EFFECTS OF SELECTED ANIONS ON THE ELONGATION OF THE LIFESPAN OF LECLANCHE CELLS



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BY

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DECLARATION

I, Yakaka Kachalla, M.ENG/SEET/2003/936 declare that this project work titled "Effects of selected anions on the elongation of lifespan of leclanche cells" is my original work.

Signature

P06/2011.

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CERTIFICATION

This is to certify that this project titled "EFFECTS OF SELECTED ANIONS ON THE ELONGATION OF THE LIFESPAN OF LECLANCHE CELLS" was carried out by Yakaka Kachalla (M.ENG/SEET/2003/936) meet the regulation governing the award of the Master of Engineering (Chemical Engineering) of Federal University of Technology, Minna and is approved for its scientific contribution to knowledge and literary presentation.

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DEDICATION

This Project work is entirely dedicated to my late Mother.

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My profound thanks goes to the Almighty God, The most high for his continuous guidance, mercies and favors throughout my life. May he continue to shower his blessings on is now and forever

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Thank You all, may Almighty God bless each and every one of us. Amen.

ABSTRACT

he effect of selected anions on the elongation of the lifespan of a Leclenche cell was nyestigated. The determination of the surface area of manganese dioxide was carried out sing adsorption from solution method and was found to be $1702.69m^2/g$. The adsorption of nese anions on manganese dioxide is to enhance the lifespan of Leclanche cell. The dsorption method by potentiometric titration was used for different anions at four different oncentrations (1M, 0.1M, 0.01M, and 0.001M) of the salt solutions at varied temperatures of 8°C, 30°C and 32°C. The electric surface charge of the anions at various temperatures and oncentrations were also determined. The quadratic models describing the adsorption process f these anions on MnO₂, were developed by factorial analysis and further optimized using tatistical Package for Social Science (SPSS) software programme. The experiments were erformed based on the factorial design technique in order to enhance determination of the urface response analysis of the relationship between the Surface charge (E) of MnO₂ and the wo factors; Concentration (X₁) and Temperature (X₂). The result showed that blending of ome anions particularly SO₄²⁻ with manganese dioxide can improve the lifespan of a cell due o its consistency in higher electric surface charge in all concentrations and temperatures.

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CHAPTER ONE

1.0 INTRODUCTION

1.1 Background

Battery is an electrochemical device that contains two or more power cells connected electrically so that the chemical energy is converted into electricity. A battery powers products that require electricity to work. They are useful because they allow us to transport electricity and use products in locations where there no electrical outlets.

In a battery, each cell that stores the electrical energy in a chemical state has two electrodes that react with the chemical and each other to release energy. The battery's two metal ends are called "Terminals". Terminals are positive and negative ends.

Leclanche cell is a cell dry cell made up of a zinc case as anode (negative pole) and carbon rod a cathode (positive pole). This battery is filled with a mixture of MnO_2 as an oxidant or depolarizer to lower the internal resistance of the cell.

This project work is to optimize the adsorption process of the anions namely $SO_4^{2^\circ}$, NO_3° , CI° , Br, and I on a MnO₂ in a Leclanche cell. This is expected to increase the lifespan of the battery, The lifespan of the battery is about 300 seconds on a continuous operation, this short lifespan increases the rate of replacement of these cells with its attendant consequences to the environment.

The optimum temperature range of operation is between $20 - 50^{\circ}$ C, outside this temperature range the performance deteriotes markedly.

During the potentiometric titration experiment, concentration and temperature were varied while other factors were kept constant.

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How Cells Work

Galvanic Action

In simple terms, batteries can be considered as electron pumps. The internal chemical reaction within the battery between the electrolyte and the negative metal electrode produces a build up of free electrons, \bigcirc each with a negative charge, at the battery's negative (-) terminal - the anode. The chemical reaction between the electrolyte and the positive (+) electrode inside the battery produces an excess of positive (+) ions \bigcirc (atoms that are missing electrons, thus with a net positive charge) at the positive (+) terminal - the cathode of the battery. The electrical (pump) pressure or potential difference between the + and - terminals is called voltage or electromotive force (EMF).

Different metals have different affinities for electrons. When two dissimilar metals (or metal compounds) are put in contact or connected through a conducting medium there is a tendency for electrons to pass from the metal with the smaller affinity for electrons, which becomes positively charged, to the metal with the greater affinity which becomes negatively charged. A potential difference between the metals will therefore build up until it just balances the tendency of the electron transfer between the metals. At this point the "equilibrium potential" is that which balances the difference between the propensity of the two metals to gain or lose electrons.

A battery or galvanic cell stores energy in chemical form in its active materials and can this convert this to electrical energy on demand, typically by means of an electrochemical oxidation-reduction (redox) reaction. (Note the generic name "redox" seems to have been appropriated by a recent flow battery design employing two vanadium redox couples). Each galvanic or energy cell consists of at least three and sometimes four components The anode or negative electrode (the reducing or fuel electrode) which gives up electrons to the external circuit and is oxidised during the electrochemical (discharge) reaction. It is generally a metal or an alloy but hydrogen is also used. The anodic process is the oxidation of the metal to form metal ions.

(LEO Lose Electrons - Oxidation)

- 2. The cathode or positive electrode (the oxidizing electrode) which accepts electrons from the external circuit and is reduced during the electrochemical (discharge) reaction. It is usually an metallic oxide or a sulfide but oxygen is also used. The cathodic process is the reduction of the oxide to leave the metal. (GER Gain Electrons Reduction). Remember the mnemonic of the lion growling.
- 3. The electrolyte (the ionic conductor) which provides the medium for transfer of charge as ions inside the cell between the anode and cathode. The electrolyte is typically a solvent containing dissolved chemicals providing ionic conductivity. It should be a non-conductor of electrons to avoid self discharge of the cell.
- 4. The separator which electrically isolates the positive and negative electrodes.

The model of the cell as two half cells is used by electro-chemists and cell designers to calculate electrode potentials and and characterise the chemical reactions within the cell. The **cell voltage** or **electromotive force (EMF)** for the external current derived from a cell is the difference in the standard electrode potentials of the two half cell reactions under standard conditions. But real voltaic cells will typically differ from the standard conditions. The **Nernst equation** relates the actual voltage of a chemical cell to the standard electrode potentials taking into account the temperature and the concentrations of the reactants and products. The EMF of the cell will decrease as the concentration of the active chemicals diminishes as they are used up until one of the chemicals is completely exhausted.

The theoretical energy available from the cell can be calculated using <u>Gibbs free energy</u> equation for the initial and final equilibrium states.

Fortunately such intimate knowledge of cell chemistry and thermodynamics is not usually required by the battery applications engineer.

Primary cells

In primary cells this electrochemical reaction is not reversible. During discharging the chemical compounds are permanently changed and electrical energy is released until the original compounds are completely exhausted. Thus the cells can be used only once.

Secondary cells

In secondary cells this electrochemical reaction is reversible and the original chemical compounds can be reconstituted by the application of an electrical potential between the electrodes injecting energy into the cell. Such cells can be discharged and recharged many times.

Dry cell

Leclanche or dry cell is an example of non-rechargeable primary cell, It is made up of Zinc case as anode, carbon rod in contact with carbon and MnO_2 as cathode and the electrolyte is a paste of NH_4Cl , $ZnCl_2$ (acid electrolyte).,

The e.m.f (operating voltage) of the leclanche cell is about 1.5V and the following reactions occur in the cell;

Anode (-)

Zinc case – The bottom of the battery is normally exposed and serves as a negative pole

CHAPTER TWO

2.0

LITERATURE REVIEW

The dry cell, invented in 1867 by the French engineer Georges Leclanché (1839 - 1889), is widely used as a source of electric energy in electric torches and small appliances such as transistor radios.

Alessandro Volta in 1789 took a copper rod and a zinc rod and immersed them both in an acetic acid solution. He had just constructed the first battery cell with the first electrolyte. The copper and zinc rods were the electrodes, positive and negative. The acid started to eat away the zinc rod, while the copper rod captured the energy released from the action. A voltage developed between the two electrodes. Volta had invented the battery. The electrochemical principles that he discovered are still the foundation for the battery industry.

Seventy-nine years went by before George Leclanch developed a practical cell. He used manganese-dioxide powder as the positive electrode instead of copper; he kept the zinc. He used sal ammoniac (ammonium chloride) in water for his electrolyte. A porous cup held the powder which surrounded a carbon collector. Leclanch put the whole business, or the cell, into a glass jar and invented the first wet battery.

The first dry cell battery was manufactured in 1888 under the auspices of a Dr. Gassner. It was to become the prototype for the dry cell battery industry. Gassner used zinc to hold all of the components and kept zinc for the negative electrode as well. The electrolyte material was absorbed by a porous medium. He also added zinc chloride to the electrolyte, which cut back zinc corrosion when the cell was inactive. This was a big step for longer battery storage life. Now, for the first time a dry cell battery was a neat, tightly sealed package, almost ready for mass production. It didn't take long. Batteries were first mass-produced in 1890 by the National Carbon Company at their plant in Cleveland, Ohio. Later they became the industrial giant known as Union Carbide.

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Between 1890 and the 1970's, dry cell batteries increased in popularity, but there were no significant changes in design. During the 1970's, battery technology began increasing rapidly, with new batteries and new ways of making the old batteries occurring regularly. Now, in addition to the standard dry cell batteries (Carbon Zinc and Zinc Chloride), the range of batteries also includes:

- Alkaline batteries (standard and high-performance)
- Lead-acid batteries
- Lithium batteries (Lithium Manganese, Lithium Ion, and Lithium Ion Polymer)
- Nickel-Cadmium batteries
- Nickel Metal-hydride batteries
- Silver-oxide batteries
- Zinc-air batteries

All batteries can be described as either primary or secondary. **Primary batteries** are those batteries that are used only once and then discarded; they cannot be recharged. They have the dual advantages of having both a higher initial voltage and longer life than **secondary batteries** of the same size. Secondary batteries are the rechargeable batteries. While the initial voltage and battery life is less, they have the significant advantage of being reusable.

Primary battery construction ranges from the basic construction used in carbon zinc and zinc chloride batteries to the more complex construction of more powerful batteries such as alkaline and lithium manganese. Changes in the components and the construction allow for the improved battery life of alkaline and lithium batteries.

In alkaline batteries, the zinc anode is a zinc powder in the center of the can, surrounding a brass current collector. The electrolyte is potassium hydroxide, and the zinc and potassium hydroxide are combined in a gel. The manganese-dioxide cathode is contained between the can wall and the separator, which keeps the cathode and anode from direct contact. The can wall in alkalines is steel, rather than zinc.

Table 2.1: Battery Time Line	(short history of flash light battery. Brooke Clarke 2005)
,	

Year	Name	Comment
1000	Valta	Dile of common & sine compreted by electrolyte
1800	Volta	Pile of copper & zinc separated by electrolyte
1821	Seebeck	called a thermopile (based on the "pile" name by Volta used by
		Simon Ohm 1825 to develop Ohms law
1836	Daniell	porous cup separates copper and zinc
1859	Planté	Lead Acid cell
1860	Callaud	Gravity cell eliminates the porous cup from Daniell cell
1866	Leclanché	Zinc & carbon porous cup and later without cup
1887	Gassner	Zinc carbon dry battery

2.1 Leclanche Dry Cell

French engineer who in about 1866 invented the battery that bears his name. In slightly modified form, the Leclanché battery, now called a dry cell, is produced in great quantities and is widely used in devices such as flashlights and portable radios. (Biographies of leclanche online)

George Leclanché was born in Parmain (France) in 1839. He was the son of Léopold Leclanché and Eugenie of Villeneuve. Leclanché was educated in England. He returned to France to continue his study in the Central School of Arts and Manufactures. After completing a technical education in 1860, Leclanché began work as an engineer. Six years later he developed his battery, which contained a conducting solution (electrolyte) of ammonium chloride, a negative terminal of zinc, and a positive terminal of manganese dioxide.

In 1866, Georges Leclanche patented a new system, which was immediately successful. Leclanche's original cell was assembled in a porous pot. The positive electrode consisted of crushed manganese dioxide with a little carbon mixed in. The negative pole was a zinc rod. The cathode was packed into the pot, and a carbon rod was inserted to act as a currency collector. The anode or zinc rod and the pot were then immersed in an ammonium chloride solution. The liquid acted as the electrolyte, readily seeping through the porous cup and making contact with the cathode material. Leclanche's "wet"cell (as it was popularly referred to) became the forerunner to the world's first widely used battery, the zinc carbon cell.

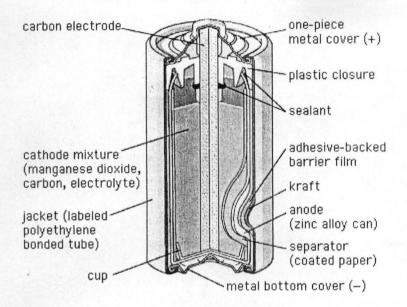


FIGURE 2.1 Leclanche Dry Cell

The Leclanche Cell consisted of a glass jar containing a porous pot with a central carbon element surrounded by powdered manganese dioxide. This formed the positive electrode. The negative electrode being a zinc rod standing in the jar which was half-filled with ammonium chloride solution, thickened by the addition of sand or sawdust. By 1868 20,000 such cells were in use and this original design, with little alteration, continued in use for nearly a hundred years. Disadvantages included its weight and bulk, the breakable glass container and the possibility of dangerous spillage. This battery was used mainly for intermittent service, such as ringing electric bells.

The e.m.f. of a Leclanche cell is about 1.5 volts buts its resistance may amount to several ohms when a porous pot is employed. It was used extensively for telegraphy, signaling and electric bell work; and for most work where intermittent current is required and where it is essential that the battery should require very little attention from time to time.

The chemical process that produces electricity begins when the atoms of zinc at the surface of the anode oxidize. A zinc atom oxidizes when it gives up both its electrons. It then becomes an ion with a positive charge. The zinc ions move away from the anode. As they do so, they leave their electrons behind on its surface. The anode thus gains an excess of electrons and becomes more negatively charged than the cathode. If a cell is connected to an external circuit, the zinc anode's excess electrons flow through the circuit to the carbon rod. The movement of electrons forms an electric current. After the electrons enter the cell through the rod, they combine with molecules of manganese dioxide and molecules of water. As these substances are reduced (gain electrons) and react with one another, they produce manganese oxide and negative hydroxide ions. This reaction makes up the second half of the cell's discharge process. It is accompanied by a secondary reaction. In the secondary reaction, the negative hydroxide ions combine with positive ammonium ions that form when ammonium chloride is dissolved in water. The secondary reaction produces molecules of ammonia and molecules of water.

$$Zn(s) + 2 MnO_2(s) + 2 NH_4Cl(aq) ----> ZnCl_2(aq) + Mn_2O_3(s) + 2 NH_3(aq) + H_2O$$
 2.1

The various chemical reactions by which a carbon-zinc cell produces electricity continue until the manganese dioxide wears away. After this cathode material has been "used up," the cell can no longer provide useful energy and is dead. Dead cells should be removed immediately. Even after a cell stops working, its electrolyte continues to eat away at the container and may puncture it. If the electrolyte leaks out, it can damage the equipment.

A carbon-zinc cell, like most primary batteries, cannot be recharged efficiently. But a device called a battery charger may extend the life of a cell for a short time. It partially restores the cell's ability to produce electricity. A battery charger functions by passing a current through the cell in a direction opposite to that of the flow of electricity during discharge.

Leclanche's invention, which was quite heavy and prone to breakage, was steadily improved over the years. The idea of encapsulating both the negative electrode and porous pot into a zinc cup was first patented by J.A. Thiebaut in 1881. But, it was Carl Gassner of Mainz who is credited as constructing the first commercially successful "dry" cell. Variations followed. By 1889 there were at least six well-known dry batteries in circulation. Later battery manufacturing produced smaller, lighter batteries, and the application of the tungsten filament in 1909 created the impetus to develop batteries for use in torches.

In 1867 George Leclanché gave up his job to devote full time to his invention; a year later it was adopted by the telegraph service of Belgium. He subsequently opened a factory to produce the battery and other electric devices; the business was taken over by his brother Maurice upon Georges's death in 1882.

2.2 Manganese Dioxide

<u>Manganese(IV) oxide</u> was used in the original type of <u>dry cell battery</u> as an electron acceptor from zinc, and is the blackish material found when opening carbon-zinc type flashlight cells. The same material also functions in newer <u>alkaline batteries</u> (usually battery cells), which use the same basic reaction, but a different electrolyte mixture.

Manganese(IV) oxide is the <u>chemical compound</u> MnO₂, commonly called manganese dioxide. This blackish or brown solid occurs naturally as the mineral <u>pyrolusite</u>, which is the main ore of <u>manganese</u>. It is also present in <u>manganese nodules</u>. The principal use for MnO₂ is for dry-cell <u>batteries</u>, such as the <u>alkaline battery</u> and the <u>zinc-carbon battery</u>. In 1976 this application accounted for 500,000 tonnes of pyrolusite.^[1] MnO₂ is also used for production of <u>MnO₄=. It is used extensively as an oxidizing agent in organic synthesis</u>, for example, for the oxidation of <u>allylic alcohols</u>.

Manganese compounds were in use in prehistoric times; paints that were pigmented with <u>manganese dioxide</u> can be traced back 17,000 years. The Egyptians and Romans used manganese compounds in glass-making, to either remove color from glass or add color to it. Manganese can be found in the iron ores used by the <u>Spartans</u>. Some speculate that the exceptional hardness of Spartan steels derives from the inadvertent production of an iron-manganese alloy

In the 17th century, German chemist <u>Johann Glauber</u> first produced <u>permanganate</u>, a useful laboratory reagent (although some people believe that it was discovered by <u>Ignites Kaim</u> in 1770). By the mid-18th century, <u>manganese dioxide</u> was in use in the manufacture of chlorine (which it produces when mixed with <u>hydrochloric acid</u>, or commercially with a mixture of dilute <u>sulfuric acid</u> and sodium chloride).

In the 20th century, <u>manganese dioxide</u> has seen wide commercial use as the object cathodic material for commercial disposable <u>dry cells</u> and dry batteries of both the standard (carbonzinc) and alkaline type.

The most important non-metallurgical application of manganes in the fore fore manganese dioxide, which is used as a depolarizer in dry-cell batteries. Dry cell consumption in the world exceeds 20 billion units per year. The function of manganese in batteries is simple. In the battery cell, the anode and cathode are essentially humid. During discharge, hydrogen generated at one of the electrodes coats the latter with a gas film, preventing any further wetting, hence cutting off electrical generation. The role of the manganese dioxide is to oxidize the hydrogen and form water. The rate at which this occurs depends on the reactivity of the dioxide.

The Leclanché cell, incorporating this process, was first developed in 1868. Today a zinc can is used as the anode, and the cathode is a rod made of a mixture of acetylene carbon black surrounded by manganese dioxide. A paste of ammonium and zinc chloride is used for the electrolyte. The manganese dioxide, as has been noted, acts as the depolarizer. In the alkaline MnO_2 zinc cell, which was put on the market in the 1950's, the cathode (MnO_2/C) is pressed against the inside wall of a steel container, and the anode is made from zinc powder. Potassium hydroxide serves as the electrolyte. This type of cell has a very low resistance and impedance, giving under certain conditions greater service life than the standard cell. Another cell used for specific purposes is the magnesium chloride-manganese dioxide cell developed for military applications.

Naturally occurring manganese dioxides (NMD) can be used in standard cells. Improved manganese dioxide grades required in high performance cells are obtained synthetically. The products are named after the processes used. EMD, or electrochemical manganese dioxide, is made through electrolysis; CMD, or chemical manganese dioxide, is produced by a purely chemical process. Combined production of both synthetic types is approximately 200 thousand tons per year, and is growing rapidly.

The market for natural manganese dioxide is about 180-200 thousand tons per year, but very few ores have the properties required for the manufacturing of dry cells. The major producing countries of natural MnO_2 are Gabon, Ghana, Brazil, China, Mexico, and India. These "natural grade battery" ores are ground into a fine powder before being used directly in the cathode mixture.

2.2.1 Physical and chemical properties of MnO₂

Formula - MnO₄

Molecular Weight - 86.94

Physical State - black powder

Melting Point - 1539°C

Specific gravity - 5

Solubility - Insoluble

pH - 9 - 10

2.3 Adsorption

Adsorption involved the transfer of a constituent of fluid (liquid or gaseous) to the surface of a liquid/solid phase. When a molecule is adsorbed on the surface of a solid, it settles on it much like a condensing molecule and is then held on the surface by attractive forces such as Vander waal force. Also in some cases depends on the natures of the molecule and the surface.

However, adsorption is the preferential concentration of a species at the interface between phases. The term rather than absorption is used when no surface penetration occurs. Adsorption results from equilibrium forces associated with surface molecules of solid or liquid. The high potential energy of these molecules is lowered by the attraction of freeing substances. The adsorbed substances show increased reactivity.

2.3.1 Types of adsorption

An adsorption phenomenon is divided into two main types;

- a. Physical adsorption
- b. Chemical adsorption or chemisorptions

2.3.1.1 Physical adsorption

Physical adsorption is non specific and similar to the process of condensation (smith).Physical adsorption or van der waal's adsorption is readily reversible process is the result of intermolecular forces of attraction between molecule of adsorbent and the adsorbate. When for example, the intermolecular attractive forces between a solid and a gas are greater than those existing between the molecules of the gas itself, the gas will condense upon the surface of the solid even though its pressure may be lower than the vapor (Trybal). In physical adsorption there is no significant redistribution of electron density in either the molecule or at the substrate surface (ISO).

Physical adsorption serves concentrate the molecule of a substance at a surface. Thos can be of importance in cases involving reaction between a chemisorbed reactant and a co-reactant which can be physically adsorbed. In such a system the catalytic reaction would rather occur between chemisorbed and physically adsorbed reactants.

The amount of physical adsorption decreases rapidly as the temperature is raised and is generally very small above critical temperatures of the adsorbed component. This indicates that physical adsorption upon a solid is exhibited at low temperature. Physical adsorption is not highly dependent on the irregularities in the nature of the surface especially near condensation temperature.

Physical adsorption studies are valuable in determining the physical properties of solid catalysts. Thus the question of surface area and pore size distribution in porous catalyst can be answered from physical adsorption measurement (smith).

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2.3.1.2 Chemisorption

Chemisorption or activated adsorption involves a chemical interaction with attendant transfer of electron between the adsorbent and the adsorbing species (adsorbate). A chemical bond, involving substantial rearrangement of electron density is formed between them (IFO). The strength of the chemical bond may vary considerably, and identifiable chemical compounds in the usual sense may not actually form, but the adhesive force is generally much greater than that found in physical adsorption. The heat liberated during chemisorptions is usually large, of the order of the heat of chemical reaction. The process is frequently irreversible and the original substance will often be found to have undergo chemical change on desorption.

Chemisorption involves high temperature and it is possible for both adsorption type and phenomenon to occur at the same time.

2.3.2 Adsorption isotherm

When a solution is allowed to allowed flow over an adsorbent containing many chemically active sites, competition between the various species in the solution phase for the active sites on the surface occur. During the competition, two processes of adsorption and desorption usually take place until an equilibrium for the rate of the two processes is established. The amount of solute adsorbed per unit gram of the solid depends solemely on the nature of the molecules involved, temperature and the specific area. Usually, the surface loses its activity when it is covered by a monolayer of adsorbed species.

The equilibrium relationship between the concentration in the fluid phase and the concentration in the adsorbent (adsorbed species) at a given temperature is called Adsorption Isotherm. Three distinguishable isotherms (shape) are;

Linear isotherm

Convex isotherm

Concave isotherms

The linear isotherm is that which represent the desired situation, it indicates that the surface does not become "saturated" with the species in question. The slope of a linear isotherm gives the distribution coefficient and, in this case, it is independent of total concentration.

i.e
$$K = C_s / C_m$$
 or $C_s = KC_m$ 2.2

K = distribution coefficient

 C_s = adsorbed concentration

 C_m = mobile phase concentration

The convex isotherm is as a result of the variation in the activity of the available adsorption sites, most system departs from linearity. Many solid-liquid systems follow a relationship known as **Freundlich isotherm**.

i.e.
$$K = Cs / Cm^{1/n}$$
 or $Cs = KCm^{1/n}$ 2.3

The concave isotherm is as a result of additional reaction that takes place on adsorption which occasionally enhances the overall absorption process. Such cases are uncommon but not unknown

In solid-gas adsorption system, the concentration is usually given in mole percent or as a partial pressure. For liquid-solid, the concentration is often expressed in mass units such as number of moles adsorbed per unit gram.

In all adsorption systems, the amount of species adsorbed decreases with an increase in temperature and of course adsorbate can be removed by raising the temperature even for the cases labelled "irreversible" (IFO).

Bond which may either be physical or chemical between the adsorbent and the adsorbate should be sufficiently strong to prevent motion of the molecule along the surface; i.e localized adsorption in contrast to mobile adsorption. Physically adsorbed molecules are mainly at low temperature localised while they are mobile at high temperature. The chemically adsorbed molecules are localized.

The various adsorption isotherrms applicable for adsorption analysis are the Gibb's, Freundlich, Langmuir and/or BET isotherms.

In principle, Gibb's isotherm can be applied to the problem of adsorption at the solid-solution interface. In this case, the surface concentration equals N/A; where N is the number of moles adsorbed per gram of solid and A is the specific area of the solid,

For strongly favorable isotherm the empirical Freundlich equation can be used to represent experimental results over a limited range.

$$N = KC^{a}$$
 2.4

Where K and a are constants with no physical significance and a < 1 is a better fit, particularly for adsorption from liquid (IFO). The limiting case of a very favorable isotherm is irreversible adsorption where the amount adsorbed is independent of concentration down to a very low value.

K and a can however be evaluated from a plot of N against log C. Equation (2.3) failed to predict the behavior usually observed at low concentration in which N is often directly proportional to concentration (C) and at high concentration where N usually approaches a constant limiting value independent of C.

1000ml volumetric flask	JAY TECH England	Analytical (fragile)	
Nitrogen gas cylinder And regulator	Switzerland	Analytical Industrial	
Tripod stand & Clamp	Technico England	Analytical	
Thermometer Gallen kamp Griffin THL – 210 - 0507	England	Analytical	

3.2 Adsorption from Solution – This method is used to determine the surface area of MnO₂

3.2.1 Procedure

Seven (7) 250ml Erlenmeyer flask were cleaned and dried. With the aid of analytical balance, 1g of manganese dioxide (MnO_2) was weighed into six of the flasks. 100ml of acetic acid of the following concentrations of 0.15, 0.12, 0.09, 0.06, 0.03 and 0.015M were then added to each of the flasks. Added also to the seventh flask containing no manganese dioxide was 100ml of 0.03 of the acetic acid as a control.

The flasks were then tight fitted with stopper and each shaken for a period of 30 minutes after which they were left over night to allow for equilibrium.

To allow for the determination of the concentration of acetic acid after adsorption, all samples were filtered through fine filter papers with the first 10mls of each of the filtrates of different concentration discarded as a precaution against adsorption of the acid by the filter paper.

Using phenolphthalein as indicator in two (different) 25ml portion of each of the different filtrate, 0.1M sodium hydroxide was titrated against the mixture to the end point.

From the values of the initial and final concentration of the acetic aid in 100ml of solution, the numbers of moles present before and after adsorption were calculated and numbers of moles N adsorbed were obtained by difference. The values of C/N versus C were plotted and the best lines through these points were drawn. C is the equilibrium concentration. The number of moles per gram Nm required to form a monolayer was then calculated from the slope. On the assumption that adsorption area of acetic acid equals 21 A^2 , the area per gram of manganese dioxde (MnO₂) was calculated.

3.3 Potentiometric Titration – This method is used to determine the electric surface charge of the anions

3.3.1 Procedure

100ml beaker and 50ml burette were cleaned, dried and rinsed with the respective solution to be placed in them.

To the 100ml beaker, 50ml of 1M solution Sodium nitrate (NaNO₃) was measured with a pipette and transferred into the beaker. To provide for a continuous stirring, a magnetic follower was placed inside the beaker. The beaker was then placed on a magnetic stirrer which was connected to a power source (off). A reference electrode and an indicator electrode (combined electrode) connected to a pH meter were introduced into the solution in the beaker via electrode holder. A nitrogen gas jet regulated by the gauge from the nitrogen gas cylinder was as well directed into the solution in the beaker such that the gas outlet is immersed in the solution.

The cleaned burette was filled with 0.1M HNO₃ solution and clamped on atripod stand such that the tip was directly pointed to the solution in the 100ml beaker.

When the arrangement of the equipment was in order, nitrogen gas regulator was opened to provide a continuous gas jetting into the solution (bubbling).

To initiate a continuous stirring, the magnetic stirrer was switched on. After a while the reading of the stabilized pH meter without a titrant (HNO₃) was recorded.

Subsequently, 0.5 ml of the titrant (HNO_3) was added from the burette and the pH recorded after 60 seconds when the indicator electrode has reached a constant value. The 0.5ml increment and the corresponding pH readings were recorded for a total of 10.0ml additions

when no significant change was observed in the pH reading. At the end, both the magnetic stirrer and the pH meter were switched off and the solution mixture disposed.

The process was repeated after the pH meter was stabilized with distilled water, but this time around, 2g of manganese dioxide (MnO_2) was added to the titrant ($NaNO_3$) and the entire process repeated for various concentrations of the titrant (1, 0.1, 0.01, & 0.001M) at three different temperatures of 28, 30 & 32°C for with and without MnO_2 . The temperature was elevated with the aid of a hot plate magnetic stirrer.

The whole procedure was also repeated using Na_2SO_4 , NaCl, NaBr & NaI for the various concentrations of 1, 0.1, 0.01. & 0.001M at three different temperatures both for with and without Manganese dioxide (MnO₂).

The volumetric readings of 0.1M HNO₃ and their corresponding pH readings for all class of titration carried out were tabulated.

Graphs were plotted for the different class of titration both for solutions with and without manganese dioxide (MnO_2) for all the concentrations at the different temperatures for the difference anions.

3.4 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 as shown in Table 3.3 and 3.4.

3.4.1 Selection of factors that affects the rate of adsorption

The rate of adsorption of the anions (adsorbents) on the MnO₂ (adsorbant) is affected by;

- i. Concentration of the solutions of the anions
- ii. Temperature
- iii. Degree of agitation or mixing

iv. Mass of the adsorbant

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

3.5 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 factors; Concentration (x₁) and temperature (x₂). X₀ is base factor selected. The sign + represent maximum value, - represent minimum value and 0 represent average value or interval of the surface response.

In this experiment, a two – variable, three level factorial designs was used. The factor and the code levels are shown in Table 3.3. Following the column of plus (+), labeled X_0 , the next 2 columns (under the headings x_1 and x_2) define the experimental design in the standard order. Thus for Run 1, all 2 variables were set to vary from their highest experimental levels. In actual conduct of the experiment, the run order would generally be randomized.

		Independent varia	ables
Levels of factors	Code	X_1 (Conc)	X ₂ (Temperature)
Base level	Xo	0	0
Interval or range	ΔX_1	0.5005	30
High level	+1	1.0	32
Low level	-1	0.001	28

Table 3.3: Factors and their Coded Levels for the Anions

3.1

-								**	**	* 7	37
Run	Xo	X_1	X ₂	X11	X ₁₂	X ₂₂	Y	Y	Y	Y	Y
No	ao	a ₁	a ₂	a ₁₁	a ₁₂	a ₂₂	SO4	NO ₃ -	Cl	Br	ľ
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	+	+	-	+	- %	+					

Table 3.4: Calculation of Matrix and the Surface Charge (Y) for 3² Factorial Design

That is, with two variables coded as x_1 and x_2 , a 9-run experiment permits unique solutions for the coefficients (parameters) of the equations 3.6.2 below.

A 2-variable, 3 level factorial arrangements provided the framework for designing the experiment.

The 3² arrangement, when applied to only 2 variables, permits uncorrelated, low variance estimates of the 6 coefficients indicated in equation 3.6.2. The numerical solution of the equation is readily obtained using computer or desk calculator (Douglas, 1991; Das, et.al, 1979; Guttman, et.al, 1982 and Betz, 1073).

3.6 Determination of Model Equation of Adsorption

Selection of model equation

A second order equation of the form,

$$Y = f(x_1, x_2)$$

$$3.2$$

 $Y = a_0 + a_1 x_1 + a_2 x_2 + a_{11} x_1^2 + a_{22} x_2^2 + a_{12} x_1 x_2$

3.3

3² quadratic factorial equation is selected

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

CHAPTER FOUR

4.0 RESULTS

The results of the experiments carried out are presented in this chapter

4.1 Results of the Adsorption from the Solution

Tables 4.1 is the result of the adsorption from solution to determine the surface area of

 MnO_2

Table 4.1: 0	Concentration and	I Number	of Mole Adsorbed
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Initial Concentration of acetic acid C ₁ (M)	Volume of acetic acid (ml)	Volume of 0.1M NaOH (ml) (average titre)	С	$N = C - C_1$	C/N
0.15	25	44	0.1760	0.026	6.7692
0.12	25	33.5	0.1340	0.014	9.5714
0.09	25	25.65	0.103	0.013	7.9231
0.06	25	16.3	0.0652	0.005	12.5385
0.03	25	6.2	0.0248	-0.005	-4.769
0.015	25	1.35	0.0054	-0.0096	-0.5625

4.2 Results for the Potentiometric Titration

Tables 4.2 - 4.21 are the results of potentiometric titration for all the anions; SO_4^{2-} ,

 $\rm NO_3^-$, $\rm CI^-$, $\rm Br^-$, $\rm I^-$ at 28°C, 30°C, and 32°C for with and without $\rm MnO_2$

Table 4.2: 1M	Na ₂ SO ₄ with and	l without MnO ₂ at	28°C, 30	°C, and 32°C
THOIC HAT THE				-,

	Na ₂ SO ₄ at 28°C		Na ₂ SO ₄ a	Na_2SO_4 at $30^{\circ}C$		Na ₂ SO ₄ at 32°C	
Volume	With	Without	With	Without	With	Without	
of HNO ₃	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂	
				pH			
0.0	6.85	6.42	7.32	8.32	6.83	6.75	
0.5	6.06	3.99	7.02	4.55	6.02	3.90	
1.0	5.73	3.66	6.82	4.08	5.81	3.51	
1.5	5.80	3.47	6.65	3.98	5.79	3.3	
2.0	5.75	3.33	6.55	3.75	5.66	3.16	
2.5	5.59	3.20	6.39	3.52	5.56	3.05	
3.0	5.40	3.12	6.28	3.39	5.44	2.97	
3.5	5.22	3.04	6.12	3.53	5.36	2.91	
4.0	5.60	2.98	6.07	3.59	5.33	2.85	
4.5	5.57	2.92	5.98	3.50	5.19	2.87	
5.0	5.46	2.88	5.89	3.44	5.12	2.74	
5.5	5.38	2.84	5.78	3.43	5.03	2.69	
6.0	5.26	2.80	5.10	3.40	5.02	2.66	
6.5	5.16	2.75	5.67	3.37	5.00	2.61	
7.0	5.08	2.73	5.58	3.35	4.98	2.58	
7.5	5.02	2.70	5.48	3.32	4.99	2.55	
8.0	4.98	2.68	5.44	3.30	4.98	2.52	
8.5	4.95	2.64	5.36	3.27	4.98	2.50	
9.0	4.90	2.61	5.38	3.25	4.97	2.47	
9.5	4.88	2.59	5.29	3.23	4.97	2.46	
10.0) 4.86	2.59	5.29	3.21		2.44	
10.5	5 4.85	-	-	3.21	-	-	

Volume of	Na ₂ SO ₄ at 28°C		Na ₂ SO ₄ at 30°C		Na ₂ SO ₄ at 32°C	
	With	Without	With	Without	With	Without
HNO ₃	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂
	pH					
0.0	7.67	5.89	8.05	6.45	2.69	5.56
0.5	6.95	3.27	7.82	3.78	6.96	3.42
1.0	6.40	3.02	7.65	3.43	6.84	3.09
1.5	6.15	2.86	7.48	3.18	6.49	2.87
2.0	5.90	2.71	7.28	3.03	6.14	2.74
2.5	5.89	2.60	7.11	2.93	6.02	2.65
3.0	5.87	2.54	6.98	2.84	5.98	2.56
3.5	5.79	2.47	6.97	2.76	5.88	2.47
4.0	5.77	2.41	6.95	2.69	5.87	2.43
4.5	5.75	2.36	6.94	2.63	5.74	2.36
5.0	5.72	2.32	6.90	2.57	5.69	2.33
5.5	5.67	2.28	6.57	2.54	5.51	2.29
6.0	5.59	2.24	6.55	2.00	5.49	2.25
6.5	5.54	2.20	6.52	2.96	5.48	2.21
7.0	5.48	2.17	6.48	2.44	5.47	2.17
7.5	5.46	2.14	6.46	2.79	5.46	2.15
8.0	5.45	2.11	6.45	2.37	5.45	2.14
8.5	5.44	2.08	6.44	2.34	5.44	2.13
9.0	5.43	2.06	6.42	2.32	5.43	2.12
9.5	5.42	2.04	6.40	2.29	5.42	2.11
10.0	5.42	2.03	6.40	2.27	5.42	2.11
10.5	-	2.00	-	2.25	- 1986 ja	

Table 4.3: 0.1M Na₂SO₄ with and without MnO₂ at 28^oC, 30^oC, and 32^oC

	1M Na ₂ S	SO ₄ at 28°C	1M Na ₂ S	SO ₄ at 30°C	1M Na ₂ SO ₄ at 32°C	
Volume of	With	Without	With	Without	With	Without
HNO ₃	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂
				pH		
0.0	8.55	6.22	9.15	6.70	8.59	6.33
0.5	8.23	3.03	8.42	3.49	8.32	3.07
1.0	7.44	2.80	8.39	3.17	8.14	2.71
1.5	7.20	2.61	8.36	2.75	7.94	2.48
2.0	7.13	2.50	8.14	2.90	7.20	2.36
2.5	6.66	2.39	7.81	2.65	7.05	2.26
3.0	6.54	2.34	7.53	2.56	6.86	2.15
3.5	6.45	2.24	7.29	2.48	6.68	2.09
4.0	6.24	2.17	7.13	2.42	6.53	2.02
4.5	6.05	2.12	7.0	2.36	6.72	1.98
5.0	5.98	2.04	6.85	2.30	6.37	1.92
. 5.5	5.82	2.03	6.77	2.25	6.22	1.88
6.0	5.80	1.99	6.73	2.21	6.12	1.84
6.5	5.74	1.96	6.53	2.16	5.95	1.8
7.0	5.68	1.93	6.34	2.14	5.87	1.76
7.5	5.63	1.90	6.21	2.12	5.78	1.73
8.0	5.65	1.86	6.16	2.10	5.61	1.7
8.5	5.65	1.84	6.08	2.08	5.55	1.67
9.0	-	1.83	6.08	2.06	5.42	1.65
9.5	-	1.80	-	2.04	5.39	1.63
10.	-	1.79	-	2.04	5.38	1.63

Table 4.4: 0.01M Na₂SO₄ with and without MnO₂ at 28° C, 30° C, and 32° C

	1M Na ₂ S	SO ₄ at 28°C	1M Na ₂ S	SO ₄ at 30°C	1M Na ₂ S	SO ₄ at 32°C
Volume of	With	Without	With	Without	With	Without
HNO ₃	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂
				pH		
0.0	8.62	5.86	9.22	6.33	9.15	5.80
0.5	8.42	2.81	8.98	3.89	8.87	2.74
1.0	8.05	2.55	8.66	3.02	8.44	2.54
1.5	7.79	2.38	8.42	2.75	8.33	2.38
2.0	7.40	2.25	8.22	2.56	8.17	2.23
2.5	7.26	2.15	8.03	2.41	8.04	2.13
3.0	6.88	2.07	7.72	2.35	7.46	2.05
3.5	6.70	2.00	7.53	2.27	7.36	1.97
4.0	6.81	1.91	7.36	2.19	7.19	1.92
4.5	6.55	1.88	7.14	2.12	7.02	1.86
5.0	6.33	1.82	6.94	2.01	6.86	1.80
5.5	6.20	1.80	6.76	2.03	6.77	1.76
6.0	6.10	1.77	6.58	1.99	6.63	1.73
6.5	6.08	1.73	6.43	1.96	6.52	1.69
7.0	6.00	1.70	6.33	1.92	6.40	1.63
7.5	5.94	1.66	6.24	1.88	5.84	1.61
8.0	5.90	1.64	6.18	1.86	5.68	1.58
8.5	4.96	1.62	6.08	1.84	5.53	1.58
9.0	4.91	1.59	6.02	1.81	5.4	1.55
9.5	4.88	1.57	6.0	1.79	5.35	1.53
10	4.87	1.57	-	1.77	5.33	1.50
10.5	-	-	- St. 3.	1.74	-	1.45

Table 4.5: 0.001M Na₂SO₄ with and without MnO₂ at 28° C, 30° C, and 32° C

R. A. S. Sta	NaNO ₃ a	at 28°C	NaNO ₃ a	at 30°C	NaNO ₃	at 32°C
Volume of	With	Without	With	Without	With	Without
HNO ₃	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂
				pH		
0.0	6.47	6.46	6.72	6.08	6.86	4.33
0.5	6.02	4.2	6.52	5.82	6.62	3.01
1.0	5.96	3.55	6.21	2.34	6.24	2.74
1.5	5.84	3.35	6.11	2.06	6.12	2.6
2.0	5.72	3.19	5.99	1.94	5.98	2.45
2.5	5.62	3.09	5.85	1.81	5.92	2.37
3.0	5.56	3.02	5.77	1.76	5.89	2.29
3.5	5.49	2.97	5.55	1.70	5.80	2.22
4.0	5.49	2.92	5.50	1.64	5.63	2.15
4.5	5.35	2.86	5.42	1.53	5.57	2.12
5.0	5.29	2.82	5.37	1.48	5.57	2.07
5.5	5.21	2.78	5.31	1.45	5.48	2.03
6.0	5.18	2.73	5.22	1.42	5.44	1.99
6.5	5.18	2.69	5.15	1.39	5.33	1.96
7.0	5.16	2.67	5.02	1.38	5.16	1.94
7.5	5.09	2.64	4.96	1.36	5.30	1.91
8.0	5.01	2.62	4.88	1.34	5.20	1.88
8.5	4.97	2.59	4.82	1.32	5.00	1.86
9.0	4.90	2.57	4.82	1.31	4.90	1.83
9.5	4.87	2.55	4.81	1.29	4.80	1.81
10	4.83	2.53	4.80	1.26	4.78	1.80
10.5	4.82	2.51	4.78	1.24	4.72	1.79
11.0	4.80	2.50	4.77	1.22	4.66	1.77
11.5	4.78	2.50	4.75	1.21	4.65	1.74
12.0	4.78	2.50	4.75	1.21	4.65	1.74

Table 4.6: 1M NaNO₃ with and without MnO₂ at 28⁰C, 30^oC and 32^oC

	0.1M Na	NO ₃ at 28°C	0.1M Na	NO ₃ at 30°C	0.1M Na	NO_3 at $32^{\circ}C$
Volume	With	Without	With	Without	With	Without
of HNO ₃	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂
				pH		
0.0	7.52	6.33	8.23	5.7	7.93	6.36
0.5	6.88	3.05	7.74	3.15	7.50	3.19
1.0	6.72	2.90	7.62	3.05	7.04	2.98
1.5	6.40	2.80	7.44	2.9	6.50	2.72
2.0	6.29	2.68	7.27	2.8	6.60	2.61
2.5	6.17	2.60	6.21	2.75	6.32	2.49
3.0	5.98	2.52	6.91	2.70	8.12	2.42
3.5	5.79	2.48	6.65	2.65	6.09	2.35
4.0	5.55	2.43	6.47	2.60	5.88	2.36
4.5	5.36	2.39	6.34	2.56	5.79	2.29
5.0	5.17	2.35	6.2	2.53	5.65	2.18
5.5	5.13	2.31	6.06	2.51	5.58	2.08
6.0	5.10	2.28	6.06	2.48	5.47	2.0
6.5	5.06	2.26	6.00	2.45	5.50	1.95
7.0	4.75	2.24	5.88	2.44	5.45	1.92
7.5	4.95	2.22	5.85	2.42	5.37	1.90
8.0	4.78	2.21	5.86	2.39	5.27	1.88
8.5	4.98	2.20	5.83	2.38	5.2	1.86
9.0	4.91	2.18	5.68	2.36	5.09	1.84
9.5	4.71	2.15	5.67	2.24	5.02	1.83
10	4.63	2.13	5.65	2.33	5.02	1.82
10.5	4.77	2.12	- 10 - 9	2.31	-	1.82
11.0	4.64	2.10	- 12	2.30		-
11.5	4.98	2.09	-	2.88	-	-
12.0	4.45	2.07	-	2.27	-	
12.5	4.47	2.05	14. juli	2.26	-	
13.0	4.44	2.05	-	2.25	-	- 10

Table 4.7: 0.1M NaNO₃ with and without MnO₂ at 28^oC, 30^oC, and 32^oC

	10.1	NaNO ₃	at 28°C	NaNO ₃ a	at 30°C	NaNO ₃ a	t 32°C
Volun	ne	With	Without	With	Without	With	Without
of HN	NO ₃	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂
					pH		
0.0	0.5	9.22	5.62	9.0	6.80	9.20	6.44
	1.0	8.05	2.68	8.89	3.05	8.76	3.02
	1.5	8.44	2.53	8.66	2.76	8.36	2.72
	2.0	8.3	2.39	8.10	2.88	8.42	2.55
	2.5	7.95	2.22	8.30	2.39	8.22	2.42
	3.0	7.67	2.14	7.71	2.32	796	2.29
	3.5	7.31	2.04	7.65	2.2	7.53	2.22
	4.0	6.92	1.99	7.21	2.15	7.41	2.15
	4.5	6.75	1.95	6.66	2.08	7.14	2.11
	5.0	6.60	1.84	6.45	2.04	6.75	2.07
	5.5	6.55	1.79	6.33	1.99	6.55	2.04
	6.0	6.33	1.74	6.18	1.96	6.48	2.00
	6.5	6.23	1.70	6.06	1.92	6.03	1.97
	7.0	6.13	1.62	5.98	1.89	5.87	1.93
	7.5	6.05	1.60	5.9	1.85	9.20	1.9
	8.0	5.99	1.56	5.87	1.83	8.76	1.87
	8.5	5.93	1.54	5.82	1.79	8.36	1.85
	9.0	5.88	1.51	5.78	1.77	8.42	1.82
	9.5	5.85	1.48	5.75	1.75	8.22	1.88
		5.82	1.46	5.72	1.73	7.96	1.76
	10.5	5.8	1.44	5.71	1.69	7.53	1.74
	11.0	-	1.41	-	1.69	7.41	1.72
	11.5	-	1.39	-	- 296-2	7.14	1.70
	12.0		1.38	-		6.75	1.69
	12.5	-	1.35	-		6.55	1.67
	13.0	-	1.34	-		6.48	1.66
	13.5	-	1.32	-	-	6.03	1.65
	14.0	-	1.29	-	-	5.87	- N.
	-	-	1.29	-		-	-

Table 4.8: 0.01M NaNO₃ with and without MnO₂ at 28⁰C, 30^oC, and 32^oC

	NaNO ₃ a	at 28°C	NaNO ₃ a	t 30°C	NaNO ₃ a	t 32°C
Volume of	With	Without	With	Without	With	Without
HNO ₃	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂
				pН		
0.0	9.77	6.40	8.67	6.24	9.82	7.04
0.5	9.48	3.20	8.38	3.34	9.53	3.33
1.0	8.99	2.80	8.16	3.02	9.28	2.72
1.5	8.81	2.56	7.92	2.82	8.93	2.65
2.0	8.53	2.40	7.69	2.76	8.66	2.46
2.5	8.08	2.30	7.24	2.68	8.58	2.31
3.0	7.38	2.22	7.16	2.60	8.45	2.21
3.5	6.97	2.15	6.95	2.56	8.31	2.13
4.0	6.69	2.08	6.80	2.51	8.19	2.08
4.5	6.56	2.04	6.71	2.46	7.99	2.03
5.0	6.38	1.99	6.62	2.43	7.73	1.99
5.5	6.22	1.95	6.47	2.39	7.50	1.96
6.0	6.10	1.91	6.38	2.36	7.06	1.92
6.5	5.98	1.88	6.29	2.33	6.88	1.89
7.0	5.90	1.84	6.15	2.31	6.69	1.86
7.5	5.87	1.82	6.07	2.28	6.54	1.84
8.0	5.81	1.79	5.99	2.26	6.43	1.82
8.5	5.76	1.77	5.96	2.24	6.37	1.8
9.0	5.72	1.74	5.91	2.23	6.35	1.78
9.5	5.69	1.71	5.88	2.21	6.34	1.77
10	5.65	1.69	5.87	2.19	6.34	1.77
10.5	-	1.64	4.86	2.18	-	-
11.0		1.62	5.29	2.16	-	S - 19
11.5	-	1.61	5.19	2.14	-	
12.0	-	1.59	5.29	2.13		-
12.5	-	1.59	5.29	2.12	-	1. - 1

Table 4.9 0.001M NaNO3 with and without MnO2 at 28°C, 30°C, and 32°C

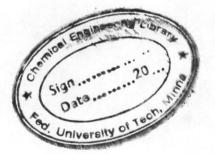
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	NaCl at 28°C		NaCl at 3	30°C	NaCl at 3	32°C
Volume of	With	Without	With	Without	With	Without
HNO ₃	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂
		Service of the		pH		
0.0	6.8	8.50	6.71	8.49	6.66	8.38
0.5	6.04	2.85	6.48	3.35	5.89	2.75
1.0	5.81	2.49	6.18	3.00	5.54	2.37
1.5	5.63	2.31	5.97	2.57	5.44	2.18
2.0	5.43	2.15	5.70	2.31	5.23	2.04
2.5	5.37	2.05	5.58	2.12	5.08	1.93
3.0	5.27	1.95	5.51	2.03	4.94	1.83
3.5	5.20	1.87	5.40	1.93	4.85	1.75
4.0	5.09	1.81	5.28	1.87	4.74	1.69
4.5	5.06	1.76	5.16	1.8	4.65	1.64
5.0	4.99	1.72	5.0	1.74	4.52	1.60
5.5	4.96	1.67	4.98	1.70	4.44	1.56
6.0	4.94	1.63	4.74	1.67	4.38	1.52
6.5	4.88	1.61	4.71	1.62	4.31	1.5
7.0	4.83	1.57	4.80	1.59	4.25	1.46
7.5	4.87	1.54	4.77	1.56	4.21	1.42
8.0	4.80	1.52	4.72	1.53	4.16	1.41
8.5	4.75	1.49	4.68	1.50	4.12	1.38
9.0	4.61	1.47	4.65	1.48	4.09	1.35
9.5	4.60	1.45	4.63	1.46	4.07	1.34
10	4.59	1.72	4.60	1.43	4.06	1.31
10.5	4.59	1.67	4.60	1.4	4.06	1.31
11.0	-	1.63		1.40	-	-
11.5	- 2013	1.61	 >> 	1.38	·	12 -
12.0	-	1.57	-	1.36	-	-
12.5	-	1.54	-	1.36		S 18

Table 4.10: 1M NaCl with and without MnO₂ at 28^oC, 30^oC, and 32^oC

	NaCl at 28°C		NaCl at 3	0°C	NaCl at 32°C	
Volume of	With	Without	With	Without	With	Without
HNO ₃	MnO ₂					
				pН		
0.0	7.75	6.29	7.80	6.44	7.77	6.07
0.5	7.00	2.85	7.55	2.86	7.31	3.11
1.0	6.67	2.50	6.74	2.58	6.90	2.75
1.5	6.41	2.31	6.38	2.29	6.63	2.48
2.0	6.20	2.16	6.4	2.15	6.58	2.31
2.5	6.10	2.07	6.25	2.07	6.37	2.16
3.0	5.98	1.98	6.06	1.99	6.21	2.08
3.5	5.88	1.93	5.98	1.91	6.14	1.99
4.0	5.79	1.87	5.89	1.84	6.08	1.93
4.5	5.65	1.81	5.78	1.79	5.93	1.87
5.0	5.54	1.77	5.77	1.75	5.83	1.83
5.5	5.43	1.73	5.68	1.70	5.72	1.78
6.0	5.39	1.69	5.56	1.65	5.78	1.74
6.5	5.34	1.65	5.50	1.63	5.72	1.70
7.0	5.25	1.62	5.44	1.61	5.67	1.67
7.5	5.18	1.60	5.38	1.57	5.61	1.64
8.0	5.14	1.57	5.34	1.56	5.56	1.61
8.5	5.10	1.54	5.31	1.53	5.51	1.58
9.0	5.05	1.51	5.28	1.51	5.48	1.55
9.5	5.03	1.50	5.26	1.48	5.45	1.54
10	5.02	1.50	5.25	1.46	5.44	1.51
10.5	-	4.14	-	1.45	1.200	1.50
11.0	-	-	-	1.45		-

Table 4.11: 0.1M NaCl with and without MnO₂ at 28^oC, 30^oC, and 32^oC



	NaCl at 28°C		NaCl at 3	0°C	NaCl at 3	S2°C	
Volume of	With	Without	With	Without	With	Without	
HNO ₃	MnO ₂						
				pН			
0.0	9.02	5.75	8.89	5.82	8.92	5.75	
0.5	8.71	2.73	8.46	2.75	8.63	2.76	
1.0	8.33	2.46	8.14	2.44	8.44	2.50	
1.5	8.65	2.31	7.42	2.30	8.26	2.32	
2.0	7.67	2.15	7.63	2.15	8.05	2.2	
2.5	7.45	2.05	7.11	2.07	7.44	2.07	
3.0	6.85	1.97	6.07	1.99	7.42	2.01	
3.5	6.66`	1.91	6.57	1.91	7.16	1.96	
4.0	6.55	1.84	6.34	1.84	6.9	1.89	
4.5	6.43	1.79	6.14	1.80	6.73	1.84	
5.0	6.35	1.74	5.98	1.76	6.70	1.80	
5.5	6.20	1.70	5.79	1.73	6.48	1.76	
6.0	6.09	1.66	5.61	1.70	6.38	1.73	
6.5	6.01	1.63	5.45	1.66	6.30	1.69	
7.0	5.93	1.60	5.38	1.62	6.16	1.66	
7.5	5.75	1.56	5.27	1.60	5.99	1.63	
8.0	5.65	1.54	5.19	1.56	5.82	1.60	
8.5	5.48	1.52	5.13	1.55	5.85	1.58	
9.0	5.35	1.50	5.09	1.53	5.65	1.56	
9.5	5.28	1.47	5.05	1.51	5.65	1.53	
10	5.26	1.40	5.03	1.48	-	1.51	
10.5	-	-	-	1.47	-	-	

Table 4.12: 0.01M NaCl with and without MnO₂ at 28⁰C, 30^oC, and 32^oC

	NaCl at 28°C		NaCl at 3	30°C	NaCl at 32°C	
Volume of	With	Without	With	Without	With	Without
HNO ₃	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂	MnO ₂
		State and		pH		
0.0	9.23	5.70	9.52	6.22	9.33	4.07
0.5	8.98	2.67	9.20	2.93	9.07	2.79
1.0	8.73	2.42	8.83	2.59	8.95	2.56
1.5	7.52	2.22	8.89	2.39	8.57	2.29
2.0	7.33	2.10	8.56	2.16	8.28	2.15
2.5	7.15	2.03	8.36	2.02	7.82	2.09
3.0	7.03	1.93	8.07	1.97	7.43	2.01
3.5	6.86	1.89	7.88	1.90	7.29	1.95
4.0	6.47	1.84	7.71	1.83	6.99	1.90
4.5	6.42	1.79	-	1.80	7.21	1.83
5.0	6.29	1.75	7.10	1.74	6.88	1.78
5.5	6.17	1.72	6.69	1.66	6.83	1.75
6.0	6.06	1.67	6.69	1.67	6.31	1.71
6.5	5.98	1.64	6.56	1.63	6.22	1.67
7.0	5.91	1.61	6.46	1.60	5.94	1.64
7.5	5.80	1.59		1.58	5.85	1.61
8.0	5.71	1.56	6.37	1.54	5.72	1.58
8.5	5.65	1.54	6.18	1.50	5.65	1.56
9.0	5.58	1.59	6.07	1.49	5.58	1.52
9.5	5.43	1.50	6.0	1.46	5.53	1.51
10	5.42	1.49	5.83	1.87	5.51	1.5
10.5	5.42	1.49	5.81	1.43	5.51	1.5
11.0	-	-	5.81	1.41		-
11.5	-	99 - 1000	0-10 mil	1.40	-	
12.0	- 7566	8 - C. S.	i - Alexan	1.40	-	1.141

Table 4.13: 0.001M NaCl with and without MnO₂ at 28^oC, 30^oC, and 32^oC

	NaI at 28°C		NaI at 30)°C	NaI at 32°C			
Volume of	With	Without	With	Without	With	Without		
HNO ₃	MnO ₂							
	pH							
0.0	8.12	8.64	8.68	6.54	8.88	6.60		
0.5	7.01	2.23	7.81	2.73	8.65	2.83		
1.0	6.06	2.04	6.90	2.37	7.40	2.41		
1.5	5.80	1.86	6.15	2.11	7.32	2.19		
2.0	5.39	1.70	5.75	1.97	6.90	2.02		
2.5	5.28	1.62	5.55	1.86	6.88	1.90		
3.0	5.13	1.54	5.32	1.77	6.73	1.81		
3.5	4.98	1.45	5.18	1.71	6.58	1.72		
4.0	4.88	1.4	5.14	1.66	6.38	1.67		
4.5	4.79	1.38	5.01	1.6	6.28	1.61		
5.0	4.70	1.34	4.89	1.55	6.11	1.56		
5.5	4.65	1.30	4.80	1.51	5.91	1.51		
6.0	4.60	1.20	4.73	1.46	5.78	1.48		
6.5	4.54	1.24	4.68	1.43	5.69	1.45		
7.0	4.50	1.22	4.64	1.41	5.60	1.43		
7.5	4.44	1.20	4.61	1.39	5.53	1.41		
8.0	4.41	1.18	4.58	1.37	5.48	1.39		
8.5	4.39	1.16	4.56	1.35	5.44	1.37		
9.0	4.37	1.13	4.55	1.34	5.42	1.36		
9.5	4.36	1.12	4.53	1.33	5.40	1.35		
10	4.35	1.11	4.51	1.32	5.38	1.35		

Table 4.14: 1M NaI with and without MnO₂ at 28^oC, 30^oC, and 32^oC

	Nal at 2	8°C	NaI at 30)°C	NaI at 32	2°C
Volume of	With	Without	With	Without	With	Without
HNO ₃	MnO ₂					
				pH		
0.0	7.61	6.55	7.62	6.44	7.77	6.67
0.5	6.14	2.59	6.43	2.85	6.6	3.63
1.0	5.55	2.28	6.02	2.49	6.02	2.68
1.5	5.27	2.09	5.89	2.25	5.8	2.31
2	5.19	1.98	5.76	2.10	5.65	2.17
2.5	5.12	1.84	5.57	1.94	5.46	2.08
3.0	5.02	1.75	5.49	1.91	5.32	1.99
3.5	4.96	1.72	5.41	1.84	5.22	1.91
4.0	4.82	1.64	5.36	1.8	5.11	1.87
4.5	4.78	1.6	5.26	1.76	5.02	1.82
5;0	4.69	1.55	5.12	1.7	4.91	1.76
5.5	7.61	1.52	5.05	1.66	4.88	1.72
6.0	6.14	1.49	4.99	1.63	4.8	1.68
6.5	5.55	1.45	4.8	1.60	4.74	1.65
7.0	5.27	1.42	4.77	1.58	4.69	1.62
7.5	5.19	1.40	4.74	1.56	4.65	1.59
8.0	5.12	1.34	4.72	1.54	4.62	1.57
8.5	5.02	1.32	4.71	1.52	4.6	1.55
9.0	4.96	1.30	4.69	1.5	4.58	1.53
9.5	4.82	1.29	4.67	1.49	4.57	1.52
10	4.78	1.29	4.66	1.49	4.56	1.52
10.5	4.78	-	-		-	-

Table 4.15: 0.1M NaI with and without MnO₂ at 28^oC, 30^oC, and 32^oC

	NaI at 2	8°C	NaI at 30)°C	NaI at 32	2°C
Volume of	With	Without	With	Without	With	Without
HNO ₃	MnO ₂					
				pH		
0.0	7.11	6.42	8.55	6.31	8.54	6.62
0.5	5.75	2.42	6.88	2.61	6.23	2.70
1.0	5.45	2.22	6.66	2.39	5.94	2.41
1.5	5.30	2.07	6.30	2.21	5.28	2.28
2.0	4.98	1.99	6.20	2.12	5.2	2.16
2.5	4.84	1.93	6.12	2.05	5.13	2.10
3.0	4.68	1.88	5.99	1.98	4.95	2.04
3.5	4.57	1.82	5.76	1.95	4.76	1.95
4.0	4.45	1.78	5.64	1.89	4.6	1.92
4.5	4.36	1.72	5.56	1.86	4.44	1.87
5.0	4.27	1.68	5.47	1.81	4.31	1.82
5.5	4.15	1.66	5.38	1.78	4.16	1.78
6.0	4.08	1.63	5.31	1.72	3.88	1.71
6.5	4.01	1.58	5.24	1.68	3.81	1.68
7.0	3.96	1.56	5.17	1.65	3.73	1.66
7.5	3.93	1.54	5.10	1.57	3.65	1.64
8.0	3.9	1.52	5.05	1.55	3.57	1.6
8.5	3.88	1.5	5.02	1.53	3.50	1.58
9.0	3.85	1.48	5.00	1.51	3.48	1.57
9.5	3.84	1.47	4.99	1.5	3.47	1.55
10	3.84	1.47	4.98	1.49	3.47	1.55

Table 4.16: 0.01M NaI with and without MnO₂ at 28^oC, 30^oC, and 32^oC

	NaI at 2	8°C	NaI at 30)°C	NaI at 32	2°C
Volume of	With	Without	With	Without	With	Without
HNO ₃	MnO ₂					
				pH		
0.0	8.70	6.75	9.4	6.52	9.29	5.57
0.5	6.11	2.70	8.15	2.77	6.44	2.82
1.0	5.60	2.53	6.69	2.50	5.83	2.68
1.5	5.88	2.35	6.20	2.37	4.99	2.4
2.0	5.36	2.22	5.32	2,22	4.89	2.26
2.5	5.34	2.14	5.15	2.19	4.33	2.17
3.0	5.03	2.05	4.89	2.08	4.22	2.06
3.5	4.82	1.97	4.53	2.01	4.11	1.99
4.0	4.61	1.92	4.38	1.95	4.03	1.94
4.5	4.48	1.85	4.05	1.89	3.64	1.88
5.0	4.34	1.82	3.35	1.84	3.25	1.81
5.5	4.22	1.79	3.09	1.80	3.11	1.77
6.0	4.14	1.75	2.91	1.77	3.01	1.74
6.5	4.08	1.72	2.80	1.74	2.92	1.71
7.0	4.04	1.68	2.69	1.71	2.85	1.69
7.5	4.01	1.65	2.61	1.69	2.79	1.67
8.0	3.98	1.62	2.58	1.67	2.74	1.65
8.5	3.96	1.59	2.52	1.64	2.69	1.63
9.0	3.95	1.57	2.47	1.61	2.66	1.61
9.5	3.94	1.56	2.41	1.59	2.62	1.59
10	3.94	1.56	2.4	1.57	2.60	1.58
10.5	-	-	-	1.57	-	1.57

Table 4.17: 0.001M NaI with and without MnO₂ at 28⁰C, 30^oC, and 32^oC

	NaBr at 2	28°C	NaBr at 3	0°C	NaBr at 3	2°C
Volume	With	Without	With	Without	With	Without
of HNO ₃	MnO ₂					
				pH		
0.0	6.74	5.71	6.60	5.81	6.86	3.26
0.5	5.21	2.91	5.25	2.50	6.54	3.01
1.0	5.11	2.50	4.95	2.16	6.24	2.74
1.5	4.19	2.28	4.80	1.97	6.12	2.60
2.0	3.98	2.16	4.68	1.82	5.98	2.45
2.5	3.74	2.01	4.53	1.71	5.92	2.37
3.0	3.62	1.93	4.40	1.63	5.89	2.29
3.5	3.45	1.88	4.28	1.58	5.80	2.22
4.0	3.32	1.83	4.13	1.52	5.70	2.15
4.5	3.17	1.76	4.01	1.47	5.63	2.12
5.0	3.06	1.72	3.88	1.43	5.57	2.07
5.5	2.96	1.68	6.60	1.37	5.48	2.03
6.0	2.88	1.64	5.25	1.33	5.44	1.99
6.5	2.81	1.60	4.95	1.30	5.33	1.96
7.0	2.78	1.57	4.80	1.27	5.16	1.94
7.5	2.59	1.55	4.68	1.24	5.13	1.91
8.0	2.55	1.53	4.53	1.22	5.10	1.88
8.5	2.51	1.50	4.40	1.20	4.90	1.86
9.0	2.48	1.48	4.28	1.98	4.80	1.83
9.5	2.46	1.46	4.13	1.97	4.72	1.81
10	2.45	1.45	4.01	1.96	4.66	1.79
10.5	-	-	3.88		4.60	1.79

Table 4.18: 1M NaBr with and without MnO₂ at 28⁰C, 30^oC, and 32^oC

	NaBr at	28°C	NaBr at 2	30°C	NaBr at 3	32°C
Volume of	With	Without	With	Without	With	Without
HNO ₃	MnO ₂					
				pH		
0.0	7.93	6.10	7.77	5.97	7.94	6.04
0.5	6.65	2.83	6.40	2.78	6.46	2.76
1.0	6.23	2.54	5.84	2.56	6.03	2.50
1.5	5.40	2.35	5.70	2.32	5.88	2.39
2.0	5.35	2.22	5.68	2.22	5.71	2.27
2.5	5.25	2.13	5.53	2.07	5.53	2.20
3.0	5.44	2.07	5,46	2.00	5.57	2.12
3.5	5.18	2.50	5.30	1.94	5.40	2.05
4.0	5.08	1.96	5.16	1.86	5.24	1.99
4.5	4.98	1.9	5.07	1.82	5.02	1.87
5.0	4.74	1.86	4.98	1.77	4.88	1.85
5.5	4.65	1.82	4.77	1.72	4.75	1.83
6.0	4.48	1.79	4.69	1.69	4.58	1.81
6.5	4.34	1.75	4.61	1.66	4.44	1.77
7.0	4.29	1.72	4.54	1.63	4.32	1.75
7.5	4.21	1.70	4.46	1.59	3.18	1.72
8.0	4.15	1.68	4.41	1.57	3.10	1.69
8.5	4.09	1.66	4.38	1.55	2.97	1.67
9.0	4.06	1.64	4.35	1.53	2.86	1.66
9.5	4.02	1.62	4.33	1.52	2.85	1.64
10	3.98	1.61	4.32	1.51	3.85	1.63
10.5	3.97	-	-	1.51	-	1.63

Table 4.19: 0.1M NaBr with and without MnO₂ at 28⁰C, 30^oC, and 32^oC

	NaBr at 2	28°C	NaBr at 30°C	2	NaBr at 32°C	2
Volume of	With	Without	With MnO ₂	Without	With MnO ₂	Without
HNO ₃	MnO ₂	MnO ₂		MnO ₂		MnO ₂
			р	H		
0.0	8.64	5.94	6.28	6.24	9.10	6.38
0.5	6.70	2.85	5.72	2.71	8.22	2.67
1.0	6.40	2.56	5.53	2.45	7.30	2.61
1.5	6.15	2.39	5.38	2.28	6.53	2.45
2.0	5.98	2.29	5.28	2.14	6.28	2.33
2.5	5.74	2.24	5.14	2.07	6.14	2.24
3.0	5.55	2.15	5.06	1.98	6.08	2.17
3.5	5.46	2.06	4.91	1.91	5.98	2.09
4.0	5.35	2.00	4.81	1.84	5.88	2.02
4.5	5.27	1.95	4.72	1.78	5.79	1.96
5.0	5.15	1.92	4.58	1.77	5.47	1.91
5.5	5.05	1.87	4.44	1.74	5.32	1.89
6.0	4.96	1.84	4.32	1.70	5.22	1.85
6.5	4.85	1.81	4.19	1.68	5.14	1.81
7.0	4.77	1.78	4.11	1.65	5.04	1.78
7.5	4.71	1.75	4.05	1.63	4.93	1.76
8.0	4.65	1.72	4.00	1.60	4.85	1.74
8.5	4.58	1.69	3.96	1.58	4.80	1.72
9.0	4.52	1.67	3.93	1.56	4.76	1.69
9.5	4.48	1.65	3.91	1.54	4.74	1.67
10	4.47	1.63	3.89	1.54	4.73	1.66
10.5	4.47	1.63	-	-		-

Table 4.20: 0.01M NaBr with and without MnO₂ at 28° C, 30° C, and 32° C

	NaBr at	28°C	NaBr at 2	30°C	NaBr at 2	32°C
Volume of	With	Without	With	Without	With	Without
HNO ₃	MnO ₂					
				pН	0	1. A.
0.0	9.4	5.77	9.06	6.15	9.40	5.95
0.5	7.81	2.73	8.21	2.78	8.76	2.93
1.0	7.64	2.54	7.57	2.65	7.04	2.64
1.5	7.87	2.34	5.81	2.50	6.35	2.40
2.0	7.15	2.26	5.62	2.41	5.36	2.27
2.5	6.67	2.16	3.96	2.31	5.21	2.17
3.0	6.53	2.10	3.71	2.26	3.46	2.08
3.5	6.45	2.04	3.55	2.19	3.35	2.02
4.0	6.15	2.00	3.41	2.13	2.9	1.94
4.5	5.90	1.95	3.34	2.09	2.64	1.93
5.0	5.64	1.89	3.26	2.06	2.55	1.89
5.5	5.58	1.87	3.18	2.00	2.46	1.90
6.0	5.46	1.83	3.11	1.96	2.37	1.88
6.5	5.36	1.80	2.98	1.95	2.28	1.86
7.0	5.29	1.76	2.83	1.92	2.22	1.83
7.5	5.26	1.74	2.75	1.90	2.13	1.80
8.0	5.09	1.71	2.70	1.88	2.05	1.78
8.5	5.03	1.69	2.66	1.86	2.01	1.78
9.0	5.00	1.67	2.63	1.83	1.95	1.74
9.5	4.98	1.65	2.60	1.82	1.88	1.72
10	4.97	1.64	2.59	1.81	1.87	1.72
10.5	-	-	-	1.81	2.54	

Table 4.21: 0.001M NaBr with and without MnO₂ at 28⁰C, 30^oC, and 32^oC

4.3 Analyzed Results

The surface area of Manganese dioxide was determined by adsorption from solution and was found to be $1702.56m^2/g$. (See Appendix A)

The value of adsorption θ is calculated using Kokarev formula (Kokarev, et.al, 1988) equation 2.9. At a given pH, the difference in volume (ΔV) between the two in each of the pH against Volume plots given in Appendix E was used to calculate the adsorption θ as illustrated in Appendix C.

4.3.1 Result of adsorption and electric surface charge for SO_4^{2-} (Sulphate ion)

from Na₂SO₄ solution

The results obtained for θ and E are presented in Tables 4.22 – 4.33.

рН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge (E) x 10 ⁻⁷ (coulombs/cm ²)
4.8	8.6	9.568	18.462
5.2	3.3	3.64	7.025
5.6	2.3	2.54	4.902
6.0	0.4	0.441	0.852
		Average	7.812

Table 4.22: 1M Na₂SO₄ Solution for SO₄²⁻ (sulphate ion) at 28°C

рН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
5.4	7.6	8.383	16.18
5.9	4.67	5.151	9.941
6.4	2.2	2.427	4.683
6.8	0.8	0.882	0.170
		Average	8.127

Table 4.23: 1M Na₂SO₄ Solution at 30°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
5.0	5.67	6.254	12.07
5.2	4.7	6.287	12.13
5.6	2.3	2.537	4.896
6.0	0.5	0.552	1.064
		Average	7.540

Table 4.24: 1M Na₂SO₄ Solution at 32°C

Table 4.25: 0.1M Na₂SO₄ Solution at 28°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
5.0	6.8	7.500	14.48
5.4	3.9	4.302	8.302
5.6	3.5	3.861	7.451
5.8	2.4	2.647	5.109
		Average	8.836

Table 4.26: 0.1M Na₂SO₄ Solution at 30°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)	
6.4	7.0	7.721	14.09	

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
4.8	9.4	10.37	20.01
5.2	6.0	6.618	12.77
5.6	4.0	4.412	8.515
		Average	13.765

Table 4.27: 0.1M Na₂SO₄ Solution at 32°C

Table 4.28: 0.01M Na₂SO₄ Solution at 28°C

pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
5.6	7.0	7.721	14.90
5.8	5.5	6.067	11.71
6.0	4.0	4.412	8.515
		Average	11.708

Table 4.29: 0.01M Na₂SO₄ Solution at 30°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
6.0	8.9	9.817	1.895
6.2	7.5	8.273	1.597
6.4	6.8	7.500	1.448
6.6	6.0	6.618	1.277
		Average	15.543

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
5.4	8.9	9.817	1.895
5.6	7.95	8.769	1.692
6.0	6.4	7.059	1.362
6.2	5.4	5.956	1.150
		Average	15.248

Table 4.30: 0.01M Na₂SO₄ Solution at 32°C

Table 4.31: 0.001M Na₂SO₄ Solution at 28°C

pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
4.8	9.8	10.81	2.086
5.2	8.15	8.989	1.735
5.6	6.8	7.500	1.448
5.8	6.0	6.618	1.277
		Average	16.365

Table 4.32: 0.001M Na₂SO₄ Solution at 30°C

pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
6.0	8.8	9.706	1.873
6.2	7.5	8.273	1.597
6.3	7.0	7.721	1.490
		Average	16.533

pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
5.4	9.0	9.922	1.916
5.6	8.2	9.045	1.746
5.8	7.5	8.273	1.597
		Average	17.530

Table 4.33: 0.001M Na₂SO₄ Solution at 32°C

4.3.2 Results of Adsorption and electric Surface charge for NO₃⁻ (Nitrate ion)

from NaNO₃ Solution

The results obtained for θ and E are presented in tables 4.34 - 4.43.

pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
4.8	9.1	10.04	9.686
5.2	5.2	5.736	5.535
5.6	2.2	2.437	2.342
6.0	0.3	0.331	0.319
		Average	5.189

Table 4.34: 1M NaNO3 solution at 28°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
4.8	8.2	9.045	8.728
5.4	4.4	4.853	4.683
5.8	2.6	2.868	2.767
6.0	2.0	2.206	2.127
		Average	4.577

Table 4.35: 1M NaNO3 solution at 30°C

Table 4.36: 0.1M NaNO₃ Solution at 28°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
5.0	5.2	5.736	5.535
5.4	4.3	4.743	4.577
5.8	3.5	3.861	3.725
6.2	2.4	2.647	2.555
		Average	4.098

Table 4.37: 0.1M NaNO₃ Solution at 30°C

pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface Charge E x 10 ⁻⁷ (coulombs/cm ²)	
5.6	9.0	9.922	9.580	

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
5.2	8.3	9.155	8.834
5.6	5.0	5.515	5.322
6.0	3.8	4.191	4.045
6.2	2.8	3.088	2.980
		Average	5.295

Table 4.38: 0.1M NaNO₃ Solution at 32°C

Table 4.39: 0.01M NaNO3 solution at 30°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
5.8	8.0	8.824	8.515
6.2	5.4	5.956	3.748
6.6	4.0	4.412	4.258
6.8	3.8	4.191	4.045
		Average	5.642

pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
5.2	8.8	9.706	9.367
5.6	7.4	8.162	7.877
6.0	6.0	6.618	6.386
6.4	5.5	6.067	5.854
		Average	7.371

Table 4.40: 0.01M NaNO_3 solution at $32^{\circ}C$

Table 4.41: 0.001M NaNO3 solution at 28oC

pH ΔV 5.6 9.5		Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface Charge E x 10 ⁻⁷ (coulombs/cm ²) 10.11	
		10.48		
6.0	6.4	7.059	6.812	
6.4	5.0	5.515	5.322	
		Average	7.415	

Table 4.42: 0.001M NaNO₃ solution at 30°C

pH ΔV 5.8 9.5		Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²) 10.11	
		10.48		
6.0	7.6	8.383	8.089	
6.2	6.5	7.170	6.919	
		Average	8.373	

pH ΔV		Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	$\begin{array}{ll} \text{n capacity}(\theta) & \text{Surface charge E x 10} \\ \text{nol/cm}^2) & (\text{coulombs/cm}^2) \end{array}$	
6.4	8.0	8.824	8.515	
6.6	7.5	8.273	7.983	
6.8	6.8	7.500	7.238	
7.0	6.0	6.618	6.386	
		Average	7.531	

Table 4.43: 0.001M NaNO3 solution at 32°C

4.3.3 Results of adsorption and electric surface charge for CI (Chloride ion)

from NaCl solution.

The result obtained for θ and E are presented in tables 4.44 – 4.53.

pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
4.6	8.7 9.596		9.260
5.0	4.7	5.184	5.003
5.4	1.7	1.875	1.809
6.0	0.3	0.331	0.319
		Average	4.098

Table 4.44:	1M NaCl	solution	at 28'	'C

pH ΔV		Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)	
4.6	8.6	9.486	9.154	
4.8	5.6	6.171	5.955	
5.4	3.3	3.640	3.513	
6.0	1.2	1.324	1.277	
6.4	0.4	0.441	0.426	
		Average	4.975	

Table 4.45: 1M NaCl solution at 30°C

Table 4.46: 1M NaCl solution at 32°C

pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
4.4	5.4	5.4 5.956 5.	
4.6	4.5	4.964	4.780
5.0	2.7	2.978	2.874
5.6	0.8	0.882	0.852
		Average	3.566

	Table	4.47:	0.1M	NaCl	solution	at 28°	C
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pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
5.0	8.8	9.706	9.367
5.4	7.5	8.273	7.983
5.8	4.0	4.412	4.258
6.2	2.0	2.206	2.129
		Average	5.934

pH ΔV		Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)	
5.2	9.5	10.48	10.11	
5.6	5.9	6.508	6.280	
6.0	3.0	3.309	3.193	
6.4	1.5	1.655	1.597	
		Average	5.295	

Table 4.48: 0.1M NaCl solution at .	I solution at 30°C	
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Table 4.49: 0.1M NaCl solution at 32	2°C	2
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pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
5.5	8.5	9.376	9.047
5.6	7.4	8.162	7.877
5.8	5.0	5.515	5.322
6.0	4.2	4.633	4.470
		Average	6.679

Table 4.50:	0.01M NaCl	solution at 28°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
5.2	9.8	10.81	10.43
5.4	8.8	9.706	9.367
5.6	8.0	8.824	8.515
5.8	7.2	7.942	7.664
		Average	8.994

pH ΔV		Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
5.2	7.9	8.714	8.409
5.4	6.5	7.140	6.919
5.6	6.0	6.618	6.386
5.8	5.5	6.067	5.854
		Average	6.892

Table	4.51:	0.01M	NaCl	solution	at 30°C
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Table 4.52: 0.001M NaCl solution at 28°C	Table 4.52:	0.001M	NaCl sol	ution	at 28°	C
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pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
5.4	9.5	10.48	10.11
5.5	9.2	10.15	9.792
5.6	8.5	9.376	9.047
		Average	9.650

pH ΔV		Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
4.6	3.3	3.640	3.513
5.0	2.6	2.868	2.767
5.6	1.7	1.875	1.809
6.4	1.3	1.434	1.384
		Average	2.368

4.3.4 Results of Adsorption and surface electric charge for Br- (bromide ion)

from NaBr solution.

The results obtained for θ and E are presented in tables 4.54 – 4.65.

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
2.8	5.9	6.508	6.280
3.2	4.0	4.412	4.258
4.0	1.7	1.875	1.809
5.0	1.0	1.103	1.064
		Average	3.353

Table 4.54:	1M NaH	3r sol	ution	at 28°C	-

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
3.2	9.1	10.04	9.686
4.0	4.2	4.633	4.470
4.6	2.2	2.427	2.342
5.0	0.9	0.993	0.958
5.2	0.4	0.441	0.426
		Average	6.067

Table 4.55: 1M NaBr solution at 30°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
3.8	4.4	4.853	4.683
4.6	2.6	2.868	2.767
5.2	1.35	1.489	1.437
5.8	0.4	0.441	0.426
		Average	3.286

Table 4.56: 1M NaBr solution at 32°C

Table 4.57: 0.1M NaBr solution at 28°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
4.2	7.2	7.942	7.664
5.0	4.37	4.820	4.651
5.4	1.4	1.544	1.490
6.0	1.2	1.324	1.277
		Average	3.771

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
4.4	7.4	8.167	7.877
5.0	5.67	6.254	6.035
5.4	3.2	3.530	3.406
5.8	1.0	1.103	1.064
		Average	4.596

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
4.0	8.1	8.934	8.622
4.6	5.8	6.397	6.173
5.2	3.9	4.302	4.151
5.8	1.8	1.985	1.916
		Average	5.216

Table 4.59: 0.1M NaBr solution at 32°C

Table 4.60: 0.01M NaBr solution at 28°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
4.8	6.4	7.059	6.812
5.2	4.7	5.184	5.003
5.6	3.0	3.309	3.193
5.8	2.4	2.647	2.555
		Average	4.391

Table 4.61:	0.01M	NaBr	solution	at 30°C

pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
4.6	4.7	5.184	5.003
5.0	3.17	3.497	3.374
5.4	1.4	1.544	1.490
5.8	0.4	0.441	0.426
		Average	3.531

рН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
4.8	7.8	8.603	8.302
5.2	5.87	6.475	6.248
5.8	4.4	4.853	4.683
6.2	2.2	2.427	2.342
		Average	5.394

Table 4.62:	0.01M	NaBr	solution	at 32°C
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Table 63: 0.001M NaBr solution at 28°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
5,0	8.1	8.934	8.622
5.2	7.5	8.273	7.983
5.6	7.0	7.721	7.451
5.7	4.8	5.294	5.109
		Average	7.291

Table 4.64:	0.001M	NaBr so	lution	at 30°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
2.8	6.5	7.170	6.919
4.0	2.4	2.647	2.555
4.8	2.0	2.206	2.129
5.4	1.8	1.985	1.916
6.0	1.5	1.655	1.597
		Average	3.023

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
4.0	2.4	2.647	2.555
4.6	2.2	2.427	2.342
5.2	2.0	2.206	2.129
5.8	1.8	1.985	1.916
		Average	2.236

Table 4.65:	0.001M	NaBr	solution	at 32°	C

4.3.5 Results of Adsorption and electric surface charge for I- (iodide ion) from

from NaI solution.

The results obtained for θ and E are presented in Tables 4.66 – 4.77.

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
4.4	7.05	7.776	7.504
5.0	3.2	3.530	3.406
5.8	1.3	1.434	1.386
6.4	0.6	6.618	6.386
		Average	4.670

Table 4.66: 1M NaI Solution at 28°C

pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
4.8	7.3	8.052	7.770
5.2	3.3	3.640	3.513
5.8	2.0	2.206	2.129
6.2	1.3	1.434	1.384
		Average	3.699

Table 4.67: 1M NaI Solution at 30°C

Table 4.68: 1M NaI Solution at 32°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
5.4	8.27	9.122	8.803
5.8	5.9	6.508	6.280
6.2	4.4	4.853	4.683
6.5	3.8	4.191	4.045
		Average	5.953

Table 4.69: 0.1M NaI Solution at 28°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface Charge E x 10 ⁻⁷ (coulombs/cm ²)
4.6	5.4	5.956	5.748
5.0	2.8	3.088	2.980
5.6	0.9	0.992	0.958
6.2	0.5	0,552	0.532
		Average	5.908

рН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
4.8	6.3	6.949	6.706
5.4	3.37	3.717	3.587
5.8	1.8	1.985	1.916
6.2	0.8	0.882	0.852
		Average	5.181

Table 4.70: 0.1M NaI Solution at 30°C

Table 4.71: 0.1M NaI Solution at 32°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
4.8	5.9	6.508	6.280
5.4	2.6	2.868	2.767
5.8	1.37	1.511	1.458
6.2	0.7	0.772	0.745
		Average	4.489

Table 4.72:	0.01M NaI	Solution	at 28°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
4.0	6.1	6.728	6.493
4.6	3.0	3.309	3.193
5.2	1.57	1.732	1.671
6.0	0.4	0.441	0.426
		Average	3.904

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
5.0	8.27	9.122	8.803
5.4	5.1	5.625	5.428
5.8	3.5	3.861	3.725
6.2	2.0	2.206	2.129
		Average	5.021

Table 4.73: 0.01M NaI Solution at 30°C

Table 4.74: 0.01M NaI Solution at 32°C

pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10 ⁻⁷ (coulombs/cm ²)
3.8	6.0	6.618	6.386
4.6	3.73	4.114	3.970
5.6	1.27	1.401	1.352
6,2	0.4	0.441	0.426
		Average	3.992

Table 4.75: 0.001M NaI Solution at 28°C

pН	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
4.2	5.1	5.625	5.428
4.8	3.3	3.640	3.513
5.4	1.87	2.063	1.990
6.2	0.4	0.441	0.426
		Average	3.797

pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
3.4	4.6	5.074	4.896
4.4	3.73	4.114	3.970
5.0	2.6	2.868	2.767
6.0	1.6	1.765	1.703
		Average	3.334

Table 4.76:	0.001M NaI	Solution a	it 30°C

Table 4.77: 0.001M NaI Solution at 32°C

pH	ΔV	Adsorption capacity(θ) x10 ⁻¹² (mol/cm ²)	Surface charge E x 10^{-7} (coulombs/cm ²)
3.0	5.6	6.177	5.963
4.0	3.7	4.088	3.938
4.8	1.87	2.063	1.990
5.8	1.2	1.324	1.277
		Average	3.292

4.4 Statistical Results

The factorial analyzed results are also presented in Tables 4.78 - 4.88.

Degree of Freedom	x _o	x ₁	X2	Y x 10 ⁻³ (Coulombs/m ²)
1	+	+	+	0. 754
2	+	0	+	1.254
3	+		+	1.753
4	+	+	0	0.813
5	+	0	0	1.233
6	+		0	1.653
7	+	+	-	0.781
8	+	0	-	1.209
9	+			1.637

Table 4.78: Factorial Result for SO₄²⁻ (sulphate ion) as Na₂SO₄

Degree of Freedom	Xo	x1	X2	$\frac{Y}{x \ 10^{-3} (coulombs/m^2)}$
1	+	+	+	0.00
2	+	0	+	0.377
3	+	-	+	0.753
4	+	+	0	0.458
5	+	0	0	0.648
6	+		0	0.837
7	+	+	-	0.519
8	+	0	13. - 11	0.630
9	+	-	-	0.742

Table 4.79: Factorial Result for NO3⁻ (Nitrate ion) as NaNO3

Degree of Freedom	X _o	\mathbf{x}_1	X2	Y x 10 ⁻³ (coulombs/m ²)
1	+	+	+	0.357
2	+	0	+	0.178
3	+	-	+	0.00
4	+	+	0	0.498
5	+	0	0	0.367
6	+	-	0	0.237
7	+	+	-	0.410
8	+	0		0.687
9	+	-	-	0.965

Table 4.80: Factorial Result for CI (Chloride ion) as NaCl

Degree of Freedom	X ₀	x ₁	x ₂	Y x 10 ⁻³ (Coulombs/m ²)
1	+	+	+	0.329
2	+	0	+	0.276
3	+		+	0.224
4	+	+	0	0.607
5	+	0	0	0.455
6	+	-	0	0.302
7	+	+	-	0.335
8	+	0	-	0.532
9	+		-	0.729

Table 4.81: Factorial Result for Br⁻ (Bromide ion) as NaBr

Degree of Freedom	X ₀	x ₁	x ₂	Y x 10 ⁻³ (coulombs/m ²)
1	+	+	+	0.595
2	+	0	+	0.462
3	+	-	+	0.329
4	+	+	0	0.370
5	+	0	0	0.352
6	+	-	0	0.333
7	+	+	-	0.467
8	+	0	-	0.423
9	+	-	-	0.380

Table 4.82: Factorial Result for I - (Iodide ion) as NaI

Table 4.83: Calculation of Matrix and the Surface Charge (E) of the Anions

Run	Xo	X_1	X ₂	X11	X ₁₂	X ₂₂	Y	Y	Y	Y	Y
No	ao	aı	a ₂	a ₁₁	a ₁₂	a ₂₂	SO4 ²	NO3 ⁻	Cl-	Br ⁻	Ι-
1	+	+	+	+	+	+	7.540	0	3.566	3.286	5.953
2	+	0	+	0	0	+	12.535	3.766	1.783	2.761	4.623
3	+	-	+	+	-	+	17.530	7.531	0	2.236	3.292
4	+	+	0	+	0	0	8.127	4.577	4.975	6.067	3.699
5	+	0	0	0	0	0	12.330	6.475	3.672	4.545	3.517
6	+	-	0	+	0	0	16.533	8.373	2.368	3.023	3.334
7	+	+	-	+	-	+	7.812	5.189	4.098	3.353	4.670
8	+	0	-	0	0	+	12.089	6.302	6.874	5.322	4.234
9	+	+	-	+	-	+	16.365	7.415	9.650	7.291	3.797

 $E = Y \times 10^{-7}$ (coulombs/cm²) for 3² Factorial Design

4.5 Determination of Regression Coefficients of the Model Equation

obs	\mathbf{x}_1	x ₂	Significance of variance = 0 Y
1	1	32	7.540
2	0.501	32	12.535
3	0.001	32	17.530
4	1	30	8.127
5	0.501	30	12.330
6	0.001	30	16.533
7	. 1	28	7.812
8	0.501	28	12.089
9	0.001	28	16.365

Table 4.84: Determination of Significance of data for SO_4^{2-}

			Significance of variance $= 1$
obs	x1	x ₂	Y
1	1	32	0
2	0.501	32	3.766
3	1	32	7.531
4	1	28	4.577
5	0.501	30	6.475
6	1	30	8.373
7	0.501	28	5.189
8	1	32	6.302
9	0.501	32	7.415

Table 4.85: Determination of Significance of Data for NO₃

			Significance of variance $= 2$
obs	x ₁	X2	Y
1	1	32	3.566
2	1	32	1.783
3	1	32	0
4	0.501	30	4.975
5	0.501	30	3.672
6	0.501	30	2.368
7	0.001	28	4.098
8	0.001	28	6.874
9	0.001	28	9.650

Table 4.86: Determination of Significance of Data for Cl⁻

			Significance of variance $= 1$
obs	x ₁	X2	Y
1	1	32	3.286
2	0.501	32	2.761
3	1	32	2.236
4	1	28	6.067
5	0.501	30	4.545
6	1	30	3.023
7	0.501	28	3.353
8	1	32	5.322
9	0.501	32	7.291

Table 4.87: Determination of Significance of Data for Br

ant i			Significance of variance $= 2$
obs	X1	X2	Y
	1	32	5.953
2	1	32	4.623
3	1	32	3.292
1	0.501	30	3.699
5	0.501	30	3.517
5	0.501	30	3.334
7	0.001	28	4.670
8	0.001	28	4.234
9	0.001	28	3.797

Table 4.88: Determination of Significance of Data for I

CHAPTER FIVE

5.0 DISCU

DISCUSSION, CONCLUSION AND RECOMMENDATION

5.1 Discussion of Results

The results obtained are hereby discussed.

5.1.1 Determination of surface area of Mno2

The volumetric analysis (titration) between various concentration of acetic acid including a control show a gradual increase in the titre value 0.1M NaOH thus reflecting in the increase in the concentration of acetic acid. A plot of C/N versus C gave a straight line graph and the slope N_m was used to calculate the surface area of MnO₂. The surface area of MnO₂ was found to be 1702.69 m²/g.

5.1.2 Effect of concentration of anions on adsorption (θ)

The result showed that the lower the concentration of the anions the higher the adsorption of the anions. This is a complete deviation from the fact that the higher the concentration of the anions (greater gradient) the higher the adsorption of the adsorbate. The fact is that the higher the concentration of the anions the less the kinetic energy of the anions and the chances of being adsorbed with time. However, the lower the concentration of the anions the higher the concentration of the anions and the chances of being adsorbed as a result of lesser concentration of the anions.

5.1.3 Effect of concentration and temperature of anions on surface charge (E)

The lower the concentration of the anions the higher the surface charge posed on the MnO_2 . Similarly, the surface charge of different concentration of anions with respect to a selected temperature of $30^{\circ}C$ shows that

SO4: 0.001M>0.01M>0.1M>1M

NO3: 0.1M>0.001M>0.01M>1M

Cl: 0.01M>0.1M>1M>0.001M

Br: 1M>0.1M>0.01M>0.001M

I: 0.1M>0.01M>1M>0.001M

The surface charge of some concentration of anions at 30°C show that

For 1M, $SO_4^{2-} > Br^- > Cl^- > NO3^- > l^-$

For 0.1M. $SO_4^{2-} > NO_3^{-} > Cl_{-} > I_{-} > Br_{-}$

For 0.01M. $SO_4^{2-} > Cl- > NO_{3-} > I- > Br-$

For 0.001M. $SO_4^{2-} > NO_{3-} > I_{-} > Br_{-} > Cl_{-}$

The above comparism shows that the surface charges of SO_4^{2-} is higher than all the anions namely NO₃-, Cl-. Br-, and I- for all the concentrations.

5.1.4 Effect of pH on MnO₂

As the titration proceeds with additional volume of the titrant, a sudden but gradual decrease of the pH solution with MnO_2 was observed. The pH value ends towards greater acidity. Generally, the starting pH values of the titrand in each of the concentration of the anion, is greater with MnO_2 than those without MnO_2 . This is because the MnO_2 is alkaline in nature.

The plot of pH against the volume of titrant HNO_3 showed that those without MnO_2 fall below those with MnO_2 , this is because the addition of MnO_2 into the titrand results in increase in pH value but this suddenly decreases as the hydrogen ions of the titrant get adsorbed unto the MnO_2 thereby decreasing the anion concentration from the solution making the solution tends towards acidity due to less anions in the solution. At a stage there will be no further change in the pH values (see appendix E). This is possible because when all the adsorption sites have been fully covered by the anions, further addition will not yield any change in the pH values of both the solutions of with and without MnO_2 .

5.1.5 Result of regression analysis

In statistical analysis attempt was made to discover and establish relationship between the different variables such as pH, temperature and concentration involved in the analysis. To this effect the chapter served as an attempt to evaluate the determination of surface electric charge of anions.

This was done by checking the type of relationship that exists between the dependent variable (Nitrate, Chloride, Sulphate, Bromide and Iodide) and Concentration of the Anions and Temperature of the anions.

This was done through the use of regression analysis. The computational device is the statistical package (SPSS) software programme.

The result of the regression model equation for SO4²⁻

 $Y_{sul} = 10.8567 - 8.9733x_1 + 0.3841x_2 - 3.4465x_{12}$

The F- statistics shows that the equation or model employed is statistically significant

With P-value = 0.00. P- Value < 0.05 is significant interaction (See Appendix D)

The result of the regression model equation for NO3⁻

 $Y_{Nat} = -278.7760 - 0.4735x_1 + 37.2464x_2 - 17.6362x_{12}$

The P-value of 0.8511 is statistically insignificant since it is > 0.05.

The result of the regression model equation for Cl

 $Y_{Cl} = 98.2619 + 2.6224x_1 + 0.1642x_2 + 0.4306x_{12}$

This model equation is statistically insignificant with p-value of 0.058 which is slightly > 0.050.

The result of the regression model equation for Br

 $Y_{Br} = 80.6951 - 1.0034x_1 + 0.1652x_2 - 0.1658x_{12}$

p-value = 0.6911 is statistically insignificant interaction

The result of the regression model equation for I-

 $Y_1 = 104.9618 + 3.6541x_1 + 0.2279x_2 + 0.8328x_{12}$

p-value = 0.3125 which means statistically insignificant interaction

5.2 Conclusion

The result obtained and its analysis showed that

- 1. The surface area of MnO2 was found to be 1702.69m2/g
- 2. Manganese dioxide (MnO₂) used as a depolarizer in a dry cell can be improved if properly blended with alkaline anions especially SO_4^{2-} ion. This is because their presence will increase the surface charges which in effect result in enhanced voltage output and extension of cells lifespan due to its greater surface charge.
- The investigation showed that the use of SO₄²⁻ ion can be justified because of its consistent increase in its surface charges at different concentrations and temperature compared with NO₃⁻, Cl⁻, Br⁻, and I⁻.
- 4. The adsorption of these anions on the MnO₂ as a depolarizer will increase the lifespan of Leclanche cell in the following decreasing order; SO₄²⁻ (99%) > Cl⁻ (48%) > NO₃⁻ (14%) > Br⁻ (12%) > I⁻ (10%).

5.3 Recommendations

- Leclanche cell will last longer by blending of the MnO₂ with 0.001M SO₄²⁻ at 32°C and pH of 5.4
- 2. Further research work in all areas of battery technology should be carried out to improve the lifespan of batteries to reduce environmental impact due to their disposal problem
 - Provision of necessary and adequate equipment/chemicals to be provided by the department.

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APPENDIX A

Determination of Surface Area of MnO₂ by Adsorption from Solution

i. Concentration of the given stock of acetic acid

 $C_{c} = \frac{\% \text{ purity x S.G x 1000}}{M.\text{wt x 100}}$

where $C_c = concentration of stock acetic acid$

% purity = percentage purity of stock acetic acid

S.G = specific gravity of stock acetic acid

M. wt = molecular weight of acetic acid

The assays on the stock bottle of acetic acid are:

S.G = 1.0495

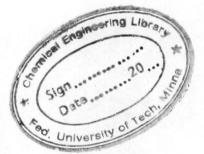
M.wt = 60.05g

% purity = 99%

Using (1) above, we have

 $C_{c} = \frac{99 \times 1.0495 \times 1000}{60.05 \times 100}$

= 17.3M



1

ii. To obtain the volume of stock acid solution required to be made up to 1000ml, in order to have 0.15M acetic acid solution, the relation

$$C_c V_c = C_d V_d$$

Where $C_c = \text{concentration stock acetic acid (M)}$

 $V_c =$ Volume (ml) of stock acid solution required dilution

 C_d = Desired concentration of needed acetic acid solution

 $V_d = Volume of desired acid solution$

2

Applying (2) $C_{c}V_{c} = C_{d}V_{d}$ Where $C_{d} = 17.3M$, $V_{c} = ?$, $V_{d} = 1000ml$ $17.3 \times V_{c} = 0.15 \times 1000$ $V_{c} = \frac{0.15 \times 1000}{17.3} = 8.67ml$

Therefore 8.67ml of the given stock acetic acid is required to be measured and made up to 100ml of solution to obtain 0.15M acetic acid solution needed.

Also 0.12, 0.9, 0.09 0.06, 0.03 and 0.015M acetic acid were obtain by respectively making up 80, 60, 40, 20 and 10ml of 0.15M acetic acid solution up to 100ml with distilled water.

iii. Calculation of equilibrium concentration of acetic acid after adsorption from solution.

The final concentration (equilibrium concentration) of acetic acid is determined from the results of its titration with 0.1M NaOH.

3

Considering the stoichiometric expression below;

 $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

We have that

$$\frac{\underline{C}_{\underline{A}}\underline{V}_{\underline{A}}}{\underline{C}_{B}\underline{V}_{B}} = \frac{\underline{n}_{\underline{a}}}{\underline{n}_{b}}$$

Where C_A = Final concentration of acetic acid

 $V_A = Volume of acetic acid used = 25ml$

 C_B = Concentration of NaOH = 0.1M

 $V_B = Average Titre (ml)$

 $n_a = number of moles of acid = 1$

 $n_b = number of moles of base = 1$

From equation 3 $C_A V_A = C_B V_B$

 $C_A = \frac{C_B V_B}{V_A}$

By applying (4)

For 0.15M solution of acetic acid:

$$C_A = 0.1 \times 44 = 0.1760$$

4

For 0.12M

$$C_A = 0.1 \times 33.5 = 0.1340M$$

For 0.09M

$$C_A = \frac{0.1 \times 25.65}{25} = 0.103M$$

For 0.06M

$$C_A = 0.1 \times 16.3 = 0.0652M$$

For 0.03M

$$C_A = 0.1 \times 6.2 = 0.0248M$$

For 0.015M

$$C_A = 0.1 \times 1.35 = 0.0054M$$

The initial concentration of acetic acid were labeled as C_1 while the final concentrations were labeled as C

iv. Calculation of slope from the graph of C/N against C

Slope =
$$\Delta y = y_2 - y_1 = \frac{8.6 - 6.0}{0.125 - 0.09}$$

$$=$$
 $\frac{2.6}{0.035}$ = 74.286

From the equation plotted i.e. $C/N = C/N_m + 1/kN_m$

Slope = $1/N_m$

 $N_m = 1/slope = 1/74.286 = 0.01346076$

v. Calculation of specific area, A

The specific area, A (in m^2/g) for adsorption is given by

 $A = N_m N_o \sigma \times 10^{-20}$

Where Nm = Number of adsorption sites

= 0.01356076

No = Avogadro's number = 6.023×10^{23}

 σ = Area occupied by an adsorbed molecule on the surface

= 21A

Therefore,

$$A = 0.01346076 \times 6.023 \times 10^{23} \times 21 \times 10^{-20}$$

 $= 1702.55731 \text{ m}^2/\text{g} = 1702.56\text{m}^2/\text{g}$

APPENDIX B

Potentiometric Titration

Preparation of Standard Solutions

0.1M NaOH solution, the following calculations were made,

Molecular weight of NaOH

23+16+1 = 40g

Therefore to prepare IM NaOH, 40g is required to be dissolved in distilled water and made up to 1000ml.

Therefore, for 0.1M, the amount of NaOH required to be dissolved is given by

 $0.1/1 \times 40 = 4g$

1M solution of Na₂SO₄, 142.02g is required to dissolved in distilled water and made

of 1000ml

Dilution of 1M solution of Na2SO4 to obtain 0.1, 0.01, and 0.001M,

We used the dilution formula

 $C_1V_1 = C_2V_2$

Where C_1 = concentration of stock solution

 V_1 = Volume of stock solution required

 C_2 = concentration required

V2 = volume of required concentration

For 250ml solution of 0.1M Na₂SO₄

 $C_1 V_1 = C_2 V_2$

 $1 \ge V_1 = 0.1 \ge 250$

 $V_1 = \frac{0.1 \times 250}{1} = 25ml$

1M solution acts as the stock solution. Hence, 25ml of the 1M solution is required to be made up to 250ml with distilled water.

Same applies to;

 $1M\ NaNO_3~$ - $85g\ dissolved\ in\ 1000ml$

- 1M NaBr 102.9g in 1000ml
- 1M NaI 149.8g in 1000ml

APPENDIX C

Surface electric charge of $SO_4^{2^-}$, NO_3^- , Cl^- , Br^- , I^- on MnO_2 at different temperature,

pH and concentration.

To obtain surface charge due to the deposition of particle on adsorbent, the relation

 $E = nF\theta$

E = surface charge

n = number of ionic charge of the anions for SO₄²⁻, n = -2

 $\theta = adsorption capacity (mol/m²)$

f = Faraday's constant = 96500Coulombs

The adsorption capacity, surface area of the adsorption of MnO_2 and the concentration

of titrant used are related by the expression;

 $\theta = \frac{C \times \Delta V}{S \times 1000}$

C =concentration of the titrant; 0.1M NaOH solution

 ΔV = change in volume (ml) of the titrant between curves at which the adsorbent was added and at which it was not

 $S = surface area of MnO_2 (m^2/g)$

 $= 1702.56 \text{m}^2/\text{g}$

APPENDIX D

Regression data analysis and interpretation of result

MODEL 1:

Multiple R: 0.99563

R-Square: 0.99127

Adjusted R-square: 0.98837

Standard Error: 0.42139

F- Statistics: 340.82759

The result of the regression equations are presented below:

Sulphate / Concentration of the anions

Ysul = 16.818307 - 8.9733ca

(68.921) (-7.214)

* The parenthesized figures below the coefficients are the t-values.

Sulphate / Temperature of the anions

Ysul = 4.895000 + 0.384083ta

(0.007) (0.008)

* The parenthesized figures below the coefficients are the t-values.

The Multiple R is 0.9956 which suggests a positive relationship between the dependent variable (that is, Sulphate) and the independent variables which is Concentration of the anions and Temperature of the anions. The adjusted R^2 of 0.988 suggests that 99% of the total change in sulphate can be attributed to the independent variables (concentration of the anions and temperature of the anions).

The F – statistics shows that the equation or model employed is statistically significant at a value of 340.827 with p value (significant F = 0.000) which means that the relationship between sulphate and the independent Variables (concentration of the

anions and temperature of the anions) is statistically significant (sig f < 0.0500 is statistically significant) The judgment and estimation is based on the independent variable as well as the appropriate expectation and the ratio will be taken into consideration.

Concentration of the anions is found to be highly negative and significant at a t- ratio of -7.214 and it has a negative impact on sulphate, Having the value of its coefficient as -8.973285.

Temperature of the anions is found to be highly positive and insignificant at a t- ratio of 0.008 and it is has a positive impact on sulphate, having the value of its coefficient as 0.384083

MODEL 2:

Multiple R: 0.07343

R-Square: 0.00539

Adjusted R-square: -.13670

Standard error: -.13670

F- Statistics: 0.03794

The result of the regression equations are presented below:

Nitrate / Concentration of the anions

Ynit = 5.830099 – 0.473499ca

(3.140) (-.195)

* The parenthesized figures below the coefficients are the t-values.

Nitrate / Temperature of the anions

Ynit = -551.722 + 37.2464ta

(-1.117) (1.132)

* The parenthesized figures below the coefficients are the t-values.

The Multiple R is 0.07343 which suggests a positive relationship between the dependent variable (that is, nitrate) and the independent variables which is concentration of the anions and temperature of the anions. The adjusted R^2 of -.13670 suggests that 14% of the total change in Nitrite can be attributed to the Independent variables (concentration of the anions and temperature of the anions).

The F – statistics shows that the equation or model employed is statistically insignificant at a value of 0.03794 with p value (significant F = 0.8511) which means that the relationship between nitrate and the independent Variables (concentration of the anions and temperature of the anions) is statistically insignificant (sig f > 0.0500 is statistically insignificant) The judgment and estimation is based on the independent variable as well as the appropriate expectation and the ratio will be taken into consideration.

Concentration of the anions is found to be highly negative and insignificant at a tratio of -0.195 and it is has a negative impact on nitrate, having the value of its coefficient as -0.473499.

Temperature of the anions is found to be highly positive and insignificant at a t- ratio of 1.132 and it is has a positive impact on nitrate, having the value of its coefficient as 37.246450

MODEL 3:

Multiple R: 0.78246 R-Square: 0.61225 Adjusted R-square: 0.48299 Standard Error: 2.04812

F- Statistics: 4.73686

The result of the regression equations are presented below:

Chloride / Concentration of the anions

Ychl = 6.881718 + 2.622386 ca

(5.802) (0.452)

* The parenthesized figures below the coefficients are the t-values.

Chloride / Temperature of the anions

Ychl = 189.642 + 0.164208ta

(0.583) (0.454)

* The parenthesized figures below the coefficients are the t-values.

The Multiple R is 0.78246 which suggests a positive relationship between the dependent variable (that is, chloride) and the independent variables which is concentration of the anions and temperature of the anions. The adjusted R^2 of 0.48299 suggests that 48% of the total change in chloride can be attributed to the Independent variables (concentration of the anions and temperature of the anions).

The F – statistics shows that the equation or model employed is statistically insignificant at a value of 4.73686 with p value (significant F = 0.0583) which means that the relationship between chloride and the independent Variables (concentration of the anions and temperature of the anions) is statistically insignificant (sig f > 0.0500 is statistically insignificant) The judgment and estimation is based on the independent variable as well as the appropriate expectation and the ratio will be taken into consideration.

Concentration of the anions is found to be highly positive and insignificant at a tratio of 0.452 and it is has a positive impact on chloride, having the value of its coefficient as 2.622386.

Temperature of the anions is found to be highly positive and insignificant at a t- ratio of 0.454 and it is has a positive impact on chloride, having the value of its coefficient as 0.164208

MODEL 4:

Multiple R: 0.15469

R-Square: 0.02393

Adjusted R-square: -0.11551

Standard Error: 1.80183

F- Statistics: 0.17160

The result of the regression equations are presented below:

Bromide / Concentration of the anions

Ybrm= 4.990207 - 1.003407ca

(2.522) (-.414)

* The parenthesized figures below the coefficients are the t-values.

Bromide / Temperature of the anions

Ybrm = 156.400000 + 0.165150ta

(0.436) (0.416)

* The parenthesized figures below the coefficients are the t-values.

The Multiple R is 0.15469 which suggests a positive relationship between the dependent variable (that is bromide) and the independent variable which is concentration of the anions and temperature of the anions. The adjusted R^2 of -.11551

suggests that 12% of the total change in Bromide can be attributed to the Independent variables (concentration of the anions and temperature of the anions).

The F – statistics shows that the equation or model employed is statistically insignificant at a value of 0.17160 with p value (significant F = 0.6911) which means that the relationship between bromide and the independent Variables (concentration of the anions and temperature of the anions) is statistically insignificant (sig f > 0.0500 is statistically insignificant) The judgment and estimation is based on the independent variable as well as the appropriate expectation and the ratio will be taken into consideration.

Concentration of the anions is found to be highly negative and insignificant at a tratio of -0.414 and it is has a negative impact on bromide, having the value of its coefficient as -1.003407.

Temperature of the anions is found to be highly positive and insignificant at a t- ratio of 0.416 and it is has a positive impact on bromide, having the value of its coefficient as 0.165150

MODEL 5:

Multiple R: 0.56690

R-Square: 0.32137

Adjusted R-square: 0.09517

Standard Error: 0.81529

F- Statistics: 1.42070

The result of the regression equations are presented below:

Iodide / Concentration of the anions

Yiod= 4.236931 + 3.654087ca

(8.974) (1.581)

* The parenthesized figures below the coefficients are the t-values.

Iodide / Temperature of the anions

Yiod = 205.686667 + 0.227875ta

(1.589) (1.581)

* The parenthesized figures below the coefficients are the t-values.

The Multiple R is 0.56690 which suggests a positive relationship between the dependent variable (that is, iodide) and the independent variables which is concentration of the anions and temperature of the anions. The adjusted R^2 of 0.09517 suggests that 10% of the total change in Iodide can be attributed to the Independent variables (concentration of the anions and temperature of the anions).

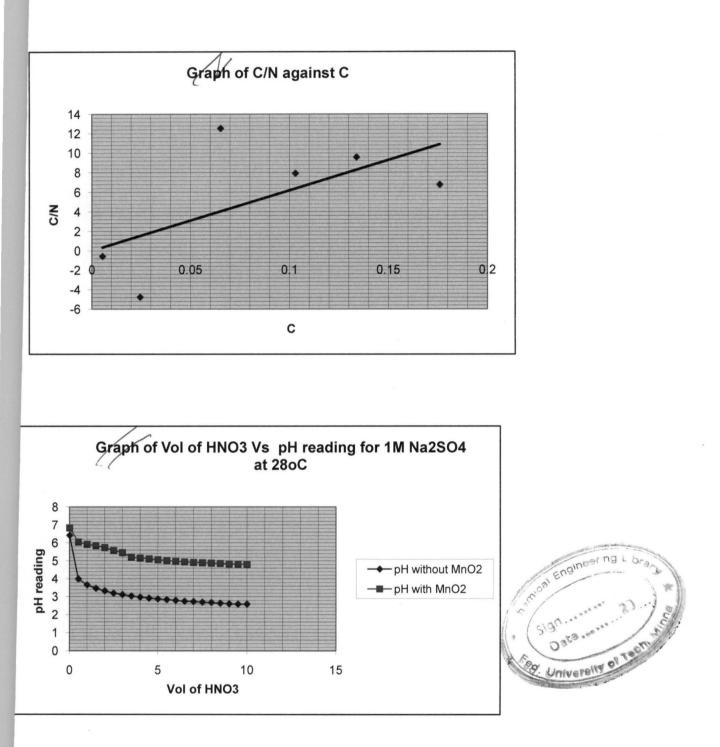
The F – statistics shows that the equation or model employed is statistically insignificant at a value of 1.42070 with p value (significant F = 0.3125) which means that the relationship between iodide and the independent Variables (concentration of the anions and temperature of the anions) is statistically insignificant (sig f > 0.0500 is statistically insignificant) The judgment and estimation is based on the independent variable as well as the appropriate expectation and the ratio will be taken into consideration.

Concentration of the anions is found to be highly positive and insignificant at a tratio of 1.581 and it is has a positive impact on iodide, having the value of its coefficient as 3.654087.

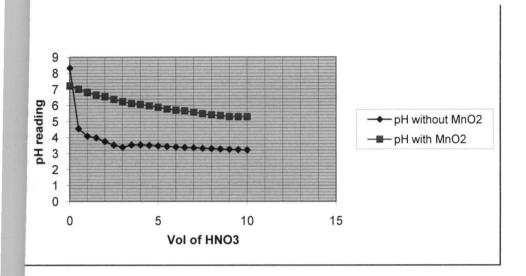
Temperature of the anions is found to be highly positive and insignificant at a t- ratio of 1.581 and it is has a positive impact on iodide, having the value of its coefficient as 0.227875.

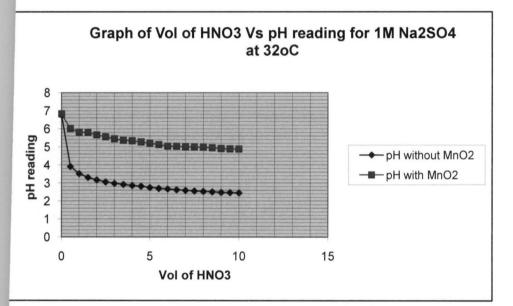
APPENDIX E

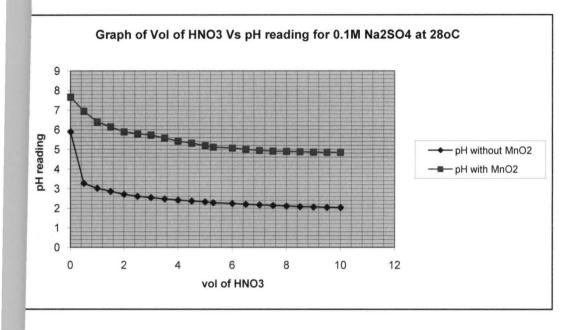
0.176	0.134	0.103	0.0652	0.0245	0.0054
6.7692	9.5714	7.9231	12.5385	-4.7697	-0.5625

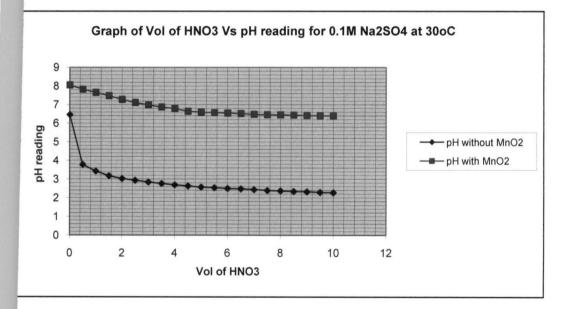


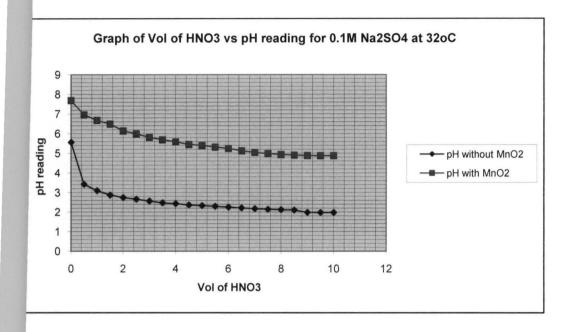
Graph of vol of HNO3 Vs pH for 1M Na2SO4 at 30oC

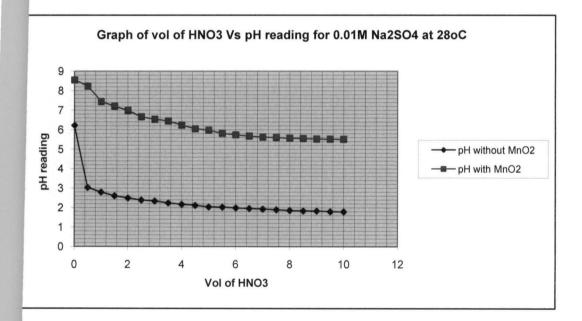


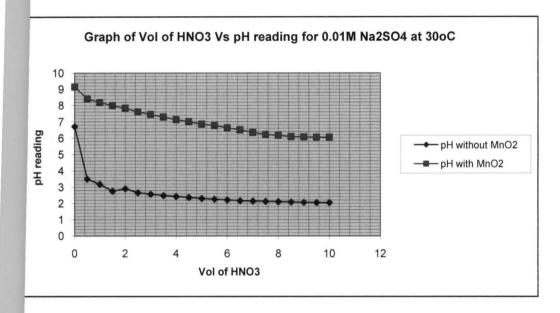


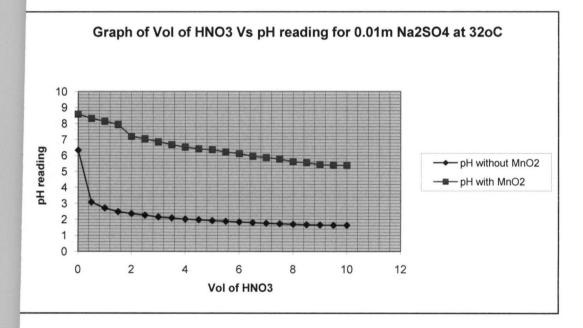


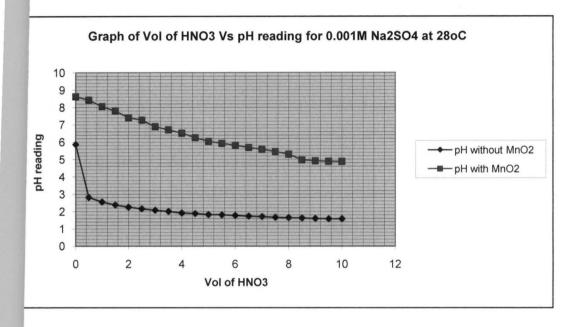


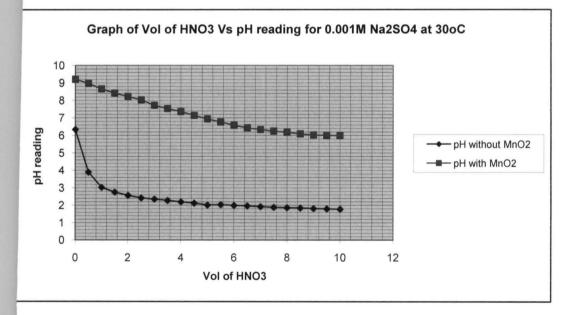


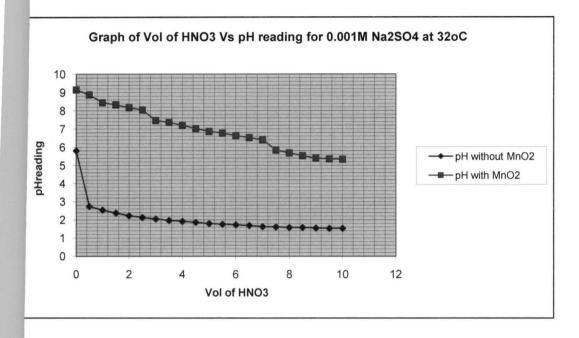


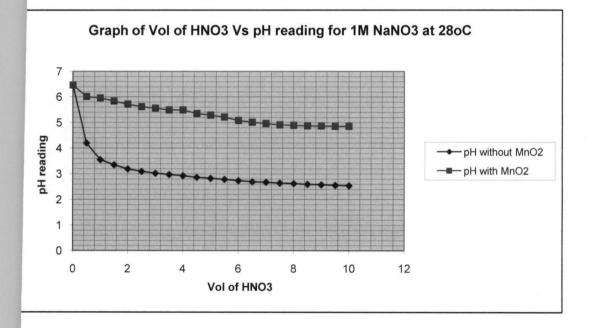


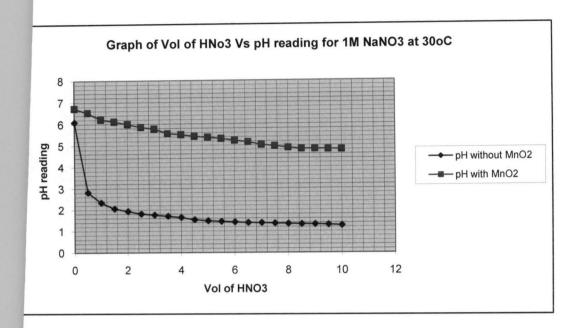


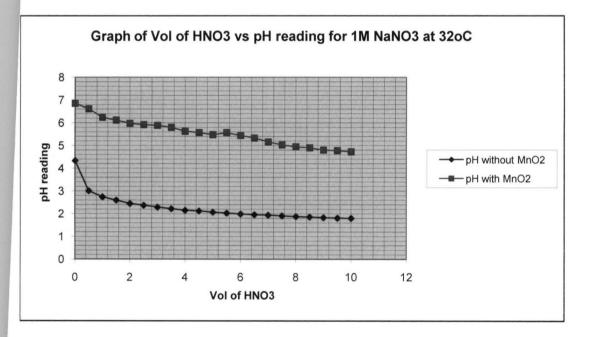


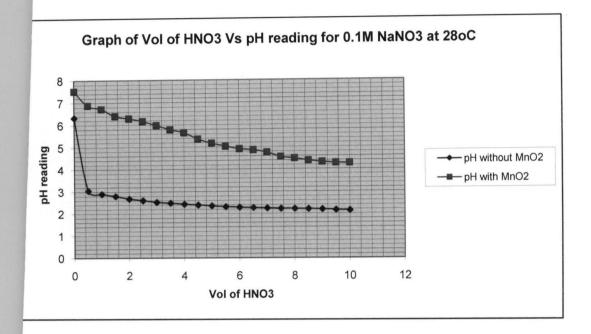


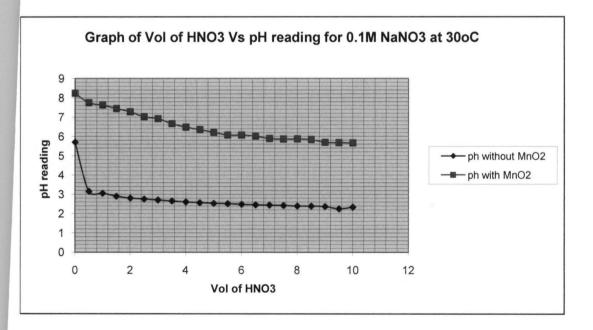


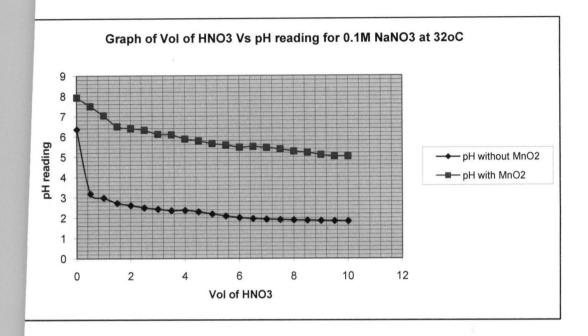


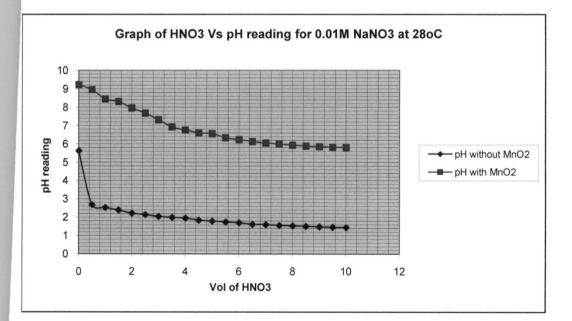


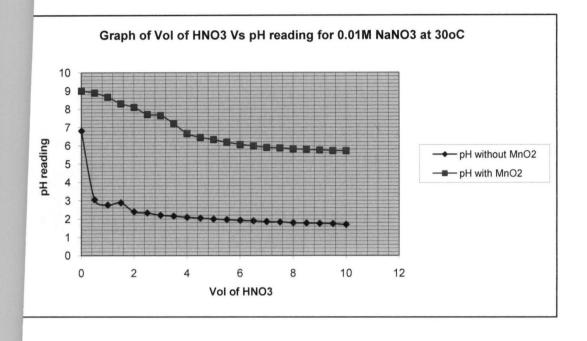


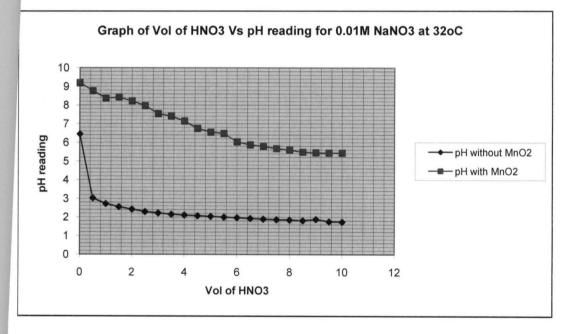


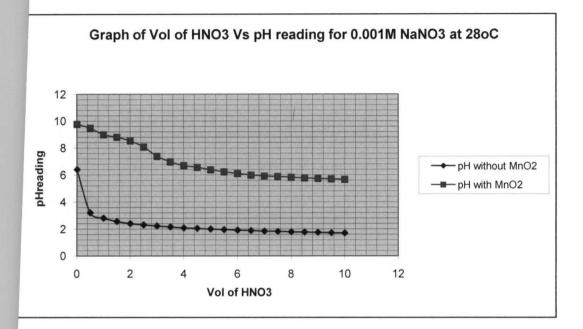


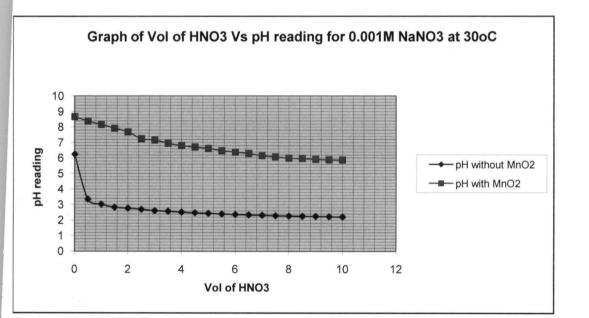




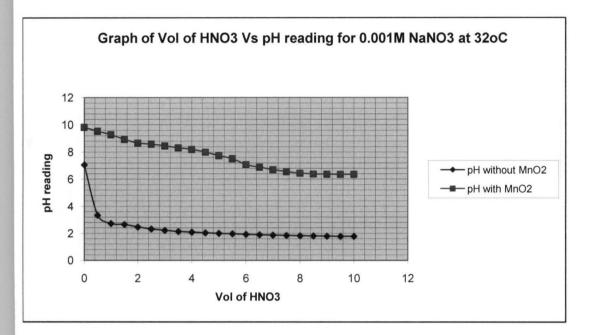


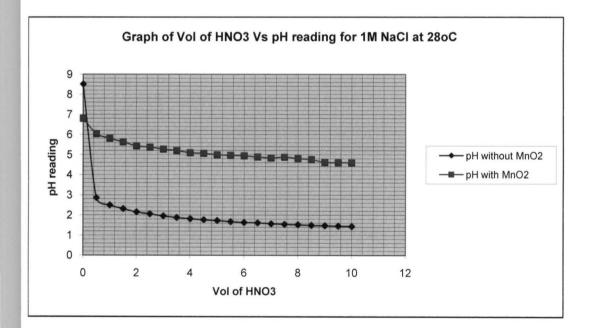


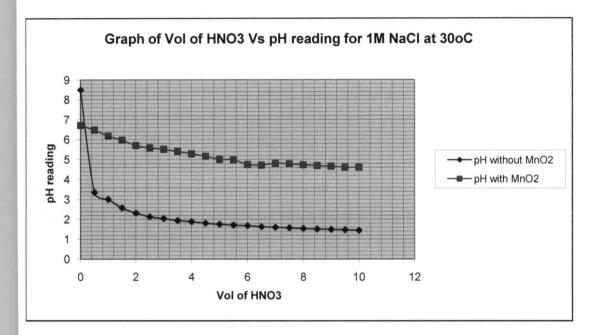


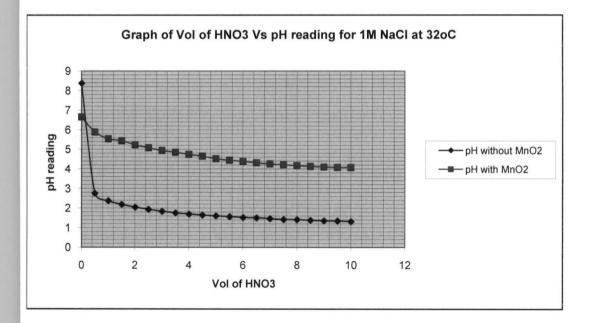


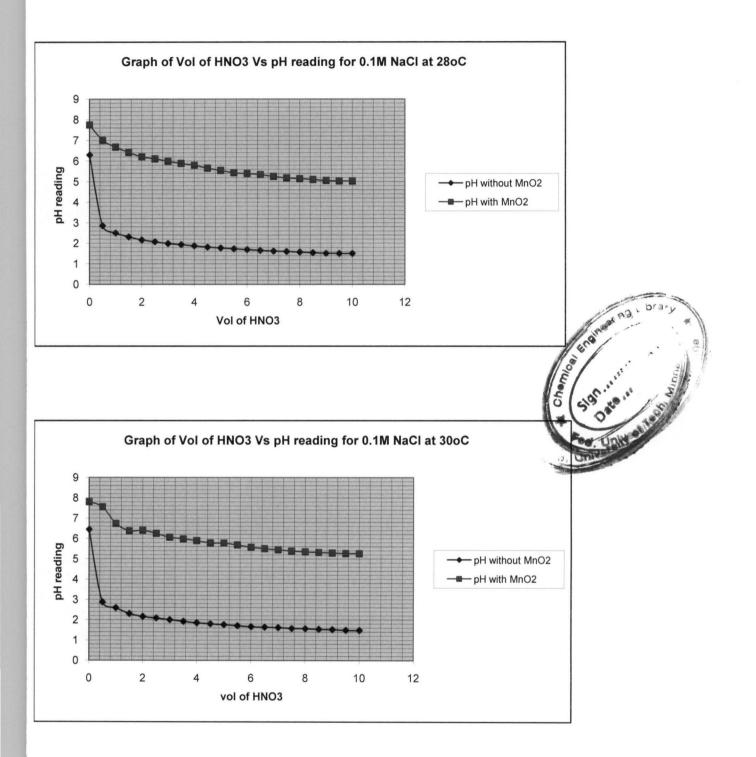


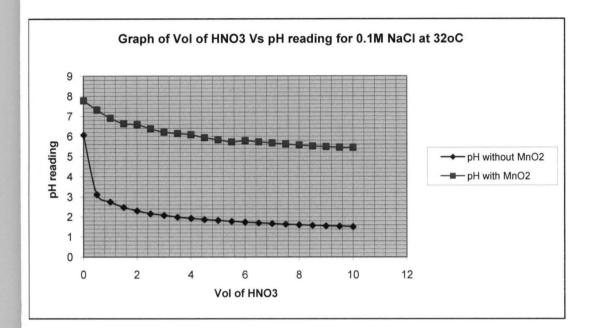


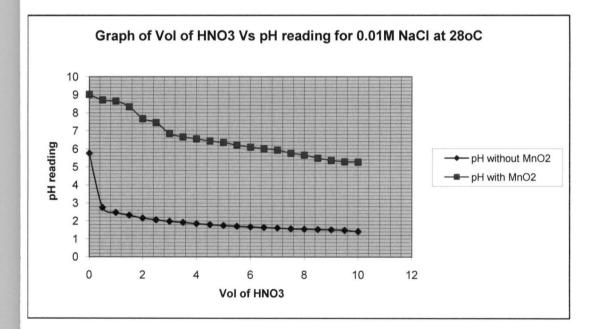


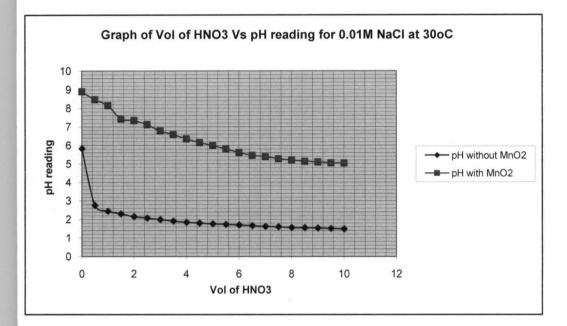


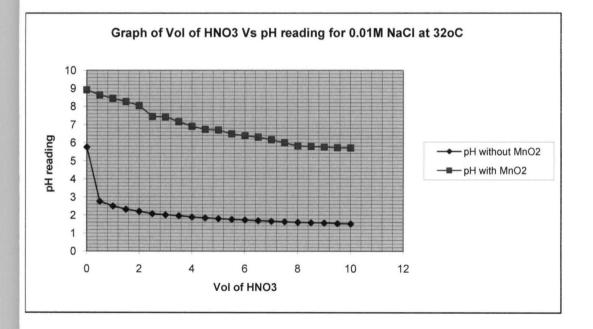


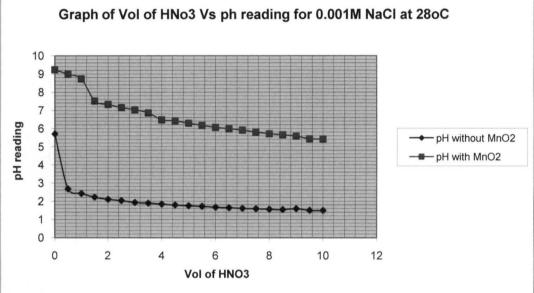


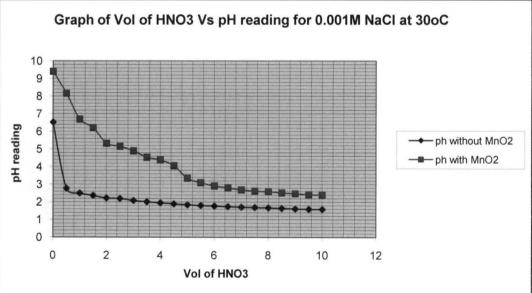












Vol of HNO3

