

# Computer Aided Factorial Analysis of the Adsorption of Calcium ion ( $\text{Ca}^{2+}$ ) on Manganese (IV) oxide used in Leclanche dry cell

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**Abstract:** The adsorption of calcium ions on manganese (IV) oxide was investigated by pH measurement in potentiometric titration of 1M, 0.1M, 0.01M, and 0.001M solutions of the ions without and with 2g of manganese (IV) oxide at temperatures of 28°C and 30°C; using 0.1M trioxonitrate (V) acid solution as titrant. The factorial method of design; using Minitab® was employed to obtain the effects of each factor on adsorption, the effects of the interactions of the factors on adsorption and a linear model equation in terms of the factors and their interactions, for the ion. The results show that increasing temperature and concentration, and decreasing pH increases adsorption of calcium ions. The linear model equation is:

$$E_{\text{Ca}^{2+}} = -2.63176 + 0.100048X_1 + 2.10185X_2 + 0.837110X_3 - 0.070034X_1X_2 - 0.0310782X_1X_3 - 0.853669X_2X_3 + 0.0290082X_1X_2X_3$$

The optimization of the equations with the target value of 1 for electric surface charge yielded the optimal values of temperature, concentration and pH as 29.1250°C, 0.001M, 2.5 respectively.

**Key words:** Leclanche dry cell; Calcium ion; Manganese (IV) oxide; Factorial design; Minitab®; Electric surface.

## Introduction and Experiment

Mathematical modelling is a mathematical representation of subsystems. It is a general characterization of a process in terms of mathematics and the equations obtained to describe the existing relationships among set of variables usually ordinary or partial differential, integration or integral differential in nature<sup>1</sup>. Adsorption is the process of selective affinity of an ion to a solid from a liquid bulk. In other words, adsorption is the selective transfer of one or more solutes from a fluid phase to a batch of rigid particles (adsorbents)<sup>1</sup>.

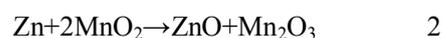
It was noted that multiple linear ordinary differential equation of the form:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_{12}X_1X_2 \quad 1$$

was a good model to represent the adsorption of some cations on manganese dioxide ( $\text{MnO}_2$ )<sup>2</sup>.

Leclanche dry cell-a primary cell<sup>3</sup>, has become a familiar household item and has a major influence in our ways of life since it was invented in the 1860s. It is an ingeniously engineer device that has a rather unusual half reactions and half-cell but it operates through electrochemical principles<sup>4</sup>. Some other improvements made on Leclanche dry cell have their shortcomings. Alkaline battery and silver (Button) battery are very expensive<sup>4</sup>. Mercury cells release toxic metal when discarded<sup>4</sup>. Several attempts have been made to correct the polarisation effect as well as to improve the capacity of dry cell. Zinc chloride was included in electrolyte with the aim of reducing the polarisation process<sup>5</sup>.

The general chemical reaction taking place in Leclanche dry cell is as follows<sup>5</sup>.



The hydrogen gas produced from equation 3 seriously reduces the efficiency of the dry cells in two ways:

- a) It increases the electrical resistance of the system.
- b) It forms a back electromotive force (E.M.F) with Zinc cathode.

The two effects combined to reduce the life span of a Leclanche dry cell. The manganese dioxide in the cell serves to minimise the effect by depolarising H<sub>2</sub> formation as given in Equation 4



However, MnO<sub>2</sub> does not totally eliminate the hydrogen gas produced and water is also forming which make the battery swells up with time. The inclusion of Calcium chloride in the electrolyte was suggested to improve the ionic conductivity of the electrolyte<sup>6,7</sup>.

Hence, this research aims at optimise some variables that influence the rate of adsorption of Ca<sup>2+</sup> on Manganese (iv) oxide used in Leclanche dry cell using computer Aided Factorial Analysis inbuilt in Minitab® in order to improve the depolarising effect of Manganese(iv) oxide.

### Procedure for the Determination of Surface area of Manganese (IV) Oxide

To seven clean and well labelled 250ml Erlenmeyer flasks, 100ml of acetic acid solution each of concentration 0.015M, 0.03M, 0.06M, 0.09M, 0.12M and 0.15M were measured with a pipette and added to their separate flask. Then 2g of the manganese (IV) oxide was added to the flasks containing the given concentrations of the acetic acid but the seventh flask contained 0.015 acetic and served as a control. The seven flasks were then stoppered and each flask was shaken periodically for thirty (30) minutes and was allowed to stand in a water bath at 25°C for 24 hours. When equilibrium has been reached (after 24 hours), the solutions were filtered into clean conical flask, but the first 10ml of the filtrate for each of the mixtures was discarded as a precaution against adsorption of the acid by the filter paper.

Two 25ml portions of the filtrate (aliquots) were taken with a pipette and titrated against 0.1M sodium hydroxide solution using phenolphthalein as an indicator. The same procedure was repeated for the remaining concentrations of the acetic acid solutions. From the titre values, the new concentrations of the acetic acid solutions were calculated and the difference obtained. These values were

used to calculate values for C/N and hence plot C/N against C. the slope of the straight line obtained was calculated and used for the calculation of the adsorption area of manganese (IV) oxide<sup>8</sup>.

### Potentiometric Titration Procedure

1M, 0.1M, 0.01M and 0.001M solutions of calcium nitrate [Ca (NO<sub>3</sub>)<sub>2</sub>] were prepared and 50ml of each solution for the salt per time was measured into a clean dry 100ml beaker into which; a magnetic stirrer follower for continuous stirring; a nitrogen gas jet to provide an inert environment and a reference electrode connected to a calibrated and stabilized pH meter were placed. The magnetic stirrer and gas jet were turned on and each solution of the salt without manganese dioxide (depolarizer) at 28°C and 30°C and with 2g of manganese dioxide (depolarizer) at 28°C and 30°C was titrated against 0.1M trioxonitrate (V) acid (HNO<sub>3</sub>) placed in a burette by addition of 0.5ml of the acid per time for a total volume of 10ml addition of the acid. In each case, the pH meter reading before titration and 1 minute after each 0.5ml addition of the titrant was recorded. The pH versus the volume of the titrant obtained was plotted both for the adsorption of cations without and with MnO<sub>2</sub> on the same graph. At a given pH, the difference in volume ( $\Delta V$ ) between the two graphs was used to calculate adsorption. The value of absorption ( $\Psi$ ) is calculated using:

$$\Psi = \frac{\Delta V \times C}{A \times 1000} \text{ (mole/cm}^2\text{)} \quad 5$$

Where C= Conc. of HNO<sub>3</sub> in mole/litre and A= Surface area in m<sup>2</sup>/g

The electric surface charge of [Ca (NO<sub>3</sub>)<sub>2</sub>] adsorbed, E in Coulomb/cm<sup>2</sup> is given by:

$$E = nF\psi \quad 6$$

n= absolute no of ionic charge and F = Faraday's constant

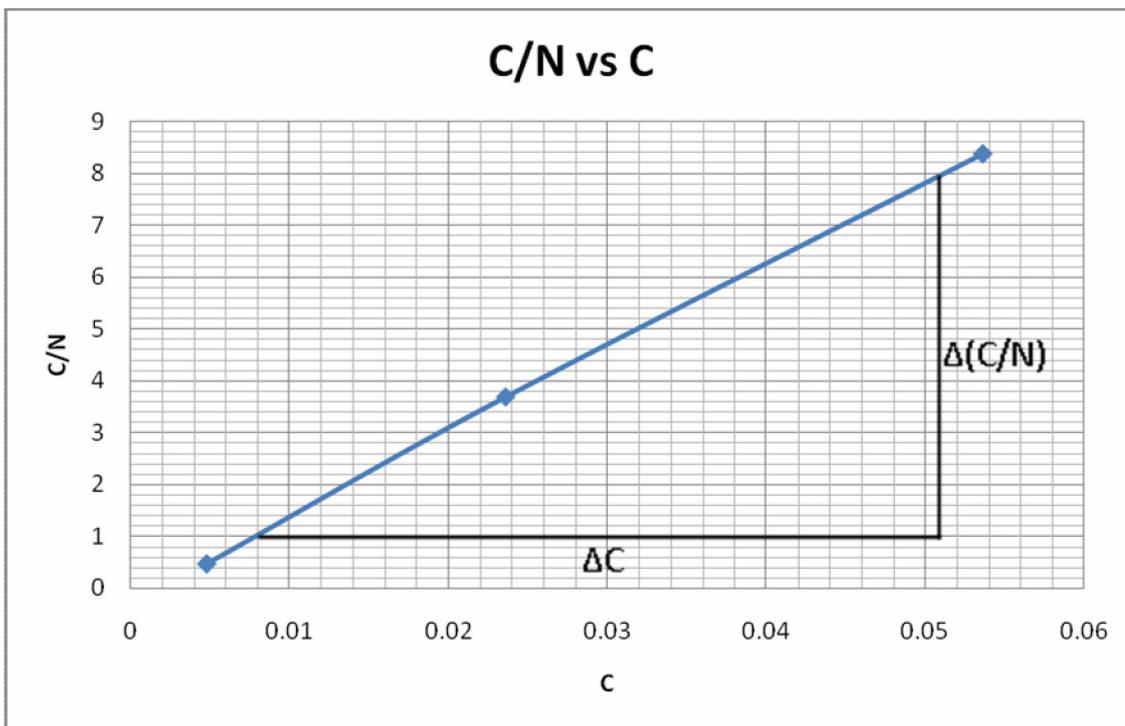
The same experiment procedures was repeated for different concentration (1M, 0.1M, 0.01M and 0.001M) of [Ca (NO<sub>3</sub>)<sub>2</sub>]<sup>8</sup>.

### Results and Discussion

The experimental results obtained for the determination of surface area of Manganese (IV) oxide are shown in Table 1.

**Table 1: Results for the determination of surface area of  $MnO_2$**

S/N	Initial acetic acid conc. $C_a$	vol. of 0.1M NaOH VB (ml)	final Acetic acid conc. $C$	Conc. Difference, $N$	$C/N$
1	0.015	1.2	0.0048	0.0102	0.470588
2	0.03	6	0.024	0.006	4
3	0.06	13.4	0.0536	0.0064	8.375
4	0.09	18.7	0.0748	0.0152	4.921053
5	0.12	24.8	0.0992	0.0208	4.769231
6	0.15	32.5	0.13	0.02	6.5



**Figure 1: Plot of  $C/N$  against  $C$**

**Specific surface area**

Specific surface area of adsorption,

$$A = N_m \times N_o \times \sigma \tag{7}$$

$N_m$  = number of moles per gram required to form a monolayer = 0.006143

$N_o$  = Avogadro's number =

$$6.023 \times 10^{23}$$

$\sigma$  = Area occupied by an adsorbed molecule on the surface =  $21 \text{ \AA}^2 = 21 \times 10^{-20} \text{ m}^2$

From fig.1, the slope of the plot which is equal to  $1/N_m$  was found to be 162.79

On substitution to equation 7, the specific surface area was calculated to be  $776.9851 \text{ m}^2/\text{g}$

From fig.1 the change in concentration of acetic acid is highest for initial concentration of 0.12M and lowest for initial acetic acid concentration of 0.03M. This is due to the fact that the rate of adsorption of adsorbate is proportional to external surface area of the solid and concentration difference across the boundary film<sup>9</sup>.

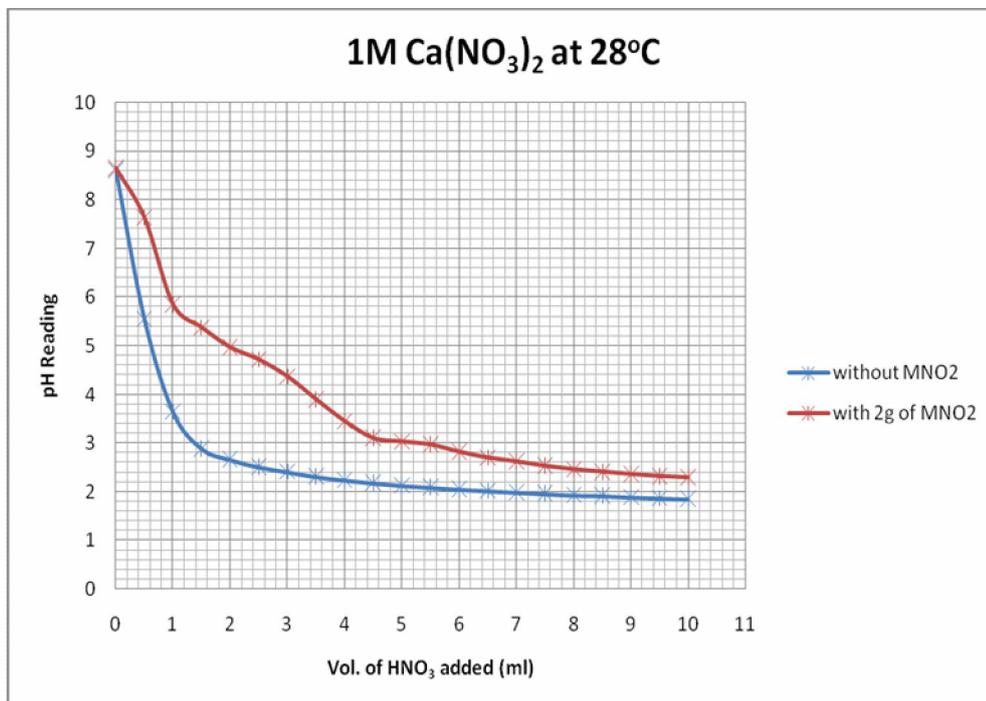


Figure 2: Plot of pH against Volume of titrant for 1M Ca (NO<sub>3</sub>)<sub>2</sub> at 28°C

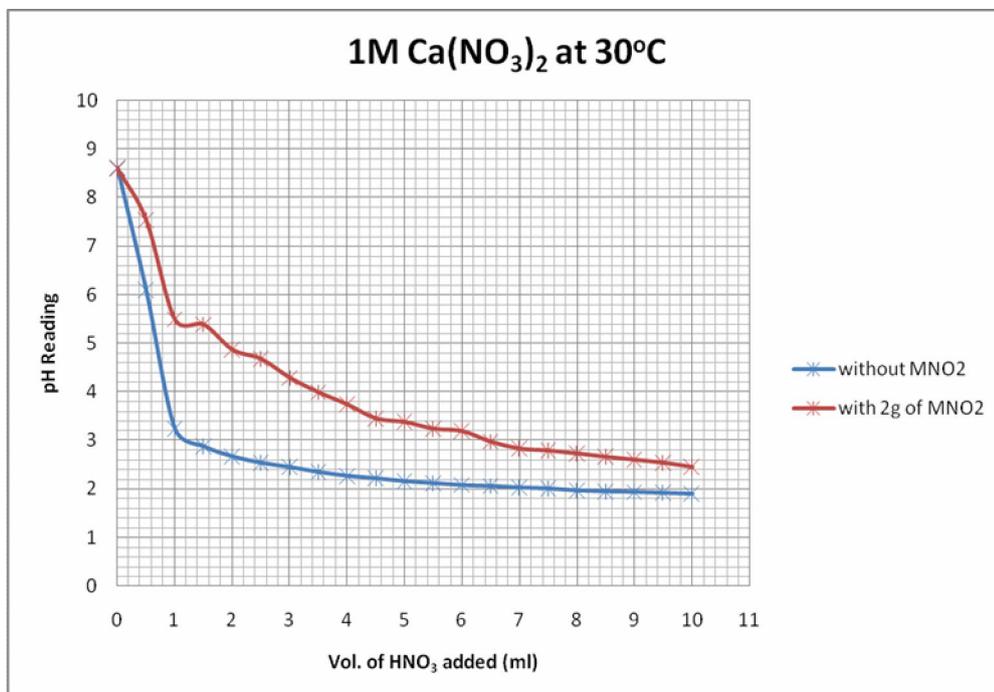


Figure 3: Plot of pH against Volume of titrant for 1M Ca (NO<sub>3</sub>)<sub>2</sub> at 30°C

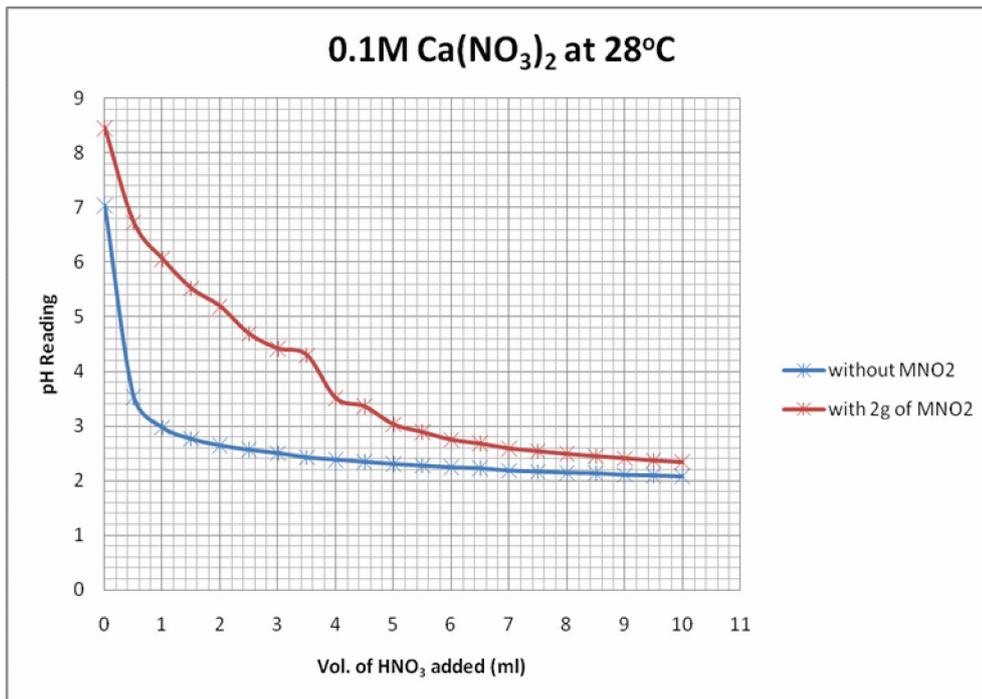


Figure 4: Plot of pH against Volume of titrant for 0.1M Ca (NO<sub>3</sub>)<sub>2</sub> at 28°C

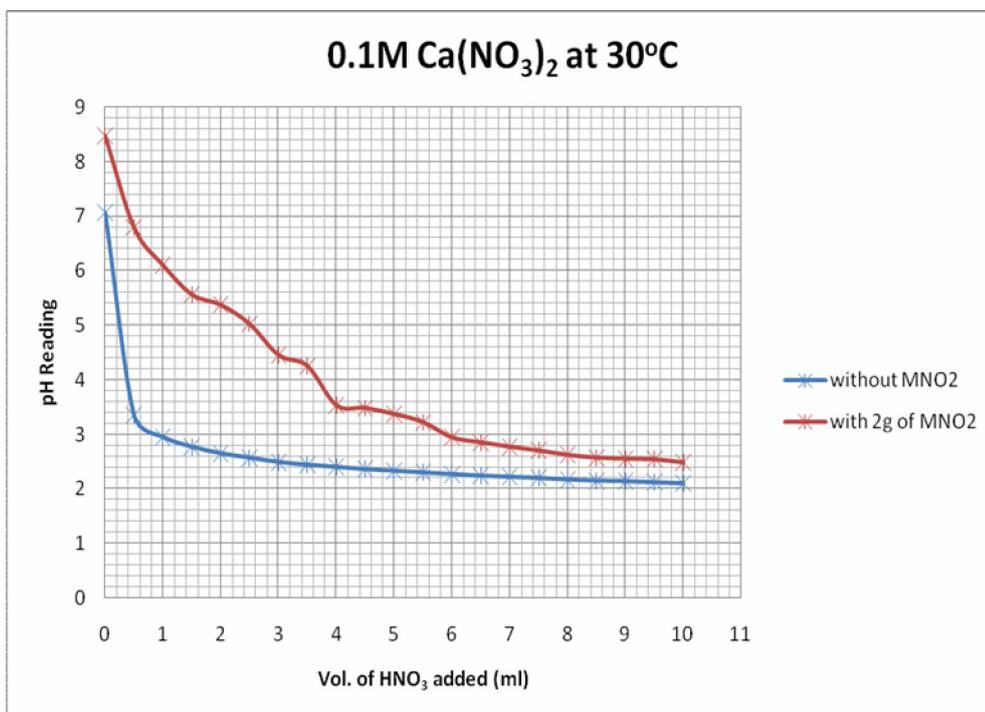


Figure 5: Plot of pH against Volume of titrant for 0.1M Ca (NO<sub>3</sub>)<sub>2</sub> at 30°C

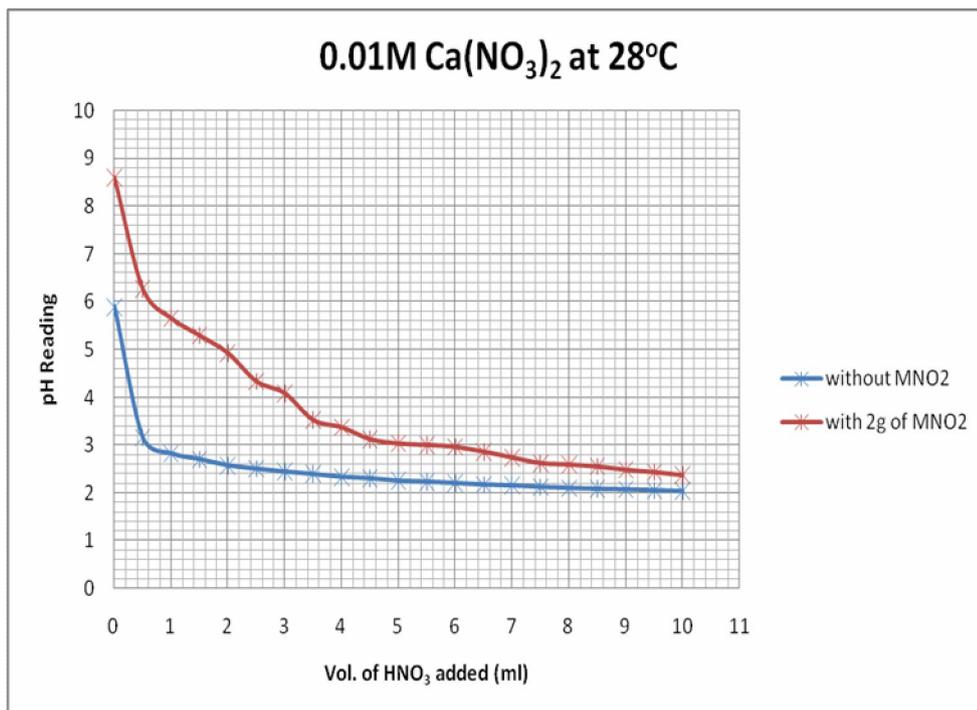


Figure 6: Plot of pH against Volume of titrant for 0.01M Ca (NO<sub>3</sub>)<sub>2</sub> at 28°

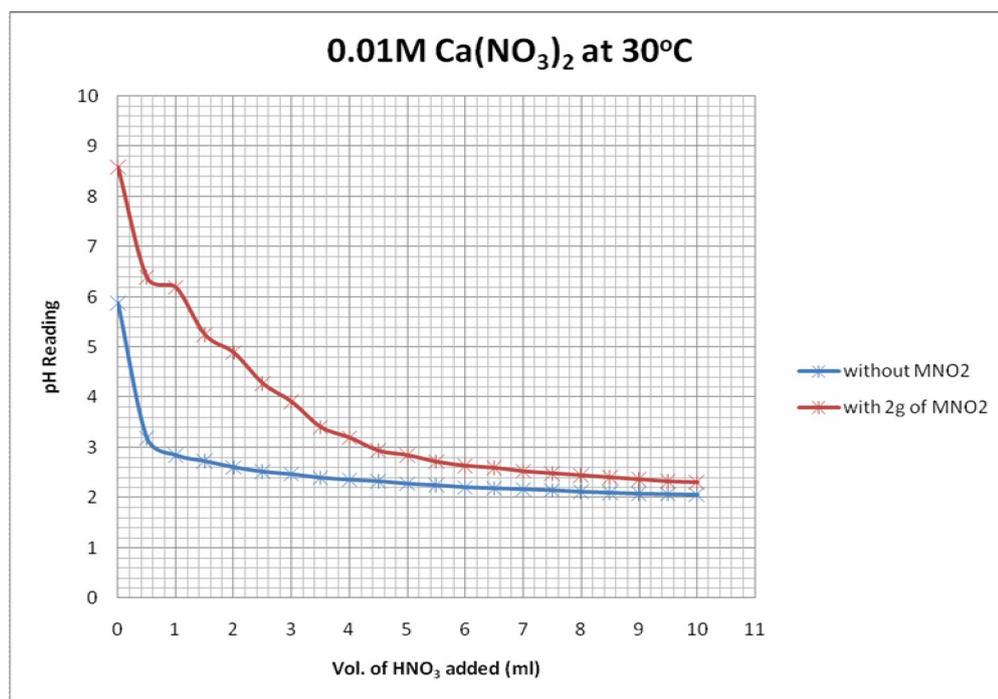


Figure 7: Plot of pH against Volume of titrant for 0.01M Ca (NO<sub>3</sub>)<sub>2</sub> at 30°

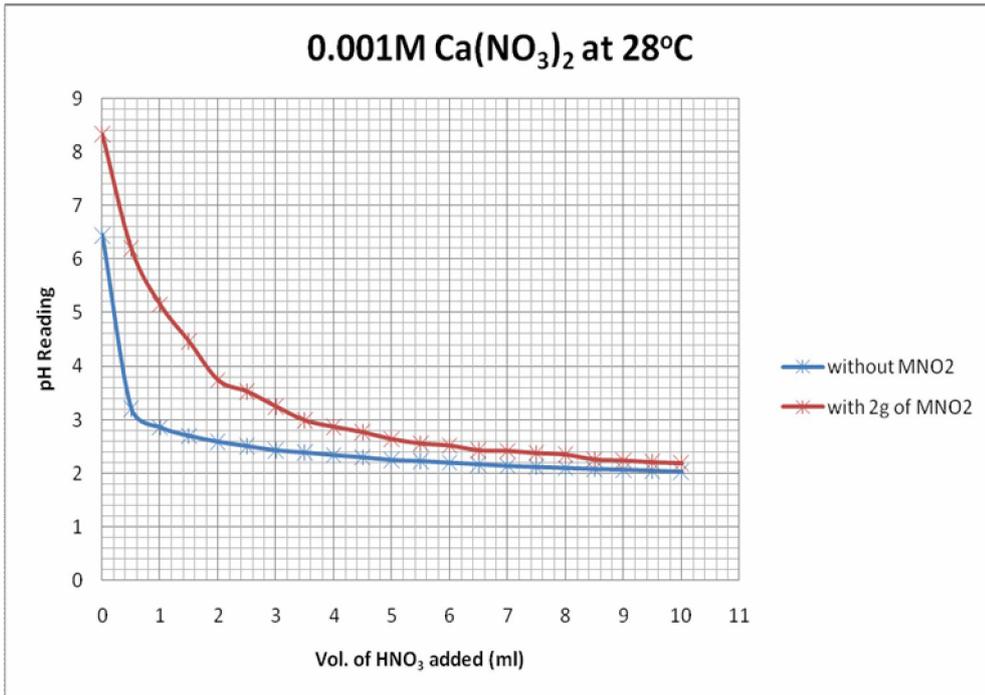


Figure 8: Plot of pH against Volume of titrant for 0.001M Ca (NO<sub>3</sub>)<sub>2</sub> at 28°C

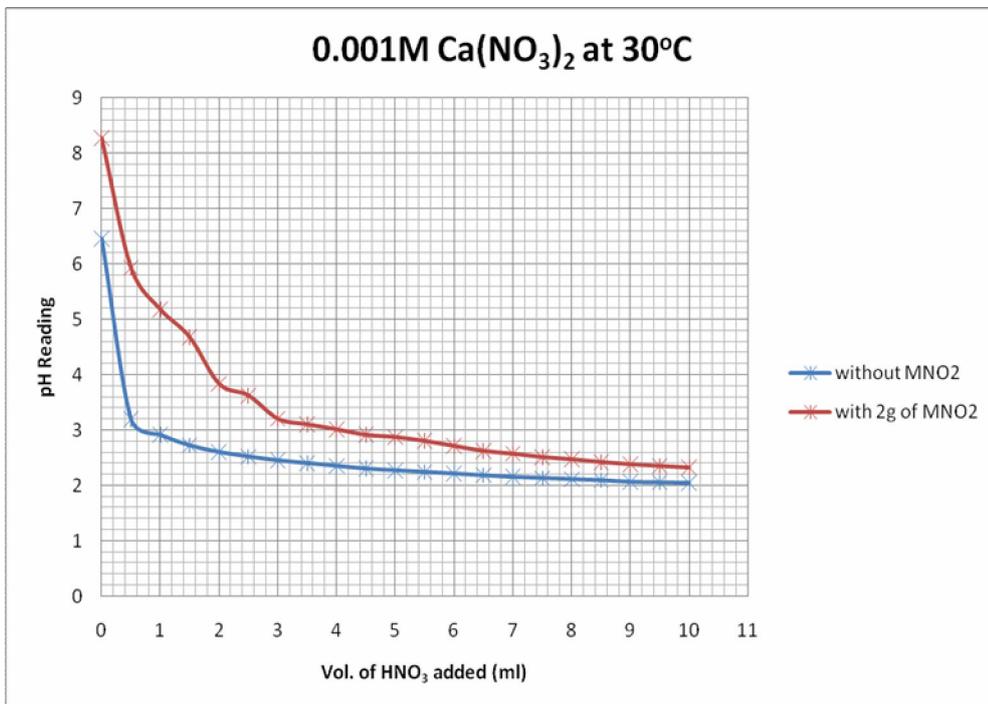


Figure 9: Plot of pH against Volume of titrant for 0.001M Ca (NO<sub>3</sub>)<sub>2</sub> at 30°

**pH responses during potentiometric titration**

From fig.2-9, it was observed that as more volume of titrants (HNO<sub>3</sub>) was added to the solution, the pH value of the solution tends toward acidity. It was also noted that at any given equal volume of titrant added, the pH value of the solution with MnO<sub>2</sub> was higher than those without MnO<sub>2</sub>.The reason was that from the depolarizing equation $3Ca^{2+}$  ions react with water produced and one of

products of that reaction is a base which increases the alkalinity of the solution. It was also observed that the change in pH with successive addition of titrant (HNO<sub>3</sub>) to the solution decreases as the titration progresses. This was true for both solution with and without MnO<sub>2</sub>.This was due to the fact that as the adsorption of Ca<sup>2+</sup> progresses, the number of available sites left for further adsorption decreases. This result is in conformity with<sup>8</sup>.

**Table 2: Electric surface charge of 1M Ca (NO<sub>3</sub>)<sub>2</sub> and adsorption on MnO<sub>2</sub>**

S/N	pH	1M Ca(NO <sub>3</sub> ) <sub>2</sub> at 28oC			1M Ca(NO <sub>3</sub> ) <sub>2</sub> at 30oC		
		ΔV (ml)	$\Psi = \frac{\Delta V \times C}{A \times 1000}$	E = nFψ	ΔV (ml)	$\Psi = \frac{\Delta V \times C}{A \times 1000}$	E = nFψ
1	2.5	5	6.43513E-07	0.124198	7	9.00918E-07	0.173877
2	2.8	4.4	5.66291E-07	0.109294	5.4	6.94994E-07	0.134134
3	3.1	3.2	4.11848E-07	0.079487	5.1	6.56383E-07	0.126682

**Table 3: Electric surface charge of 0.1M Ca (NO<sub>3</sub>)<sub>2</sub> and adsorption on MnO<sub>2</sub>**

S/N	pH	0.1M Ca(NO <sub>3</sub> ) <sub>2</sub> at 28oC			0.1M Ca(NO <sub>3</sub> ) <sub>2</sub> at 30oC		
		ΔV (ml)	$\Psi = \frac{\Delta V \times C}{A \times 1000}$	E = nFψ	ΔV (ml)	$\Psi = \frac{\Delta V \times C}{A \times 1000}$	E = nFψ
1	2.5	5.2	6.69254E-07	0.129166	7	9.00918E-07	0.173877
2	2.8	4.4	5.66291E-07	0.109294	5.3	6.82124E-07	0.13165
3	3.1	4.1	5.27681E-07	0.101842	5	6.43513E-07	0.124198

**Table 4: Electric surface charge of 0.01M Ca (NO<sub>3</sub>)<sub>2</sub> and adsorption on MnO<sub>2</sub>**

S/N	pH	0.01M Ca(NO <sub>3</sub> ) <sub>2</sub> at 28oC			0.01M Ca(NO <sub>3</sub> ) <sub>2</sub> at 30oC		
		ΔV (ml)	$\Psi = \frac{\Delta V \times C}{A \times 1000}$	E = nFψ	ΔV (ml)	$\Psi = \frac{\Delta V \times C}{A \times 1000}$	E = nFψ
1	2.5	6.5	8.36567E-07	0.161457	4.8	6.17772E-07	0.11923
2	2.8	5.7	7.33605E-07	0.141586	4.1	5.27681E-07	0.101842
3	3.1	4	5.1481E-07	0.099358	3.7	4.762E-07	0.091907

**Table 5: Electric surface charge of 0.001M Ca (NO<sub>3</sub>)<sub>2</sub> and adsorption on MnO<sub>2</sub>**

S/N	pH	0.001M Ca(NO <sub>3</sub> ) <sub>2</sub> at 28oC			0.001M Ca(NO <sub>3</sub> ) <sub>2</sub> at 30oC		
		ΔV (ml)	$\Psi = \frac{\Delta V \times C}{A \times 1000}$	E = nFψ	ΔV (ml)	$\Psi = \frac{\Delta V \times C}{A \times 1000}$	E = nFψ
1	2.5	3.5	4.50459E-07	0.086939	5.3	6.82124E-07	0.13165
2	2.8	3.2	4.11848E-07	0.079487	4.3	5.53421E-07	0.10681
3	3.1	2.7	3.47497E-07	0.067067	3	3.86108E-07	0.074519

**Optimization results for Ca<sup>2+</sup>**

Selecting temperature, concentration, pH as the factors; each of two levels denoted by + (the highest value of a factor) and – (the lowest value of a factor), and electric

surface charge as the response denoted by E, the actual design matrix and the values of the factors at the two levels are shown in Table 6 and Table 7 respectively.

**Table 6: Values of the selected factors**

S/N	Factors	Temperature	Concentration	pH
1	+	30	1	3.1
2	-	28	0.001	2.5

**Table 7: Actual 2<sup>3</sup> factorial design matrix for Ca (NO<sub>3</sub>)<sub>2</sub>**

S/NO	Temperature, X1	Concentration, X2	pH, X3	Electric surface charge, E
1	28	0.001	2.5	0.086939
2	30	0.001	2.5	0.13165
3	28	1	2.5	0.124198
4	30	1	2.5	0.173877
5	28	0.001	3.1	0.067067
6	30	0.001	3.1	0.074519
7	28	1	3.1	0.079487
8	30	1	3.1	0.126682

**Estimated Coefficients for Electric surface charge, E**

Term	Coefficient
Constant	$a_0 = -2.63176$
Temperature (X <sub>1</sub> )	$a_1 = 0.100048$
Concentration (X <sub>2</sub> )	$a_2 = 2.10185$
pH (X <sub>3</sub> )	$a_3 = 0.837110$
Temperature*Concentration (X <sub>1</sub> X <sub>2</sub> )	$a_{12} = -0.0700340$
Temperature*pH (X <sub>1</sub> X <sub>3</sub> )	$a_{13} = -0.0310782$
Concentration*pH (X <sub>2</sub> X <sub>3</sub> )	$a_{23} = -0.853669$
Temperature*Concentration*pH (X <sub>1</sub> X <sub>2</sub> X <sub>3</sub> )	$a_{123} = 0.0290082$

The model equation of the electric surface charge of Ca (NO<sub>3</sub>)<sub>2</sub> is:

$$E_{Ca^{2+}} = -2.63176 + 0.100048X_1 + 2.10185X_2 + 0.837110X_3 - 0.070034X_1X_2 - 0.0310782X_1X_3 - 0.853669X_2X_3 + 0.0290082X_1X_2X_3$$

Factorial plots for  $\text{Ca}^{2+}$

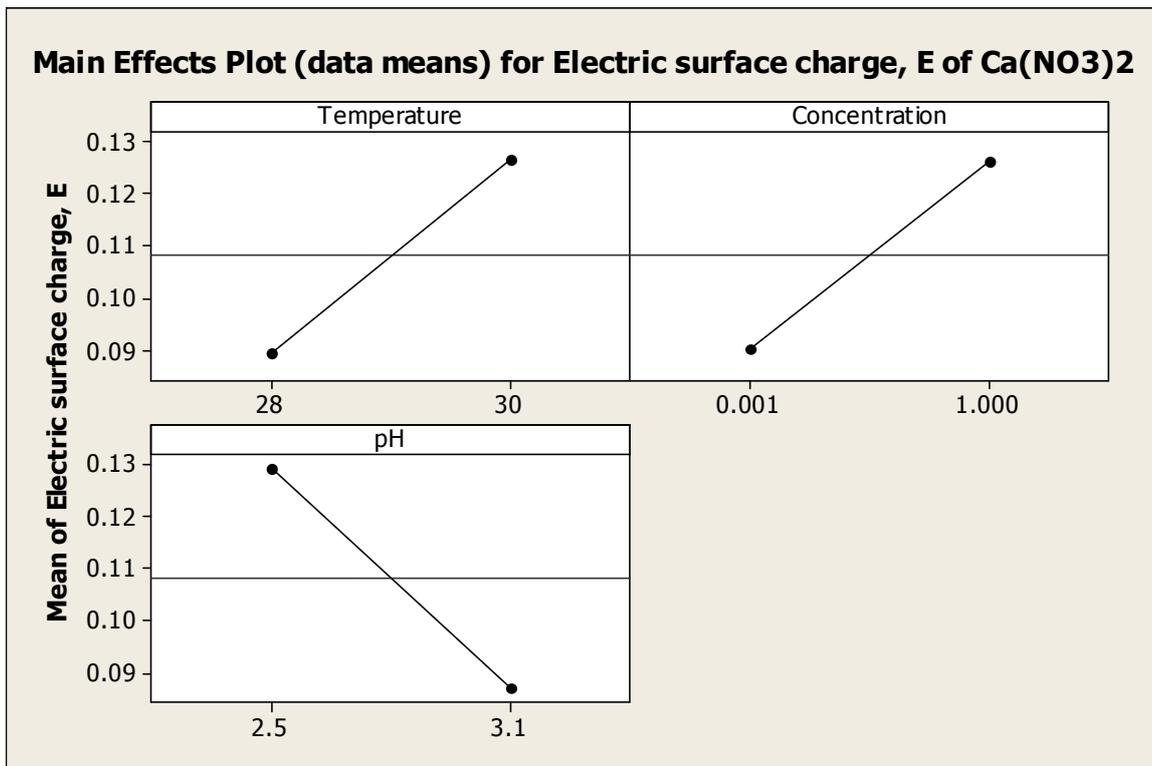


Figure10: Effects plot for electric surface charge of  $\text{Ca}(\text{NO}_3)_2$

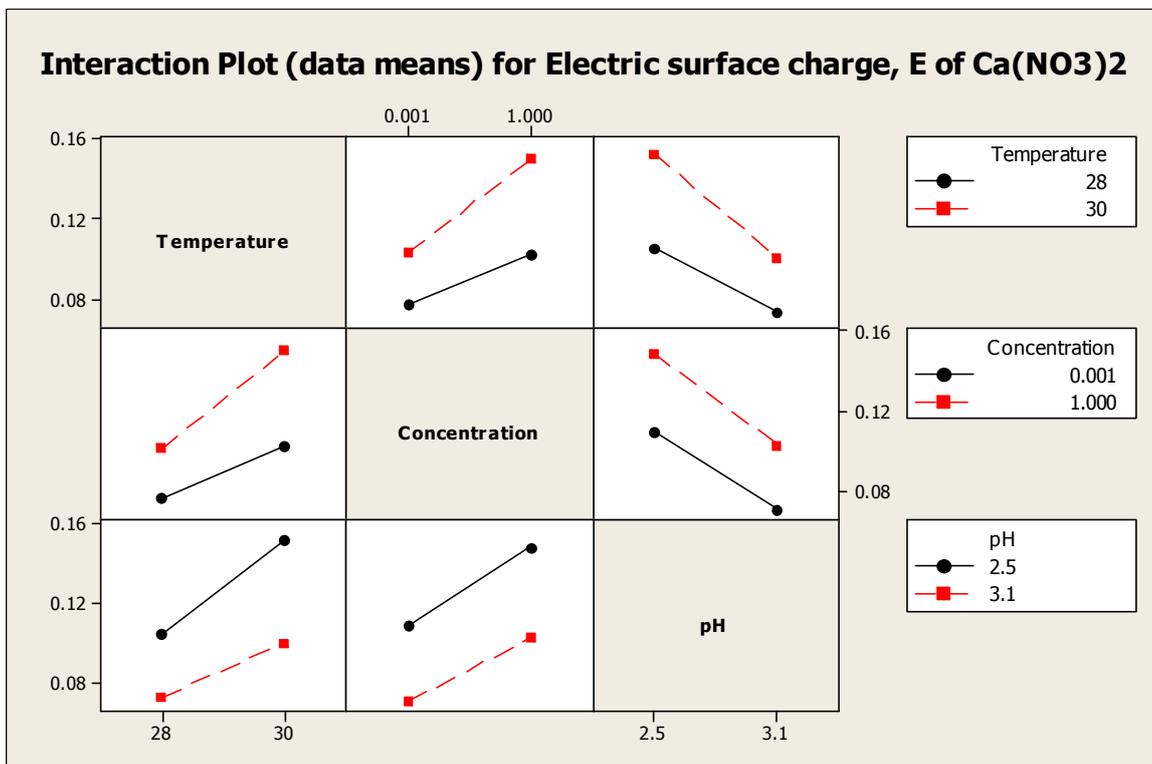
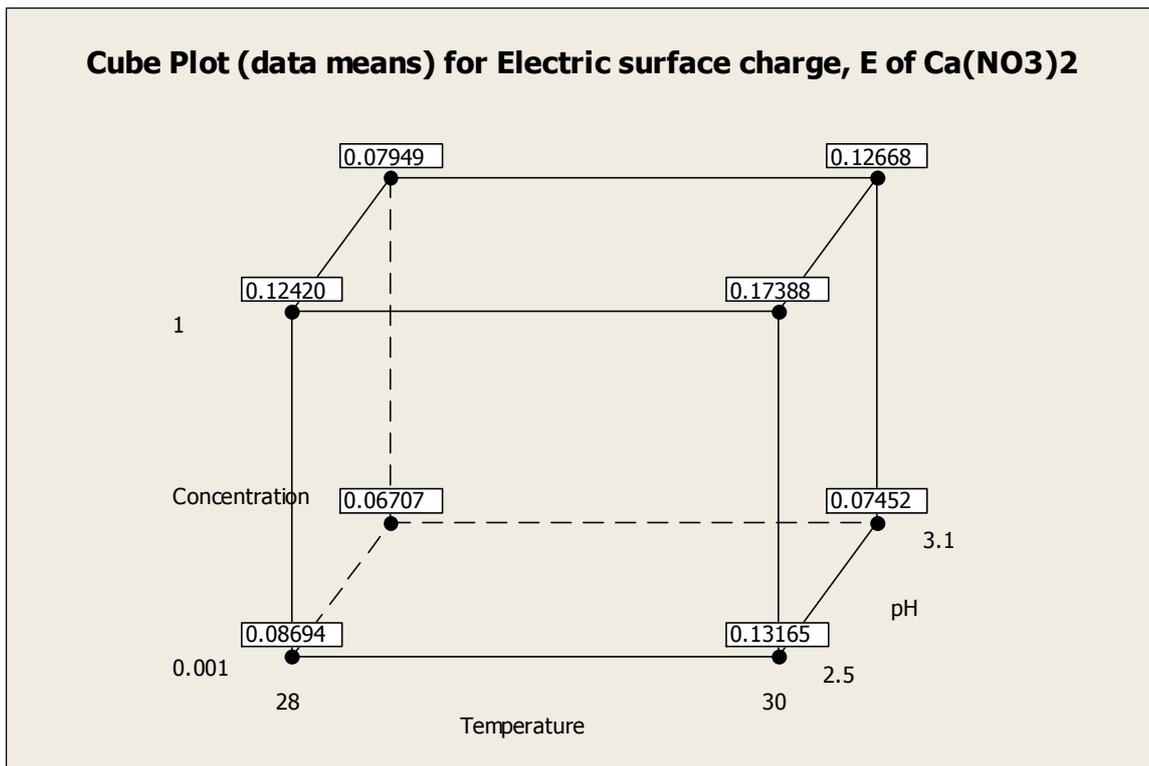


Figure 11: Interaction plot for electric surface charge of  $\text{Ca}(\text{NO}_3)_2$



**Figure12: Cube plot for Electric surface charge of Ca (NO<sub>3</sub>)<sub>2</sub>**

### Discussion of optimized results

On the main effect plot shown in fig.10, it was observed that the average effect of increasing temperature from 28°C to 30°C resulted to increase in electric surface charge by 0.03726. This indicated that the adsorption process is endothermic<sup>10</sup>. That is, increase in temperature leads to increase in adsorption and increase in surface charge. Similarly, increase of concentration from 0.001M to 0.1M resulted to increase in the electric surface charge by 0.03602. This is in conformity with boundary film theory that adsorbate is transferred to an adsorbent at a rate which depends upon the external surface area of the solid and upon concentration difference across the boundary. However, increase of pH from 2.5 to 3.1 resulted to decrease in electric surface charge by 0.04224. This shows that adsorption of Ca<sup>2+</sup> is favored in acidic medium.

On the interaction plot shown on fig.11, it was observed that high electric surface charge and high adsorption could be achieved at high temperature and high concentration but at low pH.

The cube plot shown on fig.12 summarized the model for the electric surface charge of Ca<sup>2+</sup> on MnO<sub>2</sub>. The edge of each cube plot shows various interactions of the factors and the corresponding value of response (electric surface charge). The electric surface charge at the high level of temperature, low level of pH and high level of concentration is 0.17388 and the value of electric surface charge at low level of temperature, high level of pH and low level of concentration, is 0.6707 which were the highest and lowest responses respectively.

### Conclusion

Concentration, temperature and pH and their interactions all have significant effects on the adsorption of calcium ions on manganese (IV) oxide. The optimal conditions of temperature, concentration and pH for calcium ions (Ca<sup>2+</sup>) are 29.1250°C, 0.001M and 2.5 respectively.

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