MATHEMATICAL MODELING AND COMPUTER SIMULATION FOR ADSORPTION OF CATIONS

ON [MnO_2] USED IN DRY CELL.

BY

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PROJECT SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENT FOR THE AWARD OF BACHELOR OF ENGINEERING (B-ENGR.) IN THE DEPARTMENT OF CHEMICAL ENGINEERING,

FEDERAL UNIVERSITY OF TECHNOLOGY; MINNA

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OCTOBER, 2003

DECLARATION.

I, BAMIDELE OLUFEMI RAMON, declare that this project is my original research work, and has never to my knowledge, been submitted else where

BAMIDELE O RAMON	**SIGNATURE AND DATE**

CERTIFICATION

This is to certify that I have supervised, read and approved this project work, which I found adequate both in scope and quality, for the partial fulfillment of the requirement for the award of bachelor of engineering degree in chemical engineering department.

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EXTERNAL EXAMINER	**SIGNATURE AND DATE**

DEDICATION.

This research project is dedicated to the will of Almighty GOD, who command man to" read and teaches the use of pen and taught men that he know not", (Q 96:3-6). An to the memory of my grand father, LATE PRINCE BAMIDELE MOHAMMED LAWAL, and my grandmother, MADAM OKE BAMIDELE, for the foundation well laid and to my parents, for their LOVE and concern in my LIFE.I remain grateful.

ACKNOWLEDGEMENT

Foremost glory and adoration to the Almighty (ALLAH) GOD, the most beneficent the most merciful, for the health, strength and drive which it has pleased HIM to endow on me during my sojourn so far in LIFE and particularly at F.U.T. Minna.

MY sincere appreciation goes to my parents, brothers, sisters and the entire BAMIDELE family, who have always been there for me when I need them most. My gratitude also goes to my able supervisor, DR F. DUNCAN ALOKO, whose sound understanding of the subject matter and enlightment, constructive criticism helped in bringing out the best in me during the course of my research work.

I sincerely appreciate the effort of the head of department, DR F.B. ABERUAGBA and other members of departmental staff, Engr. M.A. OLUTOYE, Engr. A. SAKA, Engr. MRS E. ETERIGHO, Engr. YEMI AGBAJELOLA, Engr. AKPAN, DR F.K. ONIFADE, and the associate professor J .O ODIGURE.

T his acknowledgement would leave much to be desired without mentioning my precious ones, the entire family of DR and MRS T .A O. SALAU, of MECHANICAL ENGINEERING DEPARTMENT, UNIVERSITY OF IBADAN, for the moral and financial support.

Finally acknowledgement goes to my dearest sisters PEJU AND TAYO BAMIDELE, SUNKANMI TOOGUN, LAOLU

GABRIEL ONI, CEIK, IMOH IMEH, and finally CHINYERE ROSELINE ENYA. To my preferred friends, Abdullah, Kunle Asunmo, Rotimi, Eedris Adeniji, Nike, Basirat, Ramon, and Quadri KELANI, Seun Kuye, Fatimah Abdulateef. Finally my appreciation goes to my dearest friend and soul mate ROSE CHICHI, and to the last that shall surely be the first, the princess of my heart, LOLA RUKAYAT. I appreciate you a lot.

ABSTRACT

Mathematical model equations were developed to predict the adsorption capacity of cations [$Zn^{2+}$and Pb^{2+}] on $Mn0_2$.The data used were from previous experimental work.

The model equations obtained are,

$$Y= -4.925E-06 - 2.146E-06*[C] +5.782E-07*[pH] + 3.291E-05*[C]*[pH],$$

$$Y= -4.693E-06 -5.013E-04*[C] + 4.471E-07*[pH] + 4.889E-05*[C]*[pH]$$

for both Zn^{2+} and Pb^{2+} respectively at constant temperature($33^{O}C$). The coefficient of regression(R^2) for both Zn^{2+} and Pb^{2+} are 88.68% and 97.3% respectively.

The model equations derived showed that high adsorption capacity on MnO_2 was obtainable at lower concentrations and higher pH values of the solutions.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 GENERAL

Modern engineering practice is becoming increasingly mathematical, predictive and computerized and so a great deal of effort, time and money are now being dedicated to the search for systematic and generalized models of as wide applicability as possible leading to widespread advancement in modeling, simulation and computer control of process.

In chemical engineering, modeling of processes and operations such as adsorption have greatly increased the understanding of man and continue to give insight into the behavior of such systems and principles upon which they are based. The mathematical model is a general characterization of a process in terms of mathematics, therefore enabling the relatively simple manipulations of variables to be accomplished in order to determine how the process would behave under a variety of operating conditions.

The understanding gained from modeling enables the system to be stripped of its "extraneous confusion factors" and thus making visible the cause and effect relationship between the variables describing the system. The bases of the models are the

fundamental physical and chemical laws such as those of the conservation of mass energy and momentum.

The equations obtained to describe the existing relationship amongst the set of variables are usually ordinary or partial differential, integration or integral-differential in nature. As such the solution are quite complex to obtain analytically or by hand computation, despite the simplifying assumptions that are taken into consideration. Thus mathematical modeling is a prerequisite and more often than not a precursor to computer simulation.

Computer simulation is a computerized technique of analyzing an operating system by deducing criteria for success, by trail and error, from processes in which the model of the system is dynamically studied. There are two types of simulation method used in system or process design: Analogue and digital simulations. However, digital simulation is more frequently used because of the enhanced capabilities and operational speed of modern electronic computers, which are used in executing computer algorithms of the models.

1.2 AIMS AND OBJECTIVES:

The objective of this study is to develop a mathematical model for the adsorption of cations on MnO_2 used in dry cell and simulate the adsorption process operated during the adsorption of the cations on MnO_2 used in dry cell.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 BATTERY

A battery is a device, which transforms chemical energy into electrical energy. The term is usually applied to a group of two or more electric cells connected together electrically. In common usage, the term battery is also applied to a single cell, such as a flash light battery.

2.1.1 TYPES OF BATTERY

There are in general two types of batteries:

A) Primary batteries

B) Secondary storage or accumulator batteries

2.1.1.1 PRIMARY BATTERIES:

Primary types of batteries, although sometimes consisting of the same plate- active materials as secondary types, are constructed so that only one continuous or intermittent discharge can be obtained.

2.1.2 SIZE OF BATTERIES

Primary cells are manufactured in many sizes and designs from the small electric wristwatch battery and the small pin-light battery to the large sub-marine battery, where a single cell can weigh as much as one tone. In all applications the cells must be

constructed for its particular service so that the best performance may be obtained consistent with cost, weight, space and operational requirements.

Automotive and aircraft batteries, generally use thin positive and negative plates with thin separation to conserve space and weight and to provide high rates of current discharge at low temperatures. Stand-by batteries use thick plates and thick separators to provide long life. Notable size and weight reductions have been made through the use of new plastic materials, active materials and methods of construction

2.1.3 RATINGS OF BATTERIES:

Since the power that can be obtained from a cell varies with its temperature and the rate of current discharge, the power output rating is very important. Common secondary battery practice is to rate cells in terms of ampere-hours (discharge rate in amperes times hours of discharge) and to specify the hourly rate of discharge. By multiplying ampere-hours by average voltage during discharge, watt-hour rating is obtained.

Ratings must be made to be a specified final voltage, which is either at the point of rapid voltage drop or at a minimum usable voltage.

The rating of primary batteries is generally stated as the number of hours of discharge, which can be obtained when discharging through a specified final voltage

2.1.4 BATTERY'S LIFE SPAN:

Life span of cells varies from the single discharge obtainable from primary types to 10,000 or more discharge-charge cycle obtainable from some secondary cells obtained at very short times. Automatic batteries may generally be expected to give approximately 300 cycles, or at least two years. Industrial truck sizes may be expected to give 1500 – 3000 cycles in five to ten years. Stand by sizes may be expected to float across the direct-current bus eight to thirty years. Generally the most costly, largest and heaviest cells are the longest lined.

To obtain life from batteries, certain precautions are necessary. The state shelf life and temperature of inert wet primary cells must not be exceeded. For dry reverse electrolyte primary cells and secondary cells of the dry construction with charged plates, the cell or battery container must be protected against moisture, and storage must be within prescribed temperature limits. Wet charged secondary batteries require periodic charging and water addition depending upon the kind of construction.[4],.[3]

2.1.5 BATTERY'S RELIABILITY

Batteries are probably the most reliable source of power known. In fact most artificial electric circuit are protected in some manner by battery power. There are no moving parts and with good quality control in component materials and construction, one can be assured of power, particularly since adequate checks to indicate the condition of the cells usually exists. To ensure reliability, manufacturers stipulations on storage and maintenance must be followed.

2.1.6 APPLICATION OF PRIMARY CELL OR BATTERY

Primary cells or batteries are used as a source of direct current power, where the following requirements are important:

- Electrical charging equipment or power is not readily available.
- Convenience is of major importance assign the case of the hand or pocket flash - light.
- Stand-by power is desirable without cell deterioration during periods of non - use for days or years.
- The cost of a discharge is not of primary importance.

2.2 DRY CELL

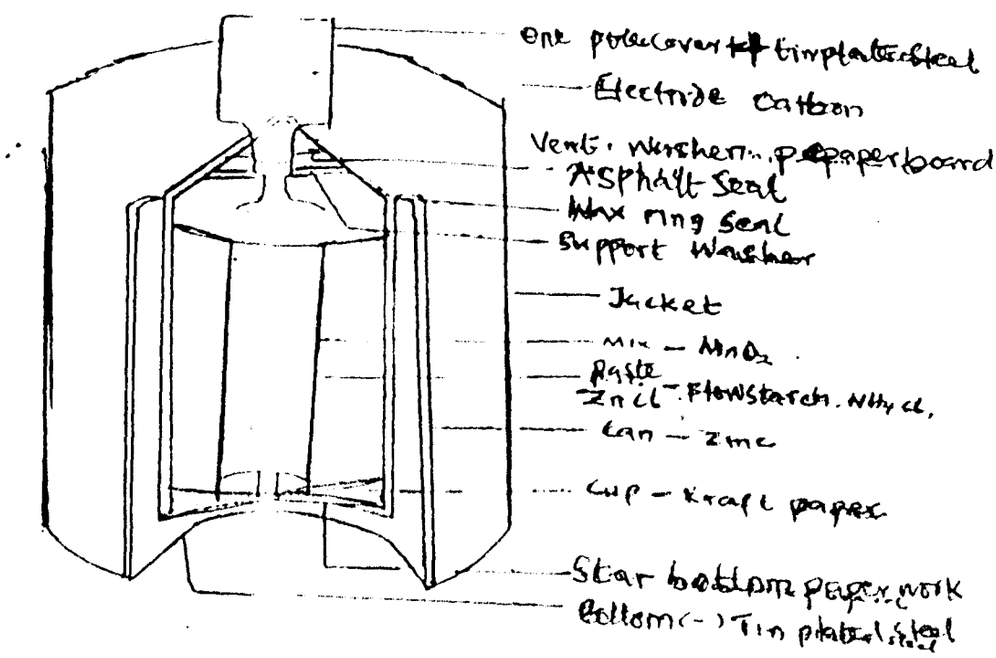
A primary cell in which the electrolyte is absorbed in a porous medium, or otherwise restricted from flowing is referred to as dry cells.

Common practice limits the terms dry cell to the Leclanche' cell which is the major commercial type of dry cells. Other types of dry cells, includes the mercury cells, the alkaline – zinc – manganese dioxide cell and the air – depolarized cell. These cells all use aqueous electrolytes immobilized in absorbent materials or gels.

2.2.1 CONSTRUCTION OF TYPICAL DRY CELL: (Le CLANCHE` CELL)

The Le clanche` cell is made in a variety of sizes. It is either round or flat in shape. American National Standard Specification for dry cells and batteries. C. 18.1 –1972, list the smallest cylindrical cell as the 0 cell, 0.328cm^3, 0.9g

To the largest, the number 6,483cm^3, 990g[10].



2.2.1.2 FLAT TYPE CELLS.

Flat type cells are available in multiple cell batteries only. They range in size from the F 12 cell, $2cm^2$ in cross section and 0.17 cm thick to the F100, which is $27.35cm^2$ by 1.04 cm. The energy volume ratio of flat cell batteries is about twice that of batteries made with round cells because of;

- The absence of an expansion chamber and carbon rod.
- Their rectangular form, which eliminates waste space in assembled batteries and voids between cells.

The negative electrode is usually solid zinc, either in cup form (cylindrical cell) or in sheet form (flat cell). The carbon positive electrode, is embedded in a black mixture of manganese dioxide (MnO_2) and carbon black. The carbon is either a rod located in the center of a cylindrical cell or a coasting on the back of the flat zinc electrode in the flat cell. The separator between the black mix and the zinc electrode consists of a paper barrier coated with cereal or methylcellulose. In older construction, the separator was composed of a gelatinous paste, which also held the electrolyte. Not only does the paper barrier give about 30% more volume for the depolarized mass, but it also decreases the internal resistance of the cell and reduces the number of manufacturing operations.

2.2.1.3 DRY CELL CHEMISTRY

At the anode (zinc), the zinc oxidizes to zinc ion and simultaneously liberates electrons to the external circuit, at a rate

proportional to current. For each ampere, which flows, 1.2g of zinc per hour are converted to zinc ion.

At the cathode (MnO_2) the electrons from the external circuit reduces the MnO_2 to three different substances depending on circumstances, which have not yet been thoroughly explained. Studies have shown however that the total ampere – hour output of the cell can be accounted for by analyzing the cathode mixture for the following substances: soluble manganese (Mn++), each grams of which accounts for nearly 1A- hr of discharge, insoluble magnetite (MnOOH), each grams of which account for about 0.3A-hr of discharge, insoluble heteroclite ($ZnO.\ Mn_2O_3$), each gram of which accounts for about 0.22A-hr of discharge. The electrochemical reduction of the manganese dioxide (MnO_2) has been reported to occur as the reaction form soluble manganese as shown as reaction (I). This occurs only when the cell delivers current.

$$MnO_2 + 4H^+ + 2e^- \Rightarrow Mn^{++} + 2H_2O \quad \text{I}$$

Two secondary reactions II and III can then occur

$$MnO_2 + Mn^{++} + 2OH^- \Rightarrow 2MnOOH \sim \text{II}$$

$$MnO_2 + Mn^{++} + 4OH^- + Zn^{++} \Rightarrow ZnO.\ Mn_2O_3 + 2H_2O \sim \text{III}$$

Reaction III occurs only if zinc is in the solution in the cathode mix.

2.2.1.4 OPERATING CHARACTERISTICS OF DRY CELL

The service capacity of dry cells is not a fixed number of ampere – hour but varies with current drain, operating schedule, cut–off voltage, operating temperature and storage conditions prior to use.

Most cells are tailor made for their related end use. For example, D-size cells can be rated as general purpose, industrial flashlight, transistor, electronic flash and photoflash. Number 6 cells are specially formulated for bell ringing, telephone, protective alarm and general purpose.

2.2.1.5 TEMPERATURE EFFECT

The higher the temperature during discharge, the greater the energy output. Conversely, the lower the temperature, the lower the energy output. At $-23^{O}C$, the battery is virtually inoperative. However, self-life is influenced in the reverse direction by environmental temperatures. Better low temperature output can be obtained with special electrolyte and cell structures giving a high ratio of electrode area to mix thickeners and special types of MnO_2.

2.2.1.6 SHELF LIFE

This is the period of time that a battery can be stored before it drops to 90% of its capacity when tested fresh at 21% and 50% relative humidity. Deterioration of a dry cell takes place in a number of ways:

- Zinc can oxidize by reaction with the electrolyte; thus the reaction produces hydrogen.
- MnO_2 can be reduced by carbon and by organic materials used in the cells. This can produce carbon dioxide.

- H_2O can be evaporated from the electrolytes. This increases the cell resistance and alters the composition of the electrolyte uniformly.

In general, shelf life decreases as the cell becomes smaller. With well constructed cells a shelf life of three years with a number 6 telephone cell and 10 months with a penlight cell.

High temperature redness shelf life, and at 32% the shelf life of a battery is about one third that of one stored at 21^{o}C. Low temperature storage increases the shelf life of batteries.

2.2.1.7 RECHARGING

It is possible to recharge dry cell batteries for five six cycles provided the following precautions are taken

- The batteries should be subject to only shallow discharges between cycles.
- Must be used immediately after charging.
- Charged over a ten to fifteen hour period at constant current and not overcharged.

2.2.1.8 ZINC CHLORIDE CELL

The zinc chloride cell is a variation of the standard Leclanche carbon zinc cell, differing mainly in the quantity of zinc chloride and ammonium chloride in the electrolyte. Infact whereas the standard carbon zinc cells uses mostly ammonium chloride with a small percentage of zinc chloride, the zinc chloride cell uses primarily zinc chloride with little or no ammonium chloride.

Most physical and electrical characteristics of the zinc chloride cells are essentially the same as those of the standard carbon zinc cells, for example, watt-hour per kilogram, watt-hour per cubic centimeter, emf (open circuit voltage), voltage under load and flash current.

The electrolyte is a solution of ammonium chloride and zinc chloride in water. The cell enclosure consists of a top seal in the cylindrical cell or thin plastic wrapping for the flat cell.

Zinc electrolyte: - Zinc cans (cup form of electrode) are made by drawing or impact extrusion. A typical alloy for extruded cans contains 1.0% lead, 0.05% cadmium and the remainder zinc. The zinc used is of 99.99% purity. The alloying elements improve the mechanical properties and decrease wasteful corrosion. The cell capacity is less than that theoretically possible from the weight of zinc. This is because zinc is used as the container. The limiting factor being the manganese dioxide. The actual capacity depends on the depolarized composition and the rate of discharge.

BLACK MIX: The black mix is composed of manganese dioxide mixed with carbon black. The MnO_2 is usually obtained from natural ore (mainly from Gabon, Greece and Mexico), but may be a synthetic product prepared by chemical precipitation or by electrolytic methods. Mixtures of the natural and synthetic oxides are also used. The carbon black is usually acetylene black made by thermal decomposition of acetylene. Graphite is used to a lesser extent.

MnO_2 has a theoretical capacity of about 0.3 Alm/g. the practical capacity is somewhat less.

The carbon black is used in varying proportions depending on design factors. It serves the double purpose of increasing the conductivity of the manganese dioxide and absorbing the electrolyte. For cells that require a high capacity at low current drains (for example transistor use) the ratio of MnO_2 to carbon may be 10:1, and at the other extreme, for cells requiring a very high flash current (for example, photoflash), the ratio may be as low as 1:1. In addition to these components, the black mix also contains electrolyte amounting to about 25% of the total weight

CARBON ROD: - The carbon rod used in a cylindrical cell serves as the conductor of electricity for the positive electrode; it also serves as a vent to allow gas to escape. Carbon rods are usually made from petroleum coke, which is calcined, ground and mixed with pitch. The "gree" rods are baked to form a hard carbon, having low electrical resistance. They may be partially waterproof by inpregnation with oil or paraffin wax to prevent capillary creepage of electrolyte out of the cell.

Flat cells are usually made with duplux electrodes. The zinc is coated on one side with a carbonaceous coating, which serves to conduct electricity between the zinc and the black mix of the adjacent cell.

SEPARATOR: - The modern method of separating the two electrodes is to use kraft paper, which has been coated on the side

adjacent to the zinc with a film of cereal or methylcellulose containing mercurous (or mercuric) chloride. The latter corresponds to a mercury concentration of 0.155mg/cm^2 of paper area.

ELECTROLYTE: - The electrolyte is made by dissolving ammonium chloride and zinc chloride in water makes the electrolyte. For paste cells a small amount of mercuric chloride is usually added.

This composition, however, converts to zinc chloride as soon as the zinc and electrolyte come into contact. Mercury then plates out on the zinc. The composition of the electrolyte depends on the cell design.

During discharge, the composition of the electrolyte changes. In one test in which D- size cell was discharged through a four-Ohm resistor, the pH of the paste layer next to the zinc changes from 5.7 to 3.8 (more acid) while the pH of the innermost portion of the mix went from 5.8 to 10.1 (more alkaline).

Ordinary dry cell electrolyte has a resistivity of 2.42 ohm-cm at 20^{O}C. For low temperature operation, special electrolytes have been developed. An electrolyte of 12%zinc chloride, 15% lithium chloride, 8% ammonium chloride and 65% water is fluid at –40^{O}C. Other electrolytes for low temperature operation use a mixture of calcium chloride, zinc chloride and ammonium chloride solutions.

Flat cells use thin plastic wrappings around the edges of each cell. This confines the electrolytes to individual cells and avoids internal discharge in a stack. The wrappings are sufficiently gas permeable to prevent the building up of pressure in the cells. After the

requisite numbers of cells are stacked, the stack is bound together by tapes and dipped in molten for further moisture proofing.

However, the zinc chloride cell does have significant advantages in the following areas

- Better low temperature performance.
- Better continuous and high drain capacity due to more efficient depolarization.
- Better leakage resistance because H_2O is consumed along with the entire materials, making the cell practically dry at the end of discharge. The major disadvantage of the zinc chloride cell is the need for an improved seal because of its high sensitivity to moisture loss.

2.2.1.9 MODIFICATIONS

In addition to the systems above, the following combinations have been developed

- The magnesium with magnesium per chlorate and with bromide and with manganese dioxide modification is more expensive than the Leclanche type. It exhibits the delayed voltage at the commencement of discharge characteristics of magnesium cells and has excellent storage properties. It has a higher initial voltage than the standard dry cell.
- The cell modification of aluminum and aluminum chlorides and ammonium chlorate and MnO_2 is attractive on account of the lower density and electrochemical equivalent of aluminum compared with zinc.

2.3 ADSORBENTS

Adsorbents are natural or synthetic materials of amorphous or microcrystalline structure. Those used on a large scale include activated carbon, activated alumna, silica gel, fullers, earth and other clay sand molecular sieves [1].

Adsorbents solids are normally used in granular form, varying in sizes from roughly 12mm in diameter to as much as 50um [2].

2.3.1 FACTORS AFFECTING CHOICE OF ADSORBENT

1 Engineering properties: The solids must possess certain engineering properties depending upon the application to which they are put. If they are used in a fixed bed through which a liquid or gas is to flow, they must not offer too great a pressure drop for flow nor must they easily be carried away by the flowing stream.

2 Hardness and strength: they must have adequate strength and hardness so as not to reduce in size during handling or crushed in supporting their own weight in beds of the required thickness

3. Chemical nature of the adsorbent to aid sufficient specificity and adsorbent capacity

4. Large surface per unit weight is essential to all useful adsorbents [2].

2.3.2 MANGANESE IV OXIDE (MnO_2)

Pyrolusite (MnO_2) was thought to be oxide of iron until the mid 18th century, when it began to be suspected that the substance contains not iron but an element unknown to science. In 1774, the Swedish chemist Carl Wilhelm Schede demonstrated that it contains a

new element, and that same year, his friend John Amn Gothlieb Gahn produced a small sample of this new material by burning pyrolnsite with charcoal [1]

2.3.2.1 LABORATORY PREPARATION OF (MnO_2)

MnO_2 can be manufactured in the laboratory by heating Mn $(NO_3)_2$ at (180 – 200^{O}C) or by heating a mixture of manganese carbonate $MnCO_3$ and potassium chlorate at 300^{O}C. The purest product contains just 98% MnO_2 and MnO_3.

2.3.2.2 PRODUCTION OF MANGANESE IV OXIDE (MnO_2).

MnO_2 used in dry cell (Leclanche dry cell) or for other use is manufactured either by the following processes:

- Activatedly – Activated manganese dioxide (AMD)
- Electrolytically – Electrolytic manganese dioxide (EMD)
- Chemically – Chemical manganese dioxide (CMD)

2.3.2.3 CMD TECHNOLOGICAL PROCESS OF PRODUCTION

The following steps are the technological steps involved in the production of CMD. Pyrolusite (natural and impure MnO_2) are reacted with nitrogen dioxide (NO_2),in the presence of water to yield impure nitrates,$Mn(NO_3)_2$. This is further treated with hydrogen sulphide (H_2S) with the pH being regulated to produce pure $MnNO_3$.

The pure Mn $(NO_3)_2$ is then treated with ammonium carbonate to yield an impure precipitate of manganese carbonate $MnCO_3$, which is further made pure by washing and drying. The pure $MnCO_3$ now

reacts with oxygen present in the air to produce an indefinite variable oxide (MnO_x) of manganese.

MnO_x is treated with sodium chlorate $NaClO_3$ and H_2SO_4 to yield MnO_2, which is then washed and the drying being regulated to yield pure form of chemically produced MnO_2

The following reactions summarize the process

- $MnO_2 + 2NO_2 \Rightarrow Mn(NO_3)$ (impure)
- $Mn(NO_3)_2 \Rightarrow Mn(NO_3)_2$ (pure)
- $Mn(NO_3)_2 \Rightarrow MnCO_3$ (impure) $+ 2NH_4NO_3$

  $MnCO_3 \Rightarrow MnCO_3$ (pure)
- $MnCO_3 \Rightarrow MnCO + MnO_x$
- $MnO_X + NaClO_3 + H_2SO_4 \Rightarrow MnO_2 + NaCl + Na_2SO_4$
- $MnO_2 \Rightarrow MnO_2$ (pure)

2.3.2.4 PROPERTIES OF MnO_2

- Solubility: - it reacts with H_2SO_4

  $2MnO_2 + 2H2SO_4 \Rightarrow 2MnSO_4 + O_2 + 2H_2$
- It reacts with fused potassium hydroxide to form potassium manganese and hence potassium per manganese $KMnO_4$.
- Colour – MnO_2, which has a gray black colour, is by far the most important oxide of manganese.

2.3.2.5 MODIFICATION OF MANGANESE IV OXIDE MnO_2 [2]

There are five existing modifications of MnO_2;

- MnO_2 – alpha
- MnO_2 – beta
- MnO_2 – gamma
- MnO_2 – delta
- MnO_2 – epsilon

The classification of MnO_2 is based on these modifications, which differs in size of crystal, form, and specific bond rotation. The crystal in its entire plays an important role to determine the quantity of MnO_2 as an active material in a dry cell.

2.4 ADSORPTION

Adsorption is the selective transfer of one or more solute from a fluid phase to a batch of rigid particles (adsorbents). The usual selectivity of a sorbent (adsorbent) between the solute and the carrier fluid or between different solutes makes it impossible to separate certain solutes from the carrier or from one another.

Adsorption involves, in general, the accumulation of solute molecules at an interface (including gas-liquid, as in foam fractionation separations and liquid-liquid). Considering gas-solid and liquid-solid interfaces, with solute from the fluid attaching selectively to the solid. The accumulation per unit area is small, thus highly porous solid with very large internal area per unit volume are preferred.

The surface are usually irregular, and the bonding energies (primarily from Van-der Waal forces as in vapor consideration vary widely from one site to another.

In adsorption from the gas phase, usually part of the solid surface is vacant, as the fluid phase concentration of solute increases, the vacant area diminishes and the sorption (adsorption) level of the solid increases. Adsorption processes are of two types, physical and chemical adsorption.

2.4.1 PHYSICAL ADSORPTION

Physical adsorption or physiosorption occurs at ordinary temperatures, adsorption is usually caused by inter molecular forces rather than by formation of new chemical bonds.

2.4.2 CHEMISORPTIONS ADSORPTION

Chemisorption's adsorption process occurs at high temperatures, above $200^{O}C$ or $400^{O}F$, the activated energy is available to make or break chemical bonds. [1].

2.4.1.1 APPLICATION OF ADSORPTION PROCESS

Major uses of liquid-phase adsorption include;

- Decolorizing drying or degumming of fuel and lubricants, organic solvents, vegetable oils and animal oils.
- Recovery of biological chemicals (antibiotics, vitamins, flavoring) forms fermentation broth or plant extracts.
- Clarification of food and drug products
- Decolourization of crude sugar syrups.

- Purification of process effluence for pollution control.
- Water supply treatment for color taste or color improvement.

2.5 MODELING

Modeling can be defined as the method of establishing inter-relationship between important entities of a system, where models are represented in terms of goals, performance criteria and constraints (Dragomiller et al). Modeling has an interactive (cyclic) character i.e. the consequence of many feed back loop from the result of every stage of modeling procedure.

Modeling can be sub-divided into physical, mental and symbolic modeling depending on the type of modeling used.[7].

2.5.1 MATHEMATICAL MODELING

Mathematical models can be defined as the mapping of relationship between the physical of the system to be modeled onto its corresponding mathematical structures. Mathematical models can either be static or dynamic in character. Static character mathematical model can be represented by algebraic equation. Completely dynamic mathematical model can be described by a system of differential equations.

In a nutshell, mathematical modeling is the general characterization of a process or concept in mathematical terms, thus enabling the relative sample manipulation of variables to be accomplished in order to determine how the process or concept would behave in different situations [7].

Mathematical modeling attempts to describe the functional relationship of the variables.

2.5.2 PRINCIPLES OF MATHEMATICAL MODEL FORMATION

In deriving a mathematical model for a system, the following steps r important:

- Modeling aims must be stated as clearly and unambiguously as possible.
- Various kinds of consultants must be taken into account.
- Gencral assumptions and omissions must be carefully argued.
- The possibility of measurement and experimentation on the system being studied must be investigated [6].

2.5.3 BASIS

The basis for mathematical models are the fundamental physical and chemical laws, such as the laws of mass conservation, energy and momentum conservation stated in their time derivative forms. Others include parameters such as mass transfer coefficient, pH, concentration and surface charge, which are either obtained experimentally or from processes operating databank [6].

2.5.4 ASSUMPTIONS

There is the need to make simplifying but reasonable assumptions about the system while modeling. The outcome of the model is dependant on the assumptions as they impose limitations on the model. A simple model needs many assumptions and yields an

approximate result quickly, whereas a more complicated model (of the same system) needs fewer assumptions and yields a more accurate answer by mere advanced mathematical techniques.

Thus, the assumptions must be carefully considered when evaluating results.

2.5.5 MATHEMATICAL CONSISTENCY OF MODEL

Care must be taken not to under specify or over specify the number of variables or equations describing the system because in order to obtain a solution, the number of variables must equal the number of equations i.e. degree of freedom of the system must be zero. There must be a consistency in the units of the terms of the equation.

Consistency checks are necessary as they save many hours of frustration, confusion and wasted computer time.

2.5.6 PROPOSED MATHEMATICAL MODELS

The mathematical models that would be used are

- Ordinary differential equations in the form

$$Y = A_o + A_1X_1 + A_2X_2$$

- Ordinary differential equations in the form

$$Y = A_o + A_1X_1 + A_2X_2 + A_3X_1 * X_2$$

In the three equations above, Y would be dependent variable, which in this case is adsorption while X_1 and X_2 are the independent variable, which stand for concentration of additive and of electrolyte respectively. The boundary conditions (constants) are as follows

X_1 = 1M - > 0.001 M

9.0 < = X_2 < = 12 with increment of 0.25

2.5.7 SOLUTION OF THE MODEL EQUATION

Available solution techniques and tools must be kept in mind as the model is being developed, as a model that contains unknown and immeasurable parameters is unsolvable amounts to a waste of time and energy. In the search for a method of solution, possible approximations for the defining equations, boundary and initial conditions and an acceptable final solution are considered.

2.5.8 VERIFICATION

The need to prove the validity of a model is an important part of mathematical modeling. Because of the complex nature of the model, it is often neglected. However, one way of achieving this objective is by comparing average experimental results, for a similar operating condition, to the computed results.

2.6 SIMULATION

Simulation is the technique of constructing and running a model of a real system in order to study its behavior without disrupting the environment of the real system. If simulation is carried out normally, at best it would be tedious and time consuming. However, with the advent of computers, most simulations of models are carried out on it.

Computer simulation involves the running of a special program on a suitable type of computer, which generates time responses of the model, which imitate the behavior of the process being studied.

2.6.1 COMPUTER SIMULATIONS

Computer simulation can be sub divided into Analog simulation, digital simulation and hybrid simulation.

2.6.1.1 ANALOG SIMULATION

The electronic analog computer has become a valuable tool for control system analysis through simulation. A process with its control system is simulated on an analog computer by wiring the computer components into an electrical network, which represents the mathematical models of the process and control systems.

2.6.1.2 DIGITAL SIMULATION

Digital simulation involves the use of digital computers capable of performing arithmetic and logic operations at very high speeds. Good for storing many processes and large amounts of data. The digital simulation procedure involves the use of computer language such as Fortran, Algol, Pascal, and e.t.c.

2.6.1.3 HYBRID SIMULATION

Hybrid simulation involves the use of hybrid computer, which consists of one or more analog computer and a general-purpose digital computer liked by a special interface into a single computer system. The hybrid computer combines the advantages of the analog and digital of computers.

2.6.2 SIMULATION PROCESS

Simulation can be described as a three-step process:

- A mathematical model is first created to describe the behavior of the system being studied.
- The mathematical model is manipulated whenever possible and practicable to give the desired information concerning the system.
- Wherever conventional mathematical manipulation is impractical, the analog/digital computers may be used to simulate the mathematical model.

2.6.3 SIMULATION PROCEDURE

The procedure for carrying out the manipulations stated above is as follows:

- Data Collection
- Problem analysis
- Simulation model specification
- Model programming
- Model verification
- Simulation experimentation
- Evaluation and interpretation of simulation results
- Report generation [6], [7].

CHAPTER THREE

3.0 MATHEMATICAL MODEL OF THE SYSTEM

As stated earlier in the thesis, the proposed mathematical models are of two types.

1. Multiple linear ordinary differential equation form;

   $Y = a_o + a_1 x_1 + a_2 x_2$ --- 3.1

2. Multiple linear ordinary differential equation in the form;

   $Y = a_o + a_1 x_1 + a_2 x_2 + a_3 \ (x_1 * x_2)$--- 3.2

In the above equation

Y = adsorption

X_1 = concentration additive

X_2 = concentration of Electrolyte

For the concentration of additive value of

$(1 \leq x_1 \leq 0.001)$ M

For electrolyte, the values considered were between 9 and 12 with increment of 0.25.

3.1 EXPERIMENTAL DATA TABLE

3.1.1 ADSORPTION CAPACITY OF Zn^{2+} CATION AT DIFFERENT pH AND CONCENTRATION AT 33°C AND 40°C

TABLE 3.1.1.1 Zn^{2+} cations AT T = 33°C.

C [X_1]	pH [X_2]	$\triangle$ V	Y X10^{-7}
1	9.00	0.50	11.1
1	9.50	0.63	14
1	10.00	1.00	22.2
1	10.50	1.10	24
1	11.00	1.75	28
0.1	9.00	0.15	3.3
0.1	9.50	0.25	5.6
0.1	10.00	0.50	11.1
0.1	10.50	0.70	15.6
0.1	11.00	1.00	22.2
0.01	9.00	0.2	4.4
0.01	9.50	0.25	5.6
0.01	10.00	0.33	7.3
0.01	10.50	1.35	7.8
0.01	11.00	1.45	10

TABLE 3.1.1.2 Zn^{2+} cations AT T = 40^{O}C.

C [X_1]	pH [X_2]	$\triangle$ V	Y
1	9.00	0.45	10E – 07
1	9.50	0.48	10.6E – 07
1	10.00	0.73	16.2E – 07
1	10.50	0.75	16.7E – 07
1	11.00	1.62	36E – 07
0.1	9.00	0.38	8.5E – 07
0.1	9.50	0.48	10.7E – 07
0.1	10.00	0.58	12.9E – 07
0.1	10.50	0.78	17.3E – 07
0.1	11.00	1.20	26.6E – 07
0.1	11.50	1.70	37.8E – 07
0.01	9.00	0.12	2.7E – 07
0.01	9.50	0.15	3.3E – 07
0.01	10.00	0.25	5.6E – 07
0.01	10.50	1.35	7.8E – 07
0.01	11.00	0.40	8.9E – 07
0.01	11.50	0.60	13.3E – 07

ADSORPTION CAPACITY OF Pb^{2+} AT DIFFERENT pH AND CONCENTRATION (WHEN T=33^{O}C and 45^{O}C).

TABLE 3.1.2.1 Pb^{2+} AT 33^{O}C.

C [X_1]	pH [X_2]	$\triangle$ V	Y
0.01	11.00	0.30	6.7E-07
0.01	11.25	0.35	7.8E-07
0.01	11.50	0.45	10E-07
0.01	11.75	0.55	12.2E-07
0.01	12.00	0.73	16.2E-07
0.001	11.00	0.15	3.3E-07
0.001	11.25	0.10	3.3E-07
0.001	11.50	0.20	4.4E-07
0.001	11.75	0.30	6.7E-07
0.001	12.00	0.35	7.8E-07

TABLE 3.1.2.2 Pb^{2+} AT $45^{O}C$

C [X_1]	pH [X_2]	△ V	Y
0.01	11.00	0.2	4.4E - 07
0.01	11.25	0.25	5.6E - 07
0.01	11.50	0.30	6.7E - 07
0.01	11.75	0.40	8.9E - 07
0.01	12.00	1.00	22.2E - 07
0.001	11.00	0.45	10E - 07
0.001	11.25	0.25	5.6E - 07
0.001	11.50	0.50	11.1E - 07
0.001	11.75	0.60	13.3E - 07
0.001	12.00	1.20	26.7E - 07

3.2 POLYMATH 5.1

Using the polymath 5.1, The mathematical model equations were derived for two different cations.

The polymath 5.1 is chemical engineering software used for general numerical analysis. However, the general procedures carried out by the computer can be down this,

i. For linear equation in the computer

$$y = B_o + B_1 + X_1 + B_2 + X_2 \text{ --- } 3.5$$

The original multiple equation would be in the following of

$$y = \alpha + B_1 + X_1 + B_2 + X_2 + \text{---} + B_1 + X_1 \text{ --- } B_n + X_n \text{ ---} 3.4$$

in this case the number of variables for X is 2 this n = 2.

The regression line considered the best representation of the data points if probability P of all values of y occurring simultaneously is a maximum, which will occur when α and B are chosen to minimize the sum of squares.

i.e $S + (y - \alpha - B_1 + X_1 - B_2 + X_2)^2$ ----- 3.5

For S to be minimum $\frac{ds}{d\alpha} = \frac{ds}{dB} = 0$

and also $\&_1$ b_1 & b_2 will be replaced by the estimates a_1 b_1 and b_2

Defining

$$Cij = \mathcal{E}x_i x_j - \frac{\mathcal{E}x_i \mathcal{E}x_j}{m} \text{ --- 3.6}$$

$$Ciy = \mathcal{E}x_i y - \frac{\mathcal{E}x_i \mathcal{E}y}{m} \text{ --- 3.7}$$

$$Cyy = \mathcal{E}y^2 - \frac{\mathcal{E}y^2}{m} \text{ --- 3.8}$$

where m = number of observations which varies for different solution considered.

Thus leads to n simultaneous linear normal equations

$$C_{11} b_1 + C_{12} b_2 = C_{1y}$$

$$C_{12} b_1 + C_{22} b_2 = C_{2y}$$

$$C_{n1} b_1 + C_{n2} b_2 = C_{ny} \text{ ---------- 3.9}$$

together with

$$a = \bar{y} - \mathcal{E}_i b_i \bar{x}_i \text{ ---------- 3.10}$$

Hence, to find the values of b_1 and b_2, we can make use of a Gaussian elimination procedure. Once the values of b_1 and b_2 are found the value of a is subsequently derived and hence we derived our linear equation.

ii. for linear equation in the form

$$y = B_o + B_1 + X_1 + B_2 + X_2 + B_3 X_1 X_2 \text{ --- } 3.11$$

The original multiple regression equation would be in the form of:

$$y = B_o + B_1 + X_1 + B_2 + X_2 + B_3 (X_1 X_2) \text{ --- } 3.12$$

i.e the number of variables are $3(X_1, X_2,$ and $(X_1$ and $X_2)$.

Using the same procedure outlined for the linear regression, minimize the sum of square

$$S = (y - \alpha - B_1 * X_1 - B_2 * X_2 - B_3 X_1 * X_2)^2 \text{ ----- } 3.13$$

For S to be a minimum, $\frac{ds}{d\alpha} = 0$, $\frac{ds}{dB} = 0$.

and also α, $B_1 + B_2$ and B_3 will be replaced by the estimates b_O, b_1, b_2 and b_3.

Defining:

$$C_{ij} = \mathcal{E} x_i x_j - \frac{\mathcal{E} x_i \mathcal{E} x_j}{m} \text{ --- } 3.14$$

$$C_{iy} = \mathcal{E} x_i y - \frac{\mathcal{E} x_i \mathcal{E} y}{m} \text{ --- } 3.15$$

$$C_{yy} = \mathcal{E} y^2 - \frac{\mathcal{E} y^2}{m} \text{ --- } 3.16$$

Where m = number of observation which varies for different solution considered.

Thus leads to n - simultaneous linear equation.

$$C_{11}\, b_1 + C_{12}\, b_2 + C_{13}\, b_3 = C_{1y}$$

$$C_{12}\, b_1 + C_{22}\, b_2 + C_{13}\, b_3 = C_{2y}$$

.

.

.

$$C_{n1}\, b_1 + C_{n2}\, b_2 + C_{n3}\, b_3 = C_{ny} \text{ ..... } 3.17$$

Together with

$$a = \bar{y} - \sum_i b_i \bar{x}_i \text{ ---------- } 3.18$$

Using Gaussian elimination procedure, the values of b_o, b_1, b_2 and b_3 are found and the multiple linear equations are derived. In solving the n set of equations in other to get the final mathematical model, the most reliable Gaussian procedure in the Gauss Jordan reduction method.

3.3.0 MATHEMATICAL MODELS (THE EQUATION).

3.3.1 MODEL EQUATIONS

A. For Zn^{2+} cations at $33^{O}C$ with and without interaction of the species.

i. With interaction,

$$Y = -4.925E-06 - 2.146E-06X_1 + 5.782E-07\, X_2 + 3.291E-07\,(X_1 * X_2) \text{ ---------- } 3.19$$

ii. Without interaction,

$$Y = -6.142E-06 + 1.145E-06X_1 + 70.0E-06\, X_2 \text{ ... } 3.20$$

3.3.2 MODEL EQUATIONS

B. For Zn^{2+} cations at $40^{O}C$ with and without interaction of the species.

i. With interaction,

$$Y = - 6.445E - 06 - 3.752E - 06X_1 + 7.298E - 07\ X_2 + 4.719E - 07\ (X_1 * X_2) \text{ ---------- } 3.21$$

ii. Without interaction,

$$Y = - 8.539E - 06 + 9.936E - 07X_1 + 9.362E - 07\ X_2 \ldots 3.22$$

3.3.3 MODEL EQUATIONS

C. For Pb^{2+} cations at $33^{O}C$ with and without interaction of the species.

. With interaction,

$$Y = - 4.693E - 06 - 5.013E - 04X_1 + 4.471E - 07\ X_2 + 4.889E - 05\ (X_1 * X_2) \text{ ---------- } 3.23$$

ii. Without interaction,

$$Y = - 7.785E - 06 + 6.089E - 05X_1 + 7.16E - 07\ X_2 \ldots 3.24$$

3.3.4 MATHEMATIC MODEL EQUATION

D. For Pb^{2+} cations at $45^{O}C$ with and without interaction of the species.

1 With interaction,

$$Y = - 1.764E - 05 + 7.044E - 05X_1 + 1.654E - 06\ X_2 - 9.778E - 06\ (X_1 * X_2) \text{ ---------- } 3.25$$

2. Without interaction,

$$Y = - 1.702E - 05 - 4.2E - 05X_1 + 1.6E - 06\ X_2 \ldots 3.26$$

3.4 COMPUTER SIMULATION PROGRAM BASED ON MATHEMATICAL MODEL

```
CLS
 PRINT "DO YOU WANT TO DO ADSORPTION WITH
INTERACTION OF SPECIES OR WITHOUT?"
 INPUT " TEMPERATURE THAT WAS CONSIDERED"; T
PRINT "ADSORPTION AT TEMPERATURE OF "; T
5 PRINT " IF INTERACTION PRESS 1!"
PRINT "WITHOUT INTERACTION PRESS 2!"
INPUT "TYPE OF ABSORPTION"; J
IF J = 1 GOTO 10
IF J = 2 GOTO 20
IF J > 2 GOTO 40
10 INPUT "X1 AS CONCENTRATION "; X1
INPUT "A0"; A0
INPUT "A1"; A1
INPUT "A2"; A2
INPUT "A3"; A3
GOTO 30
20 INPUT "X1 AS CONCENTRATION "; X1
INPUT "A0"; A0
INPUT "A1"; A1
INPUT "A2"; A2
PRINT "A3 = 0"
A3 = 0
30 PRINT "ADSORPTION = Y"
```

```
FOR X2 = 9 TO 12 STEP 0.25
Y = A0 + A1 * X1 + A2 * X2 + A3 * X1 * X2
PRINT Y
NEXT X2
GOTO 50
40 PRINT "YOU HAVE TO INPUT A VALUE BASED ON
THE TYPE OF ADSORPTION"
PRINT " i.e 1 OR 2"
PRINT " DO YOU STILL WANT TO TRY IF YES PRESS 1
IF NO PRESS 2"
INPUT S
IF S = 1 GOTO 5
IF S = 2 GOTO 45
IF S > 2 GOTO 50
45 PRINT " YOU DO NOT KNOW WHAT TO DO"
50 END
```

CHAPTER FOUR

4.0 SIMULATED RESULTS FROM MODEL EQUATION

4.1 TABLE OF RESULT.

4.1.1 Simulated result for Zn^{2+} cation at $33^{O}C$ with and without interaction of the species.

Concentration of additive C $[X_1]$	Concentration of Electrolyte pH $[X_2]$	Simulated Results	
		Model Results with interaction	Model Results without interaction
1	9.00	1.10E – 06	1.30E – 06
1	9.50	1.55E – 06	1.65E – 06
1	10.00	2.00E – 06	2.00E – 06
1	10.50	2.46E – 06	2.35E – 06
1	11.00	2.91E - 06	2.70E - 06
0.1	9.00	3.61E – 07	2.72E – 07
0.1	9.50	6.67E - 07	6.22E – 07
0.1	10.00	9.72E - 07	9.72E – 07
0.1	10.50	1.28E - 07	1.32E – 06
0.1	11.00	1.58E - 07	1.67E – 06
0.01	9.00	2.88E - 07	1.69E - 07
0.01	9.50	5.78E - 07	5.19E - 07
0.01	10.00	8.69E - 07	8.69E - 07
0.01	10.50	11.6E - 07	1.22E - 06
0.01	11.00	14.5E - 07	1.57E - 06

TABLE 4.1.2; Simulated result for Zn^{2+} cation at $40^{O}C$ with and without interaction of the species.

Concentration of additive C $[X_1]$	Concentration of Electrolyte pH $[X_2]$	Simulated Results	
		Model Results with interaction	Model Results without interaction
1	9.00	6.18E – 07	8.8E – 07
1	9.50	1.22E – 06	1.35E – 06
1	10.00	1.82E – 06	1.82E – 06
1	10.50	2.42E – 06	2.28E – 06
1	11.00	3.02E - 06	2.75E - 06
0.1	10.00	9.50E – 07	9.22E – 07
0.1	10.50	1.34E - 06	1.36E – 06
0.1	11.00	1.73E - 06	1.86E – 06
0.01	9.00	1.28E - 07	-1.03E - 07
0.01	9.50	4.95E - 07	3.65E - 07
0.01	10.00	8.63E - 07	8.33E - 07
0.01	10.50	1.23E – 06	1.30E - 06
0.01	11.00	1.60E – 06	1.77E - 06

TABLE 4.1.3 Simulated result for Pb^{2+} cation at $33^{O}C$ with and without interaction of the species.

Concentration of additive C [X_1]	Concentration of Electrolyte pH [X_2]	Simulated Results	
		Model Results with interaction	Model Results without interaction
0.01	11.00	5.90E – 07	7.00E – 07
0.01	11.25	8.24E – 07	8.79E – 07
0.01	11.50	1.06E – 06	1.06E – 06
0.01	11.55	1.29E – 06	1.24E – 06
0.01	12.00	1.53E - 06	1.42E – 07
0.001	11.00	2.62E – 07	1.52E – 07
0.001	11.25	3.86E - 07	3.31E – 07
0.001	11.50	5.10E - 07	5.10E – 07
0.001	11.55	6.34E - 07	6.89E – 07
0.001	12.00	7.58E - 07	8.68E – 07

TABLE 4.1.4 Simulated result for Pb^{2+} cation at $45^{O}C$ with and without interaction of the species.

Concentration of additive C [X_1]	Concentration of Electrolyte pH [X_2]	Simulated Results	
		Model Results with interaction	Model Results without interaction
0.01	11.00	1.83E – 07	1.56E – 07
0.01	11.25	5.72E – 07	5.56E – 07
0.01	11.50	9.61E – 07	9.56E – 07
0.01	11.75	1.35E – 06	1.36E – 06
0.01	12.00	1.74E - 06	1.76E – 06
0.001	11.00	5.17E – 07	5.34E – 07
0.001	11.25	9.28E - 07	9.34E – 07
0.001	11.50	1.34E - 06	1.33E – 06
0.001	11.75	1.75E - 06	1.73E – 06
0.001	12.00	2.16E - 06	2.13E – 06

CHAPTER FIVE

5.0 DISCUSSION OF RESULT.

In statistic analysis of the model results, both the polymath 5.1 and QBasic software's program will be used.

Using the polymath 5.1 software program, the statistical analysis of the various mathematical models derived was carried out, thus a set of tables were generated for Zn^{2+} cations at temperature of $33^{O}C$ and $45^{O}C$, and for Pb^{2+} cations model at different temperature of $33^{O}C$ and $45^{O}C$

For statistical analysis of the mathematical model, the parameters of interest are, the multiple regression, root mean standard error (Rmsd) and the variance, significance F. there defunction is given in the table below.

Regression coefficient (multiple R) – This is the numerical representation of the degree of condition between two steps of data.

For regression coefficient close to unity it means the model equation best fit the data being considered.

Standard Error:- This is the error encountered during the polynomial fitting when deriving the mathematical model. Variance measures the difference between two set of date.

5.1 STATISTICAL REGRESSION ANALYSIS FOR Zn^{2+} AT $33^{O}C$ WITH INTERACTION.

Regression Statistics	Variable Coefficient	Values Coefficient	95% Confidenc
$R^n2 = 0.8867831$	a_0	- 4.925E – 06	3.14E – 06
R^n adj = 0.8559058	a_1	- 2.146E – 06	5.412E – 06
Rmsd = 6.639E - 08	a_2	5.782E -- 07	3.32E – 07
Variance = 9.015E - 14	a_3	3.291E – 07	5.398E – 07

Analyzing adsorption of Zn^{2+} cation at $33^{O}C$ with and with interaction,

For adsorption with interaction of species, adsorption capacity increasing proportional to the increment in pH value, of the electrolyte while it decrease with increase in the concentration of the additive. The interaction coefficient is positive for adsorption capacity, so it increases the adsorption capacity for increment in both pH value of electrolyte and additive concentration. The correlation coefficient, which is a measure of agreement between experimental and simulated value, is 0.8867831 and the variance is 9.025E – 14.

5.2 FOR Zn^{2+} AT $33^{O}C$ WITHOUT INTERACTION.

Regression Statistics	Variable Coefficient	Values Coefficient	95% Confidenc
R"2 = 0.86827493	a_o	- 6.142E – 6	2.478E – 6
R" adj = 0.8462908	a_1	1.145E – 6	3.903E – 7
Rmsd = 7.161E - 08	a_2	7.0E – 7	2.467E – 7
Variance = 9.616E - 14			

For adsorption capacity of Zn^{2+} at 33 without the interaction of the species, the adsorption capacity depends more on the concentration of the additive as both the concentration of additive and pH value of the electrolyte increase. The correlation coefficient was 0.8682493 and variance was 9.616E – 14:

5.3 COMPARISON OF ANALYSIS OF ITEM 5.1 AND 5.2

From the correlation coefficient values and variance, it could be seen that multiple R is highest for adsorption capacity involving interaction of species and with least variance between the experimental and simulated result.

This simply means that the mathematical models that best represent the experimental data is the form of $Y = a_o + a_1 x_1 + a_2 x_2 + a_3 x_1 * x_2$.

Furthermore, R = 0.8867831, which in closer to unity than R = 0.8682493 for adsorption without interaction, therefore the best mathematical model equation that best fit the experimental data is the multiple linear regression equation, that of interaction i.e.

$$Y = - 4.925E - 06 - 2.146E - 06\ X_1 + 5.782E - 07\ X_2 + 3.291E - 07\ X_1 * X_2.$$

5.4 STATISTICAL REGRESSION ANALYSIS FOR Zn^{2+} AT $40^{O}C$ WITH INTERACTION.

Regression Statistics	Variable Coefficient	Values Coefficient	95% Confidence
R^2 = 0.7144951	a_o	- 6.445E – 06	7.396E – 06
R^ adj = 0.6193268	a_1	-3.752E – 06	1.131E – 05
Rmsd = 1.336E – 07	a_2	7.298E – 07	1.261E – 07
Variance = 3.354E – 13	a_3	4.710E – 07	1.23E – 06

Analyzing the adsorption of Zn^{2+} at $40^{O}C$ interaction of the species;

. For adsorption with interaction of species, the adsorption capacity increases with the increasing value of electrolyte i.e pH value. The interaction of the species also increases the adsorption capacity of Zn^{2+}, but as concentration of additive increases, the adsorption capacity decreases. The correlation coefficient of Zn^{2+} adsorption capacity with experimental data is 0.7144915 and it variance is 3.354E - 13.

5.5 STATISTICAL REGRESSION ANALYSIS FOR Zn^{2+} AT $40^{O}C$ WITHOUT INTERACTION SPECIES.

Regression Statistics	Variable Coefficient	Values Coefficient	95% Confidenc
R^2 = 0.6858106	a_0	- 8.539E – 06	5.359E – 06
R adj = 0.6229728	a_1	9.936E – 07	7.683E – 07
Rmsd = 1.402E – 07	a_2	9.362E – 07	5.242E – 07
Variance = 3.321E – 13			

For adsorption without interaction, both the additive concentration of the electrolyte i.e pH values increase the adsorption capacity of MnO_2 as the value increases, but the value of correlation coefficient given without interaction is 0.6858106 and variance of 3.32E – 13.

5.6 COMPARISON ANALYSIS OF ITEM 5.4 AND 5.5

From the correlation coefficient value, it can be seen that the highest value for multiple R recurred where there was interaction between the species which is 0.7144951 as compared with R value for adsorption without interaction of the same and concentration of additive and electrolyte

This simply means that the mathematical model equation that best represents the linear regression equation modeled is of the form of multiple linear regression equation i.e Y = -6.445E – 06 – 3.752E – 06 X_1 + 7.298E – 07 X_2+ 4.719E – 07 X_1* X_2.

5.7 STATISTICAL REGRESSION ANALYSIS FOR Pb^{2+} AT 33^{O}C WITHOUT INTERACTION SPECIES.

Regression Statistics	Variable Coefficient	Values Coefficient	95% Confidenc
R"2 = 0.9730874	a_o	- 4.603E – 06	3.253E – 06
R" adj = 0.9595312	a_1	-5.013E– 04	4.578E – 04
Rmsd = 2.004E – 08	a_2	4.471E – 07	2.828E – 07
Variance = 6.693E – 15	a_3	4.889E- 05	3.979E – 05

Analyzing the adsorption of Pb^{2+} cation at 33^{O}C with interaction of the species.

. For adsorption with interaction of species, the adsorption capacity of MnO_2 increases as the concentration of the electrolyte i.e PH increases, the interaction of species also increase the adsorption capacity, but increase of the concentration of the additive has negative effect on the adsorption capacity.

The correlation coefficient of Pb^{2+} adsorption capacity with the experimental data is 0.9730874 and its variance is 6.693E – 15.

5.8 STATISTICAL REGRESSION ANALYSIS FOR Pb^{2+} CATION AT 33^{O}C WITHOUT INTERACTION SPECIES.

Regression Statistics	Variable Coefficient	Values Coefficient	95% Confidenc
R^2 = 0.9326444	a_o	- 7.785E – 06	2.921E – 06
R^ adj = 0.9132713	a_1	6.089E– 05	1.993E – 05
Rmsd = 3.173E – 08	a_2	7.16E – 07	2.537E – 07
Variance = 1.43E – 13			

For adsorption without interaction, both the additive concentration and electrolyte concentration have positive effect on the adsorption capacity of MnO_2 as their value increases, but the correlation coefficient without interaction is 0.9325444 and it's variance is 1.438e – 13 compared with the experimental data.

5.9 COMPARISON OF ANALYSIS OF ITEM 5.7 AND 5.8

From the correlation coefficient values, multiple R has highest value for interaction of species, which is 0.9730874 as compared with that without interaction, which is 0.9325444. Therefore the mathematical model, that best represent the experimental data is of the form;

$$Y = a_o + a_1 x_1 + a_2 x_2 + a_3 x_1 \cdot x_2.$$

Since R = 0.9730874, the equation is thus.

$$Y = - 4.693E - 06 - 5.013E - 04 X_1 + 4.471E - 07 X_2 + 4.889E - 05 X_1 \cdot X_2$$

5.10 STATISTICAL REGRESSION ANALYSIS FOR Pb^{2+} CATION AT $45^{O}C$ WITH INTERACTION OF SPECIES.

Regression Statistics	Variable Coefficient	Values Coefficient	95% Confiden
R^2 = 0.7105263	a_o	- 1.76E – 05	1.955E – 05
R adj = 0.5657894	a_1	7.044E– 05	0.0027511
Rmsd = 31.204E – 07	a_2	1.654E – 06	1.699E – 06
Variance = 2.417E– 13	a_3	-9.778E – 06	2.391E – 04

Analyzing the adsorption capacity of Pb^{2+} cation on MnO_2 with interaction of species at $45^{O}C$.

For adsorption capacity of Pb^{2+} cation on MnO_2 with interaction of species, the adsorption capacity on MnO_2 increases with increases in both the additive and electrolyte concentration.

The correlation coefficient of model values compared with experimental values is 0.7105263 and it its variance is 2.417E – 13.

5.11 STATISTICAL REGRESSION ANALYSIS FOR Pb^{2+} CATION AT $45^{O}C$ WITHOUT INTERACTION OF SPECIES.

Regression Statistics	Variable Coefficient	Values Coefficient	95% Confiden
R^2 = 0.7100432	a_o	- 1.702E – 05	1.109E – 05
R adj = 0.6271984	a_1	- 4.2E– 05	7.571E – 05
Rmsd = 1.205E – 07	a_2	1.6E – 06	9.636E – 07
Variance = 2.075E– 13			

For adsorption capacity without interaction, the adsorption capacity increases with increase in the electrolyte concentration i.e pH, but decreases with increase in the concentration of the additive, the correlation coefficient of the model values compared with the experimental value was 0.7100432 and its variance was 2.075E – 13.

5.12 COMPARISON OF ANALYSIS OF ITEM 5.10 AND 5.11

From the correlation coefficient values, multiple R is highest for adsorption capacity on MnO_2 with interaction of species which is 0.7105265 as compared with adsorption capacity without interaction which is 0.710043

Therefore the best mathematical model that best represent the experimental data is of the form,

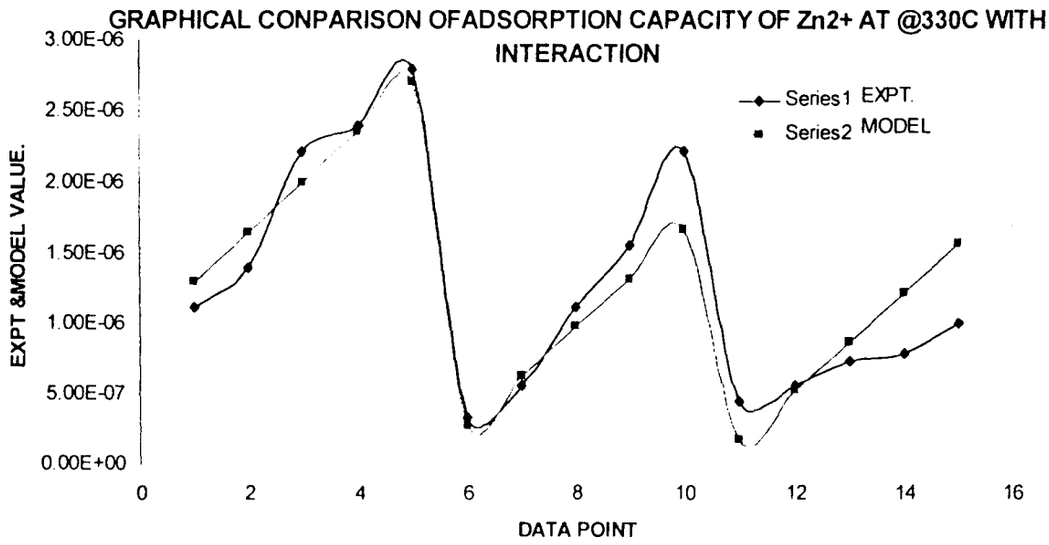
$$Y = a_o + a_1 x_1 + a_2 x_2 + a_3 x_1 x_2.$$

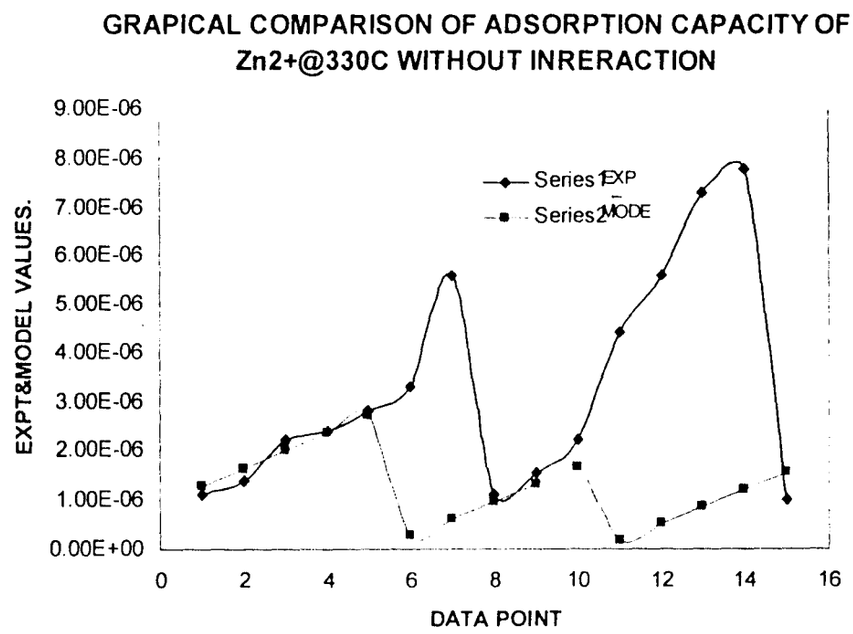
Since R = 0.7105265 > 0.7100432.

the equation is thus.

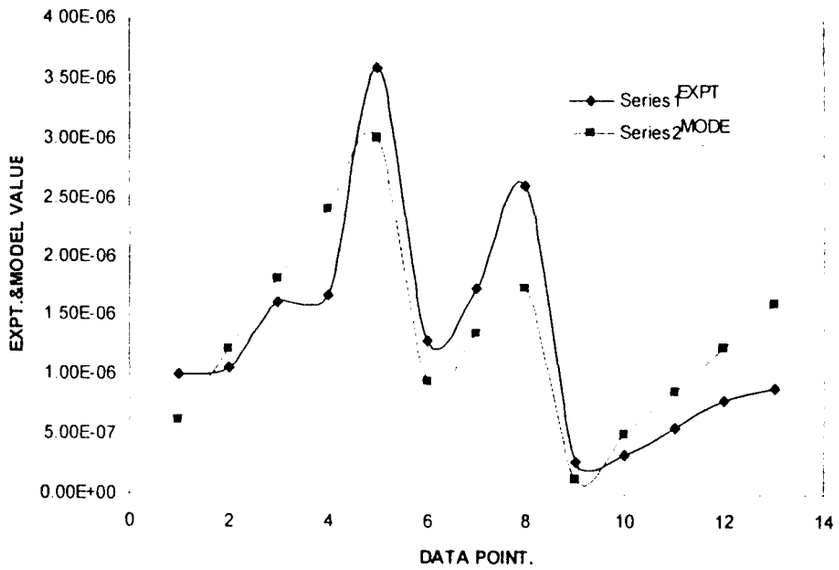
$$Y = - 1.76E - 05 + 7.044E - 05 X_1 + 1.65E - 06 X_2 - 9.778E - 06 X_1 * X_2.$$

5.13 GRAPHIC COMPARISON OF THE EXPERIMENTAL DATA AND SIMULATED VALUES OF Y THAT BEST FITS THE DATA IS SHOW BELOW.

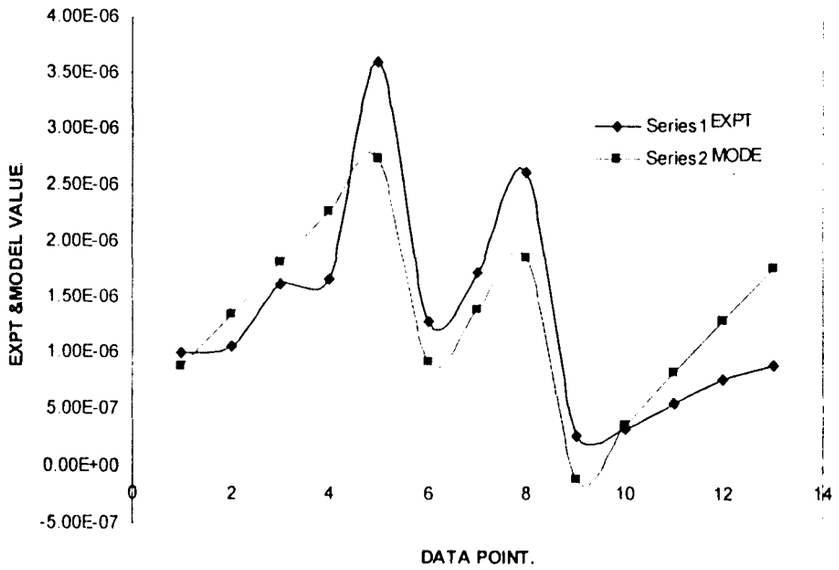




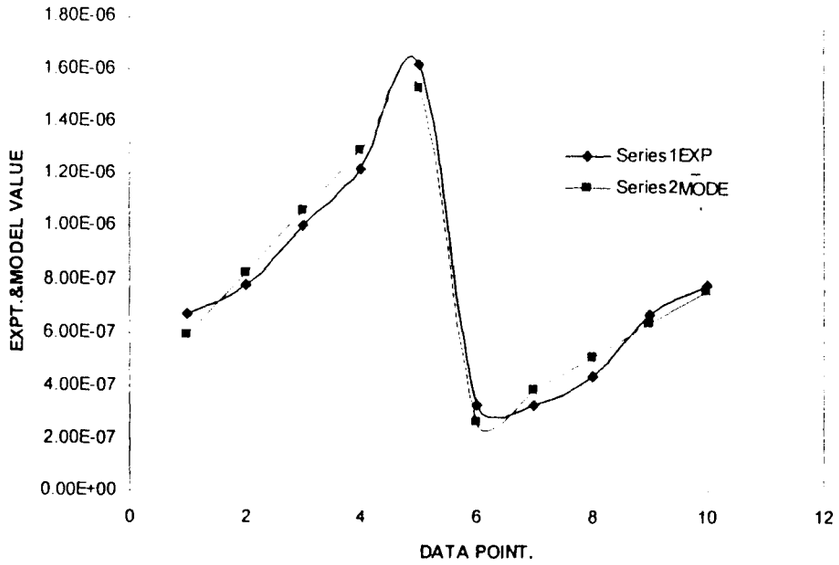
GRAPHICAL COMPARISON OFADSORPTION CAPACITY OF Zn2+ @400C WITH INTERACTION



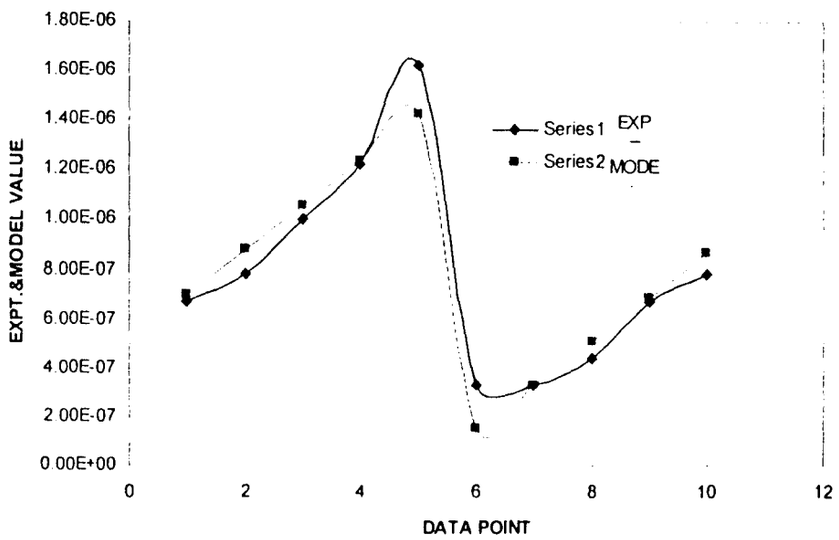
GRAPHICAL COMPARISON OF ADSORPTION CAPACITY OF Zn2+ @400C WITHOUT INTERACTION.



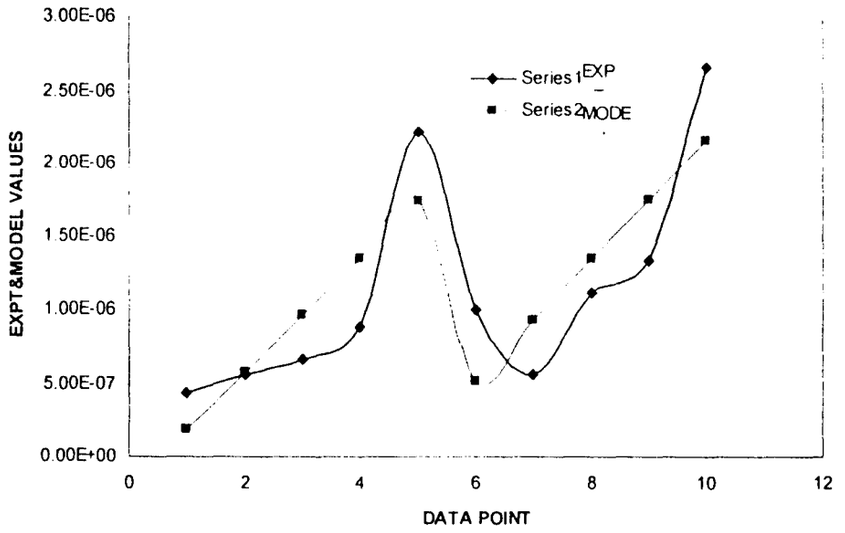
GRAPHICAL COMPARISON OFADSORPTION CAPACITY OF Pb2+ @330C WITH INTERACTION.



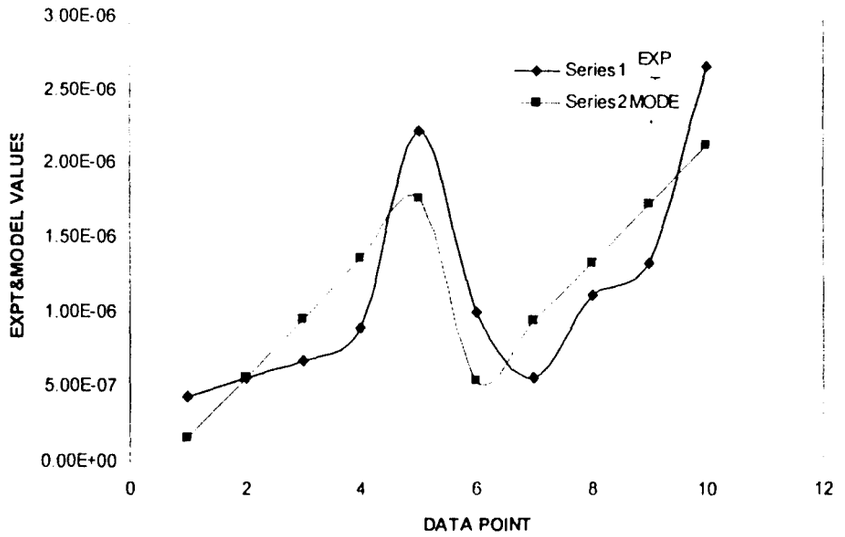
GRAPHICAL COMPARISON OF ADSORPTION CAPACITY OF Pb2+ @330C WITHOUT INTERACTION



GRAPHICAL COMPARISON OF ADSORPTION CAPACITY OF Pb2+ @450C WITH INTERACTION.



GRAPHICAL COMPARISON OF ADSORPTION CAPACITY OFPb2+ @450C WITHOUT INTERACTION



In the case of Standard Error, the values are lowest for adsorption of Zn^{2+} with infections of species; it is also lowest for adsorption of Pb^{2+} cations with interaction of species. However, since for Zn^{2+}, standard

is 6.0393E – 08 and for Pb^{2+} is 2.004E – 08, the standard errors are still within acceptable units.

Reasons for Variation in Results:

i. Understanding of data: This is the possibility that the data used in determining some parameter could contain Error e.g. during calculation of charge involve.

ii. In sufficient data to fit the polynomial equation and limitation imposed by assumption e.g content temperature for such step during experimental procedure.

CHAPTER SIX

5.0 CONCLUSION AND RECOMMENDATION.

6.1 CONCLUSION

From the simulated results obtained from the mathematical models, the following conclusion can be made;

i. Generally for divalent cations, as concentration of cations in solution reduces, a greater adsorption capacity is obtained at high values of pH,i.e as the electrolyte concentration value increases,high adsorption capacity is obtained.

ii. The adsorption operation is best carried out at ordinary temperature[physical adsorption in this case] with interaction of specie

iii The model equations derived best fit the experimental data with correlation coefficients of 0.8867831 and 0.9730874 for both Zn^{2+} and Pb^{2+} cations respectively.

6.2 RE COMMENDATION

i. Computer courses should be introduced to the department of higher level. This will improve student ability to carry out modelling and computer simulation using computer.

ii. In production of a dry cell, cations preferably Pb^{2+} cations should be blended with MnO_2 in order to enhance it activities.

iii. High pH value of electrolytes should be used in other to obtain higher adsorption capacity at ordinary temperature and at reduced concentration of the solution.

iv. High order polynomial can be used for the experimental data. This would improve the model generated.

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APPENDIX I "COMPUTER SIMULATION PROGRAM BASED ON MATHEMATICAL MODEL"

```
CLS
 PRINT "DO YOU WANT TO DO ADSORPTION WITH
INTERACTION OF SPECIES OR WITHOUT?"
 INPUT " TEMPERATURE THAT WAS CONSIDERED"; T
PRINT "ADSORPTION AT TEMPERATURE OF "; T
5 PRINT " IF INTERACTION PRESS 1!"
PRINT "WITHOUT INTERACTION PRESS 2!"
INPUT "TYPE OF ABSORPTION"; J
IF J = 1 GOTO 10
IF J = 2 GOTO 20
IF J > 2 GOTO 40
10 INPUT "X1 AS CONCENTRATION "; X1
INPUT "A0"; A0
INPUT "A1"; A1
INPUT "A2"; A2
INPUT "A3"; A3
GOTO 30
20 INPUT "X1 AS CONCENTRATION "; X1
INPUT "A0"; A0
INPUT "A1"; A1
INPUT "A2"; A2
PRINT "A3 = 0"
A3 = 0
30 PRINT "ADSORPTION = Y"
```

```
FOR X2 = 9 TO 12 STEP 0.25
Y = A0 + A1 * X1 + A2 * X2 + A3 * X1 * X2
PRINT Y
NEXT X2
GOTO 50
40 PRINT "YOU HAVE TO INPUT A VALUE BASED ON
THE TYPE OF ADSORPTION"
PRINT " i.e 1 OR 2"
PRINT " DO YOU STILL WANT TO TRY IF YES PRESS 1
IF NO PRESS 2"
INPUT S
IF S = 1 GOTO 5
IF S = 2 GOTO 45
IF S > 2 GOTO 50
45 PRINT " YOU DO NOT KNOW WHAT TO DO"
50 END
```

APPENDIX II LIST OF TABLE