9 | - |
| 7 | 9.16 | 10 | - |
| 8 | 9.19 | 11 | - |
| 9 | 9.27 | 12 | - |
| 10 | 9.29 | 13 | - |
| 11 | 9.31 | 15 | - |
| 12 | 9.33 | 16 | - |
| 13 | 9.35 | 18 | - |
| 14 | 9.54 | 20 | - |
| 15 | 9.66 | 22 | - |
| 16 | 9.78 | 24 | - |
| 17 | 9.90 | 38 | - |
| 18 | 9.90 | 42 | - |
| 19 | 9.93 | 45 | - |
| 20 | 9.98 | 48 | - |
| 21 | 9.87 | 50 | - |

Table 4.62; 50ml of 0.1M NaOH with 0.01M $Mg(NO_3)_2$+ 1g $MnO_2$ soln at $50^oC$

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.38 | 2 | - |
| 3 | 9.10 | 4 | - |
| 4 | 9.12 | 6 | -101 |
| 5 | 9.25 | 8 | -112 |
| 6 | 9.30 | 10 | -112 |
| 7 | 9.32 | 12 | -117 |
| 8 | 9.33 | 14 | -122 |
| 9 | 9.40 | 16 | -123 |
| 10 | 9.42 | 18 | -123 |
| 11 | 9.44 | 20 | -126 |
| 12 | 9.47 | 22 | -134 |
| 13 | 9.49 | 24 | -147 |
| 14 | 9.49 | 26 | -153 |
| 15 | 9.51 | 28 | -155 |
| 16 | 9.51 | 30 | -156 |
| 17 | 9.55 | 32 | -158 |
| 18 | 9.50 | 34 | -173 |
| 19 | 9.48 | 36 | -174 |
| 20 | 9.47 | 38 | -174 |
| 21 | 9.46 | 40 | -177 |
| 22 | 9.23 | 42 | -180 |
| 23 | 9.10 | 44 | -184 |
| 24 | 8.23 | 46 | -186 |
| 25 | 6.45 | 48 | -187 |

Table 4.63; 50ml of 0.1M NaOH with 0.001M $Mg(NO_3)_2$+ 1g $MnO_2$ Soln at 30°C

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 7.21 | - | - |
| 2 | 8.32 | 2 | -101 |
| 3 | 8.44 | 4 | -121 |
| 4 | 8.56 | 6 | -122 |
| 5 | 8.67 | 8 | -122 |
| 6 | 8.89 | 10 | -123 |
| 7 | 9.01 | 12 | -126 |
| 8 | 9.04 | 14 | -127 |
| 9 | 9.09 | 16 | -134 |
| 10 | 9.03 | 18 | -134 |
| 11 | 9.06 | 20 | -136 |
| 12 | 9.07 | 21 | -156 |
| 13 | 9.10 | 22 | -157 |
| 14 | 9.12 | 23 | -157 |
| 15 | 9.14 | 24 | -164 |
| 16 | 9.16 | 26 | -165 |
| 17 | 9.19 | 27 | -165 |
| 18 | 9.22 | 28 | -166 |
| 19 | 9.25 | 30 | -171 |
| 20 | 9.26 | 32 | -183 |
| 21 | 9.29 | 34 | -188 |
| 22 | 9.31 | 36 | -188 |
| 23 | 9.32 | 38 | -189 |
| 24 | 9.37 | 40 | 190 |
| 25 | 9.40 | 42 | -194 |
| 26 | 9.42 | 44 | -198 |

Table 4.64; 50ml of 0.1M NaOH with 0.001M $Mg(NO_3)_2$+ 1g $MnO_2$ soln at 50$^oC$

| S/N | PH | VOL.(ml) | E(mV) |
|---|---|---|---|
| 1 | 6.54 | - | - |
| 2 | 7.88 | 2 | -092 |
| 3 | 8.73 | 4 | -102 |
| 4 | 9.32 | 6 | -106 |
| 5 | 9.33 | 8 | -110 |
| 6 | 9.37 | 10 | -111 |
| 7 | 9.41 | 11 | -112 |
| 8 | 9.56 | 12 | -122 |
| 9 | 9.66 | 13 | -122 |
| 10 | 9.68 | 14 | -123 |
| 11 | 9.73 | 15 | -123 |
| 12 | 9.77 | 16 | -137 |
| 13 | 9.78 | 18 | -144 |
| 14 | 9.78 | 20 | -141 |
| 15 | 9.79 | 22 | -151 |
| 16 | 9.80 | 24 | -165 |
| 17 | 9.81 | 26 | -166 |
| 18 | 9.82 | 28 | -167 |
| 19 | 9.83 | 30 | -170 |
| 20 | 9.84 | 34 | -171 |
| 21 | 9.86 | 38 | -177 |
| 22 | 9.87 | 42 | -187 |
| 23 | 9.86 | 46 | -198 |
| 24 | 9.82 | 48 | -198 |
| 25 | 9.71 | 50 | -211 |

## 4.2 Results

The Electric Surface Charge ($E_v$) is calculated from equation 1.1 The pH versus the volume of the titrant obtained was plotted for both the neat electrolyte and neat electrolyte with 1g $MnO_2$ on the same graph. (pH Meter, model 209 by Hanna inst. was used to read the corresponding pH as the titration proceeded). At a given pH, the difference in volume ($\Delta V$) between the two graphs was used to calculate adsorption ($\theta$). The value of adsorption ($\theta$) is calculated using Kokarev's formula (Kokarev, et.al, 1988) equation 1.3

The surface areas (s) of both Chemical Manganese Dioxide and Electrolytic Manganese Dioxide were determined using a method called "Adsorption from Solution" and found to be 1719.3$m^2$/g and 4637.88 $m^2$/g respectively (Aloko D.F et al). In this work the chemical value is used because the reagent is laboratory chemical type. Whereas $\Delta v$ = changes in volumes of electrolyte between that with and without $MnO_2$ at variable cations (i.e $Na^+$, $Ca^{++}$, $Pb^{++}$, $Mg^{++}$) concentrations (C). So, the adsorption term ($\theta$) can be related to the hydrogen ion concentration (PH) as

$$\theta = f(PH) \qquad \text{.............4.1}$$

The figures (4.1 - 4.32) are showed in appendix 2.

### 4.2.2 Results of Adsorption and Electric Surface Charge (E.F.C)

The calculations of adsorption and surface charge of the cations on $MnO_2$ at various concentrations and temperatures are presented in tables 4.65 to 4.96.

Table 4.65: 1.0M Sodium ion ($Na^{+)}$ analysis at 30°C

| PH value | Change in volume (ΔV), (ml) | Adsorption(θ), (mole/cm$^2$) X $10^{-12}$ | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.00 | 3.60 | 3.932 | 3.794 |
| 9.50 | 4.00 | 4.369 | 4.216 |
| 10.00 | 5.20 | 5.680 | 5.481 |
| 11.00 | 4.40 | 4.806 | 4.638 |
| Average | | | 4.532 |

Table 4.66: 1.0M Sodium ion ($NA^+$) analysis at 50°C

| PH value | Change in volume (ΔV), (ml) | Adsorption(θ), (mole/cm$^2$) X $10^{-12}$ | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.50 | 9.60 | 10.486 | 10.119 |
| 10.00 | 8.00 | 8.738 | 8.432 |
| 10.80 | 12.80 | 13.981 | 13.492 |
| 11.50 | 16.60 | 18.132 | 17.489 |
| Average | | | 12.383 |

Table 4.67: 0.1M Sodium ion ($Na^+$) analysis at 30°C

| PH value | Change in volume ($\Delta$V), (ml) | Adsorption($\theta$), (mole/$cm^2$) X $10^{-12}$ | Surface charge ($E_v$) (coulombs/$cm^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.60 | 10.00 | 10.923 | 10.541 |
| 10.80 | 14.40 | 15.729 | 15.178 |
| 11.20 | 17.40 | 19.006 | 18.341 |
| Average | | | 14.687 |

Table 4.68; 0.1M Sodium ion ($Na^+$) analysis at 50 °C

| Ph value | Change in volume ($\Delta$V), (ml) | Adsorption ($\theta$), (mole/$cm^2$) x $10^{-12}$ | Surface charge ($E_v$) (coulombs/$cm^2$) x$10^{-7}$ |
|---|---|---|---|
| 8.25 | 2.43 | 2.654 | 2.561 |
| 10.20 | 4.01 | 4.380 | 4.228 |
| 11.00 | 3.29 | 3.594 | 3.468 |
| Average | | | 3.419 |

Table 4.69: 0.01M Sodium ion ($Na^+$) analysis at 30°C

| pH value | Change in volume ($\Delta$V), (ml) | Adsorption ($\theta$), (mole/$cm^2$) x $10^{-12}$ | Surface charge ($E_v$) (coulombs/$cm^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.50 | 4.44 | 4.850 | 4.680 |
| 10.00 | 10.49 | 11.458 | 11.057 |
| 10.50 | 10.86 | 11.862 | 11.447 |
| Average | | | 9.061 |

Table 4.70: 0.01M Sodium ion ($Na^+$) analysis at 50°C

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption (θ), (mole/cm$^2$) X $10^{-12}$ | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| 8.80 | 3.23 | 3.304 | 3.188 |
| 9.25 | 2.42 | 2.643 | 2.550 |
| 10.80 | 6.45 | 7.045 | 6.798 |
| 11.00 | 2.63 | 2.873 | 2.772 |
| Average | | | 3.827 |

Table 4.71; 0.001M Sodium ion ($Na^+$) analysis at 30°C

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption (θ) (mole/cm$^2$) x $10^{-12}$, | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| 8.60 | 5.65 | 6.171 | 5.955 |
| 9.00 | 7.88 | 8.607 | 8.306 |
| 10.00 | 17.71 | 19.345 | 18.668 |
| 10.89 | 15.71 | 17.160 | 16.559 |
| Average | | | 12.372 |

Table 4.72: 0.001M Sodium ion ($Na^+$) analysis at 50°C

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption (θ), (mole/cm$^2$) x $10^{-12}$ | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.50 | 8.02 | 8.760 | 8.453 |
| 9.80 | 13.70 | 14.965 | 14.441 |
| Average | | | 11.447 |

Table 4.73: 1.0 M Calcium ion ( $Ca^{++}$) analysis at $30^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/$cm^2$) x $10^{-12}$ | Surface charge ($E_v$) (coulombs/$cm^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.40 | 28.99 | 31.666 | 61.115 |
| 10.00 | 33.85 | 36.974 | 71.360 |
| 10.50 | 33.01 | 36.057 | 69.590 |
| 11.00 | 27.96 | 30.541 | 58.944 |
| Average | | | 65.252 |

Table 4.74; 1.0 M Calcium ion ( $Ca^{++}$) analysis at $50^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/$cm^2$) x $10^{-12}$ | Surface charge ($E_v$) (coulombs/$cm^2$) x$10^{-7}$ |
|---|---|---|---|
| 8.80 | 4.84 | 5.287 | 10.204 |
| 9.20 | 7.26 | 7.930 | 15.305 |
| 10.50 | 25.76 | 28.138 | 54.306 |
| 11.00 | 36.23 | 39.574 | 76.378 |
| Average | | | 25.472 |

Table 4.75; 0.1 M Calcium ion ( $Ca^{++}$) analysis at $30^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/$cm^2$) X $10^{-12}$ | Surface charge ($E_v$) (coulombs/$cm^2$) x$10^{-7}$ |
|---|---|---|---|
| Average | | | 0.000 |

Table 4.76: 0.1 M Calcium ion ( $Ca^{++}$) analysis at $50^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/$cm^2$) X $10^{-12}$ | Surface charge ($E_v$) (coulombs/$cm^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.00 | 1.87 | 2.043 | 3.943 |
| 10.70 | 10.51 | 11.480 | 22.156 |
| 10.90 | 22.26 | 24.330 | 46.957 |
| 11.20 | 27.39 | 29.918 | 57.742 |
| Average | | | 32.700 |

Table 4.77: 0.01 M Calcium ion ( $Ca^{++}$) analysis at $30^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$) (mole/$cm^2$) x $10^{-12}$, | Surface charge ($E_v$) (coulombs/$cm^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.20 | 12.84 | 14.025 | 27.068 |
| 9.50 | 9.61 | 10.497 | 20.259 |
| 10.00 | 8.89 | 9.711 | 18.742 |
| 10.40 | 14.50 | 15.838 | 30.657 |
| Average | | | 24.182 |

Table 4.78: 0.01 M Calcium ion ( $Ca^{++}$) analysis at $50^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/cm$^2$) x $10^{-12}$ | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.30 | 12.83 | 14.014 | 27.047 |
| 9.55 | 6.47 | 7.067 | 13.639 |
| 10.50 | 9.60 | 10.486 | 20.236 |
| 11.00 | 19.03 | 20.786 | 40.117 |
| Average | | | 20.201 |

Table 4.79: 0.001 M Calcium ion ( $Ca^{++}$) analysis at $30^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/cm$^2$) x $10^{-12}$ | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.00 | 2.01 | 2.196 | 4.238 |
| 9.20 | 27.38 | 29.907 | 57.721 |
| 9.40 | 41.48 | 45.309 | 87.446 |
| - | - | - | - |
| Average | | | 49.802 |

Table 4.80: 0.001 M Calcium ion ( $Ca^{++}$) analysis at $50^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/$cm^2$) X $10^{-12}$ | Surface charge ($E_v$) (coulombs/$cm^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.80 | 3.53 | 3.856 | 7.442 |
| 10.00 | 8.84 | 9.656 | 18.636 |
| 10.30 | 20.11 | 21.966 | 42.394 |
| 10.50 | 24.20 | 26.434 | 51.018 |
| Average | | | 29.873 |

Table 4.81: 1.0 M Lead ion ( $Pb^{++}$) analysis at $30^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/$cm^2$) x $10^{-12}$ | Surface charge ($E_v$) (coulombs/$cm^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.00 | 2.38 | 2.600 | 5.018 |
| 9.40 | 5.76 | 6.292 | 12.144 |
| 10.20 | 2.80 | 3.444 | 6.647 |
| - | - | - | - |
| Average | | | 7.936 |

Table 4.82: 1.0 M Lead ion ( $Pb^{++}$) analysis at $50^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/$cm^2$) X $10^{-12}$ | Surface charge ($E_v$) (coulombs/$cm^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.00 | 1.40 | 3.292 | 6.354 |
| 9.50 | 5.60 | 6.117 | 11.806 |
| 10.20 | 4.32 | 4.719 | 9.108 |
| Average | | | 9.089 |

Table 4.83: 0.1 M Lead ion ( $Pb^{++}$) analysis at $30^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), ($mole/cm^2$) x $10^{-12}$ | Surface charge ($E_v$) ($coulombs/cm^2$) $x10^{-7}$ |
|---|---|---|---|
| Average | | | 0.000 |

Table 4.84: 0.1 M Lead ion ( $Pb^{++}$) analysis at $50^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), ($mole/cm^2$) x $10^{-12}$ | Surface charge ($E_v$) ($coulombs/cm^2$) $x10^{-7}$ |
|---|---|---|---|
| 9.50 | 5.61 | 6.128 | 11.827 |
| 10.00 | 5.70 | 6.226 | 12.016 |
| 10.80 | 8.09 | 8.837 | 17.055 |
| Average | | | 13.633 |

Table 4.85: 0.01 M Lead ion ( $Pb^{++}$) analysis at $30^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), ($mole/cm^2$) x $10^{-12}$ | Surface charge ($E_v$) ($coulombs/cm^2$) $x10^{-7}$ |
|---|---|---|---|
| 9.20 | 10.65 | 11.640 | 22.465 |
| 10.00 | 1.61 | 1.759 | 3.395 |
| 10.50 | 8.9 | 9.721 | 18.762 |
| Average | | | 14.874 |

Table 4.86: 0.01 M Lead ion ( $Pb^{++}$) analysis at $50^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/cm$^2$) X $10^{-12}$ | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| 8.80 | 2.02 | 2.206 | 4.258 |
| 9.20 | 2.01 | 2.196 | 4.256 |
| 10.50 | 4.40 | 4.806 | 9.276 |
| Average | | | 5.930 |

Table 4.87: 0.001 M Lead ion ( $Pb^{++}$) analysis at $30^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/cm$^2$) X $10^{-12}$ | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.20 | 8.84 | 9.656 | 18.636 |
| 9.50 | 3.19 | 3.484 | 6.724 |
| 10.20 | 6.48 | 7.078 | 13.661 |
| Average | | | 13.005 |

Table 4.88: 0.001 M Lead ion ( $Pb^{++}$) analysis at $50^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/cm$^2$) x $10^{-12}$ | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| 8.80 | 5.35 | 5.843 | 11.277 |
| 9.00 | 9.61 | 10.497 | 20.259 |
| 9.50 | 7.32 | 7.996 | 15.432 |
| 10.00 | 4.90 | 5.352 | 10.329 |
| Average | | | 14.324 |

Table 4.89: 1.0 M Magnesium ion ( $Mg^{++}$) analysis at $30^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$) (mole/cm$^2$) x $10^{-12}$, | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| 8.50 | 8.87 | 9.689 | 18.700 |
| 9.00 | 8.88 | 9.670 | 18.663 |
| 9.50 | 4.80 | 5.243 | 10.119 |
| 10.5 | 6.08 | 6.641 | 12.817 |
| Average | | | 15.075 |

Table 4.90: 1.0 M Magnesium ion ( $Mg^{++}$) analysis at $50^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/cm$^2$) x $10^{-12}$ | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.00 | 3.63 | 3.965 | 7.652 |
| 9.50 | 3.22 | 3.517 | 6.788 |
| 10.00 | 4.00 | 4.369 | 8.432 |
| 11.00 | 6.00 | 6.554 | 12.649 |
| Average | | | 8.880 |

Table 4.91: 0.1 M Magnesium ion ( $Mg^{++}$) analysis at $30^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/cm$^2$) x $10^{-12-}$ | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| Average | | | 0.000 |

Table 4.92: 0.1 M Magnesium ion ( $Mg^{++}$) analysis at $50^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/$cm^2$) x $10^{-12}$ | Surface charge ($E_v$) (coulombs/$cm^2$) x$10^{-7}$ |
|---|---|---|---|
| 8.60 | 3.63 | 3.965 | 7.652 |
| 9.00 | 3.64 | 3.976 | 7.674 |
| 9.50 | 4.80 | 5.243 | 10.119 |
| 11.00 | 6.21 | 6.788 | 13.101 |
| Average | | | 9.637 |

Table 4.93: 0.01 M Magnesium ion ( $Mg^{++}$) analysis at $30^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/$cm^2$) x $10^{-12}$ | Surface charge ($E_v$) (coulombs/$cm^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.60 | 12.07 | 13.184 | 25.445 |
| 9.80 | 10.10 | 11.032 | 21.292 |
| 10.00 | 10.51 | 11.480 | 22.156 |
| Average | | | 22.964 |

Table 4.94: 0.01 M Magnesium ion ( $Mg^{++}$) analysis at $50^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/$cm^2$) $10^{-12}$ | Surface charge ($E_v$) (coulombs/$cm^2$) x$10^{-7}$ |
|---|---|---|---|
| 8.50 | 2.42 | 2.643 | 5.101 |
| 9.30 | 8.44 | 9.219 | 17.793 |
| 9.50 | 16.12 | 17.608 | 33.983 |
| Average | | | 18.959 |

Table 4.95: 0.001 M Magnesium ion ( $Mg^{++}$) analysis at $30^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/cm$^2$) X $10^{-12}$ | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| 8.50 | 2.43 | 2.654 | 5.122 |
| 9.20 | 8.09 | 8.834 | 17.050 |
| 9.40 | 15.28 | 16.690 | 32.212 |
| 9.60 | 22.59 | 24.675 | 47.623 |
| Average | | | 25.502 |

Table 4.96: 0.001 M Magnesium ion ( $Mg^{++}$) analysis at $50^0C$

| pH value | Change in volume ($\Delta V$), (ml) | Adsorption ($\theta$), (mole/cm$^2$) x $10^{-12}$ | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| 8.50 | 3.63 | 3.965 | 7.652 |
| 9.00 | 4.84 | 5.287 | 10.204 |
| 9.50 | 4.81 | 5.254 | 10.140 |
| 9.80 | 14.50 | 15.838 | 30.567 |
| Average | | | 14.641 |

### 4.2.3 FACTORIAL ANALYSIS TABLES

Table 4.97: Factorial Experimental Result for Sodium ion ($Na^+$) as $NaNO_3$

| Degree of freedom | $X_0$ | $X_1$ | $X_2$ | Y x $10^{-3}$ (coulombs/$m^2$) |
|---|---|---|---|---|
| 1 | + | + | + | 1.2383 |
| 2 | + | 0 | + | 1.1915 |
| 3 | + | - | + | 1.1447 |
| 4 | + | + | 0 | 1.0163 |
| 5 | + | 0 | 0 | 0.8966 |
| 6 | + | - | 0 | 0.7769 |
| 7 | + | + | - | 0.4532 |
| 8 | + | 0 | - | 0.8452 |
| 9 | + | - | - | 1.2372 |

Table 4.98: Factorial Experimental Result for Calcium ion ($Ca^{++}$) as $Ca(NO_3)_2$

| Degree of freedom | $X_0$ | $X_1$ | $X_2$ | Y x $10^{-3}$ (coulombs/$m^2$) |
|---|---|---|---|---|
| 1 | + | + | + | 2.5472 |
| 2 | + | 0 | + | 2.7651 |
| 3 | + | - | + | 2.9873 |
| 4 | + | + | 0 | 2.7062 |
| 5 | + | 0 | 0 | 3.0935 |
| 6 | + | - | 0 | 3.4809 |
| 7 | + | + | - | 6.5252 |
| 8 | + | 0 | - | 5.7527 |
| 9 | + | - | - | 4.9802 |

Table 4.99: Factorial Experimental Result for Lead ion ($Pb^{++}$) as $Pb(NO_3)_2$

| Degree of freedom | $X_0$ | $X_1$ | $X_2$ | Y x $10^{-3}$ (coulombs/$m^2$) |
|---|---|---|---|---|
| 1 | + | + | + | 0.9089 |
| 2 | + | 0 | + | 1.1707 |
| 3 | + | - | + | 1.4324 |
| 4 | + | + | 0 | 1.0744 |
| 5 | + | 0 | 0 | 0.9849 |
| 6 | + | - | 0 | 1.0739 |
| 7 | + | + | - | 0.7936 |
| 8 | + | 0 | - | 2.0941 |
| 9 | + | - | - | 1.3005 |

Table 4.100: Factorial Experimental Result for Magnesium ion ($Mg^{++}$) as $Mg(NO_3)_2$

| Degree of freedom | $X_0$ | $X_1$ | $X_2$ | Y x $10^{-3}$ (coulombs/$m^2$) |
|---|---|---|---|---|
| 1 | + | + | + | 0.8880 |
| 2 | + | 0 | + | 1.1761 |
| 3 | + | - | + | 1.4641 |
| 4 | + | + | 0 | 1.3029 |
| 5 | + | 0 | 0 | 1.6523 |
| 6 | + | - | 0 | 1.5885 |
| 7 | + | + | - | 1.5075 |
| 8 | + | 0 | - | 2.0289 |
| 9 | + | - | - | 2.5502 |

ere

= Base

$X_1$ = concentration

$X_2$ = temperature

Y = mean response or yield

\+ = maximum value

\- = minimum value

0 = average value

Table 4.101: Calculation Matrix and the Surface charge of the four cations

(Ev = Y x $10^{-3}$coulombs/$m^2$) for $3^2$ Factorial design.

| Run | $x_0$ | $X_1$ | $X_2$ | $X_{11}$ | $X_{12}$ | $X_{22}$ | Y | Y | Y | Y |
|---|---|---|---|---|---|---|---|---|---|---|
| No | $a_0$ | $a_1$ | $a_2$ | $a_{11}$ | $a_{12}$ | $a_{22}$ | $Na^{++}$ | $Ca^{++}$ | $Pb^{++}$ | $Mg^{++}$ |
| 1 | + | + | + | + | + | + | 1.2383 | 2.5472 | 0.9089 | 0.8880 |
| 2 | + | 0 | + | 0 | 0 | + | 1.1915 | 2.7651 | 1.1707 | 1.1761 |
| 3 | + | - | + | + | - | + | 1.1447 | 2.9873 | 1.4324 | 1.4641 |
| 4 | + | + | 0 | + | 0 | 0 | 1.0163 | 2.7062 | 1.0744 | 1.3029 |
| 5 | + | 0 | 0 | 0 | 0 | 0 | 0.8966 | 3.0935 | 0.9849 | 1.6523 |
| 6 | + | _ | 0 | + | 0 | 0 | 0.7769 | 3.4809 | 1.0739 | 1.5885 |
| 7 | + | + | - | + | - | + | 0.4532 | 6.5252 | 0.7936 | 1.5075 |
| 8 | + | 0 | - | 0 | 0 | + | 0.8452 | 5.7527 | 2.0941 | 2.0289 |
| 9 | + | + | - | + | - | + | 1.2372 | 4.9802 | 1.3005 | 2.5502 |

## 4.3 DEVELOPMENT AND OPTIMIZATION OF THE MODEL EQUATIONS OF ADSORPTION

Since the selected second order model equation is of the form y = f($x_1$, $x_2$)

therefore, Equation 3.5 was used and the regression coefficients (a) and the response(Y) are calculated using computer software and optimized as follows.

### 4.3.1 Determination of regression coefficients of the model equation and optimization using minitab computer software

Table 4.101a,b,c,d: Determination of significance of data

a

| Na$^+$ | | | significant var | 1 |
|---|---|---|---|---|
| X1 | X2 | Y | | |
| 1 | 50 | 1.2383 | | |
| 0.501 | 50 | 1.1915 | | |
| 1 | 50 | 1.1447 | | |
| 1 | 30 | 1.0163 | | |
| 0.501 | 40 | 1.8966 | | |
| 1 | 40 | 0.7769 | | |
| 0.501 | 30 | 1.4532 | | |
| 1 | 50 | 0.8452 | | |
| 0.501 | 50 | 1.2372 | | |

b

| $Ca^{++}$ | | | significant<br>var | 2 |
|---|---|---|---|---|
| X1 | X2 | Y | | |
| 1 | 50 | 2.5472 | | |
| 1 | 50 | 2.7651 | | |
| 1 | 50 | 2.9873 | | |
| 0.501 | 40 | 2.7062 | | |
| 0.501 | 40 | 3.0935 | | |
| 0.501 | 40 | 3.4809 | | |
| 0.001 | 30 | 6.5252 | | |
| 0.001 | 30 | 5.7527 | | |
| 0.001 | 30 | 4.9802 | | |

| Mg$^{++}$ | | | Significant<br>var | 2 |
|---|---|---|---|---|
| 1 | 50 | 1.4472 | | |
| 1 | 50 | 1.6651 | | |
| 1 | 50 | 1.8873 | | |
| 0.501 | 40 | 1.6062 | | |
| 0.501 | 40 | 2.0635 | | |
| 0.501 | 40 | 2.3809 | | |
| 0.001 | 30 | 5.4152 | | |
| 0.001 | 30 | 4.7117 | | |
| 0.001 | 30 | 3.9611 | | |

d

| Pb$^{++}$ | | | Significant<br>var | 0 |
|---|---|---|---|---|
| 1 | 50 | 0.909 | | |
| 0.501 | 50 | 1.171 | | |
| 0.001 | 50 | 1.432 | | |
| 1 | 40 | 1.074 | | |
| 0.501 | 40 | 0.985 | | |
| 0.001 | 40 | 1.074 | | |
| 1 | 30 | 0.794 | | |
| 0.501 | 30 | 2.094 | | |
| 0.001 | 30 | 1.301 | | |

## A. SODIUM ION RESULT

**Factorial Fit: Y versus X1,**

* NOTE * This design has some botched runs. It will be analyzed using a regression approach.

Table 4.102; Estimated Effects and Coefficients for Y (coded units)

| Term | Effect | Coef | SE Coef | T | P |
|---|---|---|---|---|---|
| Constant | | 1.2331 | 0.09836 | 12.54 | 0.000 |
| X1 | - | - | 0.09836 | -2.58 | 0.049 |
| X2 | 0.5084 | 0.2542 | 0.11186 | -0.48 | 0.653 |
| X1*x2 | - | - | 0.11186 | 1.05 | 0.653 |
| | 0.1070 | 0.0535 | | | |
| | 0.2341 | 0.1171 | | | |

S = 0.272080 R-Sq = 58.60% R-Sq(adj) = 33.75%

The obtained model is

$$Y = 1.2331 - 0.2542x_1 - 0.0535x_2 + 0.0646x_1^2 + 0.0029x_2^2 + 0.\ 1171X1*X2 \qquad \ldots\ldots 4.1$$

Table 4.103; Analysis of Variance for Y (coded units)

| Source | DF | Seq SS | Adj SS | Adj MS | F | P |
|---|---|---|---|---|---|---|
| Main Effects | 2 | 0.44277 | 0.52365 | 0.26183 | 3.54 | 0.110 |
| 2-Way Interactions | 1 | 0.08108 | 0.08108 | 0.08108 | 1.10 | 0.343 |
| Residual Error | 5 | 0.37014 | 0.37014 | 0.07403 | | |
| Lack of Fit | 2 | 0.28476 | 0.28476 | 0.14238 | 5.00 | 0.111 |
| Pure Error | 3 | 0.08537 | 0.08537 | 0.02846 | | |
| Total | 8 | 0.89399 | | | | |

Table 4.104; Factorial Analysis of Response of Sodium ion

| Obs | StdOrder | Y Fit | SE Fit | Residual | St Resid |
|---|---|---|---|---|---|
| 1 | 1.23830 | 1.04241 | 0.15210 | 0.19589 | 0.87 |
| 2 | 1.19150 | 1.31668 | 0.18344 | -0.12518 | -0.62 |
| 3 | 1.14470 | 1.04241 | 0.15210 | 0.10229 | 0.45 |
| 4 | 1.01630 | 0.91532 | 0.24525 | 0.10098 | 0.86 |
| 5 | 1.89660 | 1.48727 | 0.14209 | 0.40933 | 1.76 |
| 6 | 0.77690 | 0.97886 | 0.13604 | -0.20196 | -0.86 |
| 7 | 1.45320 | 1.65786 | 0.24611 | -0.20466 | -1.76 |
| 8 | 0.84520 | 1.04241 | 0.15210 | -0.19721 | -0.87 |
| 9 | 1.23720 | 1.31668 | 0.18344 | -0.07948 | -0.40 |

Table 4.105; Estimated Coefficients for Y using data in uncoded units

| Term | Coef | Constant | 3.62038 |
|---|---|---|---|
| X1 | -2.89569 | | |
| X2 | -0.0405664 | | |
| X1*X2 | 0.0469208 | | |

The reduced model equation is

$Y_{Na+} = 3.6204 - 2.8957x_1 - 0.0406x_2 + 8.3851x_1^2 + 0.0016x_2^2 + 0.\ 1171X1*X2$ .....4.2

Table 4.106; Least Squares Means for Y

| | Mean SE | Mean |
|---|---|---|
| X1 | | |
| 0.5010 | 1.4873 | 0.1421 |
| 1.0000 | 0.9789 | 0.1360 |
| X2 | | |
| 30 | 1.2866 | 0.1737 |
| 50 | 1.1795 | 0.1191 |
| X1*X2 | | |
| 0.5010 | 30 1.6579 | 0.2461 |
| 1.0000 | 30 0.9153 | 0.2452 |
| 0.5010 | 50 1.3167 | 0.1834 |
| 1.0000 | 50 1.0424 | 0.1521 |

**Effects Plot for Y**

The effects of the plots of the above analysis are shown in figure 4.33; a – g, in appendix 4.

a = Effects Pareto for Y

* NOTE * Some factors have more than 2 levels, no alias table was printed.

b = Normal Probability Plot of the Standard effects

c = Residual Plots for Y

d = Cube Plot (data means) for Y

e = Interaction Plot (data means) for Y

f = Main Effects Plot (data means) for Y

g = Surface Plot of Y vs X1, X2

## B. CALCIUM ION ANALYSIS

**Factorial Fit: Y versus X1, X2**

* NOTE * This design has some botched runs. It will be analyzed using a regression approach.

Table 4.107;Estimated Effects and Coefficients for Y (coded units)

| Term | Effect | Coef | SE Coef | T | P |
|---|---|---|---|---|---|
| Constant | | 4 | 0.210 | 20.27 | 0.000 |
| X1 | -2330 | -1165 | 363.692 | -3..20 | 0.019 |
| X2 | 2327 | 1163 | 363.692 | 3.20 | 0.019 |

S = 0.514853 R-Sq = 91.01% R-Sq(adj) = 88.01%

The model equation obtained with nil interaction effects is

$$Y = 4.0 - 1165x_1 + 1163x_2 + 1357225x_1^2 + 1352569x_2^2 \qquad .....4.3$$

Table 4.108; Analysis of Variance for Y (coded units)

| Source | DF | Seq SS | Adj SS | Adj MS | F | P |
|---|---|---|---|---|---|---|
| Main Effects | 2 | 16.0953 | 16.0953 | 8.0476 | 30.36 | 0.001 |
| Residual Error | 6 | 1.5904 | 1.5904 | 0.2651 | | |
| Pure Error | 6 | 1.5904 | 1.5904 | 0.2651 | | |
| Total | 8 | 17.6857 | | | | |

able 4.109; Factorial Analysis of Response of Calcium Ion

| bs | StdOrder | Y | Fit | SE Fit | Residual | St Resid |
|---|---|---|---|---|---|---|
| 1 | 1 | 2.54720 | 2.76653 | 0.29725 | -0.21933 | -0.52 |
| 2 | 2 | 2.76510 | 2.76653 | 0.29725 | -0.00143 | -0.00 |
| 3 | 3 | 2.98730 | 2.76653 | 0.29725 | 0.22077 | 0.53 |
| 4 | 4 | 2.70620 | 3.09353 | 0.29725 | -0.38733 | -0.92 |
| 5 | 5 | 3.09350 | 3.09353 | 0.29725 | -0.00003 | -0.00 |
| 6 | 6 | 3.48090 | 3.09353 | 0.29725 | 0.38737 | 0.92 |
| 7 | 7 | 6.52520 | 5.75270 | 0.29725 | 0.77250 | 1.84 |
| 8 | 8 | 5.75270 | 5.75270 | 0.29725 | 0.00000 | 0.00 |
| 9 | 9 | 4.98020 | 5.75270 | 0.29725 | -0.77250 | -1.84 |

Table 4.110; Estimated Coefficients for Y using data in uncoded units

| Term | Coef |
|---|---|
| Constant | -3482.19 |
| X1 | -2332.17 |
| X2 | 116.342 |

The reduced model equation is

$$Y_{Ca++} = -3482.19 - 2332.17x_1 - +116.342x_2 + 5439017x_1^2 + 13535.5x_2^2 \qquad .....4.4$$

Table 4.111; Least Squares Means for Y

| | Mean | SE Mean |
|---|---|---|
| X1 | | |
| 0.0010 | 1169 | 363.8 |
| 1.0000 | -1161 | 363.6 |
| X2 | | |
| 30 | -1159 | 363.6 |
| 50 | 1168 | 363.8 |

**Effects Plot for Y**

The effects of the plots of the response of the analysis are shown in figure4.34 a –g in appendix 5

a =Effects Pareto for Y

* NOTE * Some factors have more than 2 levels, no alias table was printed.

b = Residual Plots for Y

**C. LEAD ION RESULT**

**Factorial Fit: Y versus X1, X2**

* NOTE * This design has some botched runs. It will be analyzed using a regression approach.

Table 4.112; Estimated Effects and Coefficients for Y (coded units)

| Term | Effect | Coef | SE Coef | T | P |
|---|---|---|---|---|---|
| Constant | | 1.2038 | 0.1445 | 8.33 | 0.000 |
| X1 | -0.3431 | -0.1715 | 0.1769 | -0.97 | 0.377 |
| X2 | -0.2254 | -0.1127 | 0.1769 | -0.64 | 0.552 |
| X1*X2 | -0.0086 | -0.0043 | 0.2167 | -0.02 | 0.985 |

S = 0.433419 R-Sq = 21.21% R-Sq(adj) = 0.00%

$= 1.2038 - 0.1715x_1 - 0.1127x_2 + 0.0294x_1^2 + 0.0127x_2^2 - 0.\ 0043X1*X2$ .....4.5

able 4.113; Analysis of Variance for Y (coded units)

| Source | DF | Seq SS | Adj SS | Adj MS | F | P |
|---|---|---|---|---|---|---|
| Main Effects | 2 | 0.25277 | 0.252769 | 0.126384 | 0.67 | 0.551 |
| 2-Way Interactions | 1 | 0.00007 | 0.000075 | 0.000075 | 0.00 | 0.985 |
| Residual Error | 5 | 0.93926 | 0.939259 | 0.187852 | | |
| Total | 8 | 1.19210 | | | | |

Unusual Observations for Y

Table 4.114; Unusual Observations for Y:Factorial Analysis of the Response of Lead ion

| Obs | StdOrder | Y | Fit | SE Fit | Residual | St Resid |
|---|---|---|---|---|---|---|
| 8 | 8 | 2.09410 | 1.31630 | 0.22843 | 0.77780 | 2.11R |

R denotes an observation with a large standardized residual.

Table 4.115; Estimated Coefficients for Y using data in uncoded units

| Term | Coef |
|---|---|
| Constant | 1.80912 |
| X1 | -0.30880 |
| X2 | -0.0108365 |
| X1*X2 | -0.0008658 |

The reduced model equation is

$Y_{Pb++} = 1.8091 - 0.3088x_1 - 0.0108x_2 + 0.0954x_1^2 + 0.00012x_2^2 - 0.00087X1*X2$ .....4.6

Table 4.116; Least Squares Means for Y

| X1 | Mean | SE Mean |
|---|---|---|
| 0.0010 | 1.3753 | 0.2285 |
| 1.0000 | 1.0322 | 0.2284 |
| X2 | | |
| 30 | 1.3165 | 0.2284 |
| 50 | 1.0911 | 0.2284 |
| X1*X2 | | |
| 0.0010 | 30 1.4837 | 0.3613 |
| 1.0000 | 30 1.1492 | 0.3611 |
| 0.0010 | 50 1.2669 | 0.3613 |
| 1.0000 | 50 0.9152 | 0.3611 |

**Effects Plot for Y**

The effects of the plots of the responses are shown in figure 4.35a –c in appendix 6

a = Effects Pareto for Y

* NOTE * Some factors have more than 2 levels, no alias table was printed.

b = Normal probability Plots of standard effects

c = Residual Plots for Y

**D. Magnesium ion Result**

**Factorial Fit: Y versus X1, X2**

* NOTE * This design has some botched runs. It will be analyzed using a regression approach.

able 4.117; Estimated Effects and Coefficients for Y (coded units)

| erm | Effect | Coef | SE Coef | T | P |
|---|---|---|---|---|---|
| Constant | | 3 | 0.201 | 15.81 | 0.000 |
| X1 | -2326 | -1163 | 348.192 | -3.34 | 0.016 |
| X2 | 2323 | 1162 | 348.192 | 3.34 | 0.016 |

S = 0.492910 R-Sq = 91.87% R-Sq(adj) = 89.16%

$$Y = 3.0 - 1163x_1 + 1162x_2 + 1352569x_1^2 + 13500244x_2^2 \qquad .....4.7$$

Table 4.118; Analysis of Variance for Y (coded units)

| Source | DF | Seq SS | Adj SS | Adj MS | F | P |
|---|---|---|---|---|---|---|
| Main Effects | 2 | 16.4782 | 16.4782 | 8.2391 | 33.91 | 0.001 |
| Residual Error | 6 | 1.4578 | 1.4578 | 0.2430 | | |
| Pure Error | 6 | 1.4578 | 1.4578 | 0.2430 | | |
| Total | 8 | 17.9359 | | | | |

Table 4.119; Estimated Coefficients for Y using data in uncoded units

| Term | Coef |
|---|---|
| Constant | -3478.14 |
| X1 | -2328.80 |
| X2 | 116.172 |

The reduced model equation is

$$Y = -3478.14 - 2328.80x_1 + 116.172x_2 + 5423309.44x_1^2 + 13495.9336x_2^2 \qquad .....4.8$$

Table 4.120; Least Squares Means for Y

| X1 | Mean SE | Mean |
|---|---|---|
| 0.0010 | 1166 | 348.3 |
| 1.0000 | -1160 | 348.1 |
| X2 | | |
| 30 | -1159 | 348.1 |
| 50 | 1165 | 348.3 |

Table 4.121; Predicted Response for New Design Points Using Model for Y

| Point | Fit | SE Fit | 95% CI | 95% PI |
|---|---|---|---|---|
| 1 | 1.66653 | 0.28458 | (0.97019, 2.36288) | (0.27384, 3.05923) |
| 2 | 1.66653 | 0.28458 | (0.97019, 2.36288) | (0.27384, 3.05923) |
| 3 | 1.66653 | 0.28458 | (0.97019, 2.36288) | (0.27384, 3.05923) |
| 4 | 2.01687 | 0.28458 | (1.32052, 2.71321) | (0.62417, 3.40956) |
| 5 | 2.01687 | 0.28458 | (1.32052, 2.71321) | (0.62417, 3.40956) |
| 6 | 2.01687 | 0.28458 | (1.32052, 2.71321) | (0.62417, 3.40956) |
| 7 | 4.69600 | 0.28458 | (3.99965, 5.39235) | (3.30331, 6.08869) |
| 8 | 4.69600 | 0.28458 | (3.99965, 5.39235) | (3.30331, 6.08869) |
| 9 | 4.69600 | 0.28458 | (3.99965, 5.39235) | (3.30331, 6.08869) |

**Effects Plot for Y**

The effects of the analysis of response of magnesium ion are given in figure 4.36 a-e

d = Effects Pareto for Y

* NOTE * Some factors have more than 2 levels, no alias table was printed.

c = Residual Plots for Y

# CHAPTER 5

## 5 DISCUSSION OF RESULTS

### 5.1 Introduction

When a design is screened, the object is to select factors that have large effects. Now that factorial design has been created and the response data collected, a model is fitted to the results and some graphs were generated to evaluate the effects using Minitab Computer Software. The output from fitting a mathematical model is analyzed and the two graphical indices; p-value and pareto chart, are used to help see which factor is important for improving the surface charge of the leclanche' cell. The software employs a session window output which provides information as to how good the model is. It displays p-values and pareto charts criteria.

### 5.2 P-Value fitness

The values in the P column of the estimated effects and coefficients table of the factorial design run are used to determine which of the effects are significant. Using α = 0.05, the main effects for concentration of cations and the temperature interaction are tested for significance; that is, if their p-values are less than 0.05.

The data showed that the P values for $Na^{++}$,= 0.048($x_1$),0.053($x_2$),0.0343($x_1x_2$), $Ca^{++}$ = 0.019($x_1$=$x_2$), and $Mg^{++}$ = 0.016($x_1$=$x_2$), while $Pb^{++}$ =0.372($x_1$), 0.552($x_2$),0.985($x_3$). These are indicated in Tables 4.102, 4.107, 4.112 and 4. 117. That is, for sodium ion only $x_1$ is significant. Table 4.102 showed that only the concentration of the electrolyte has an active or greater effect on the adsorption process, whereas the temperature,$x_2$, and interaction effect, $x_1$*$x_2$, between the two have smaller effect in the process because their p-values are greater than 0.05. While for calcium ions, Table 4.107, both concentration, ,$x_1$ and temperature, ,$x_{2,}$ have great effect in the process except that no visible interaction effect, $x_1$*$x_{2,}$ was indicated. This is also the same, fof magnesium ions, Table 4.117, where $x_1$ and $x_2$ are significant with no $x_1$*$x_{2.}$ whereas lead ions factors are all not significant, Table 4.112, shwed that the p-values are all above the α value.

### 5.3 Pareto chart test for suitability of factors

A Pareto chart of the effects is another useful tool that was used to help determine which effects are active. The Minitab displays the absolute value of the effects on the Pareto chart.

The Pareto chart uses the same α value as the normal plot to determine the significance of effects but one very interesting point with the pareto chart is that it gives pictorial representation. So again, in Figue 4.33a in appendix 4, it can be observed that concentration ($x_1$ represented as A) of $Na^+$ is active as it crosses the right margin (numerical value of 2.571) while the temperature ($x_2$ represented as B) and the interaction ($x_1*x_2$ represented as AB) are far away from the margin (fig.44a ). $Ca^{++}$ Pareto chart (figure 4.34a in appendix 5) showed both concentration and temperature as active effects but no interaction ($x_1*x_2$ represented as AB) effect was indicated. In figure 4.35a for $Pb^{++}$ both effects are far away from the margin signifying that the effects are all inactive or not significant. Whereas figure 4.36d for $Mg^{++}$ showed that the two effects A and B are significant factors except that no visible interaction is noticed.

The factorial result was first run using regression approach to determine the coefficients of the data. The models obtained for the four cations are shown in Equations 4.1 - 4.8.

## 5.3 Fitting a Reduced Model

Later, a model was fitted without the terms which seem to be inactive described as reduced model. It was checked to see how good the model equation is after fitting the reduced model. That is the task performed was fitting a new model using only the terms identified as important by looking at the results of fitting the full model, in other words screening out the unimportant effects. After fitting the model, several plots were generated to visualize the effects, evaluate the fit of the reduced model, and do a residual analysis. (fig.4.33,.34,.35,.36c). A new model was fitted that includes concentration temperature and the interaction for the significant elements. The reduced models obtained are given below

$$Y_{Na+} = 3.6204 - 2.8957x_1 - 0.0406x_2 + 8.3851x_1^2 + 0.0016x_2^2 + 0.\ 1171X1*X2 \qquad ...5.1$$

$$Y_{Ca++} = -3482.19 - 2332.17x_1 - +116.342x_2 + 5439017x_1^2 + 13535.5x_2^2 \qquad ...5.2$$

$$Y_{Mg++} = -3478.14 - 2328.80x_1 + 116.172x_2 + 5423309.44x_1^2 + 13495.9336x_2^2 \qquad ...5.3$$

The model is further checked by using the residual plots. The fitted values are the results predicted by the model. The residuals indicate the normal probability plot of the residuals, the histogram of the residuals, the variation of the residuals to the fitted values as well as the variation with the order of the data. The residuals plot for sodium ion does not clearly fit the model and the residual order is not periodic. However, calcium and magnesium plots clearly fitted the model and orderly. Although the lead ion residuals did not fit it has a fine order.

## 54 Optimum Surface Charge from Three-Dimensional (3-D) Plot Analysis

The surface- concentration- temperature($Y$-$x_1$-$x_2$), i.e 3-D, plot for $Na^+$ is shown in Figue 4.33g. The optimum electric surface charge (Y) is 1.25 x $10^{-3}$ coulombs per square meter of manganese dioxide at a concentration of 0.75 M and temperature of 40°C. The optimum value is shown by the faded portion of the 3-D plot array.

The optimum for $Ca^{++}$ is obtainable from figure 4.34e. The faded portion of this plot is at $Y = 1.5 \times 10^{-3}$ coulombs per square meter, i.e $x_1 = 0.85$ and $x_2 = 40$ coordinates.

And Figure 4.36a is for $Mg^{++}$ ion in which the faded portion of the plot gives the optimum surface charge; $Y = 1.8 \times 10^{-3}$ coulombs per square meter, $x_1 = 0.5$ and $x_2 = 47$°C.

Lead (Pb) data were not significant and thus could not be optimized.

These optimum values of the adsorb-ability of the cations on manganese dioxide gave corresponding surface charge and current density of 1.25 x $10^{-3}$, 1500 x $10^{-3}$ and 1800 x $10^{-3}$ $C/m^2$ and 4.5$A/m^2$, 5.4$A/m^2$ and 6.5 $A/m^2$ respectively, Table 5.1 and Table 5.2.

A simple comparison of the usage life of conventional leclanche' cell free of adsorbed cations( of 300s) to the expected usage life of the cell with adsorbed cations gave 480, 575 and 690 seconds, thus higher life span. This signifies 60%, 92% and 130% increases in life span for Sodium, Calcium and Magnesium ions respectively.

## 5.3 Comparative Analysis of Current Density and Potential of Adsorb and Unadsorbed cations on $MnO_2$

### 5.3.1 Current density/Amperage Comparison

The Current density or amperage is shown in table 5.1.

Table 5.1; Current density / Amperage Analysis

| S/N | Adsorbed cations on $MnO_2$ | | | | Unadsorbed $MnO_2$ | |
|---|---|---|---|---|---|---|
| | Cations | Surface Charge $C/m^2$ | Current Amps(A)/$m^2$ | Usage ($S/m^2$) | Current Amps(A) | Usage $S/m^2$ sec |
| 1 | $Na^+$ | $1.25 \times 10^{-3}$ | 4.5 | | 0.15 | 300 |
| 2 | $Ca^{++}$ | $1.50 \times 10^{-3}$ | 5.4 | | 0.15 | 300 |
| 3 | $Pb^{++}$ | - | - | | - | - |
| 4 | $Mg^{++}$ | $1.80 \times 10^{-3}$ | 6.48 | | 0.15 | 300 |

*Current is expressed in absolute amperes per square meter of cations on $MnO_2$.

### 5.3.2 Potential Comparison

The Current density or amperage is shown in table 5.2 below and potential obtained from appendix 8.

Table 5.2 calculated Potential

| S/N | Adsorbed cations on $MnO_2$ | | | | Unadsorbed $MnO_2$ | |
|---|---|---|---|---|---|---|
| | Cations | Surface Charge | Potential | Usage | Potential | Usage |
| | | $C/m^2$ | mV | $s/m^2$(NaOH) | Volts | $s/m^2$ |
| 1 | $Na^+$ | $1.25 \times 10^{-3}$ | 4500 | 478.23 | 1500 | 300 |
| 2 | $Ca^{++}$ | $1.5 \times 10^{-3}$ | 5400 | 575.08 | 1500 | 300 |
| 3 | $Pb^{++}$ | - | - | - | - | - |
| 4 | $Mg^{++}$ | $1.8 \times 10^{-3}$ | 6480 | 690.10 | 1500 | 300 |

The usage time measured in s/m2 per mole of titrant agrees with the graphical assessment of the potential read directly from figures 4.37 – 4.40 in appendix 8.

The usage time calculated per mole of titrant (NaOH),appendix 1, shows that the for every one mole of cation involve a relative mole of titrant is used. The improvement on the voltage and time will be a function of the cation relative to titrant consumed. The potential is compare to the one obtained from figures 4.37 -4.40 measured directly by the pH meter.

Table 5.3 Potential Obtained from graphs

| S/N | Adsorbed cations on $MnO_2$ | | | | Unadsorbed $MnO_2$ | |
|---|---|---|---|---|---|---|
| | Cations | Surface Charge | Potential | Usage time | Potential | Usage time |
| | | $C/m^2$ | mV | sec | Volts | sec |
| 1 | $Na^+$ | $1.25 \times 10^{-3}$ | 2400 | 480 | 1500 | 300 |
| 2 | $Ca^{++}$ | $1500 \times 10^{-3}$ | 2180 | 540 | 1500 | 300 |
| 3 | $Pb^{++}$ | - | - | - | - | - |
| 4 | $Mg^{++}$ | $1800 \times 10^{-3}$ | 2300 | 400 | 1500 | 300 |

The time difference between the calculated time and the graphically estimated value is very slight except for Mg ion which could be attributed to approximate extrapolation carried out.

# CHAPTER SIX

## 6.0 CONCLUSIONS AND RECOMMENDATIONS

### 6.1 Conclusion

The response plots of the quadratic models gave a three dimensional array with the optimum values. It can be concluded that

i. The optimum values for the adsorbed sodium, calcium and magnesium ions are obtained when the electrolyte concentrations are set to 0.75M at 40°C, 0.85M at 40°C and 0.5M at 47°C respectively.

ii. The corresponding surface charges and current densities calculated are $1.25 \times 10^{-3}$, $1.5 \times 10^{-3}$ and $1.8 \times 10^{-3}$ C/m$^2$ and 4.5A/m$^2$, 5.4A/m$^2$ and 6.5 A/m$^2$ respectively.

iii. Leclanche cell that has these cations adsorbed on the depolarizer, $MnO_2$, will last longer since, theoretically, the Leclanche cell lasts between 120 - 300s only on a continuous usage. (chapter 2 pp 9 -11;Stephen K.L, 2004 and Brant V, 1976). Therefore, a simple comparison of the usage life of conventional Leclanche' cell to the expected usage life of the cell with adsorbed cations gives 480, 575 and 690seconds, thus higher life span. Thus, 60%, 92% and 130% increases in life span are expected from cells incorporating sodium, calcium and magnesium ions respectively.

### 6.2 Recommendation

In view of the optimization of the adsorption of cations on Manganese dioxide for leclanche' cell production, the following points are recommended.

1 Optimization technique by factorial design using other standard software for the experiment should be carried out.

2 Effect of other factors on Manganese dioxide should also be investigated.

3. This work tried to improve on the undergraduate studies in the field of electrochemistry of dry cells. It was observed that effective optimization of the linear model equations were un-obtainable hence this work on quadratic model.

However, absolute error free experiment is unachievable.

It is recommended that these experimental works are repeated to justify or otherwise verify the findings. If however, it is satisfactory, the implementation of the results will serve as contribution to improve the performance or life span of dry cell batteries, reduce environmental littering of spent batteries and to provide users with objects of more economic value.

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# APPENDIX 1

## CALCULATION OF CHANGE IN VOLUME (ΔV) OF TITRANT

0.001M $Na^{++}$ at 30°C

1. @ pH 8.6, $\Delta V = 7.26 - 1.61 = 5.65$
2. @ pH 9.0, $\Delta V = 10.29 - 2.42 = 7.88$
3. @ pH 10.0, $\Delta V = 27.41 - 17.71 = 17.71$
4. @ pH 10.89, $\Delta V = 43.12 - 27.41 = 15.71$

0.001M $Na^{++}$ at 50°C

1. @ pH 9.5, $\Delta V = 22.51 - 16.49 = 8.02$
2. @ pH 9.8, $\Delta V = 31.41 - 17.71 = 13.70$

1.0M $Ca^{++}$ at 30°C

1. @ pH 9.4, $\Delta V = 32.21 - 3.22 = 28.99$
2. @ pH 10.0 , $\Delta V = 38.69 - 4.84 = 33.85$
3. @ pH 10.50, $\Delta V = 44.30 - 11.29 = 33.01$
4. @ pH 11.0, $\Delta V = 47.25 - 19.29 = 27.96$

1.0M $Ca^{++}$ at 50°C

1. @ pH 8.8, $\Delta V = 6.45 - 1.61 = 4.84$
2. @ pH 9.2, $\Delta V = 11.29 - 4.04 = 7.26$
3. @ pH 10.50, $\Delta V = 32.21 - 6.45 = 25.76$
4. @ pH 11.00, $\Delta V = 45.91 - 9.68 = 36.23$

0.1M $Ca^{++}$ at 50°C

1. @ pH 9.0, $\Delta V = 2.68 - 0.81 = 1.87$
2. @ pH 10.7, $\Delta V = 25.8 - 15.29 = 10.51$
3. @ pH 10.9, $\Delta V = 37.82 - 15.56 = 22.26$
4. @ pH 11.2, $\Delta V = 43.49 - 16.1 = 27.39$

0.01M $Ca^{++}$ at 30°C

1. @ pH 9.2, $\Delta V = 19.29 - 6.45 = 12.84$
2. @ pH 9.5, $\Delta V = 21.71 - 12.1 = 9.61$
3. @ pH 10.0, $\Delta V = 25.8 - 16.91 = 8.89$
4. @ pH 10.4, $\Delta V = 33.79 - 19.29 = 14.5$

0.01M $Ca^{++}$ at 50°C

1. @ pH 9.3, $\Delta V = 22.51 - 9.68 = 12.83$
2. @ pH 9.55, $\Delta V = 24.99 - 18.52 = 6.47$
3. @ pH 10.5, $\Delta V = 33.79 - 24.19 = 9.60$
4. @ pH 11.0, $\Delta V = 47.25 - 28.22 = 19.03$

0.001M $Ca^{++}$ at 30°C

1. @ pH 9.0, $\Delta V = 3.22 - 1.21 = 2.01$
2. @ pH 9.2, $\Delta V = 30.6 - 3.22 = 27.38$
3. @ pH 9.4, $\Delta V = 45.1\ 3.62 = 41.48$

0.001M $Ca^{++}$ at 50°C

1. @ pH 9.8, $\Delta V = 11.28 - 7.75 = 3.53$
2. @ pH 10.0, $\Delta V = 17.71 - 8.84 = 8.84$
3. @ pH 10.3, $\Delta V = 35.4 - 15.29 = 20.11$
4. @ pH 10.5, $\Delta V = 45.1 - 20.9 = 24.20$

1.0M $Pb^{++}$ at 30°C

1. @ pH 9.0, $\Delta V = 6.4 - 4.03 = 2.38$
2. @ pH 9.4, $\Delta V = 9.6 - 3.84 = 5.76$
3. @ pH 10.2, $\Delta V = 18.4 - 15.6 = 2.80$

1.0M $Pb^{++}$ at 50°C

1. @ pH 9.0, $\Delta V = 5.4 - 4.0 = 1.4$
2. @ pH 9.6, $\Delta V = 9.6 - 4.0 = 5.6$
3. @ pH 10.2, $\Delta V = 20.1 - 15.69 = 4.32$

0.1M $Pb^{++}$ at 50°C

1. @ pH 9.5, $\Delta V = 21.71 - 16.1 = 5.61$
2. @ pH 10.0, $\Delta V = 27.41 - 21.71 = 5.70$
3. @ pH 10.8, $\Delta V = 40.3 - 32.21 = 8.09$

0.01M $Pb^{++}$ at 30°C

1. @ pH 9.2, $\Delta V = 16.1 - 20.9 = 10.65$
2. @ pH 10.0, $\Delta V = 22.51 - 20.9 = 1.61$
3. @ pH 10.5, $\Delta V = 41.11 - 32.21 = 8.90$

0.01M $Pb^{++}$ at 50°C

1. @ pH 8.80, $\Delta V = 5.24 - 3.22 = 2.02$
2. @ pH 9.2, $\Delta V = 6.45 - 4.44 = 2.01$
3. @ pH 10.5, $\Delta V = 28.59 - 24.1 = 4.40$

0.01M $Mg^{++}$ at 30°C

1. @ pH 9.6, $\Delta V = 17.71\ 5.65 = 12.07$
2. @ pH 10.0, $\Delta V = 27.41 - 16.91 = 10.51$
3. @ pH 9.8, $\Delta V = 26.61 - 16.50 = 10.10$

0.01M $Mg^{++}$ at 50°C

1. @ pH 8.5, $\Delta V = 4.03 - 1.61 = 2.42$
2. @ pH 9.3, $\Delta V = 14.49 - 6.06 = 8.44$
3. @ pH 9.5, $\Delta V = 25.8 - 9.68 = 16.12$

0.001M $Mg^{++}$ at 30°C

1. @ pH 8.5, $\Delta V = 4.44 - 2.01 = 2.43$
2. @ pH 9.2, $\Delta V = 25.8 - 17.71 = 8.09$
3. @ pH 9.4, $\Delta V = 33.79 - 18.52 = 15.28$
4. @ pH 9.6, $\Delta V = 45.1 - 22.51 = 22.59$

0.001M $Mg^{++}$ at 50°C

1. @ pH 8.5, $\Delta V = 6.45 - 2.82 = 3.63$
2. @ pH 9.0, $\Delta V = 9.28 - 4.44 = 4.84$
3. @ pH 9.5, $\Delta V = 16.1\ 11.29 = 4.81$
4. @ pH 9.8, $\Delta V = 35.4 = 20.9 = 14.5$

# APPENDIX 2

## CALCULATION OF ADSORPTION AND SURFACE CHARGE

Table 4.67: 0.1M Sodium ion ($Na^+$) analysis at 30°C

| PH value | Change in volume ($\Delta V$), (ml) | Adsorption($\theta$), (mole/cm$^2$) X $10^{-12}$ | Surface charge ($E_v$) (coulombs/cm$^2$) x$10^{-7}$ |
|---|---|---|---|
| 9.60 | 10.00 | 10.923 | 10.541 |
| 10.80 | 14.40 | 15.729 | 15.178 |
| 11.20 | 17.40 | 19.006 | 18.341 |
| Average | | | 14.687 |

1. ADSORPTION

Adsorption ($\theta$) = $\Delta V$ x C / (s x 1000)

= 10 x C/(s x 1000)

where s = 1719.3 m$^2$/g

C = concentration of NaOH (mole/liter )

= 4g/100ml = 0.04 g/ml

= 0.04g/ml x ( 1/S.G)

S.G of NaOH = 2.130 g/mole

= 0.04g/ml x (1 mole/ 2.130g)

= 0.01878 mole/ml

= 0.01878 mole/ml x 1000ml/ liter

= 18.78 mole/ liter

$$\theta = \frac{(\Delta V \text{ liter}) \times (18.78 \text{ mole/ liter})}{(1719.3\text{m}^2/\text{g}) \times (1\text{g}) \times (10^4 \text{ cm}^2/\text{m}^2) \times 1000}$$

$$= \frac{\Delta V \text{ liters } (18.78 \text{ mole/ liter})}{1719.3 m^2/g \times 1 g \times 10^4 \, cm^2/m^2 \times 1000}$$

$= (\Delta V \text{ liters}) \times 1.09231 \times 10^{-9}$

$= (\Delta V \text{ ml} \times (\text{ liters/ } 1000 \text{ ml})) \times 1.09231 \times 10^{-9}$

$= \Delta V \times 1.09231 \times 10^{-12}$ mole/ $cm^2$

So at $\Delta V = 10$ml,

$=10 \times 1.09231 \times 10^{-12} = 10.92 \times 10^{-12}$ mole/ $cm^2$

2. SURFACE CHARGE (Ev = Y)

$E_v = n F \theta$

n = number of ionic charge, F = Faradays constant = 96500 coulombs

For Na+ with $\Delta V = 10$ml, $\theta = 10.92 \times 10^{-12}$

$E_v = Y = 1 \times 96500 \times 10.92 \times 10^{-12} = 10.541 \times 10^{-6}$ coulombs/$m^2$

As the internal resistance of leclanche' cell is 10 ohms, v = I R = 10 x I = 10I

3. Charge conversion

3600 * coulombs (absolute) = amperes (absolute)

0.00125 x 3600 = 4.5A(Absolute) per square meter

0.00150 x 3600 = 5.4 A

0.00180 x 3600 = 6.48A

4. Voltage/ Potential calculation

(since the internal resistance of leclanche' cell is 10 volt, v = I R = 10 x I =10I)

Therefore,

4.5A x 10 = 45V,

5.4V x 10 = 54V

6.48 x 10 = 64.8V

and

5. Usage Time Calculation

Since , 1.5V = 300s

45V = 300s/1.5V x 45 = 9000 / $m^2$

54V = 300s/1.5V x 54 = 10800/ $m^2$

64.8V = 300s/1.5V x 64.8 = 12960/ $m^2$

9000(s/$m^2$) / 18.78 = 479.23(s/$m^2$) /NaOH

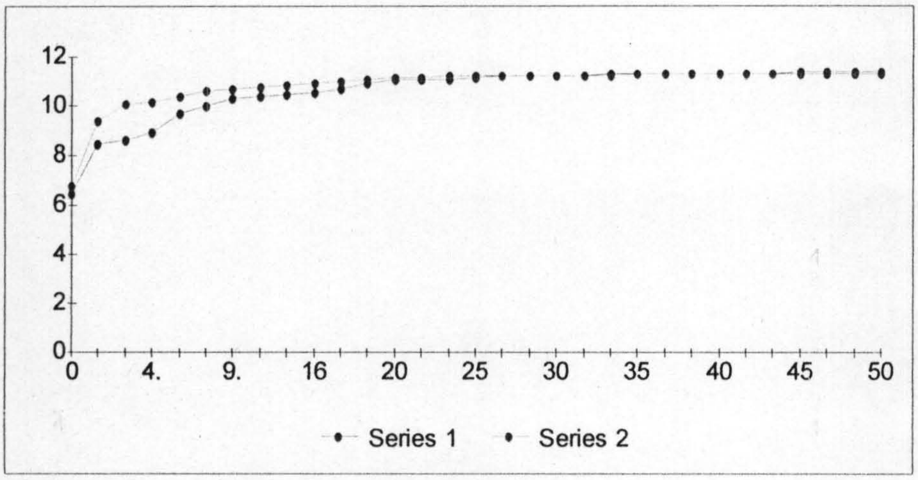
10800(s/$m^2$)/18.78 = 575.08(s/$m^2$)/NaOH

12960(s/$m^2$)/18.78 = 690.10(s/$m^2$)/NaOH

## APPENDIX 3

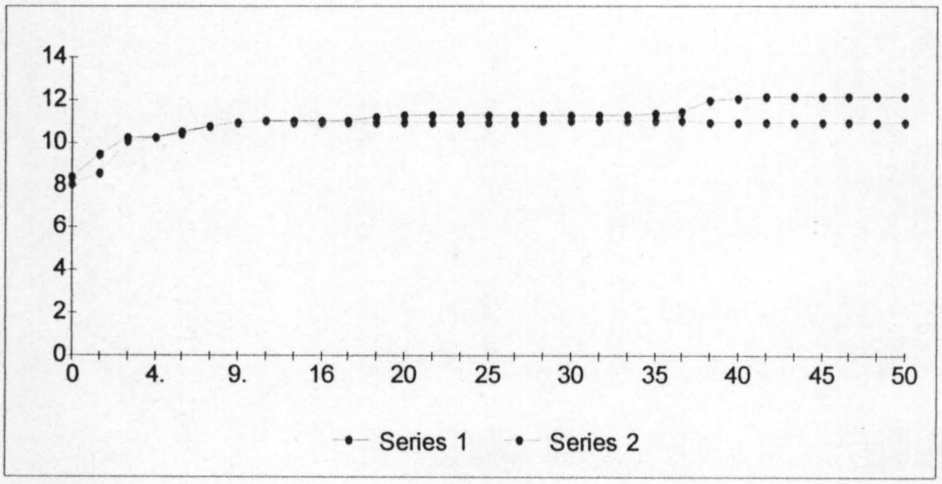
### 4.2.1 Graphical analysis of the changes in volumes of titrant

**(Series 1 and 2represent adsorption without and with $MnO_2$ respectively)**



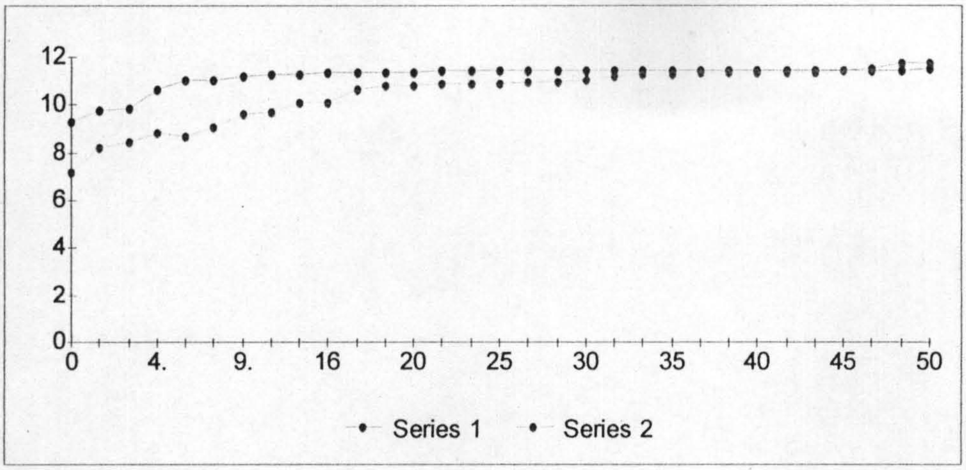
(pH = y axis, vol of titrant = x axis)

Figure. 4.1: pH vs Volume of Titrant plot for 1.0M $NaNO_3$ at 30°C



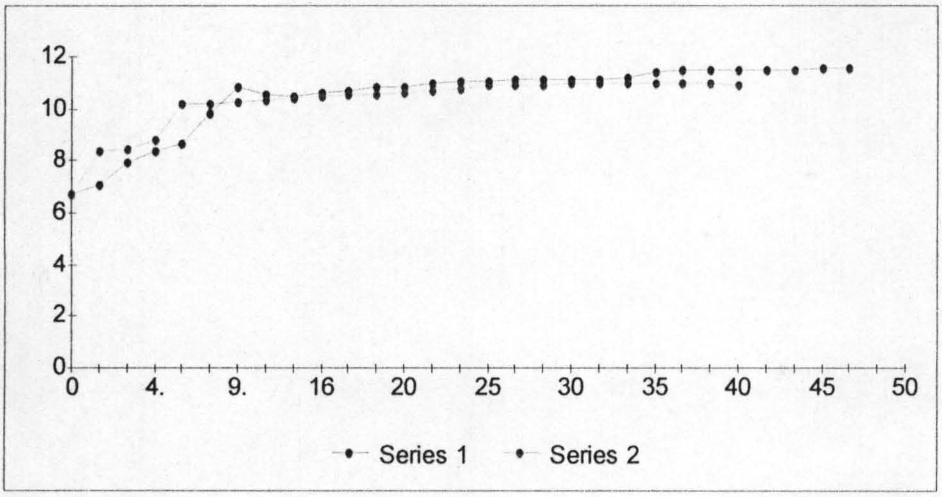
(pH = y axis, vol of titrant = x axis)

Figure 4.2: pH vs Volume of Titrant plot for 1.0M $NaNO_3$ at 50°C



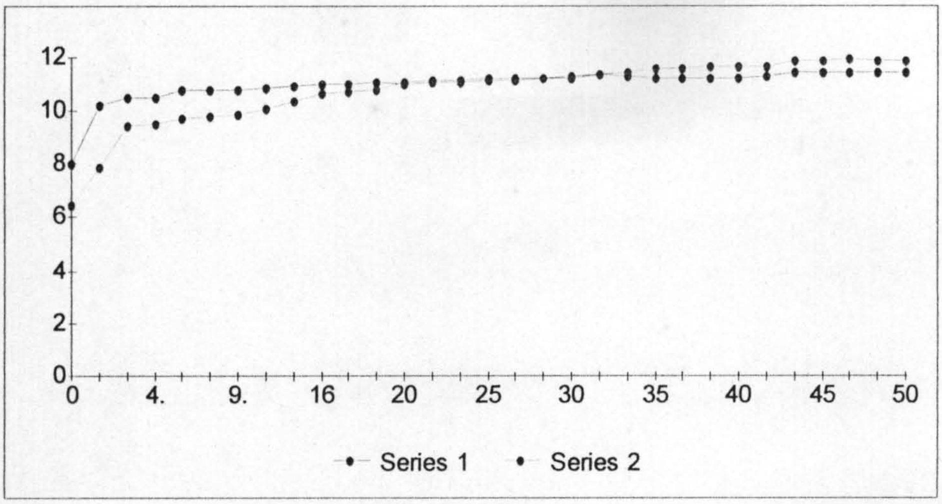
(pH = y axis, vol of titrant = x axis)

Figure 4.3: pH vs Volume of Titrant plot for 0.1M $NaNO_3$ at 30°C



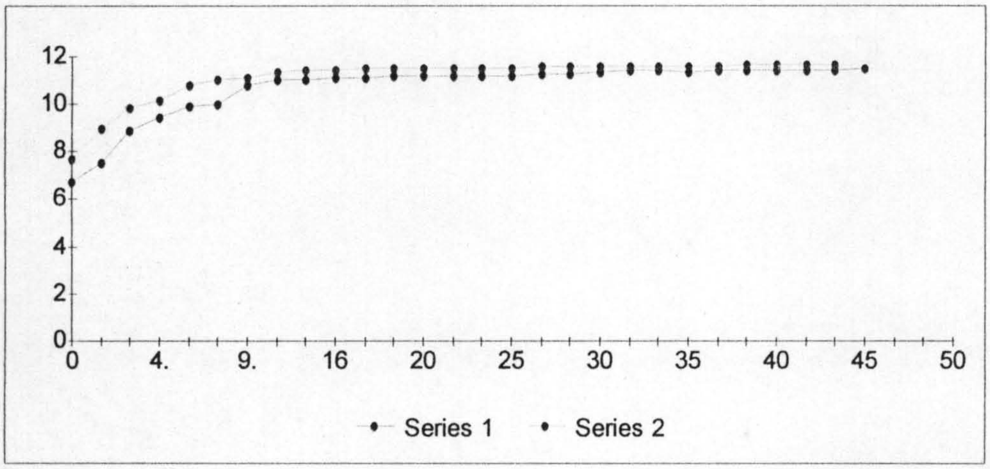
(pH = y axis, vol of titrant = x axis)

Figure 4.4: pH vs Volume of Titrant plot for 0.1M $NaNO_3$ at 50°C



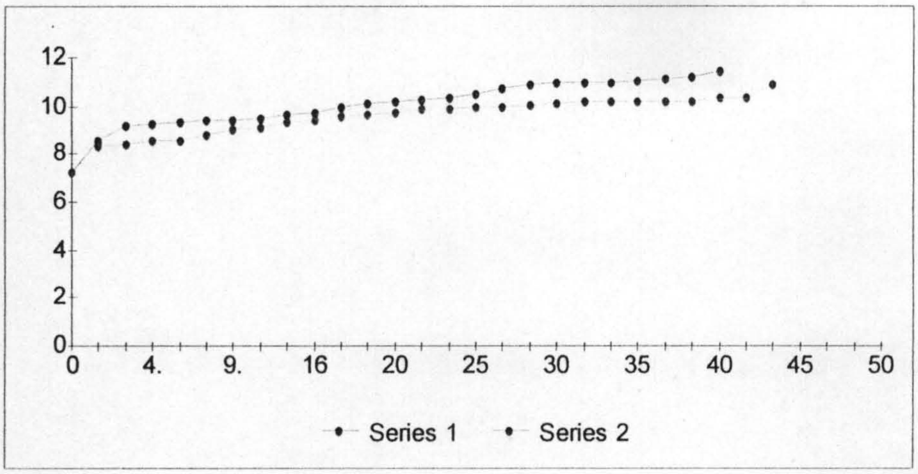
(pH = y axis, vol of titrant = x axis)

Figure 4.5: pH vs Volume of Titrant plot for 0.01M $NaNO_3$ at 30°C



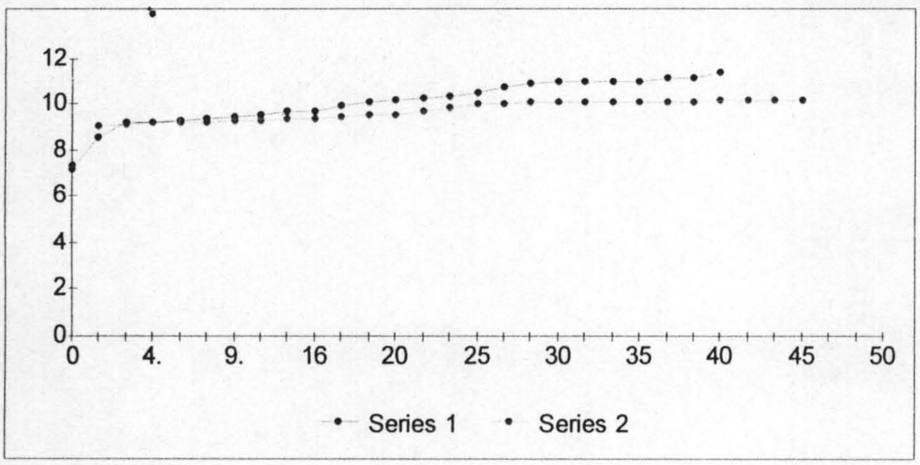
(pH = y axis, vol of titrant = x axis)

Figure 4.6: pH vs Volume of Titrant plot for 0.01M $NaNO_3$ at 50°C



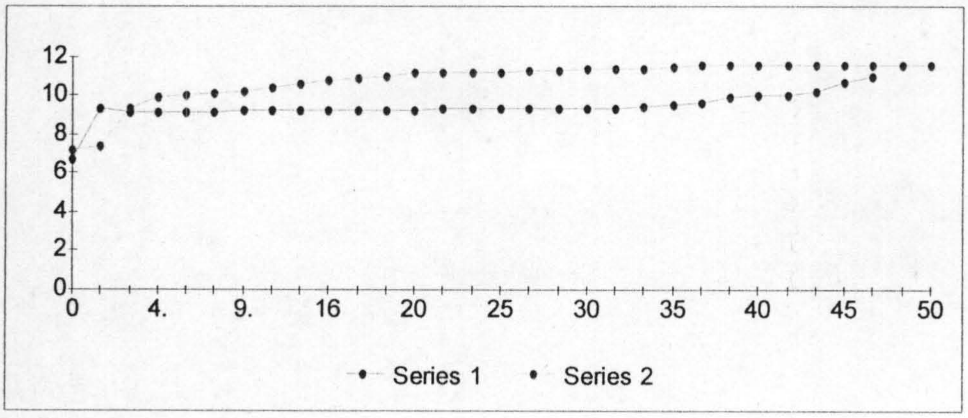
(pH = y axis, vol of titrant = x axis)

Figure 4.7: pH vs Volume of Titrant plot for 0.001M $NaNO_3$ at 30°C



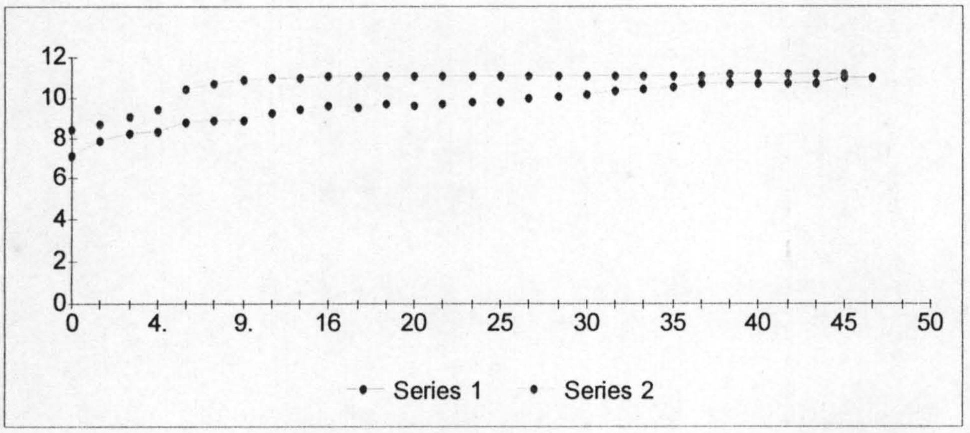
(pH = x axis, vol of titrant = y axis)

Figure 4.8: pH vs Volume of Titrant plot for 0.001M $NaNO_3$ at 50°C



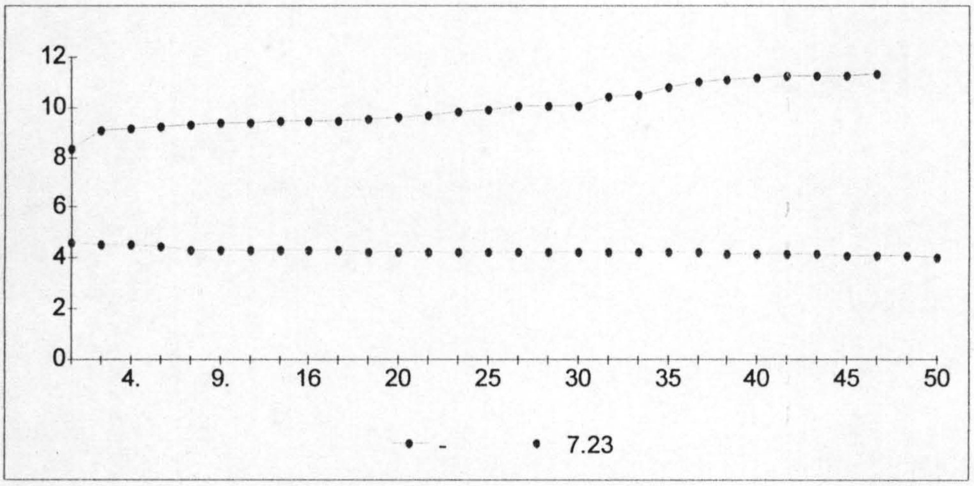
(pH = y axis, vol of titrant = x axis)

Figure 4.9: pH vs Volume of Titrant plot for 1.0M $Ca(NO_3)_2$ at 30°C



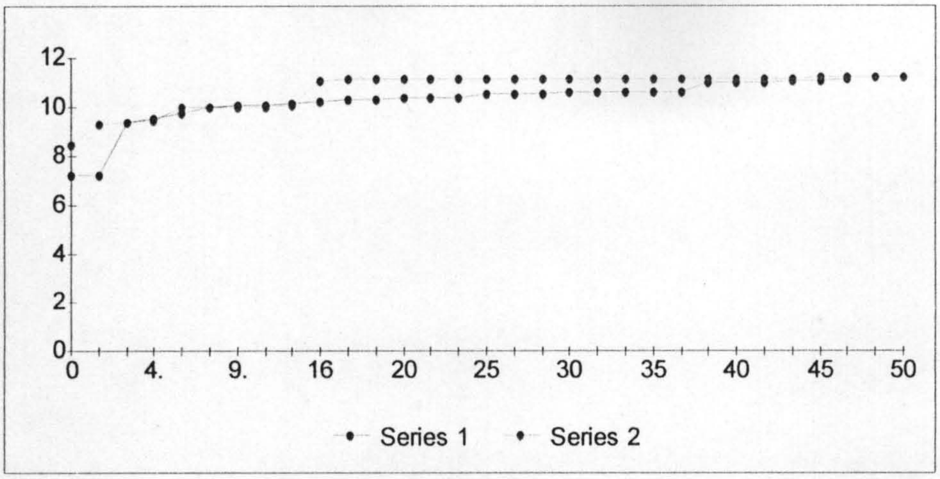
(pH = y axis, vol of titrant = x axis)

Figure 4.10: pH vs Volume of Titrant plot for 1.0M $Ca(NO_3)_2$ at 50°C



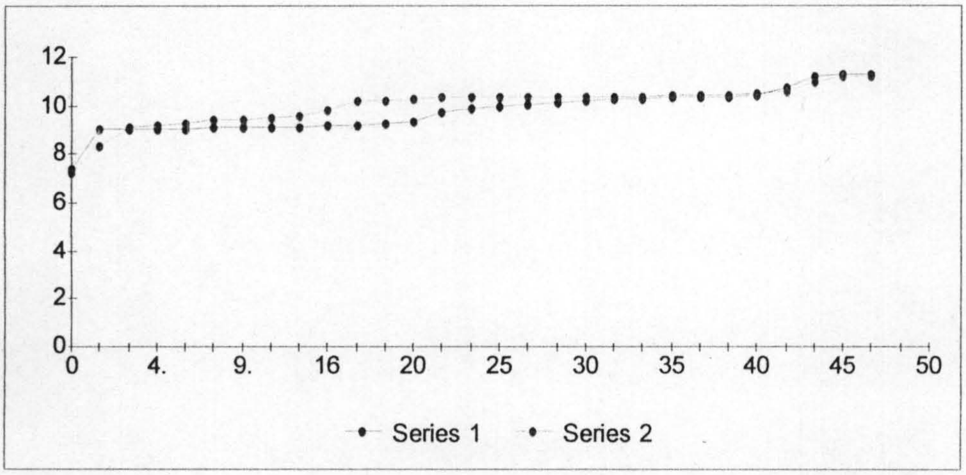
(pH = y axis, vol of titrant = x axis)

Figure 4.11: pH vs Volume of Titrant plot for 0.1M $Ca(NO_3)_2$ at 30°C



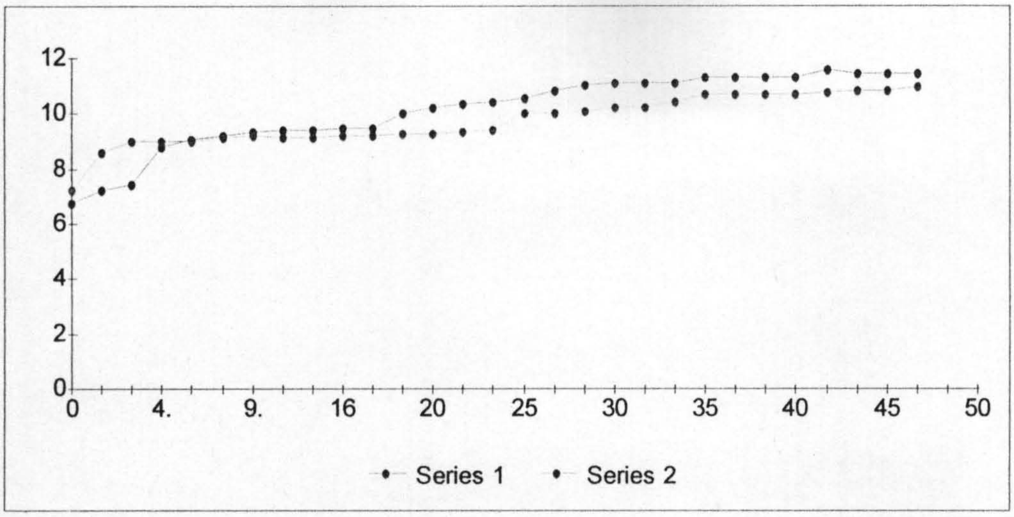
(pH = y axis, vol of titrant = x axis)

Figure 4.12: pH vs Volume of Titrant plot for 0.1M $Ca(NO_3)_2$ at 50°C



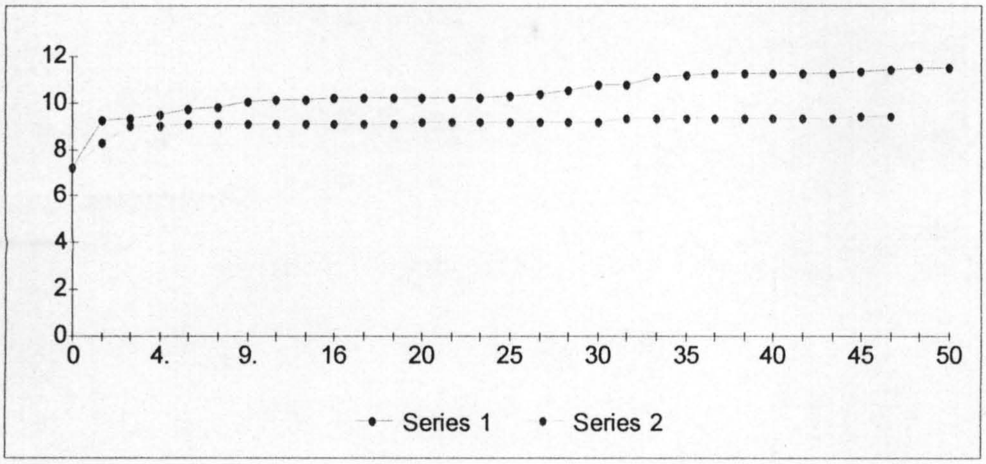
(pH = y axis, vol of titrant = x axis)

Figure 4.13: pH vs Volume of Titrant plot for 0.01M $Ca(NO_3)_2$ at 30°C



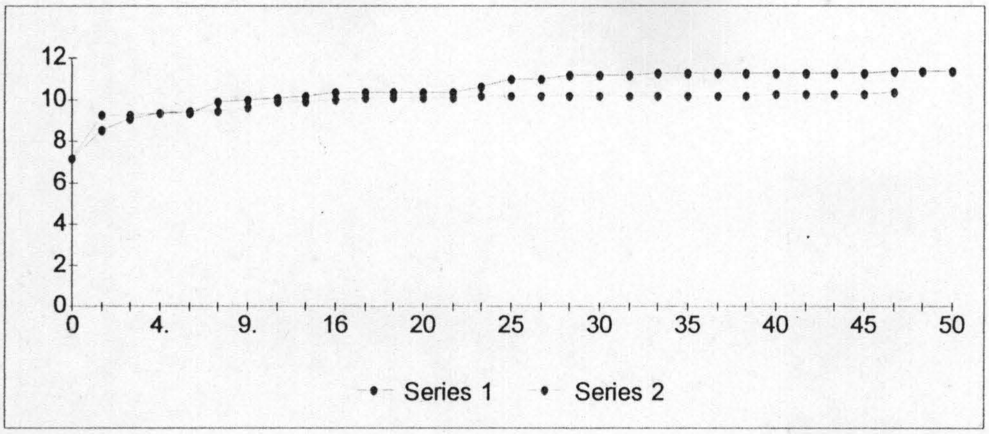
(pH = y axis, vol of titrant = x axis)

Figure 4.14: pH vs Volume of Titrant plot for 0.01M $Ca(NO_3)_2$ at 50°C



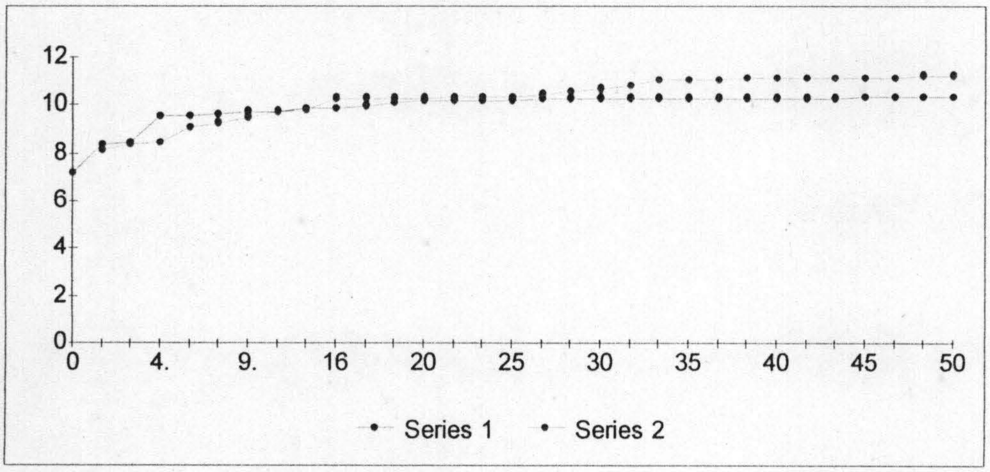
(pH = y axis, vol of titrant = x axis)

Figure 4.15: pH vs Volume of Titrant plot for 0.001M $Ca(NO_3)_2$ at 30°C



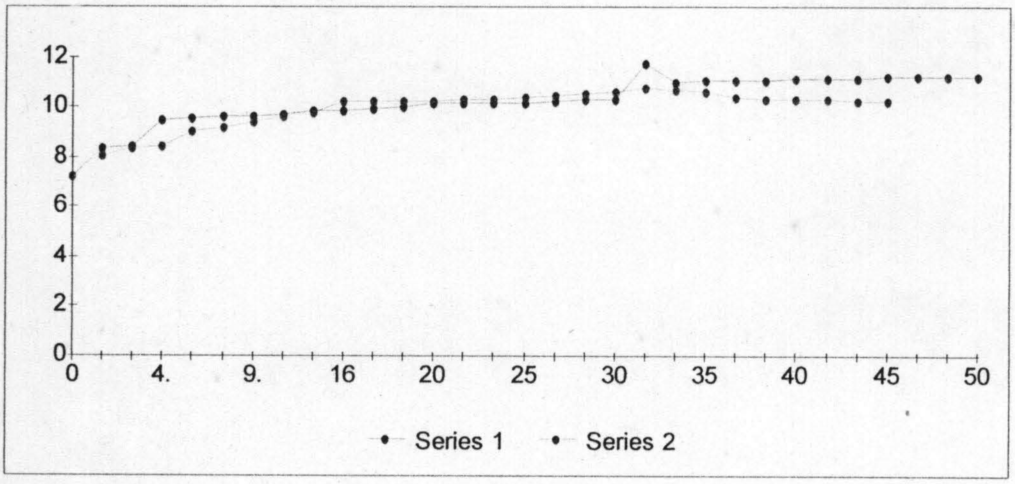
(pH = y axis, vol of titrant = x axis)

Figure 4.16: pH vs Volume of Titrant plot for 0.001M $Ca(NO_3)_2$ at 50°C



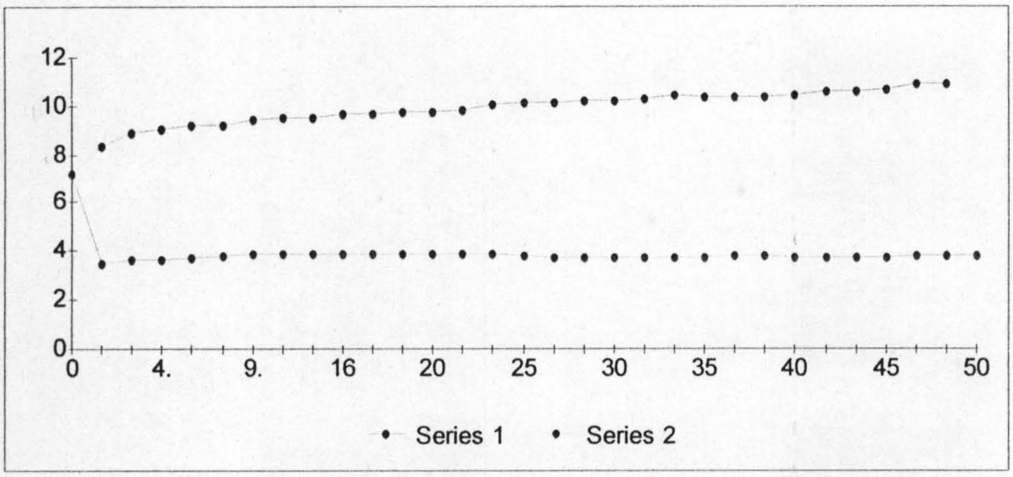
(pH = y axis, vol of titrant = x axis)

Figure 4.17: pH vs Volume of Titrant plot for 1.0M $Pb(NO_3)_2$ at 30°C



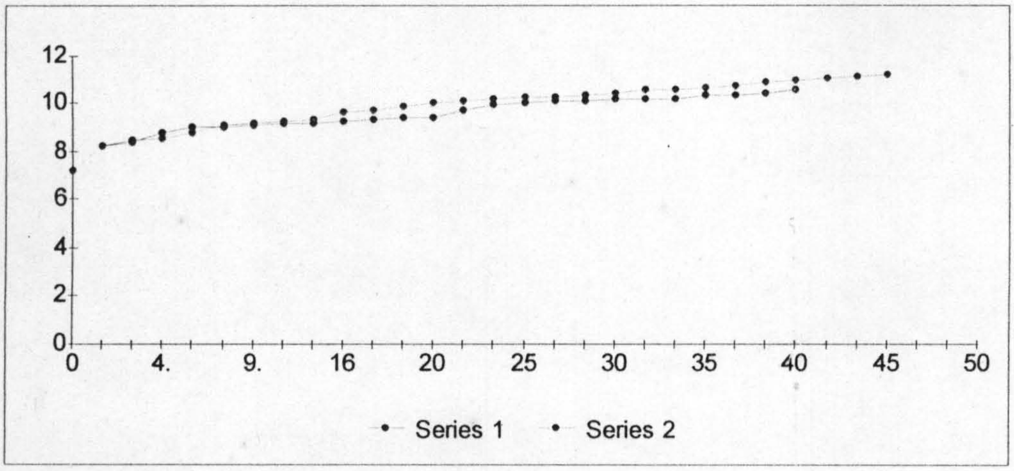
(pH = y axis, vol of titrant = x axis)

Figure 4.18: pH vs Volume of Titrant plot for 1.0M $Pb(NO_3)_2$ at 50°C



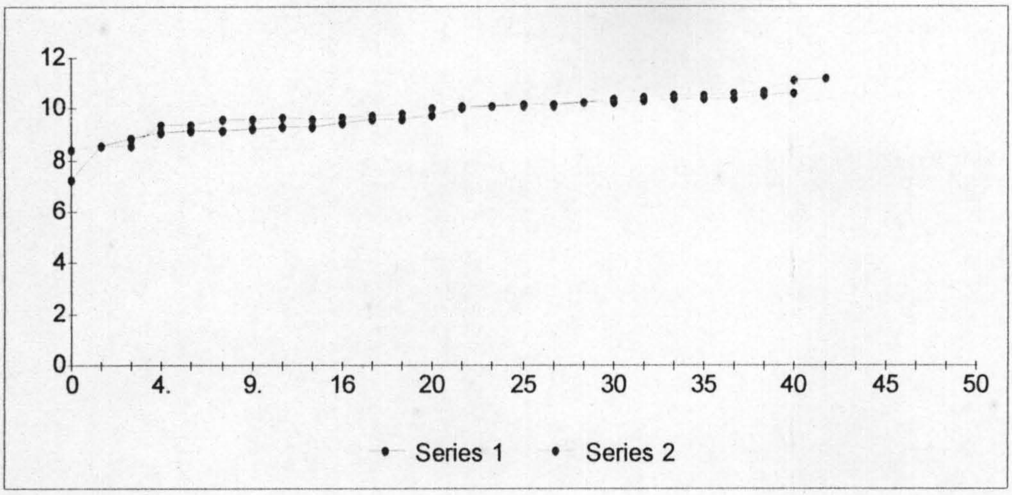
(pH = y axis, vol of titrant = x axis)

Figure 4.19: pH vs Volume of Titrant plot for 0.1M $Pb(NO_3)_2$ at 30°C



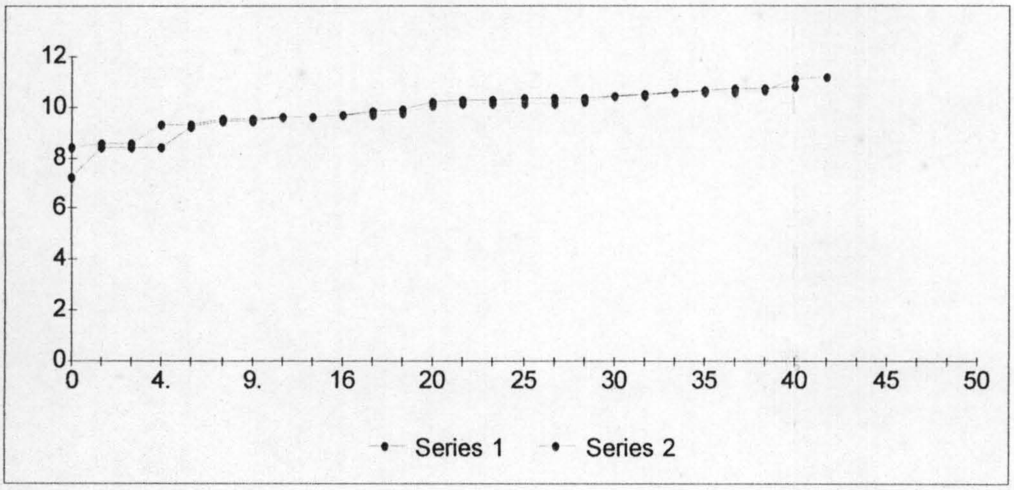
(pH = y axis, vol of titrant = x axis)

Figure 4.20: pH vs Volume of Titrant plot for 0.1M $Pb(NO_3)_2$ at 50°C



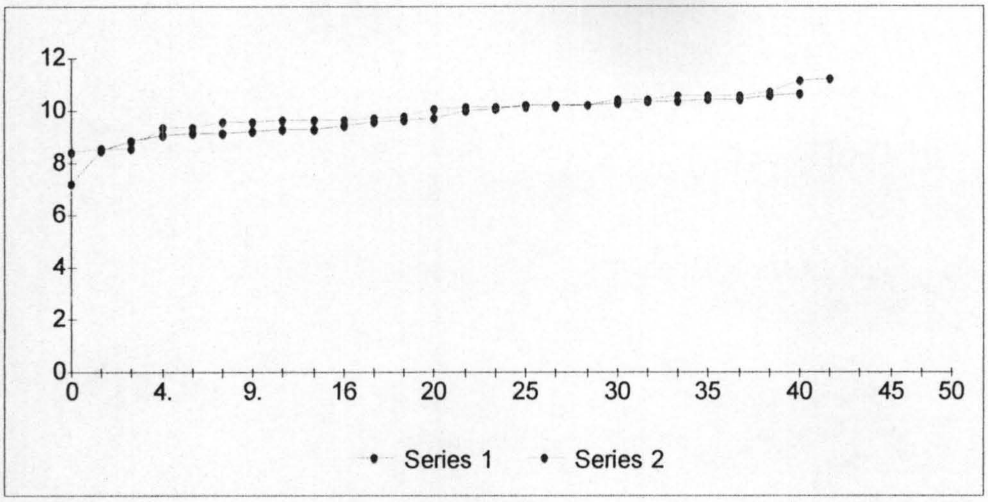
(pH = y axis, vol of titrant = x axis)

Figure 4.21: pH vs Volume of Titrant plot for 0.01M $Pb(NO_3)_2$ at 30°C



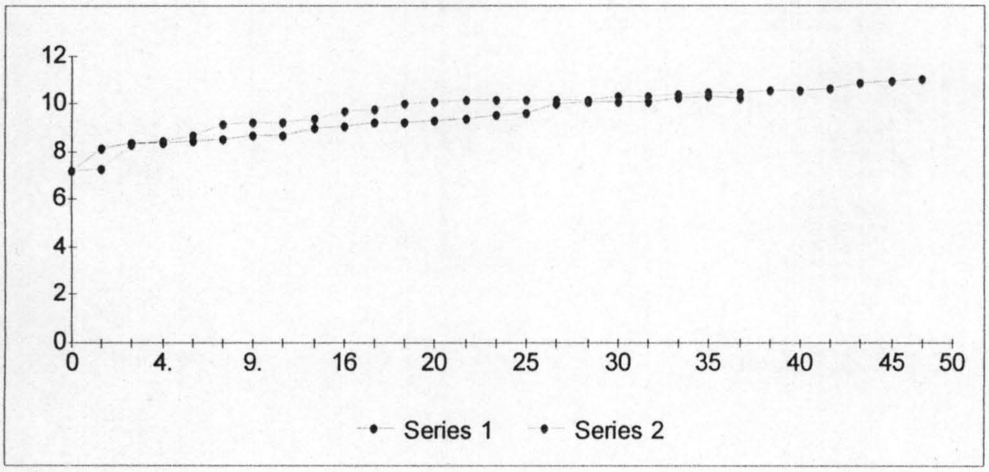
(pH = y axis, vol of titrant = x axis)

Figure 4.22: pH vs Volume of Titrant plot for 0.01M $Pb(NO_3)_2$ at 50°C



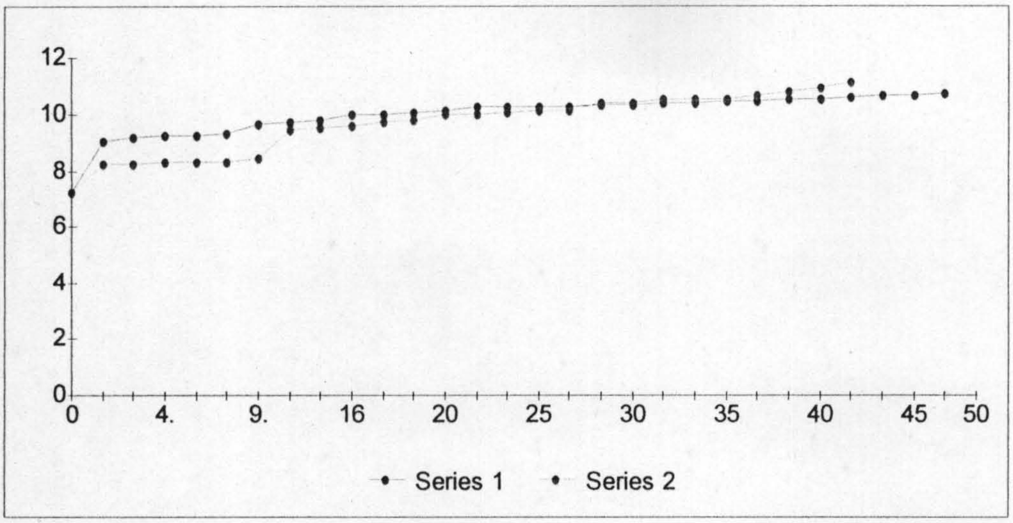
(pH = y axis, vol of titrant = x axis)

Figure 4.23: pH vs Volume of Titrant plot for 0.001M $Pb(NO_3)_2$ at 30°C



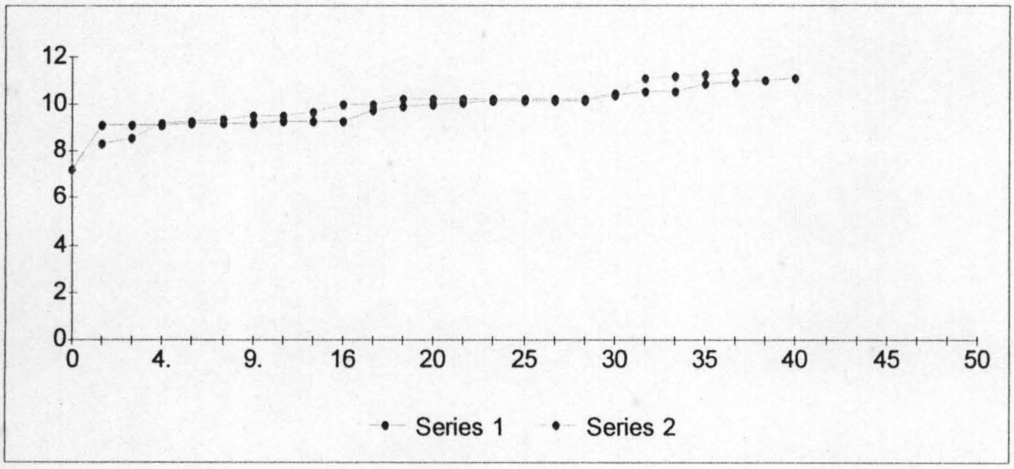
(pH = y axis, vol of titrant = x axis)

Figure 4.24: pH vs Volume of Titrant plot for 0.001M $Pb(NO_3)_2$ at 50°C



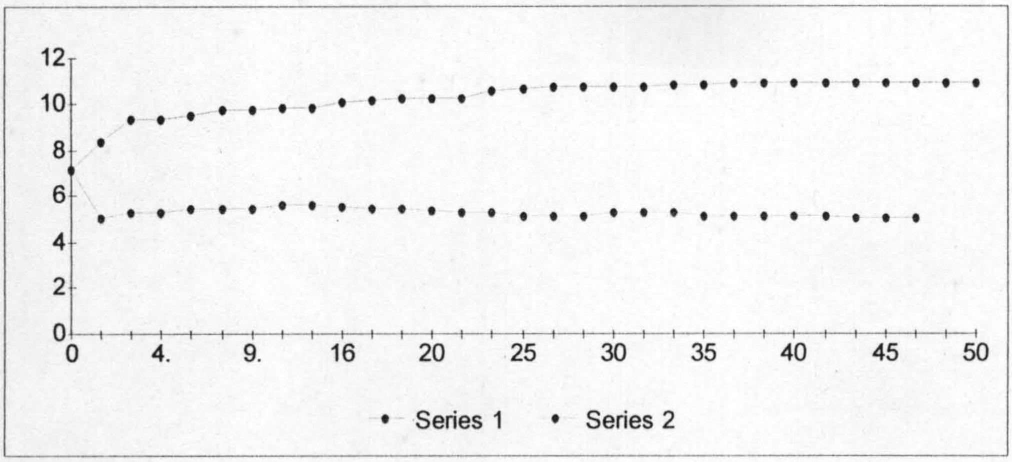
(pH = y axis, vol of titrant = x axis)

Figure 4.25: pH vs Volume of Titrant plot for 1.0M $Mg(NO_3)_2$ at 30°C



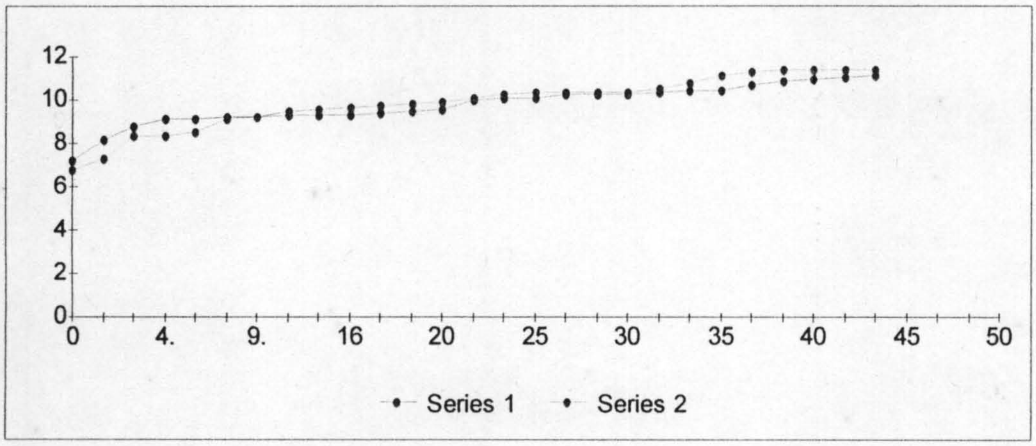
(pH = y axis, vol of titrant = x axis)

Figure 4.26: pH vs Volume of Titrant plot for 1.0M $MgNO_3)_2$ at 50°C



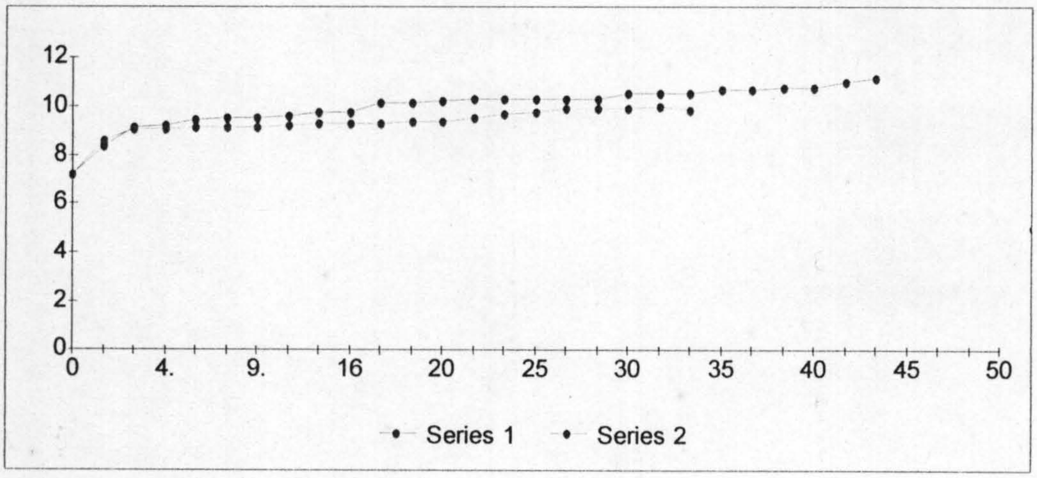
(pH = y axis, vol of titrant = x axis)

Figure 4.27: pH vs Volume of Titrant plot for 0.1M $Mg(NO_3)_2$ at 30°C



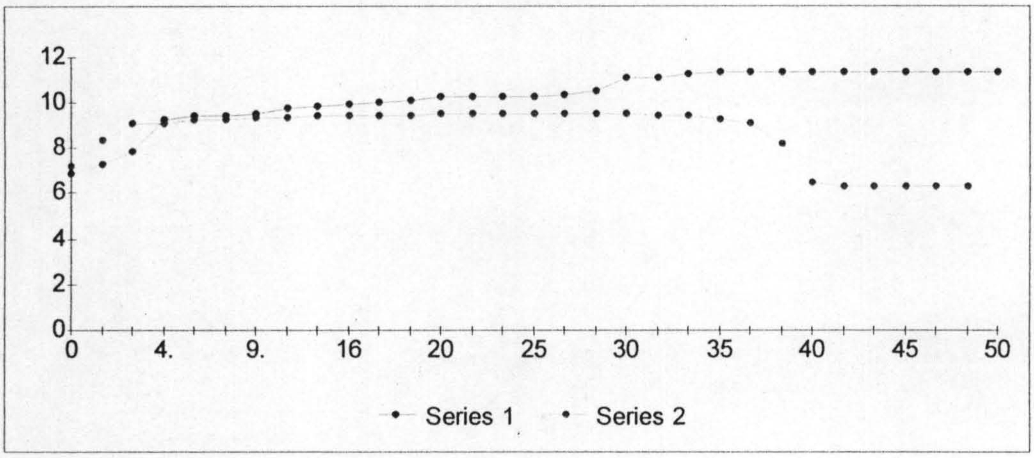
(pH = y axis, vol of titrant = x axis)

Figure 4.28: pH vs Volume of Titrant plot for 0.1M $Mg(NO_3)_2$ at 50°C



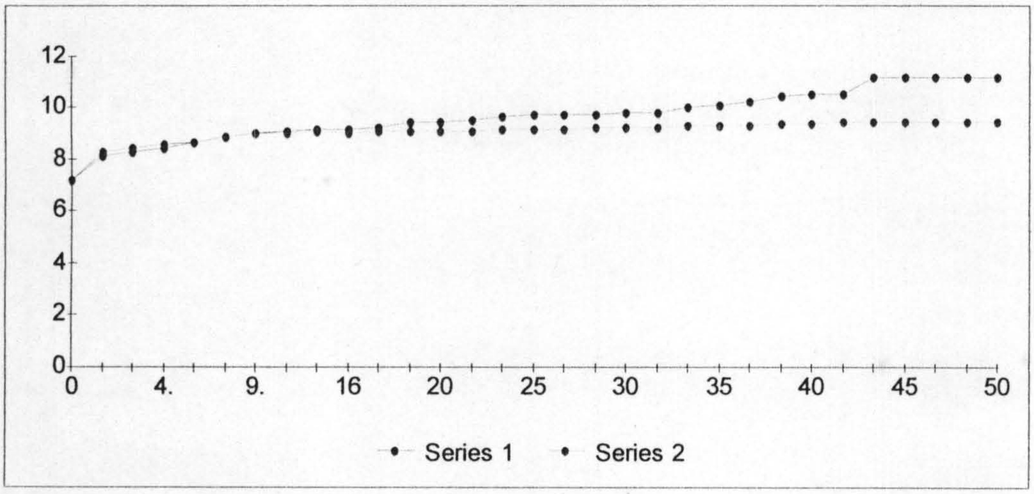
(pH = y axis, vol of titrant = x axis)

Figure 4.29: pH vs Volume of Titrant plot for 0.01M Mg(NO$_3$)$_2$ 30°C



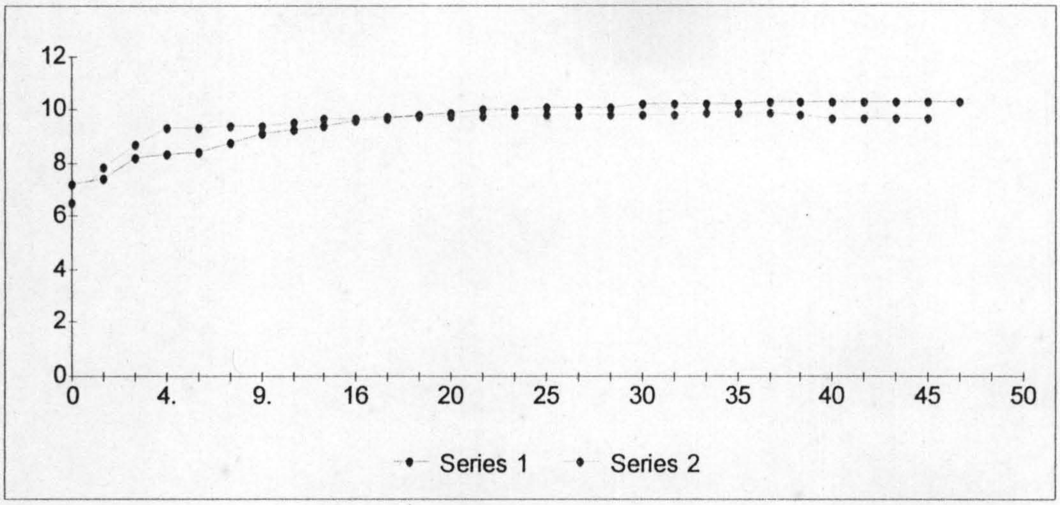
(pH = y axis, vol of titrant = x axis)

Figure 4.30: pH vs Volume of Titrant plot for 0.01M Mg(NO$_3$)$_2$ at 50°C



(pH = y axis, vol of titrant = x axis)

Figure 4.31: pH vs Volume of Titrant plot for 0.001M Mg(NO$_3$)$_2$ at 30°C



(pH = y axis, vol of titrant = x axis)

Figure 4.32: pH vs Volume of Titrant plot for 0.001M $Mg(NO_3)_2$ at 50°C

# APPENDIX 4

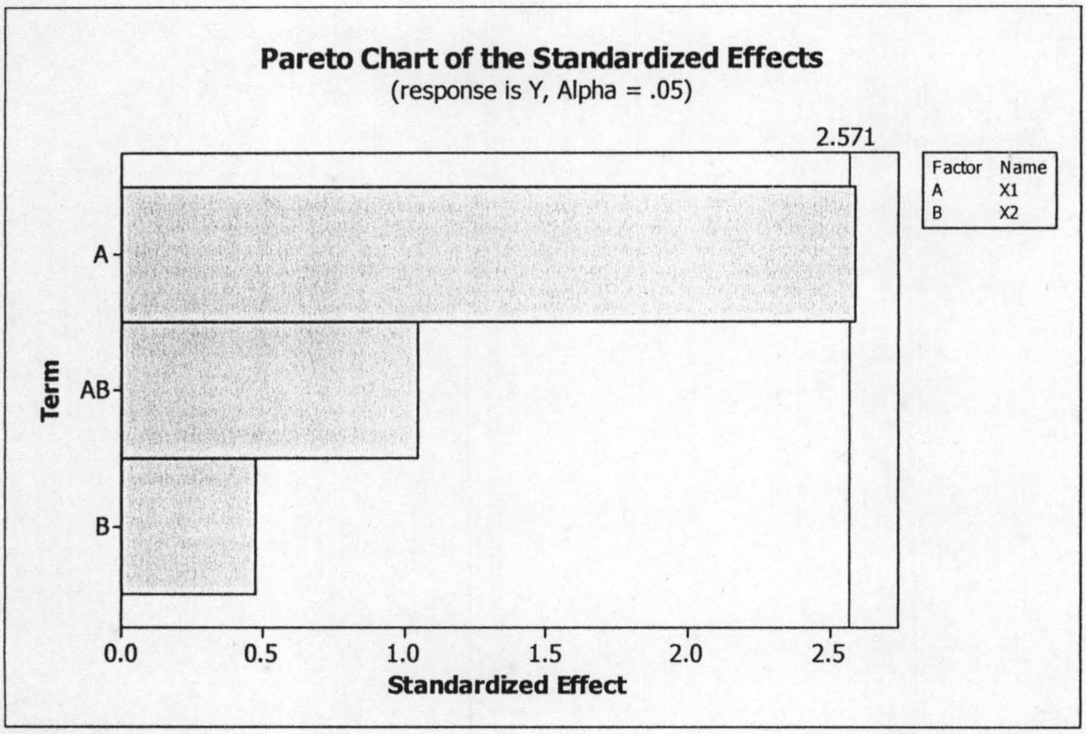


Figure 4.33a; Pareto Chart of the Standard effects

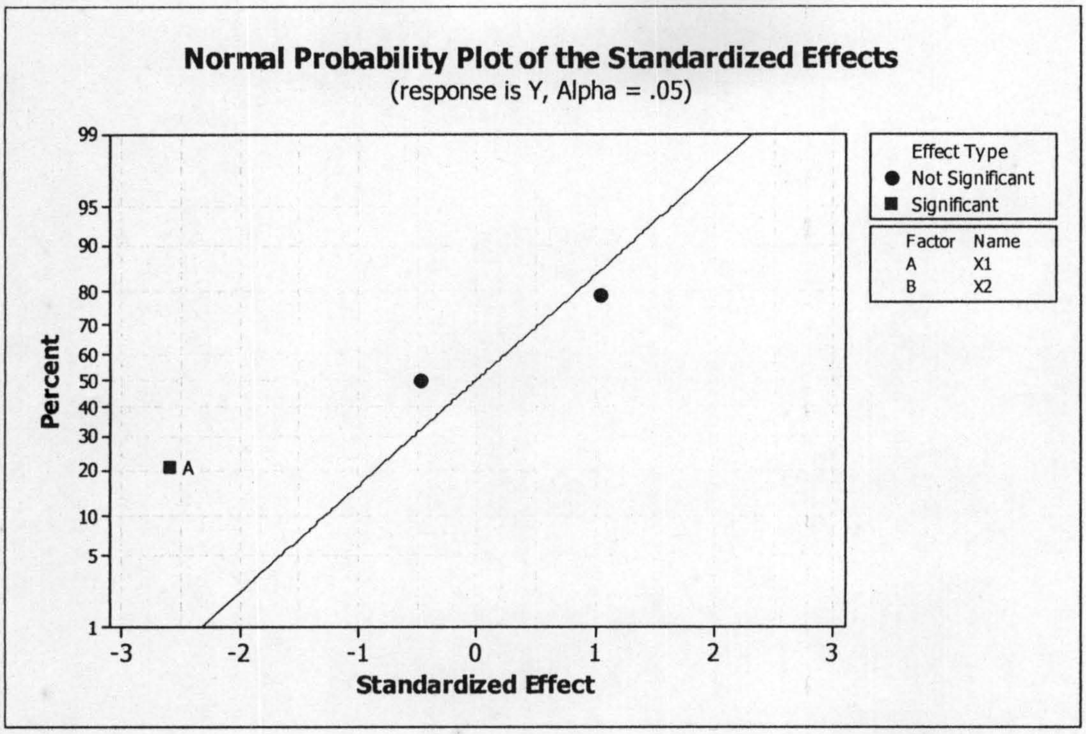


Figure 4.33 b; = Normal Probability Plot of the Standard effects

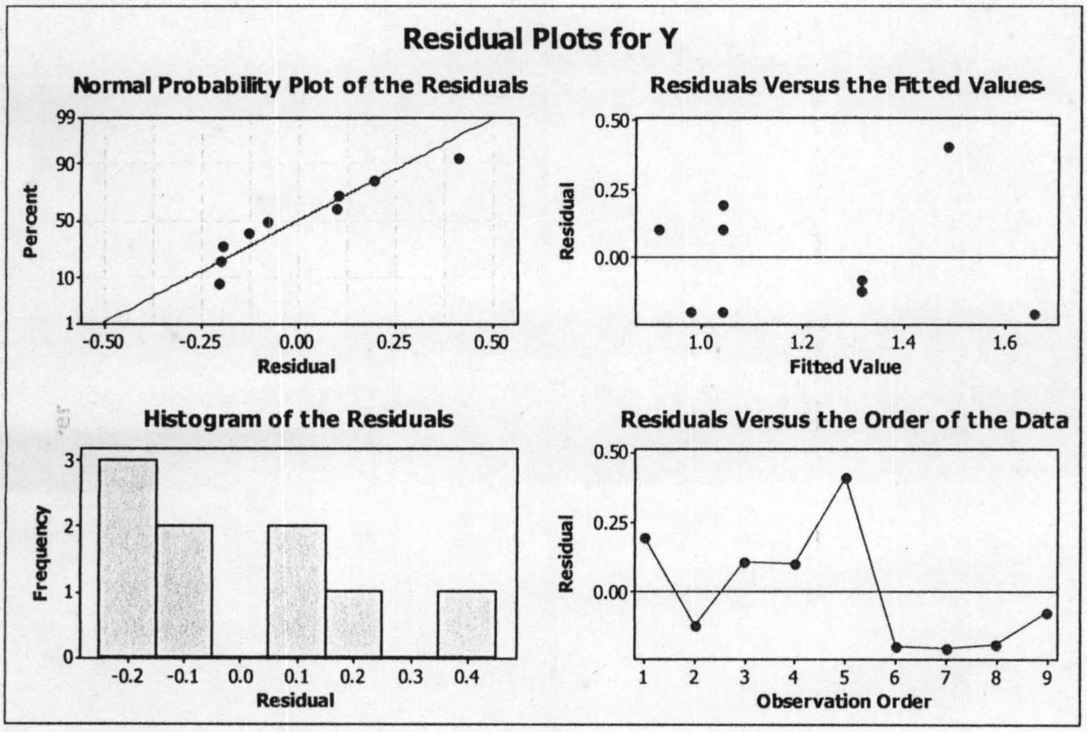


Figure 4.33c; Residual Plots for Y

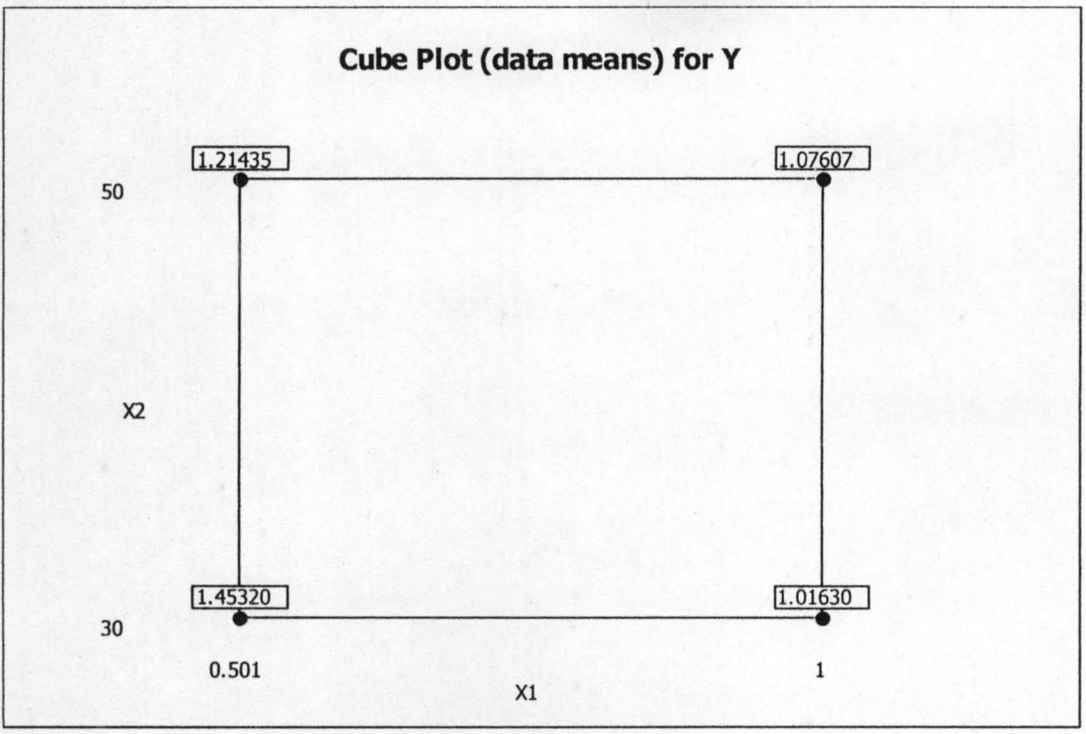


Figure 4.33d; Cube Plot (data means) for Y

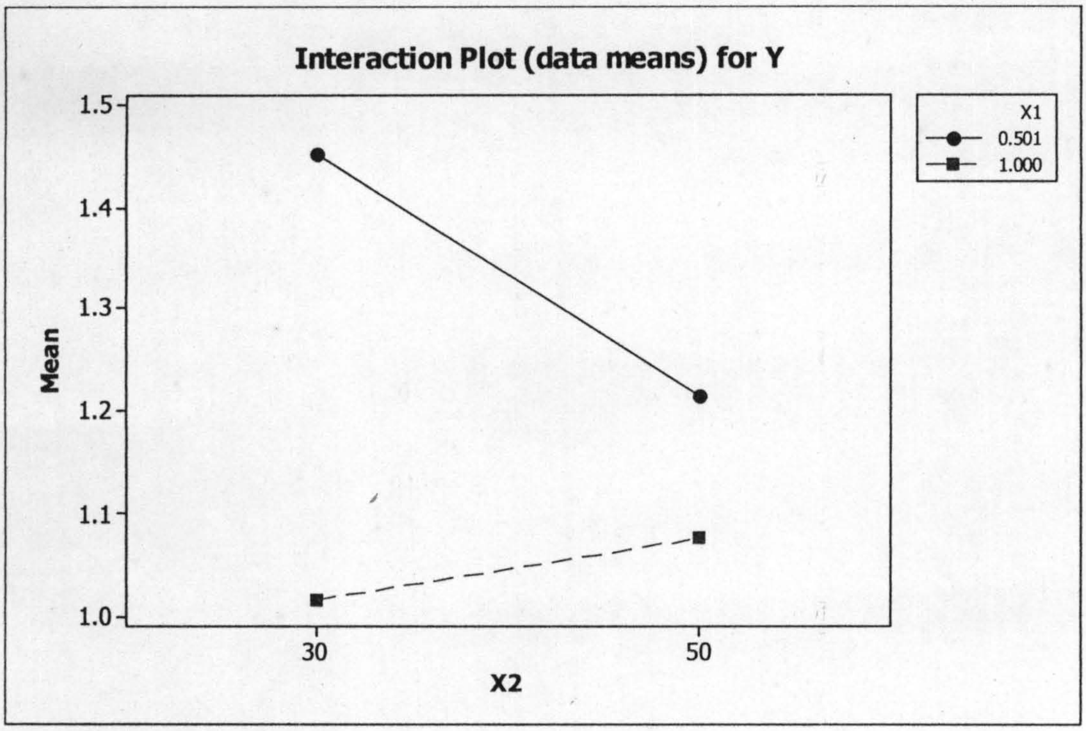


Figure 4.33e; Interaction Plot (data means) for Y

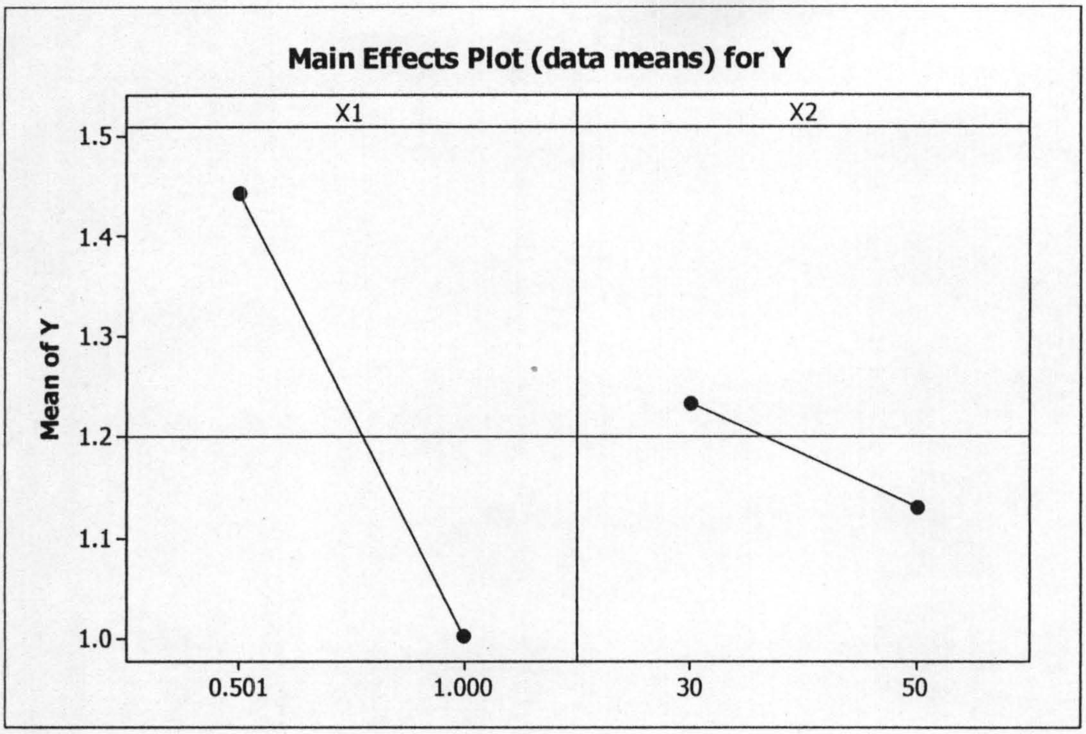


Figure 4.33f; Main Effects Plot (data means) for Y

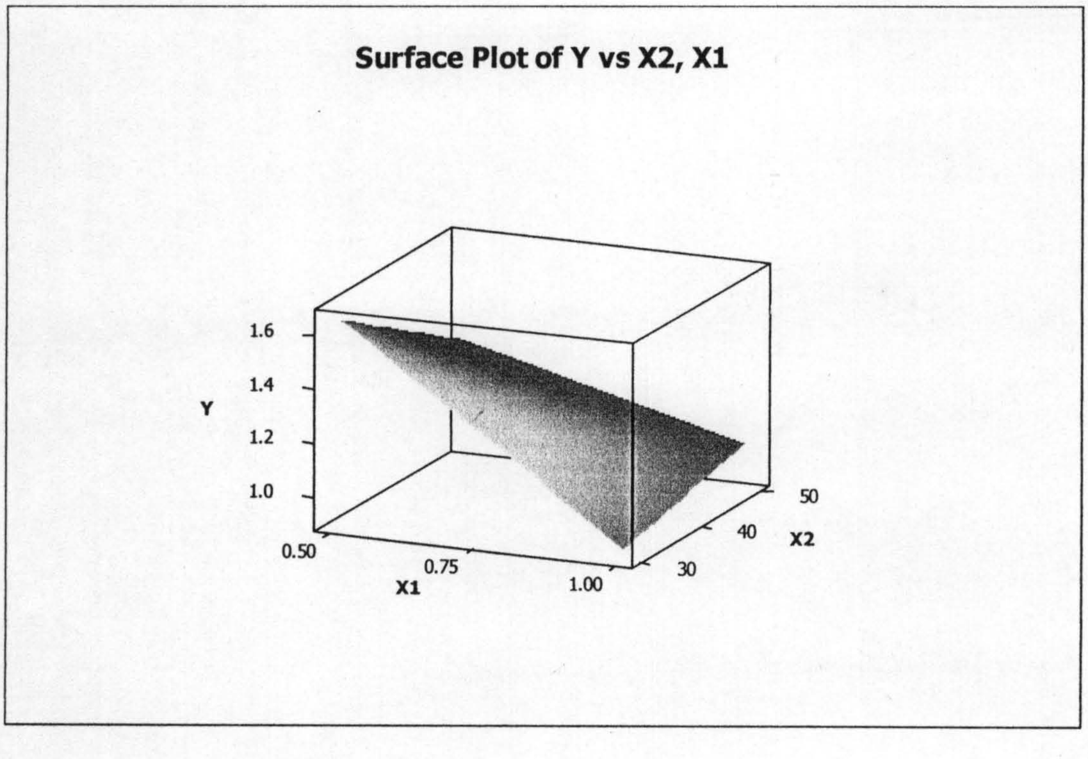


Figure 4.33g; Surface plot of Sodium Ion Response (Y) vs X1, X2

# APPENDIX 5

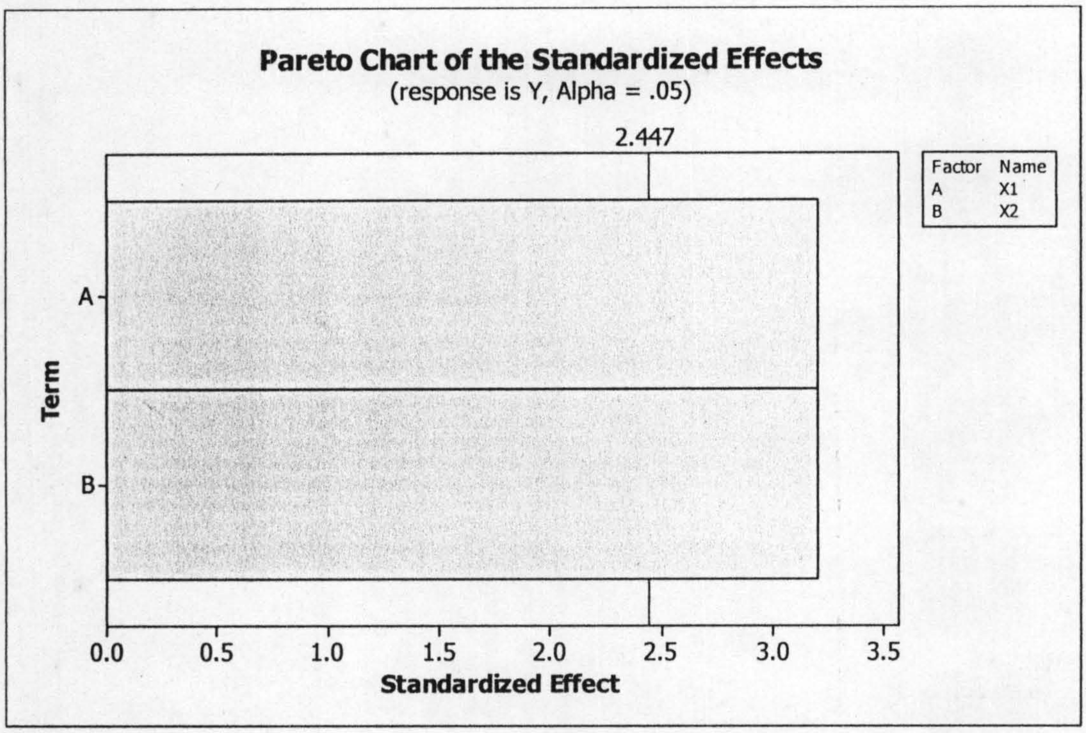


Figure 4.34a; Pareto chart of the Standard Effects

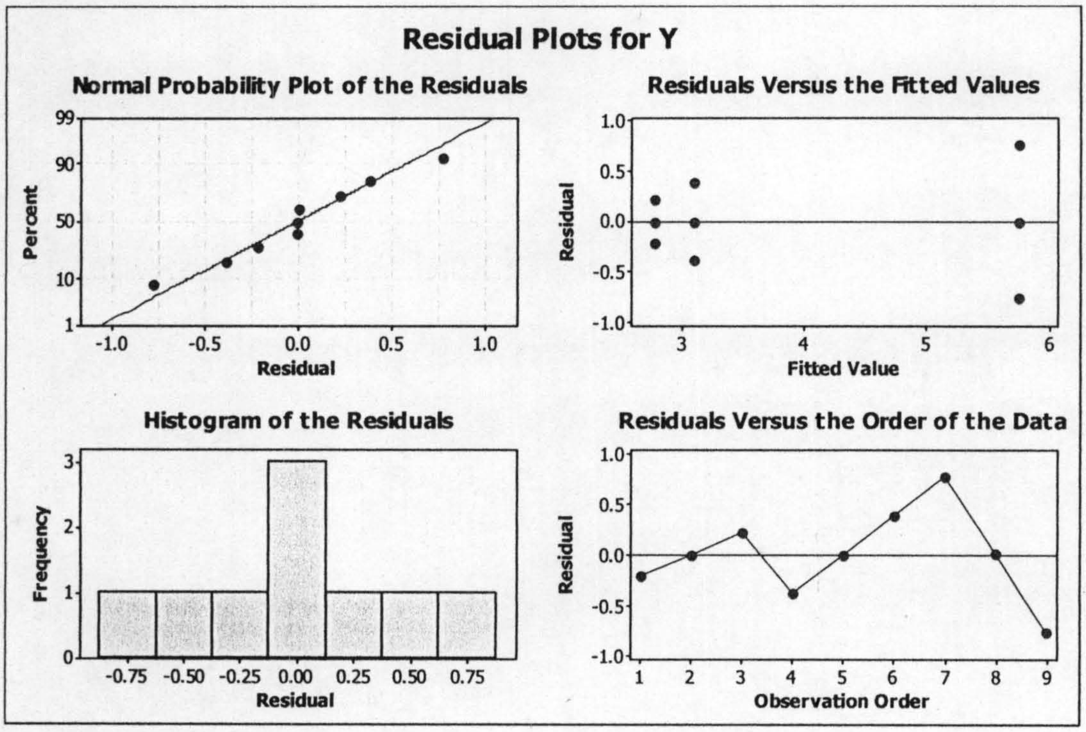


Figure 3.34b; Residual Plots for Y

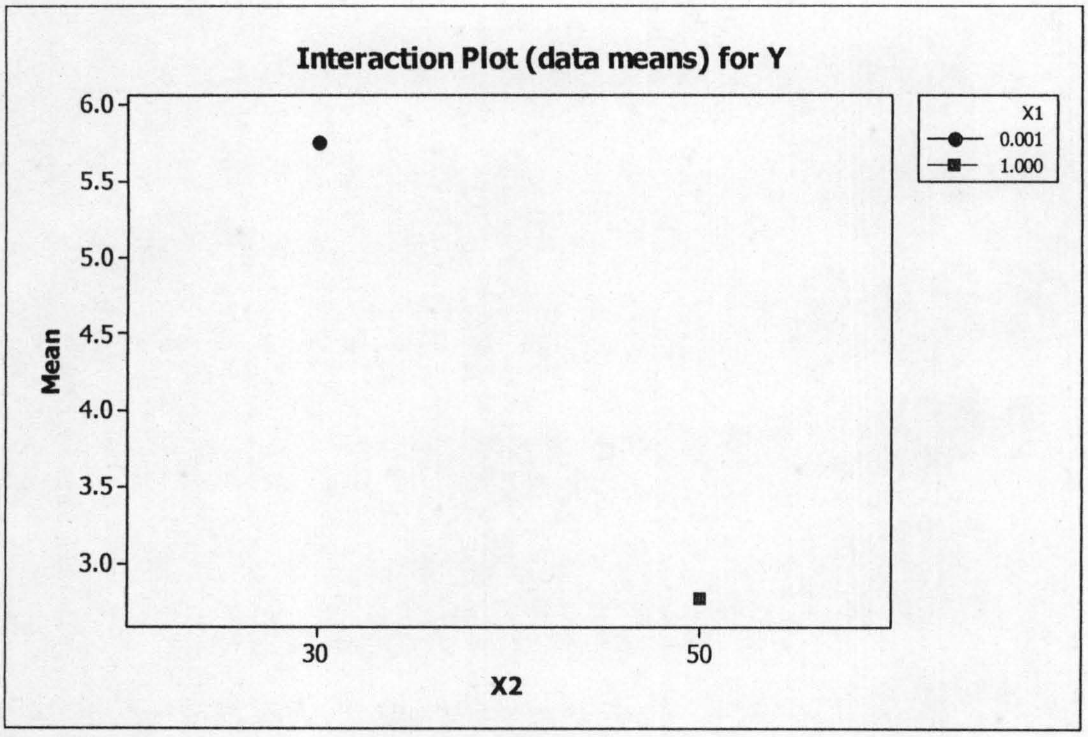


Figure 4.34c; Interaction Plot for Y

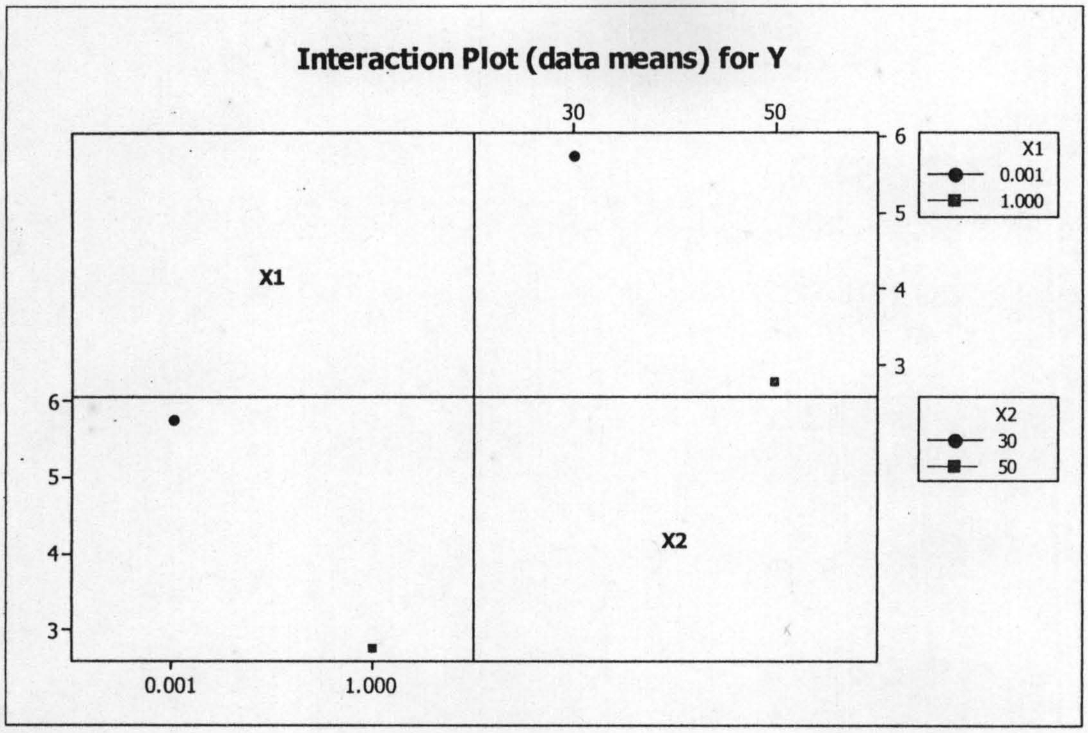


Figure 4.34d; Interaction Plot for Y

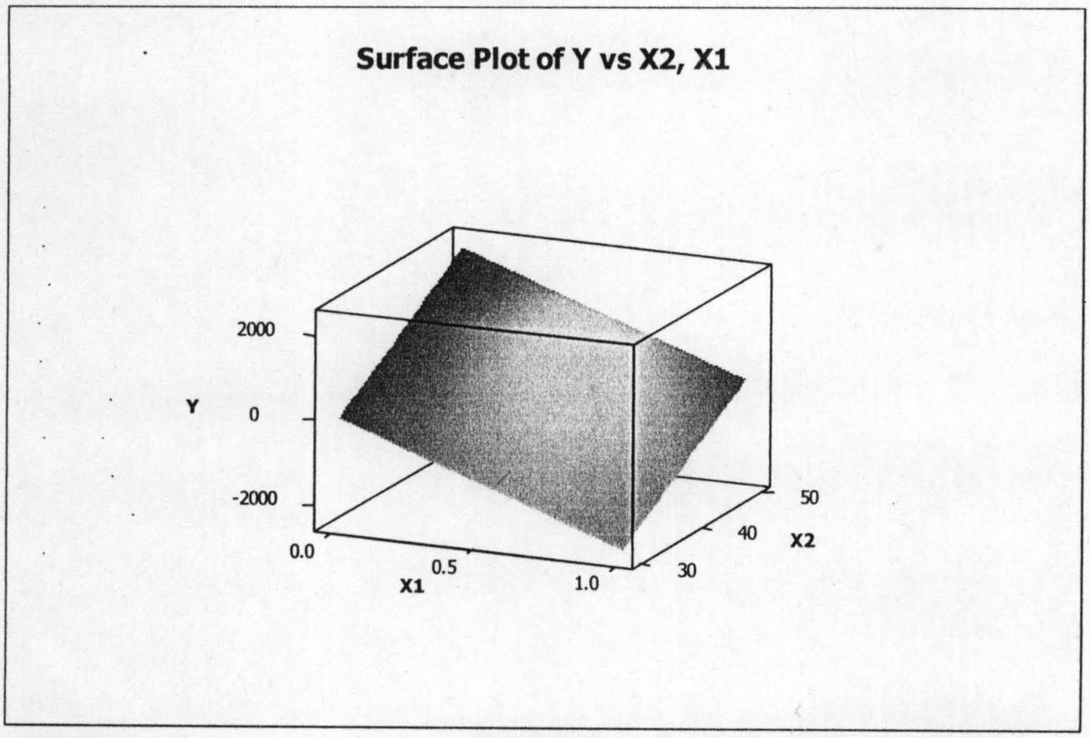


Figure 4.34e; Surface Plot for Y

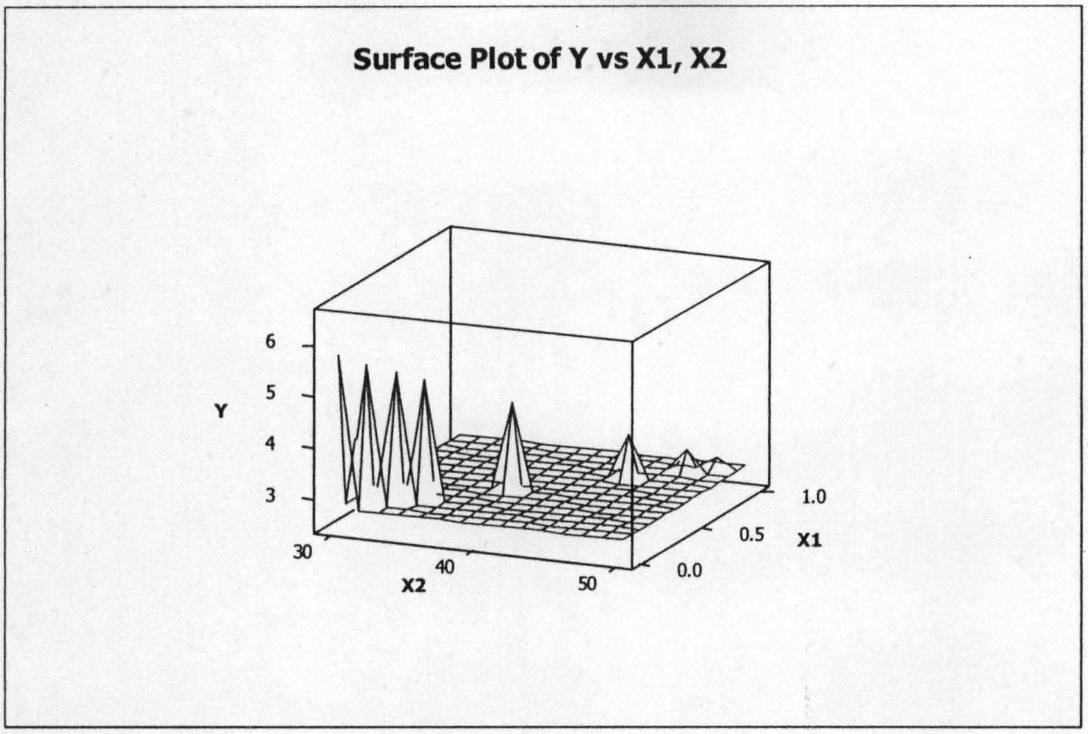


Figure 4.34f; Surface Analysis of Response vs X2, X1

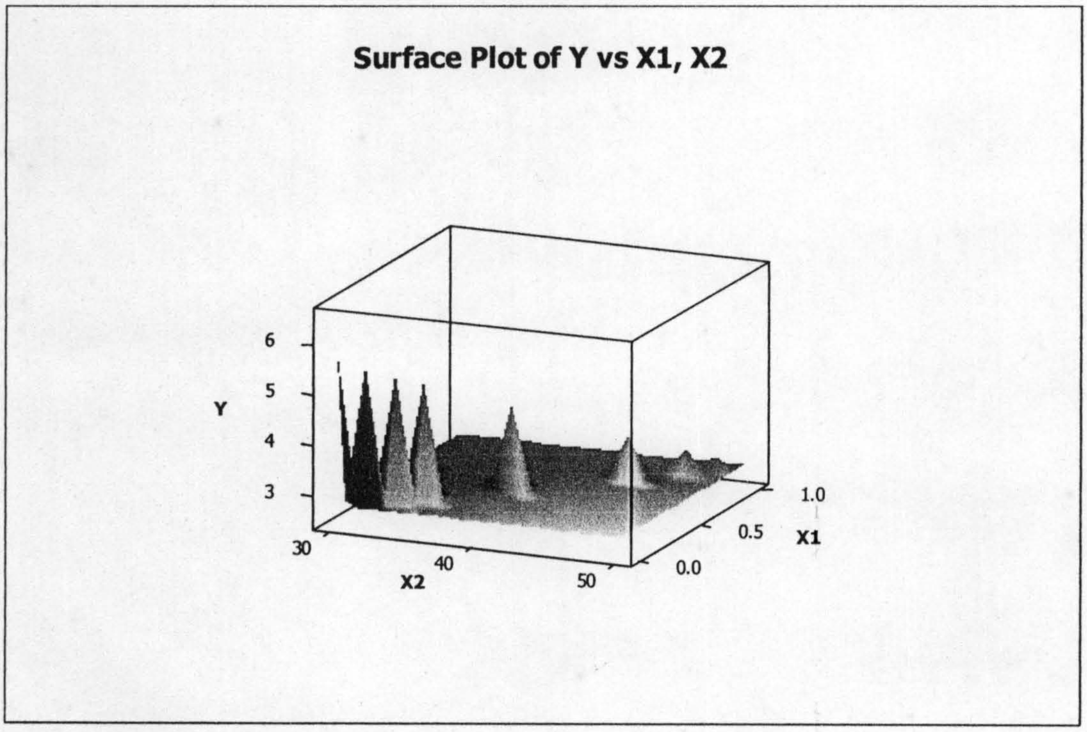


Figure 4.34g; Surface Plot of Y vs X1, x2

# APPENDIX 7

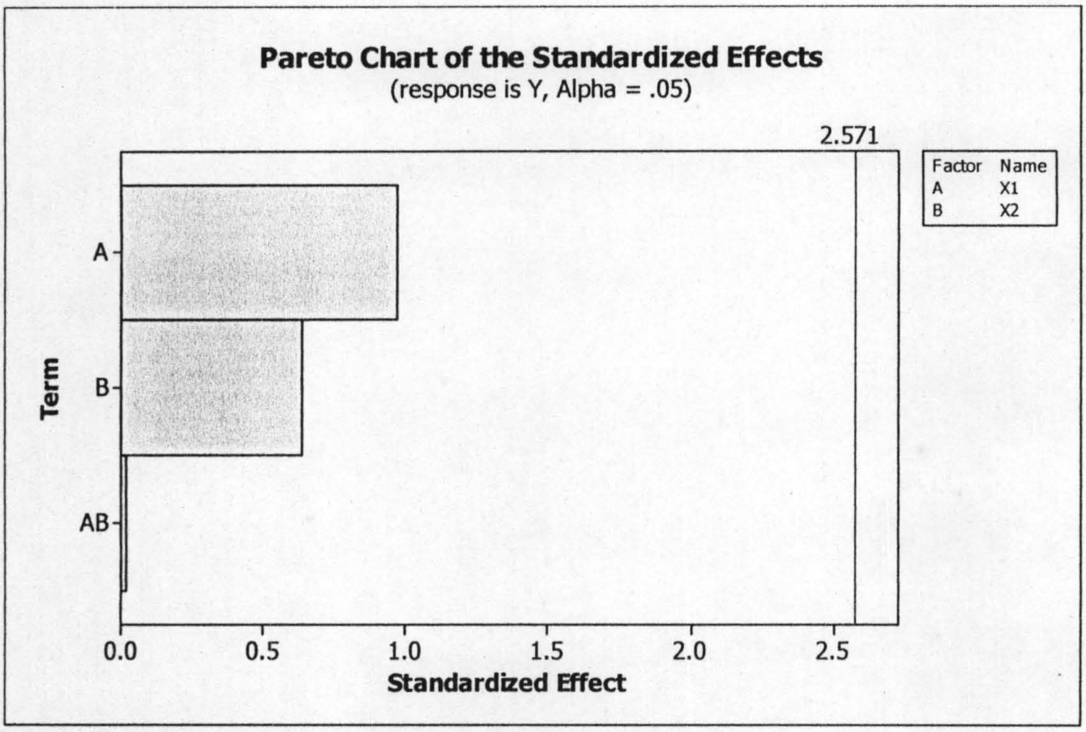


Figure 4.35a; Pareto Chart of Standard Efeects

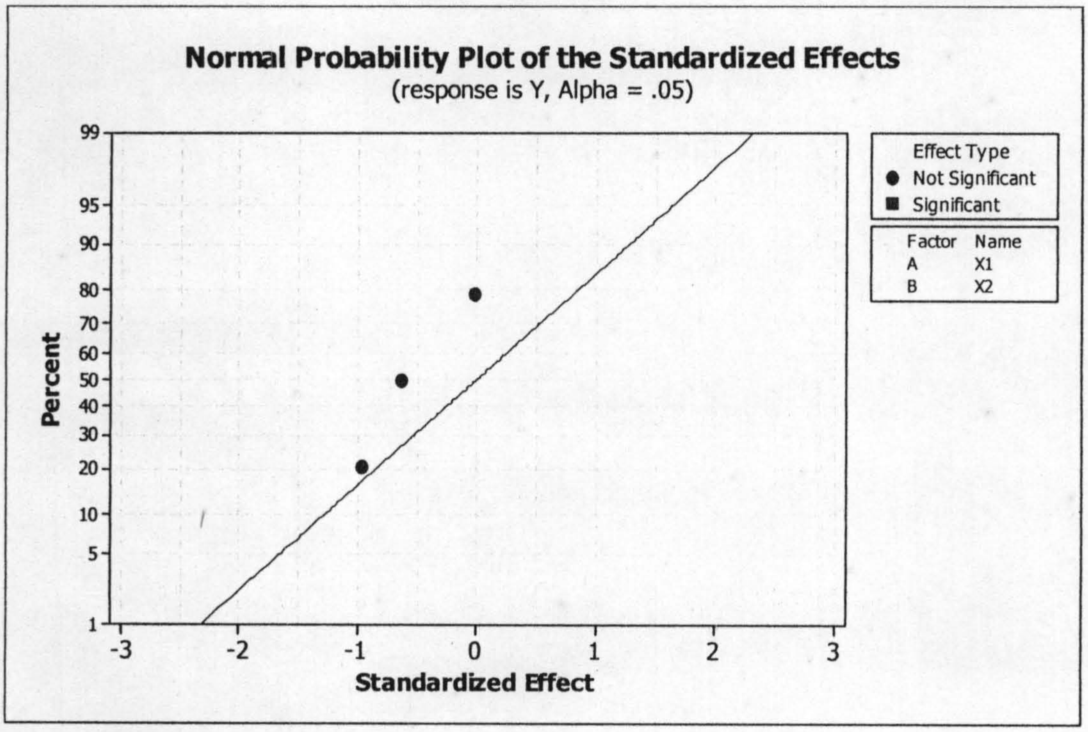


Figure 4.35b; Normal Probability Plots of Standard Effects

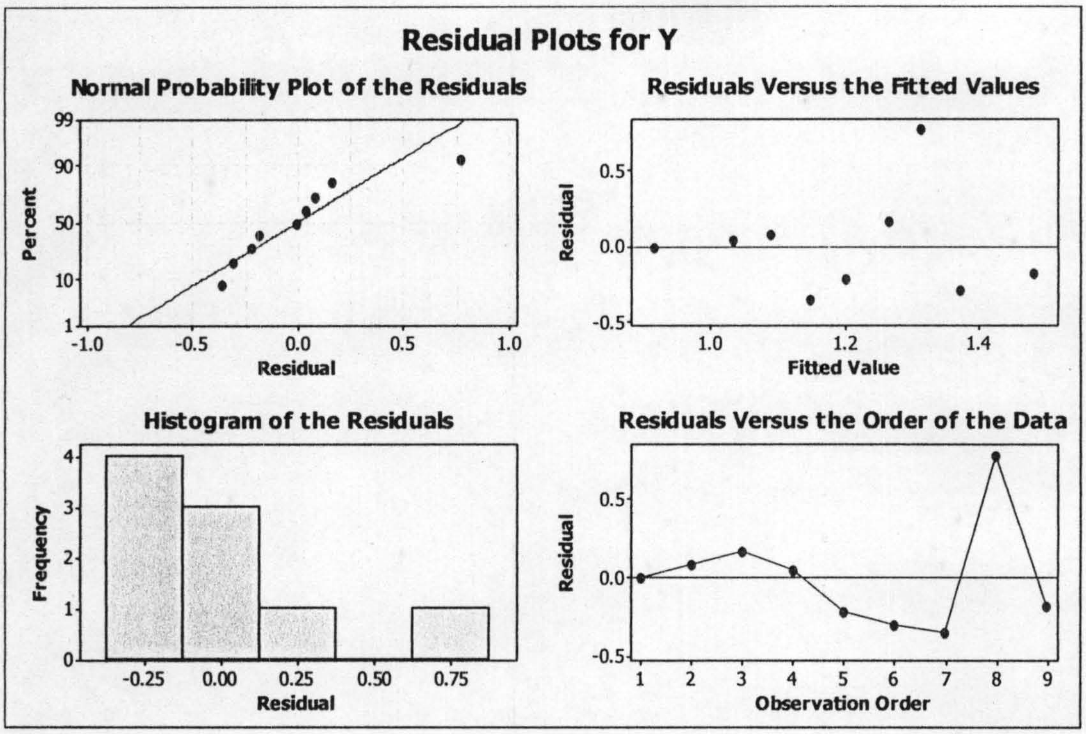


Figure 4.35c; Residual Plots for Y

# APPENDIX 8

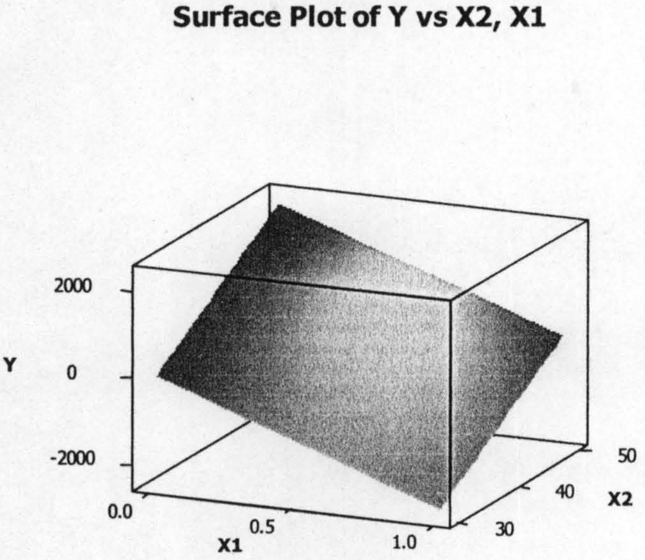


Figure 4.36a; Surface plot of Response for Magnesium Ion

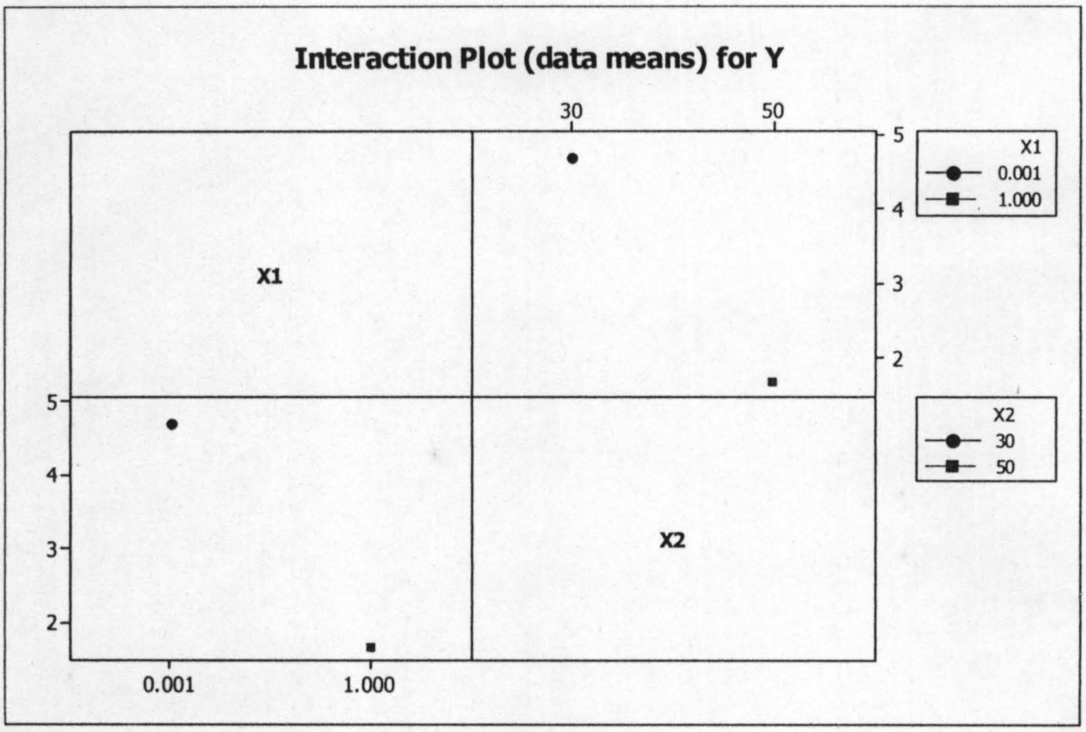


Figure 4.36b; Interaction Plot for Y

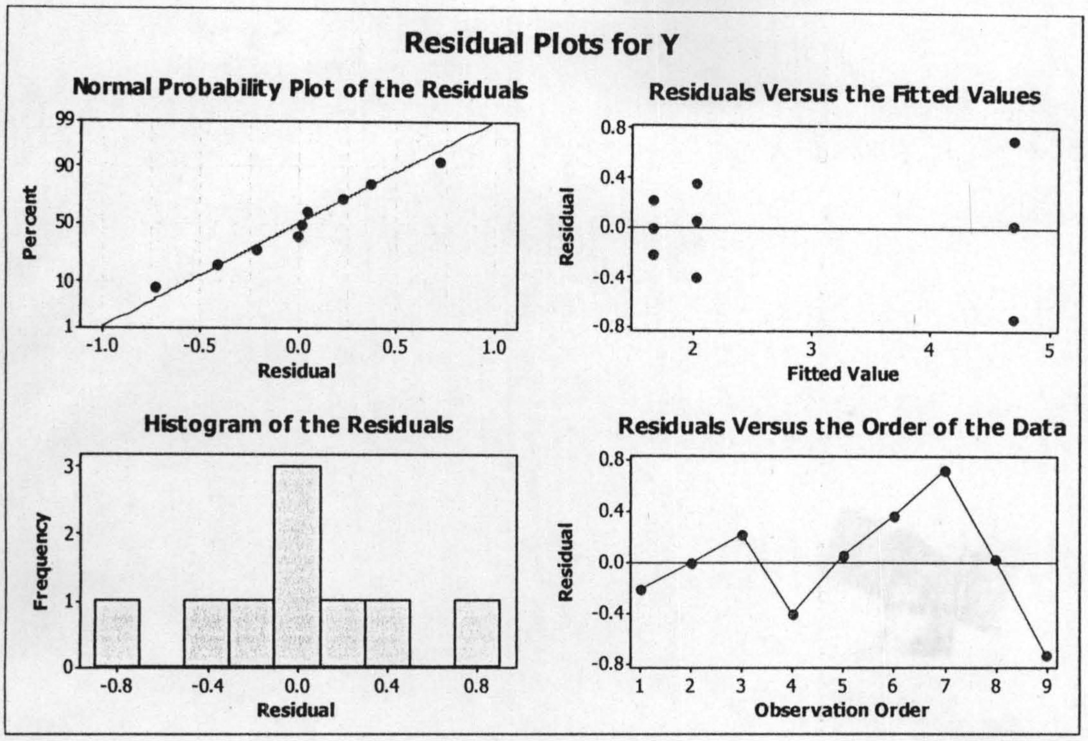
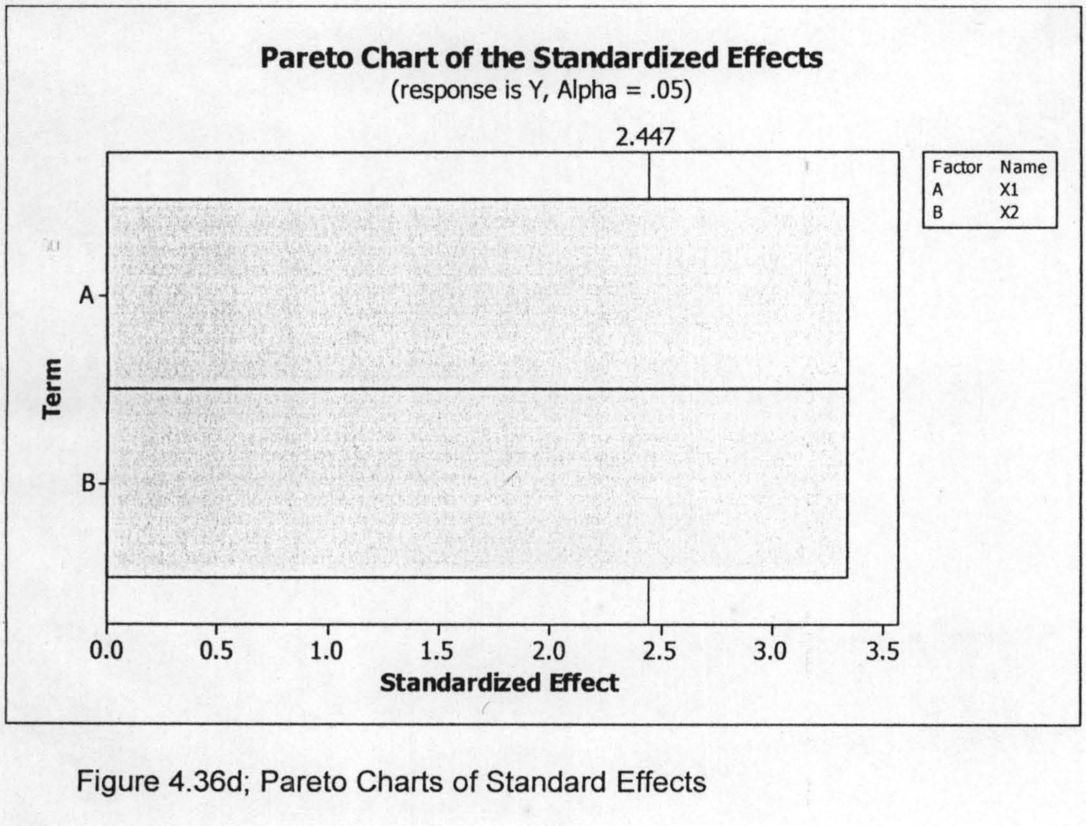
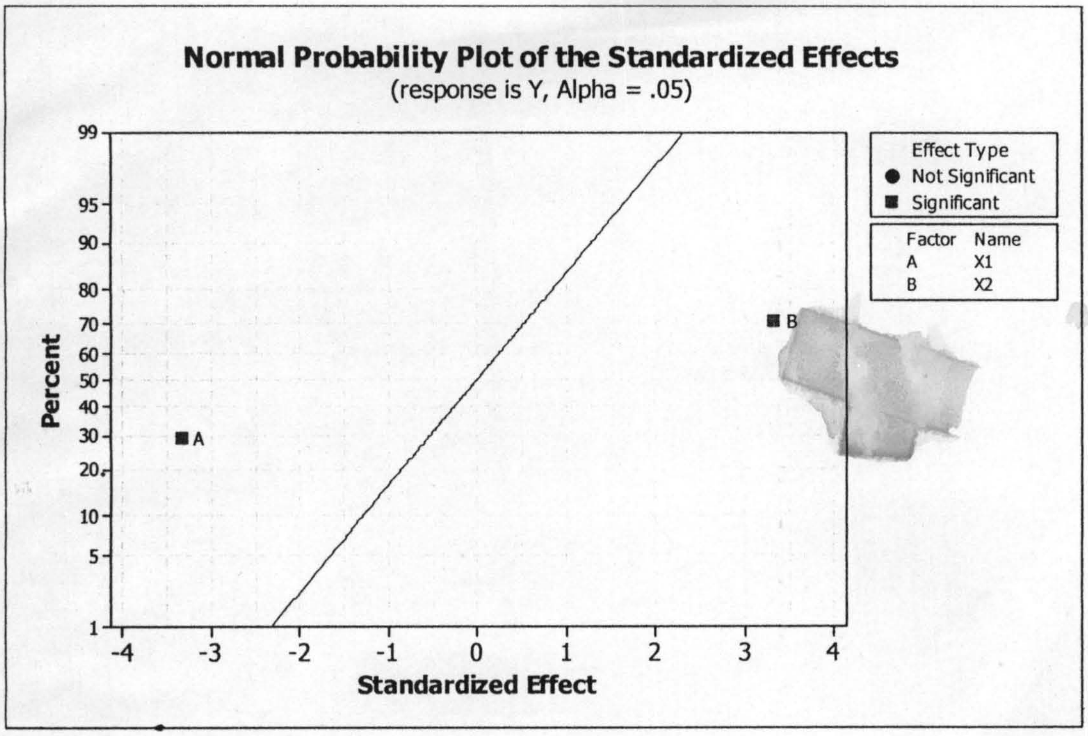


Figure 4.36c; Residual Plot for Y



d

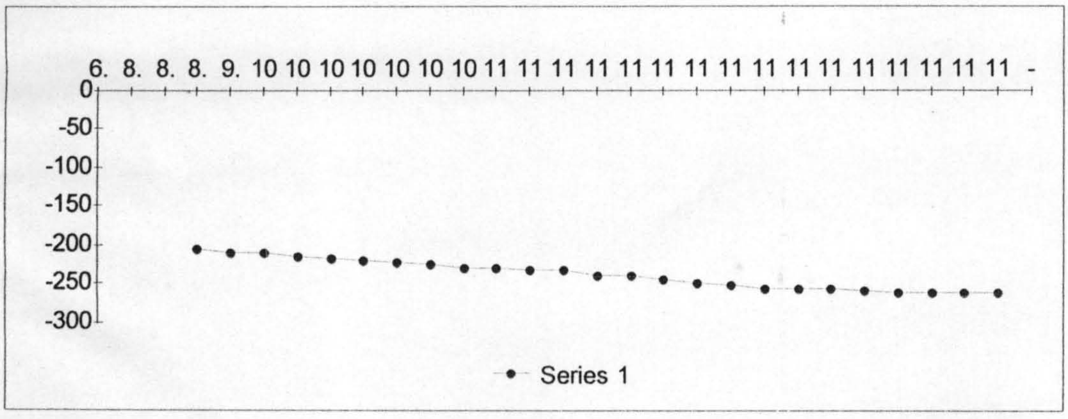
Figure 4.36d; Pareto Charts of Standard Effects



e

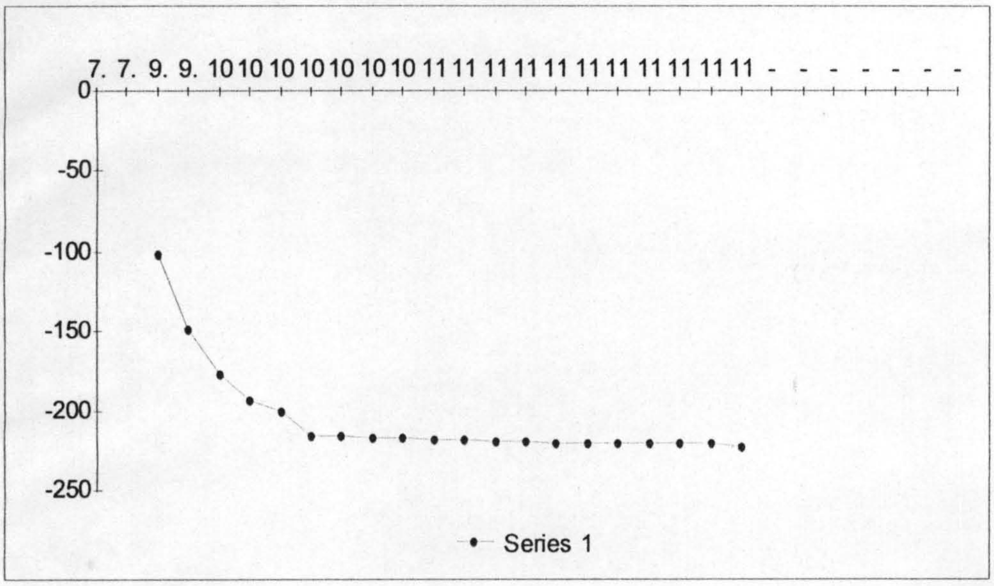
Figure 4.36e; Normal Probability

## 4.4 POTENTIAL VERSUS pH PLOTS FOR THE OPTIMUM CONDITIONS



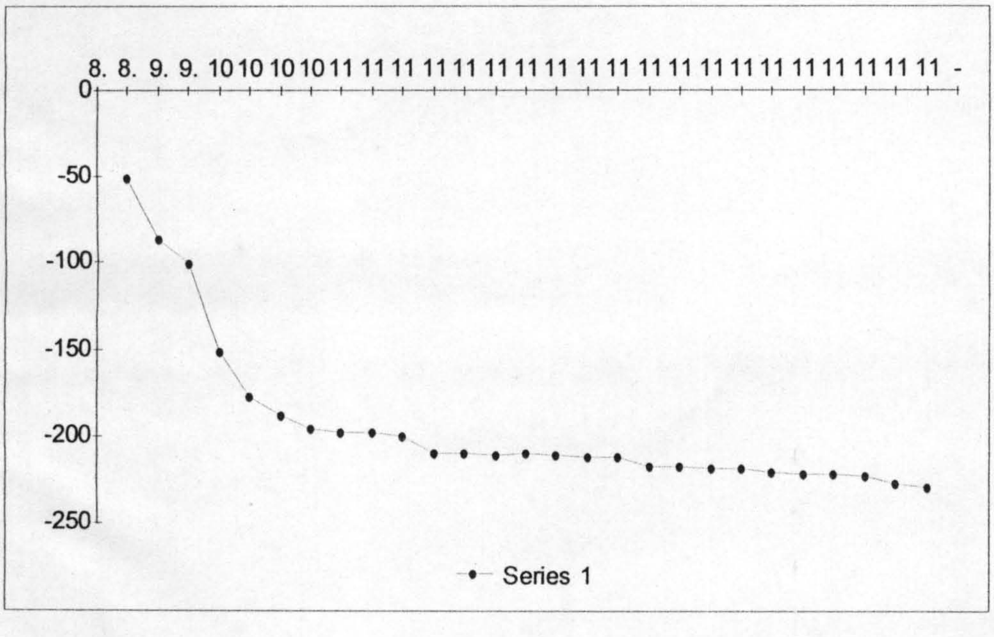
(Potential,x10 = Y axis, pH = x axis)

Fig.4.37: Potential vs pH for 1.0M Na$^{++}$ at 30$^{o}$C



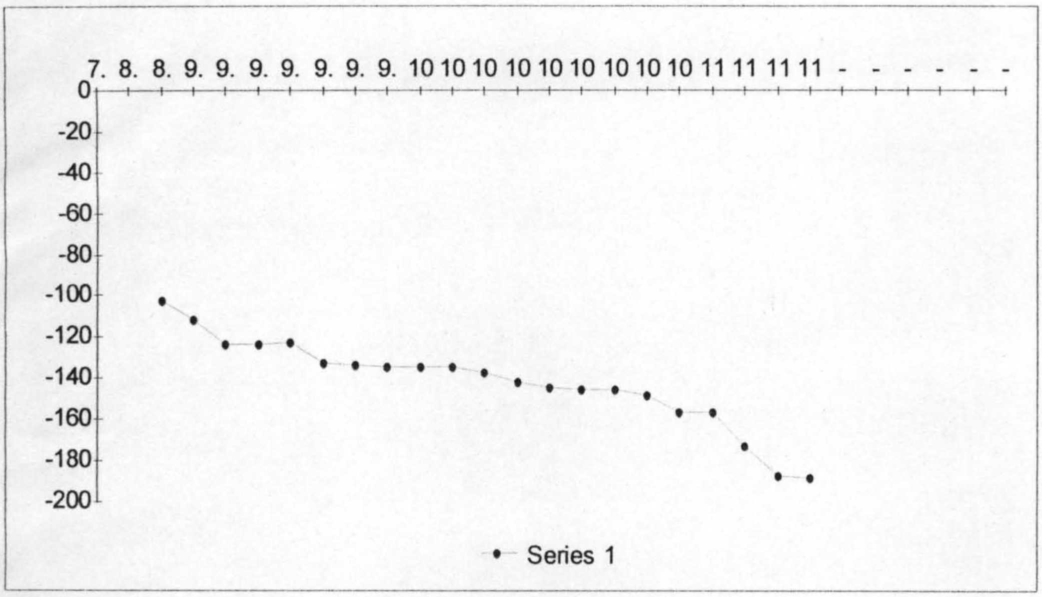
(Potential x10 = Y axis, pH = x axis)

Fig.4.38: Potential vs pH plot for 1.0M $Ca^{++}$ at 30°C



(Potential x10= Y axis, pH = x axis)

Fig.4.39: Potential vs pH plot for 1.0M $Ca^{++}$ at 50°C



(Potential = Y axis, pH = x axis)

Fig. 4.40: Potential vs pH Plots for $Mg^{++}$ at 50°C