Nigerian Journal of Technology (NIJOTECH)
Vol. 42, No. 1, March, 2023, pp.136 - 143
www.nijotech.com

Print ISSN: 0331-8443
Electronic ISSN: 2467-8821
https://doi.org/10.4314/njt.v42i1.17

RECOVERY OF MANGANESE AND ZINC FROM SPENT ZINC-CARBON DRY CELLS VIA SULPHURIC ACID LEACHING USING GLUCOSE AS REDUCTANT

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Article history: Received 09 March, 2022. Revised 06 January, 2023. Accepted 11 January, 2023

Abstract

The recovery of manganese and zinc from spent zinc-carbon dry cells using sulphuric acid and glucose as the leaching medium and reducing agent respectively was studied to determine the optimum processing parameters for increasing the recovery of the manganese content. Leaching tests were done using the Response Surface Methodology with the process variables being leaching time, temperature, acid concentration and glucose dose. Regression equations were obtained from the experimental data for the extraction of manganese and zinc, and the main effects and interactions from the leaching studies were investigated by the analysis of variance (ANOVA). Experimental results indicate that the dissolution of the battery materials depends largely on the leaching temperature and glucose dose, with the optimum yield of manganese and zin-c being 81.93 and 98.43 %, respectively corresponding to a leaching temperature of 70 °C, leaching time of 150 min, sulphuric acid concentration of 4 M and glucose dose of 0.5 g/L.

Keywords: Glucose; Manganese; Reductive leaching; Response surface methodology; Spent batteries.

1.0 INTRODUCTION

The various applications of manganese and zinc have an impact on our daily lives as consumers, be it in the production of materials such as dry cell batteries, alloys and aluminium beverage cans, or the production of various fine chemicals [1 – 5], with a substantial portion of world's total manganese production used in the production of specialty alloys such as high-carbon ferromanganese, silico-manganese, and refined ferromanganese alloys [6,7]. Zinc is commonly used in the galvanization of iron and steel to protect them from corrosion, with a substantial amount of the zinc global production finding its use in this area [8].

The increasing demands for metals, coupled with constraints raised by various legislations on environmental protection and resource management, have made it imperative to partly satisfy the need for such metals of concern from secondary sources such as spent dry cell batteries [9 – 13]. Dry cell batteries are known to contain zinc, manganese, iron, nickel, and other heavy metals [14] hence the need for recycling and recovering valuable metals from these secondary resources.

1.1 Spent Zinc-Carbon Batteries as Manganese Sources

Chemical reactions do occur between the battery's electrodes and the electrolyte to yield zinc oxide (ZnO) or manganese oxides (Mn_3O_4 or Mn_2O_3) according to equations (1) and (2) [15]:

$$2Zn + 3MnO_2 \longrightarrow Mn_3O_4 + 2ZnO \tag{1}$$

$$2Zn + 2MnO_2 \longrightarrow Mn_2O_3 + 2ZnO \tag{2}$$

Investigations on the hydrometallurgical recovery of metal values from spent dry batteries using acid or alkaline solutions have shown that while zinc oxide dissolves easily in acidic media, the manganese oxides are partially soluble in the acid due to the formation of manganese (IV) oxide [1, 16 – 17]. Equations (3) and (4) are the reactions that occur during the leaching of the manganese oxides from equations (1) and (2) in sulphuric acid media:

$$Mn_2O_3 + H_2SO_4 \rightarrow MnO_2 + MnSO_4 + H_2O \quad (3)$$

$$Mn_3O_4 + 2H_2SO_4 \rightarrow MnO_2 + 2MnSO_4 + 2H_2O \quad (4)$$

The leaching of manganese, therefore, requires the presence of a reducing agent because manganese occurs mainly as manganese dioxide in zinc-carbon dry cells.

There have been proposition of various reductants such as organic acids [14] and sulphur dioxide [18] for the acid leaching of manganese from spent dry cells. The use of hydrogen peroxide in the reductive leaching of manganese from pyrolusite ore using sulphuric acid as the leachant was reported by Nayl et al. [19], while Momade and Momade [20] reported on the use of a mixture of methanol and sulphuric acid in the reductive leaching of manganese from its ore. This study thus seeks to study the recovery of manganese from spent zinc-carbon dry cells using sulphuric acid as the leachant and glucose as the reducing agent. The design of the experiment focuses on the response surface methodology with acid concentration, glucose dosage, leaching temperature and reaction time selected as the process variables.

2.0 METHODOLOGY

2.1 Materials

Spent type AAA zinc-carbon dry cells used in the study came from various locations in Ile-Ife, Nigeria, with the collection made from households and other users within and around Obafemi Awolowo University, Ile-Ife. A reputable chemical store in Osogbo (Nigeria) supplied the glucose and sulphuric acid (BDH, 98 % w/w) used in the study.

2.2 Sample Preparation

The Zinc-Carbon dry cells were dismantled, separating the metallic components, paper and cardboard pieces, plastic films, black paste and carbon rods. The separators (cardboard and papers) and plastic films were discarded while the black paste and the metallic parts were roasted to reduce the carbon content, and sieved to obtain particles of sizes less than 145 µm (that is, 100 mesh).

The elemental composition of the roasted battery mass was determined by Particle Induced X-Ray Emission (PIXE) spectroscopy using the sample preparation and analysis methods of Obiajunwa and Nwachukwu [21], and Sanda and Taiwo [22]. The proton energy used was 2.5 MeV, while the charge and current values were 4.0 µC and 3.23 nA, respectively.

2.3 Leaching Experiments and Analysis

For the leaching experiment, 5 g of the sample and 100 ml of sulphuric acid were mixed in a 250 ml 3-necked glass reactor fitted with a reflux condenser and a thermometer. The temperature varied between 45 and 75 °C using a digital temperature controller, while the mixing was done using a magnetic stirrer. The leaching duration was varied between 15 and 150 min, while the acid concentration was varied between 0.5 and 4.0 M. Glucose was used as a reductant to aid the dissolution of manganese. At the end of each experiment, the mixture was filtered and the filtrate analyzed for its manganese content using a Thermo iCE 3300 Atomic Absorption Spectrophotometer (AAS), while the residue obtained was dried at 105 °C in an oven and weighed. The extent of dissolution of the sample was determined using the formula:

$$X = \frac{W_o - W_f}{W_o} \quad (1)$$

where X is the mass fraction of the sample dissolved, W_o is the initial mass before leaching, and W_f is the mass of the residue obtained at the end of the leaching process.

To study the effect of the various process parameters on the extent of leaching of the metal values to optimize the process, a 3-level, 4-factor Box-Behnken design was used with a total of 27 experiments generated. The process variables were temperature (°C), time (min), acid concentration (mol/L) and glucose dose (g), with their coded and uncoded levels shown in Table 1. The responses were evaluated using Minitab statistical software (version 17) and fitted to the quadratic model below:

$$Y = a_o + \sum_{i=1}^{4}(a_i X_i) + \sum_{i=1}^{4}(a_{ii} X_i^2) + \sum_{i>j}^{4}(a_{ij} X_i X_j) + \varepsilon \quad (2)$$

where Y is the predicted response (% dissolution or amount of manganese and zinc recovered), δ_o is the intercept term, a_i (i = 1,2,3,4) is the linear coefficient, a_{ij} represents the coefficients of the interaction terms, a_{ii} represents the quadratic coefficients of X_i and ε is the random error. The terms X_1, X_2, X_3, X_4 are the coded factors, which are related to the actual factors x_1, x_2, x_3 and x_4 in Table 1 by equation (3):

$$X_i = \frac{x_i - x_o}{\Delta x} \quad (3)$$

where: X_i = coded value for the ith input (that is, X_i), x_o = mid value for the experimental design, and Δx = $(x_{high} - x_o)$ = $(x_o - x_{low})$.

The terms X_{high} and X_{low} represent the upper and lower design limits, respectively.

Table 1: Coded and uncoded levels of variables for the RSM Box–Behnken design.

Variable	Symbol	Coded factor levels (X)		
		-1	**0**	**+1**
Temperature (ºC)	x_1	45	60	75
Time (min)	x_2	15	82.5	150
Acid Concentration (mol/dm^3)	x_3	0.5	2.25	4.0
Glucose Dose (g/dm^3)	x_4	0.5	2.75	5.0

3.0 RESULTS AND DISCUSSION

3.1 Elemental Composition of the Samples

The elemental analysis results of the spent battery after roasting (Table 2) shows that the elements present are Mn (31.38%), Zn (12.22%), Fe (5.22%), and Cl (12.86%), while Mg, Al, K, Ca, and Cr are minor elements in the samples. These results are in agreement with the results obtained from Baba *et al.* (2009) in the analysis of spent batteries- ash samples by ICP-MS technique and reported Zn, Fe, Mn, Ca, and Al as the major elements. Likewise, the results reported by Khan and Kurny (2012) on the analysis of the electrolyte paste of zinc-carbon dry cells by x-ray fluorescence agree well with the PIXE results presented in this study.

Table 2: Composition of the elements contained in the sample

Element	Composition by mass (wt.%)
Mg	0.17
Al	1.24
Cl	12.86
K	0.52
Ca	0.46
Ti	0.07
Mn	31.38
Fe	5.22
Zn	12.22
Ba	0.42
Pb	0.29

3.2 Leaching Studies by Response Surface Methodology (RSM)

The results obtained from experiments (Table 3) were subjected to statistical treatments using the RSM statistical tool in Minitab v.17.

The results of the analyses of variance (ANOVA) for the quadratic models are shown in Tables 4 - 6 for the dissolution studies, manganese dissolution and zinc dissolution respectively, while Table 7 shows the coefficients of the final regression equations in terms of coded terms for the responses studied. All terms in the models with p-values less than 0.05 are significant, while the bolded model terms in Table 7 are the insignificant model terms (with $p > 0.05$). From Table 4, it can be deduced that the dissolution of the battery materials depends mainly on the acid concentration (F = 191.25) and glucose dosage (F = 62.94). From Tables 5 and 6, the high F-values of 103.03 and 102.10 for manganese and zinc, respectively with corresponding low P-values implied that the models obtained are statistically significant and adequately explain the variations observed in the outputs from the leaching process.

Table 3: Results from the RSM-generated experiments

Run	Coded levels for factors				% Dissolution	% Zn leached	% Mn leached
	X_1	X_2	X_3	X_4			
1	-1	-1	0	0	66.3	63.78	70.83
2	-1	-1	0	0	63.6	59.18	72.39
3	+1	+1	0	0	65.2	79.85	81.18
4	+1	+1	0	0	64.3	83.88	78.76
5	0	0	-1	-1	62.5	88.85	84.15
6	0	0	-1	+1	65.5	51.06	72.63
7	0	0	+1	-1	67.5	82.26	80.43
8	0	0	+1	+1	70.3	82.73	83.43
9	-1	0	0	-1	68.0	78.18	76.50
10	-1	0	0	+1	72.0	47.48	67.91
11	+1	0	0	-1	66.8	84.58	80.47
12	+1	0	0	+1	68.6	76.69	81.10
13	0	-1	-1	0	67.3	70.87	77.74
14	0	-1	+1	0	58.2	82.47	82.23
15	0	+1	-1	0	54.1	67.77	78.90
16	0	+1	+1	0	74.3	79.62	80.88
17	-1	0	-1	0	66.0	64.26	74.24
18	-1	0	+1	0	64.6	58.64	69.65
19	+1	0	-1	0	57.7	66.71	74.67
20	+1	0	+1	0	70.1	93.54	85.85
21	0	-1	0	-1	67.3	74.60	80.07
22	0	-1	0	+1	65.4	83.18	79.60
23	0	+1	0	-1	63.5	99.57	83.38
24	0	+1	0	+1	72.1	50.74	75.69

25	0	0	0	0	66.2	82.70	81.47
26	0	0	0	0	66.4	82.72	81.47
27	0	0	0	0	66.2	82.70	81.45

Table 4: Analysis of variance (ANOVA) for the response model for the % dissolution of the battery materials

Source	DF	Sum of squares	Mean squares	F-Value	P-Value
Model	14	490.991	35.071	79.09	0.000
X_1	1	8.640	8.640	19.49	0.001
X_2	1	6.000	6.000	13.53	0.003
X_3	1	84.801	84.801	191.25	<0.001
X_4	1	27.907	27.907	62.94	0.000
X_1^2	1	0.496	0.496	1.12	0.311
X_2^2	1	4.333	4.333	9.77	0.009
X_3^2	1	16.800	16.800	37.89	<0.001
X_4^2	1	20.254	20.254	45.68	<0.001
X_1X_2	1	0.653	0.653	1.47	0.248
X_1X_3	1	47.610	47.610	107.37	<0.001
X_1X_4	1	1.210	1.210	2.73	0.124
X_2X_3	1	214.622	214.622	484.04	<0.001
X_2X_4	1	27.562	27.562	62.16	<0.001
X_3X_4	1	0.010	0.010	0.02	0.883
Lack-of-Fit	8	1.244	0.156	0.15	0.988
Pure Error	4	4.077	1.019		
Total	26	496.312			

Table 5: Analysis of Variance (ANOVA) for the percentage of zinc leached

Source	DF	Sum of squares	Mean squares	F-Value	P-Value
Model	14	4557.68	325.55	102.10	<0.001
X_1	1	1026.00	1026.00	321.79	<0.001
X_2	1	10.45	10.45	3.28	0.095
X_3	1	405.31	405.31	127.12	<0.001
X_4	1	1124.43	1124.43	352.66	<0.001
X_1^2	1	248.62	248.62	77.98	<0.001
X_2^2	1	41.77	41.77	13.10	0.004
X_3^2	1	74.40	74.40	23.34	0.000
X_4^2	1	31.08	31.08	9.75	0.009
X_1X_2	1	0.38	0.38	0.12	0.735
X_1X_3	1	263.25	263.25	82.56	<0.001
X_1X_4	1	130.07	130.07	40.80	<0.001
X_2X_3	1	0.02	0.02	0.00	0.945
X_2X_4	1	823.98	823.98	258.43	<0.001
X_3X_4	1	365.96	365.96	114.78	<0.001
Lack-of-Fit	8	19.56	2.45	0.52	0.798
Pure Error	4	18.70	4.68		
Total	26	4595.94			

Table 6: Analysis of Variance (ANOVA) for the percentage of manganese leached

Source	DF	Sum of squares	Mean squares	F-Value	P-Value
Model	14	566.881	40.491	103.03	<0.001
X_1	1	191.535	191.535	487.37	<0.001
X_2	1	0.077	0.077	0.20	0.666
X_3	1	33.802	33.802	86.01	<0.001
X_4	1	50.594	50.594	128.74	<0.001
X_1^2	1	75.199	75.199	191.35	<0.001
X_2^2	1	3.695	3.695	9.40	0.010
X_3^2	1	2.263	2.263	5.76	0.034
X_4^2	1	1.825	1.825	4.64	0.052
X_1X_2	1	0.034	0.034	0.09	0.773
X_1X_3	1	62.173	62.173	158.20	<0.001
X_1X_4	1	21.252	21.252	54.08	<0.001
X_2X_3	1	1.575	1.575	4.01	0.068
X_2X_4	1	13.032	13.032	33.16	<0.001
X_3X_4	1	52.708	52.708	134.12	<0.001
Lack-of-Fit	8	0.571	0.071	0.07	0.999
Pure Error	4	4.145	1.036		
Total	26	571.597			

Table 7: Regression coefficients for the fitted quadratic models in terms of Coded Factors

Coefficients	% dissolution	% Mn leached	% Zn leached
a_0	66.2667	81.4633	82.7067
a_1	-0.9000	4.2375	9.8075

a_2	0.7500	-0.0850	*-0.9900*
a_3	2.6583	1.6783	5.8117
a_4	1.5250	-2.0533	-9.6800
a_{12}	*-0.7000*	*-0.1600*	*0.5350*
a_{13}	3.4500	3.9425	8.1125
a_{14}	*-0.5500*	2.3050	5.7025
a_{23}	7.3250	*-0.6275*	0.0625
a_{24}	2.6250	-1.8050	-14.3525
a_{34}	*-0.0500*	3.6300	9.5650
a_{11}	*0.3667*	-4.5129	-8.2058
a_{22}	-1.0833	-1.0004	-3.3633
a_{33}	-1.8708	-0.6867	-3.9371
a_{44}	2.0542	-0.6167	-2.5446
R^2	*0.9893*	*0.9917*	*0.9917*
Adjusted R^2	*0.9768*	*0.9820*	*0.9821*

The bold-faced model coefficients are insignificant model terms (with $p > 0.05$)

The quadratic regression models for the dissolution process follow the general form shown in the equation below:

$$Y = a_0 + a_1X_1 + a_2X_2 + a_3X_3 + a_4X_4 + a_{12}X_1X_2 + a_{13}X_1X_3 + a_{14}X_1X_4 + a_{23}X_2X_3 + a_{24}X_2X_4 + a_{34}X_3X_4 + a_{11}X_1^2 + a_{22}X_2^2 + a_{33}X_3^2 + a_{44}X_4^2$$

where the independent variables are the coded response terms presented earlier in Table 1. The numerical values of the coefficients in the quadratic models are as presented in Table 7, while the contour plots in Figures 1 – 3 give graphical representations of the response surface quadratic models, showing the relationships between the factors and the responses. The results obtained from the response surface experiments agree with a similar work done by Biswas et al [25] using Yates' 2^4 factorial design. In the present work and the one by Biswas et al., the R^2 values are greater than 0.99 for the leaching of Mn and Zn.

It is worth mentioning that MnO_2 cannot be leached directly by sulphuric acid [26], hence the need for the addition of a reductant to obtain high leaching efficiency of manganese. The reduction and subsequent dissolution of the MnO_2 present in the battery powder on the addition of glucose to the leaching take place according to the chemical reaction below [26]:

$$12MnO_2 + C_6H_{12}O_6 + H_2SO_4 \longrightarrow 12MnSO_4 + 6CO_2 + 18H_2O$$

From Figure 1, it was observed that while the dissolution increases with temperature and acid concentration, increasing the glucose dose decreased the overall dissolution of the battery materials as indicated in Figures 1a, c and e. The same trend was observed in Figures 2 and 3. Although the purpose of adding glucose to the mixture to the mixture is to aid the dissolution of manganese, more of the manganese was leached at low glucose dosage. This observation is in agreement with Biswas et al [25] who also studied the leaching of zinc and manganese from spent batteries using glucose as reductant.

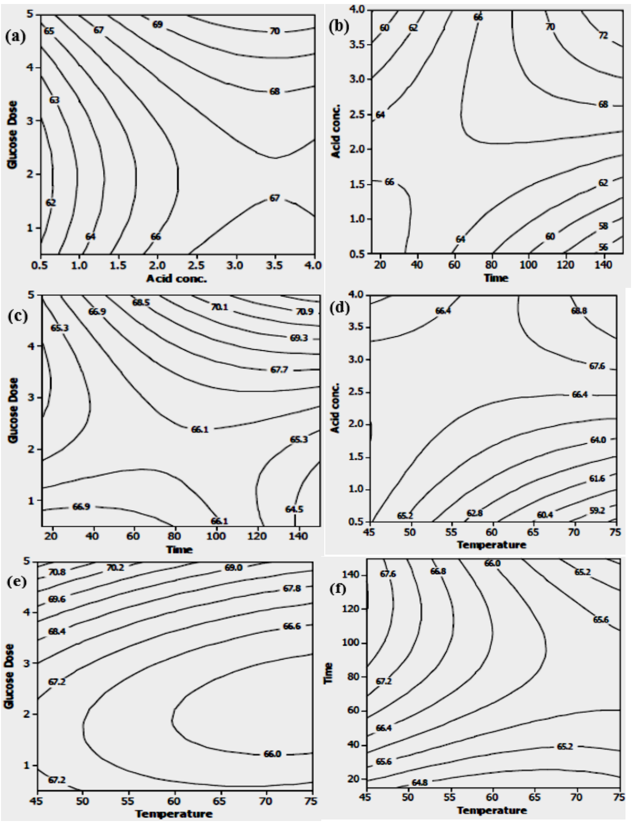

Figure 1: Contour plots showing the relationship between the percentage dissolution of the battery mass and the process variables

An objective of the study is to find the optimum process parameters for the leaching of manganese from spent zinc-carbon dry cells in sulphuric acid using glucose as a reductant. The optimum recovery of zinc and manganese was predicted by the model to be 97.07 and 82.16 %, respectively corresponding to a leach solution containing 5.30 g/l Zn and 12.89 g/l Mn, respectively, and this occurs at a leaching temperature of 70 ºC, leaching time of 150 min, the sulphuric acid concentration of 4 M and glucose dose of 0.5 g/L. The predicted percentage recovery was found to be in good agreement with the experimental values of 98.43% for zinc and 81.93% for manganese.

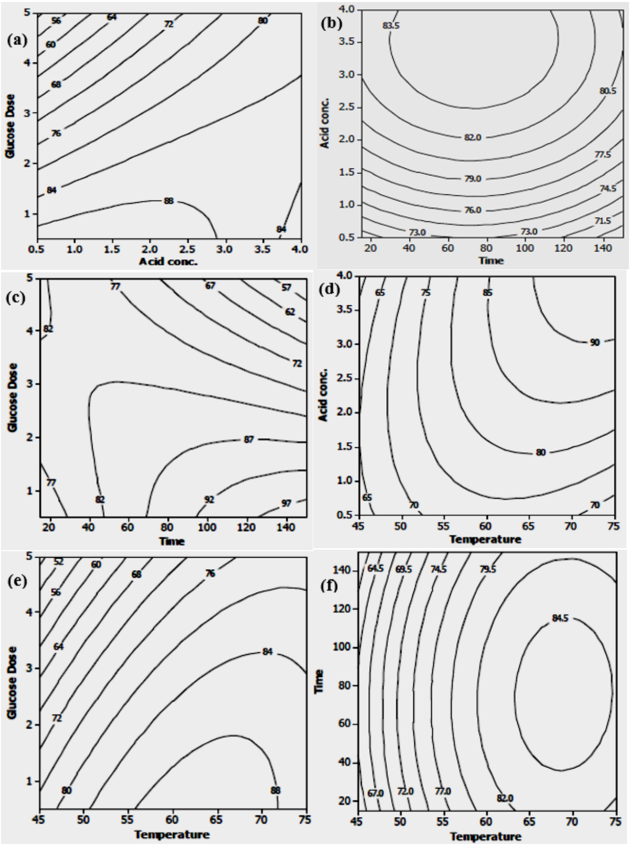

Figure 2: Contour plots showing the relationship between the percentage of zinc leached and the process variables

The optimal leaching results obtained from this study was compared with those obtained in [25] and the results are as presented in Table 8. Although the acid volume and process conditions differ, the results obtained in both cases are in agreement. In addition, the results in [25] were based on only 16 experimental runs, compared with the present work which is based on 27 runs.

Table 8: Comparison of results with those obtained by Biswas et al [25]

Optimum process parameters	Biswas et al [25]	This work
Temperature (ºC)	100	70
H_2SO_4 concentration (mol/L)	2	4
Leachate volume per run (mL)	250	100
Time (min)	60	150
Glucose dosage (g/L)	2.5	0.5
% Zn leached	>99	97.07 (predicted), 98.43 (experimental)
% Mn leached	>99	82.16 (predicted), 81.93 (experimental)

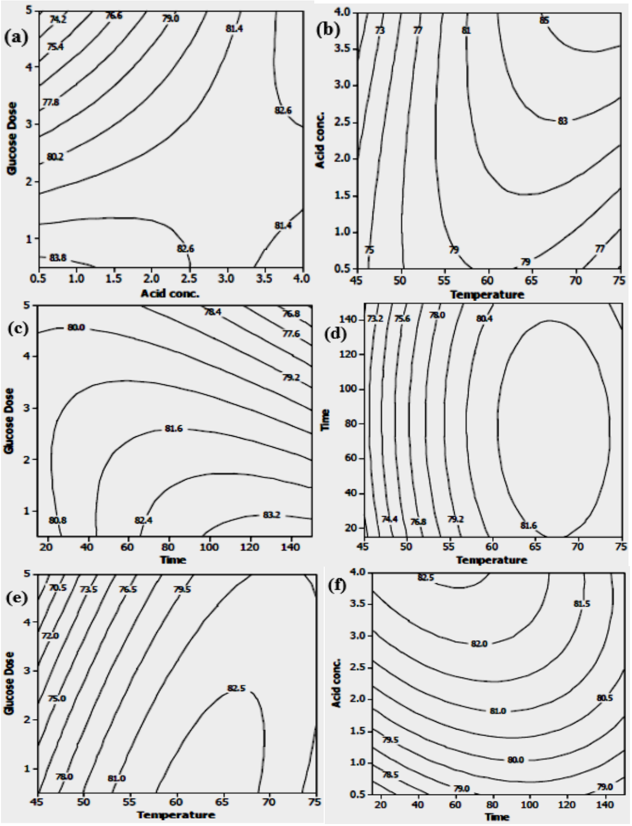

Figure 3: Contour plots showing the relationship between the percentage of manganese leached and the process variables

4.0 CONCLUSIONS

The analyses of the results of this study showed that spent zinc-carbon batteries can serve as a secondary source of manganese and zinc. The leaching tests were fitted to quadratic models which adequately described the relationship between the quantity of manganese and zinc leached and process parameters. From the leaching tests, it was found that temperature and glucose dosage have a significant influence on the rate of dissolution of zinc and manganese in sulphuric acid, with the optimum recovery of zinc and manganese occurring at a leaching temperature of 70 ºC, leaching time of 150 min, the sulphuric acid concentration of 4 M and glucose dose of 0.5 g/L. The percentage recovery of zinc and manganese-based on the optimum process conditions were 98.43% and 81.93%, respectively. Based on the foregoing, the study has shown that glucose has potential for use as a reductant in the leaching of manganese and zinc from zinc-carbon dry cells using sulphuric acid.

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