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The effect of Concentration, Temperature, and the Potency of Hydrogen on the Adsorption of Calcium on Manganese Dioxide

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Abstract

This research was carried out to determine the effect of temperature, concentration, and pH on the adsorption of Ca^{2+} in $Ca(NO_3)_2$ solution on MnO_2. The essence is to improve the depolarizing ability of MnO_2 used in a dry cell. Potentiometric titration method was used to determine the adsorption of calcium ion on MnO_2. Both unilateral and interactive effects of concentration, temperature, and pH on the calcium ion were investigated using the 2^3 factorial design. It was observed that at 40°C, 1M, and pH of 11.25, Ca^{2+} produce an electric surface charge of 0.961 coloumb/mole on MnO_2.

Keywords

Concentration, temperature, potency of hydrogen, adsorption, calcium ion, manganese dioxide, depolarization and factorial design.

1.0 Introduction

Dry cells especially Leclanche, are made in various shapes and sizes; they are potable, readily available, and relatively cheap. It is the most commonly used cell worldwide in flashlights, radios, cameras and others. The operating voltage of a Leclanche cell is in the range of 0.9-1.7 volts. The temperature by which the cell operates is of great importance. It influences below 36°C, the cells usually produce little current and change the internal morphology, resulting to internal damage and diminished performance. At the other hand, if the temperature is raised above 45°C, chemicals may evaporate or react spontaneously with one another leading to earlier failure. Adsorption involves the transfer of a constituent of a component to the surface of a liquid or solid phase Akhmetov et al (1989) when a liquid molecule is adsorbed on the surface of a solid, it settles

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on it much like a condensing molecule, and is then held on the surface by attractive forces such as van der waals forces or in some cases depends on the chemical nature of the molecule and the surface (chemisorption). Both physical and chemical (chemisorption) adsorption occurs in a particular system Akhametov et al (1989).

The forces involved in physical adsorption decreases rapidly as the temperature is increased and is generally very small above the critical temperature of the adsorbed component Ira (1989).

Adsorption isotherm deals with the relationship between concentration in the solution and the quantity adsorbed. The amount of solid adsorbed per gram of solid depends on the specific area of the solid, the equilibrium solute concentration in the solution (or pressure in the case of adsorption from the gas phase), the temperature and the type of the molecules involved.

The aim of this research work is to investigate the effect of temperature, concentration and pH on the adsorption of calcium ion on manganese dioxide (MnO_2) in a Lenclanche dry cell using potentiometric titration method. The objective is to determine the optimum temperature, concentration and pH by which calcium ion additive can be blended with manganese dioxide to enhance the performance and enable it withstand the polarization action occurring in the cell.

For an experiment involving the study of the effect of two or more factors, the factorial designs are most efficient in obtaining the response functions. Factorial designs are most effective in experiments involving several factors where it is necessary to study deeply the effect of temperature, concentration and pH; factorial design which involves planning, running and analysis of the results is incorporated.

Factorial experiments provide an opportunity to study not only the individual effects of each factor, but also their interactions. When experiments are conducted factor by factor changing the level of one factor at a time and keeping the factors at constant levels, the effects of interaction cannot be investigated. In many science trials, factors are likely to have interaction. Therefore, factorial types of experiments are more informative in such investigations. They have the further advantage of economizing experimental resources. When experiments are conducted fact or by factor, much more resources are required for the same precision than when they are tried in factorial experiments (Douglas, 1991).

The design for 2^3 full factorial which indicates the run by run experimental design is shown in Table 1 with three variables (temperature, pH and concentration represented as X_1,X_2,X_3 respectively), two levels of minimum(-) and maximum(+) runs. The complete design leads to a total of 8 runs.

Table 1 A plan for 2^3 factorial design experiments

Run	X_0	X_1	X_2	X_3	1st run, Y_1	2nd run, Y_2	Mean, Y
1	+	-	-	-			
2	+	+	-	-			
3	+	-	+	-			
4	+	+	+	-			
5	+	-	-	+			
6	+	+	-	+			
7	+	-	+	+			
8	+	+	+	+			

After planning, the experiment is run and the statistical analysis of the 2^3 factorial approach was carried out guided by the following conditions (Douglas, 1991):

The condition of homogeneity of experimental result is given as:

if $G_{cal} < G[\alpha, (r-1), N]$ 1

then, the experimental results are accepted otherwise, rejected.

Where $G[\alpha, (r-1), N] = G(0.05,1,8) = G_{table} = 0.76$

N = number of experimental run

r = number of replicates

α = level of significance

$G_{cal} = y^2 max / \sum^n_{u=1} y^2$ = maximum dispersion/sum of dispersion 2

The significance of coefficients is considered accepted

if $t_{cal} > t[\alpha,(r-1), N]$, ... 3

Where (r-1) is the degree of freedom, $t[\alpha, N(r-1), N] = t(0.05,1,8) = t_{table} = 2.306$

The calculated F-ratio of individual coefficients is accepted when compared with the F_{table} values if $F_{ratio} > F[\alpha, N(r-1), N]$......... 4

Where $F[\alpha, N(r-1), N] = F(0.05,1,8) = F_{table} = 5.32$

The condition of adequacy is met if $F_{ad} \leq F[\alpha, r, N(r-1),]$ 5

2.0 Experimental

2.1 Determination of surface area of manganese dioxide (MnO_2)

To seven clean 250ml flasks, 100ml of acetic acid solution of various concentrations of 0.015M, 0.03M, 0.06M, 0.09M, 0.12M, and 0.15M were measured into their separate flasks. The flasks were shakened periodically for a period of 30minutes, then left in water bath at 25°C for 24 hours after which the solutions were filtered and 25ml portion of each solution was taken and titrated against 0.1M NaOH using phenolphthalein as the indicator, but 10ml burette was used for 0.015M. From the titre values, the new concentrations of the acetic acid solutions calculated. Thus the number of moles present before and after adsorption was similarly calculated and the difference obtained. These values were used to calculate the ratio of concentration (C) to number of moles adsorbed (N) and hence a plot of C/N versus C was drawn. The slope of the straight line obtained, was calculated and used for the calculation of the adsorption area of manganese dioxide.

2.2 Potentiometric titration

50ml of 1M solution of $Ca(NO_3)$ was measured into a 100ml beaker at various temperatures of 36, 40 and 45°C and a magnetic follower placed inside to provide a continuous stirring. A reference electrode and an indicator electrode connected to a pH meter were hanged into the solution in a beaker. The 100ml solution in a beaker was titrated with 0.1M sodium hydroxide solution with a continuous addition of nitrogen to minimize external reaction that can be caused from the atmospheric oxygen white (1984). The pH value was noted when the solution has been stabilized. Subsequently 0.50ml of the titrant 0.1MNaOH was added from the burette and the pH value noted for every 2 minutes after every addition when the indicator electrode had reached a constant value, The 0.5ml increment and the corresponding pH value were taken for a total of 10ml additions until when no significant change was observed in the reading. At the end, both the magnetic stirrer and the pH meter were switched off and the solution mixture disposed.

Similarly, another 50ml of 1M calcium nitrate solutions was pipetted into a beaker with a magnetic follower in it and 2g manganese dioxide added. The whole set up was arranged after stabilizing the pH meter with distilled water. The same procedure was repeated as described, the volumetric readings of the 0.1M NaOH and their corresponding pH readings for all the sets of titrations carried out were tabulated. Graphs were plotted for each set of readings (both pH of solutions with and without MnO_2).

2.3 *Factorial experiment*

In the adsorption of $Ca(NO_3)_2$ on MnO_2, the base level for the factors under consideration includes: concentration 0.5M, temperature 40.50°C, and pH 10.38.

The maximum and minimum measurement used for the varying factors includes: concentration, maximum 1.0M and minimum 0.001M; temperature, maximum 45°C and minimum 36°C and these were used to determine the adsorption of $Ca(NO_3)_2$ on MnO_2.

2.4 *Procedure*

The potentimetric titration experiment described in item 2.2 were run base on the 2^3 factorial design plan of table 1. The results obtained is given in table 3.

3.0 *Results and discussion*

Table 2 and 3 are the results obtained for both potentiometric titration and 2^3 factorial experimental design respectively.

Table 2 Adsorption and surface charge at different temperatures, various pH and at different concentrations of $Ca(NO_3)_2$

pH	T	1.0M		0.1M		0.01M		0.001M	
	°C	θ	E	θ	E	θ	E	θ	E
10.50	36	1.14e-6	2.21e-1	5.54e-1	1.07e-1	1.27e-7	2.49e-2	6.45e-7	0.125
11.25	40	4.98e-6	9.61e-1	1.48e-6	2.85e-1	1.85e-6	3.56e-1	1.11e-7	0.213
10.75	45	2.06e-6	3.92e-1	2.21e-6	4.27e-1	1.29e-6	2.49e-1	6.45e-7	0.125

Where E = surface charge

θ = adsorption

Table 3 2^3 Factorial Experimental Design of $Ca(NO_3)_2$

Run	X_0	X_1	X_2	X_3	Adsorption of Ca^{2+}		
					E_1	E_2	E_3
1		36	9.0	0.001	0.014	0.0144	0.0142
2		45	9.0	0.001	0.070	0.0712	0.0712
3		36	11.75	0.001	0.114	0.114	0.114
4		45	11.75	0.001	0.242	0.242	0.242
5		36	9.0	1.0	0.120	0.130	0.125
6		45	9.0	1.0	0.434	0.420	0.427
7		36	11.75	1.0	0.267	0.267	0.267
8		45	11.75	1.0	0.800	0.800	0.890

The fitted regression model for adsorption of $Ca(NO_3)_2$ on MnO_2 using the 2^3 factorial statistical analysis is:

$$y = 0.2688 + 0.1388_{x1} + 0.1095_{x2} + 0.1585_{x3} + 0.049_{1x2} + 0.0925_{x1x3} + 0.0418_{x2x3} \quad \text{.......... 6}$$

3.1 *Adsorption of Ca^{2+}*

The adsorption of Ca^{2+} ion on MnO_2 is a method used to enhance voltage output in a dry cell. At varying concentration of $Ca(NO_3)_2$ from 1M to 0.001M solutions, it was observed that more cations were adsorbed on the surface of Ca^{2+} gave high adsorption value at 40°C and 45°C, especially in 1M concentration which was consistent resulting to a corresponding higher surface charge as shown in Table 2. The adsorption of Ca^{2+} ion at different temperatures increases in the order 40°C>45°C>36°C with increase in concentration. In the effect the adsorption of Ca^{2+} ion is more effective at 40°C and 1M. Decrease in temperature, that is at 36°C in the adsorption of Ca^{2+} on manganese slow down the adsorption process and increase in temperature that is at 45°C causes exothermic reaction and there reduces the adsorption process. These two occurrences cause chemical reaction in the system and therefore reduce electrochemical process.

3.2 *Effect of temperature on surface charge*

At the temperatures investigated (36°C, 40°C, and 45°C), the adsorption and surface charge increases with increase in temperature. At 0.1M Ca^{2+} with pH of 11.25, a remarkable increase in surface charge

36°C to 45°C was observed. More so, dilute solutions (0.01M and 0.001M) at high temperatures (45°C) shows an impressive increase in surface charge. The increase in surface charge and adsorption with respect to the increase in temperature is because high temperature energizes the molecules and facilitates the adsorption process to be achieved.

3.3 *Effect of concentration on surface charge*

The surface charge of Ca^{2+} ion increases with the increase in concentration. It can be deduced that the higher the concentration of Ca^{2+} the higher the surface charge posed on MnO_2. For instance, considering 1M concentration of Ca^{2+} ion at 40°C shows the following order of increase in adsorption and surface charge. $E_{1M} > E_{0.1M} > E_{0.01M} > E_{0.001M}$, this was observed at all the temperatures investigated. This shows consistency in order of decrease from concentrated solution to the most diluted solution. Therefore, the higher the concentration of the cation, the higher the adsorption of the adsorbate and the higher the chances of being adsorbed with time. At 36°C adsorption of Ca^{2+} decreases as concentration increases because fewer ions are present. Also the same trend is observed at 40°C and 40°C with the exception of 0.01M at 40°C and 1M at 45°C were specific adsorption might have taken place Delahay et al (1960).

3.4 *The effect of pH on surface charge*

Increase in the hydrogen ion concentration that is pH of Ca^{2+} ion increase the adsorption of the cation since more hydrogen ions create more vacant spaces on the adsorbent and hence surface charge increases except at 0.1M due specific adsorption Aloko (2002). Furthermore, 1M solution of Ca^{2+} at 40°C shows that the highest surface charge was obtained at pH of 11.25, while the least was recorded at 0.01M, 36°C and pH of 10.50. Thus, this clearly shows that lower pH values are associated with lower electric surface charge while, higher pH values gives higher electric surface charge as given in Table 2.

3.5 2^3 *Factorial design result*

The cochran test (G_{cal}) result was compared with the table value (G_{table}) and found to be less than it (G_{table}) signifying homogeneity of the results in Table 3, Das et al (1979).

Statistical significance of the regression coefficients carried out revealed that six out of the seven coefficients were accepted since their values were greater than G_{table} value. The rejected coefficient (t_{x1x2x3}) had a value of 2.2609.

The F-ratio test of coefficients of the proposed model carried out tended towards acceptability since all the calculated coefficients were greater than the F_{table} value.

The adequacy test performed on the entire proposed model proved adequate since it's calculated value was less than the $F_{adequacy}$ table value as given in equations 3, 4 and 5.

Equation 6 revealed that adsorption increases with increase in temperature(X_1), pH value(X_2) and concentration of $Ca(NO_3)_2$ (X_3) separately and with their different possible combinations(X_1X_2, X_1X_3 and X_2X_3) because of the positive values in front of these variables. Also it is observed that increase in concentration enhanced more adsorption compared with other factors (pH and temperature) separately. And in the interactions of factors, temperature and concentration interactions gave a better yield of adsorption of Ca^{2+} on MnO_2 than others. The synergy of the three factors is negligible, since $X_1X_2X_3$ did not appear in the equation.

4.0 Conclusion

In conclusion it was observed adsorption increases from 36°C-40°C and decreases at 45°C. Furthermore adsorption increases as pH increases from 10.50-11.25 and likewise as concentration decreases adsorption decreases. It was generally observed that the adsorption of Ca^{2+} on MnO_2 enhances its activity as a depolarizing agent since of this gave significant surface charge. The results of the potentiometric titrations and factorial designs were discovered and found out to be in agreement that the highest adsorption of Ca^{2+} on MnO_2 was at the highest concentration and at higher pH and temperature.

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