Electrolytic Deposition of Manganese Dioxide from Nigerian Manganese Ore Using Graphite Electrodes

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ABSTRACT

Super rich manganese dioxide got deposited at the anode when manganese sulphate solution was electrolytically decomposed, and the deposits called Electrolytic Manganese Dioxide (EMD). Manganese ore containing about 35.79% manganese from Ka'oje (Kebbi State, Nigeria) with pyrolusite (MnO_2) as the major manganese mineral alongside iron mineral present as hematite, was the resource material. Some 1973.31g of beneficiated ore sample (75 to 600μm) was isothermally reduced with charcoal (52.17% carbon) at 600^0C for one hour. The paramagnetic high oxide ore got reduced to a ferromagnetic lower oxide containing 38.90% manganese. Some 610g portions of the reduced ore were leached in varied concentrations of sulphuric acid (1.0M, 1.5M and 2.0M) at 50^0C for one hour and 42.36% leaching efficiency was achieved with 2.0M acid. Calculated elemental mass balance revealed that 2.0M acid dissolved 100.52g of manganese into the leach liquor as manganese sulphate along with 13.83g of iron and 7.47g of aluminium as the major elements. Each leach filtrate was purified with aqueous sodium hydroxide except some 600ml of filtrate from 2.0M acid leaching which was decomposed unpurified for comparison. The filtrates were respectively electrolyzed at 2.5V, 3.0V and 4.0V driving potentials for five hours using graphite electrodes. Analyses showed that the purified liquor extracted with 2.0M acid and electrolysed at 4.0V deposited the best quantity and quality of EMD, containing 98% MnO_2. This high grade EMD is a principal precursor in Ferro-alloy production for steel making and also an important raw material for electrochemical cells and other allied manganese-based chemicals.

Keywords: *Driving Potential, Electrolytic Deposition, Electrolytic Manganese Dioxide, Leaching and Purification.*

1 INTRODUCTION

Manganese occurs mostly in oxide forms or as carbonates and silicates. Available records show that Ka'oje manganese ore contains pyrolusite as the major manganese mineral along with hematite. Manganese exhibits variable oxidation states of +7, +6, +4, +3 and +2 with the one of +2 being the most stable. Higher oxides of manganese with high oxidation states are insoluble in most mineral solvents and this necessitates a reduction pre-treatment to more soluble lower oxide (Muriana *et al*,2014[a]).

Steel making accounts for most manganese demand ranging from 85 to 90% of total demand (Lennetech, 2016). Manganese is added to molten steel for deoxidation and desulphurization. It is an important alloying element in steels (improves the strength and other special properties)

and non-ferrous metals like aluminium to improve the corrosion resistance. World manganese ores are equally consumed by chemical industries. Electrolytic manganese metal (EMM), manganese sulphate fertilizers, chemical manganese metal (CMM) and electrolytic manganese dioxide (EMD) are all products of chemical industries.

Manganese dioxide (MnO_2) is the most popular among the common compounds of manganese making up 0.14% of the earth's crust. Pure form of manganese dioxide such as EMD is used in electrochemical cells and in catalysing chemical reactions such as in the preparation of oxygen from potassium chlorate.

This research focuses on electrolytic deposition of manganese dioxide from Ka'oje manganese ore using graphite electrodes. The ore is carbothermically reduced with charcoal and then leached with dilute sulphuric acid. Purified leach liquor is electrolyzed using graphite (inert

electrodes). Electrolysis is an electrochemical process that involves the decomposition of molten compound or aqueous solution by passing electric current through it. The electrolysis of the leach liquor got manganese dioxide deposited at the anode.

2   METHODOLOGY

2.1   INSTRUMENTS

The major instruments used in the research are: Electronic weighing balance: PA313 and XY1000C with readabilities of 0.001g and 0.01g respectively; Muffle furnace: 1600^0C capacity; Electric hot plates: Brentwood 221101, 230/250V, 2A and Type HE 1, 3300W, 220V; Digital DC power supply: ISO-Tech IPS-3303, 0 – 30V, 3A; Electric drying oven: 220V, ~50Hz, 2.4kW, 350^0C, all from Ajaokuta Steel Company Limited, Kogi, Nigeria. Others are XRD: GBC Enhance mini-material analyser operated over 2theta rang of 5^0 and 65^0, and XRF: EDX3600B, detects between sodium (Z = 11) and Uranium (Z = 92) operated at 40kV and 350µA from Engineering Materials Development Institute, Akure, Nigeria.

2.2   METHOD

Some sorted ore samples obtained from Ka'oje were comminuted and screened to particle size range of 75µm to 600µm. Some 1973.31g of the comminuted ore were thoroughly mixed with 986.65g of charcoal (-3000 + 800µm) which represents 2:1 of ore-to-reductant by mass making a total of 2959.96g of ore-charcoal mix. The ore-charcoal mix was isothermally roasted at 600^0C for one hour in a muffle furnace according to equation (1) (Muriana *et al*, 2014[a]). The EDX3600B XRF machine operated at 40kV and 350µA was used to determine the elemental composition of the treated ore sample while the mineralogical composition was determined by generating XRD patterns. The reduction of the high oxide manganese to a lower one was affirmed by magnetic property exhibited by the treated ore when tested with a bar magnet.

$$MnO_2 \text{ (s)} + C \text{ (s)} \rightarrow MnO \text{ (s)} + CO \text{ (g)} \qquad (1)$$

Three batches of 610g each of the treated ore were leached in three portions of 7320ml of dilute sulphuric acid with concentrations of 1.0M, 1.5M and 2.0M respectively, prepared from analytical 18M concentrated portion of the acid with 98% purity. Each leaching operation was carried out at 50^0C on electric hot plate with magnetic stirrer for one hour according to equation (2) (Muriana et al, 2014[b]). The cooled pregnant solutions were filtered with filter cloth and Ø125mm filter papers. The filtrates and residue were collected and analysed. The leaching efficiency, ξ_L for the ore leached in 2.0M sulphuric acid was calculated using equation (3). Based on 610g treated ore leached, the leach liquor was characterized based on elemental mass balance calculation of the treated ore and the leach residue from equations (9) and (10) and recorded in Table 2. The filtrates
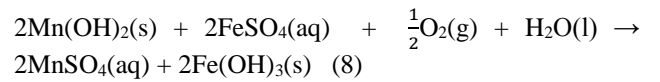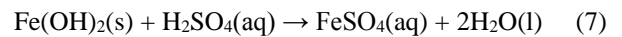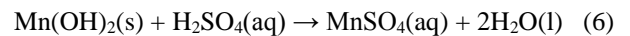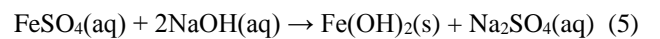
were purified using single step selective precipitation with aqueous sodium hydroxide containing 10.5g/150ml of the solution according to equations (4) through (8) (Muriana *et al*, 2014[b]). The purified filtrates of the liquors obtained from 1.0M, 1.5M and 2.0M sulpuric acid leachings were respectively labelled samples A, B and C. Only 600ml of filtrate from 2.0M sulphuric acid leaching was not purified and was labelled sample D.

$$MnO \text{ (s)} + 2H_3O^+ \text{ (aq)} \rightarrow Mn^{2+} \text{ (aq)} + 3H_2O \text{ (l)} \quad (2)$$
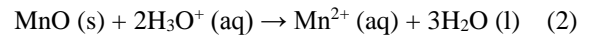
$$\xi_L = (M_1 - M_2) \times M_1^{-1} \times 100 \qquad (3)$$

Where M_1 = percentage of manganese in the reduced ore

M_2 = percentage of manganese in the leach residue

$$MnSO_4(aq) + 2NaOH(aq) \rightarrow Mn(OH)_2(s) + Na_2SO_4(aq) \quad (4)$$

$$FeSO_4(aq) + 2NaOH(aq) \rightarrow Fe(OH)_2(s) + Na_2SO_4(aq) \quad (5)$$

$$Mn(OH)_2(s) + H_2SO_4(aq) \rightarrow MnSO_4(aq) + 2H_2O(l) \quad (6)$$

$$Fe(OH)_2(s) + H_2SO_4(aq) \rightarrow FeSO_4(aq) + 2H_2O(l) \quad (7)$$

$$2Mn(OH)_2(s) + 2FeSO_4(aq) + \tfrac{1}{2}O_2(g) + H_2O(l) \rightarrow 2MnSO_4(aq) + 2Fe(OH)_3(s) \quad (8)$$

$$M_{Liquor} = M_{Treated} - M_{Residue} \qquad (9)$$

$$M_E = M_{Liquor} \times [100]^{-1} \times 610 \qquad (10)$$

Where M_{Liquor} = percentage by mass of element in leach liquor

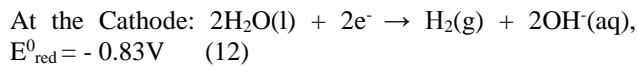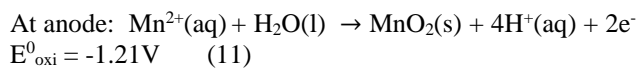$M_{Treated}$ = percentage by mass of element in treated ore

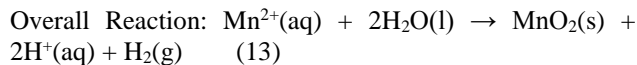$M_{Residue}$ = percentage by mass of element in leach residue

and M_E = mass of element in the leach liquor.

A threshold potential of 2.04V was calculated from the cathodic and anodic half reactions [equations (11) and (12)] with respect to their standard reduction potentials. This calculated value prompted the choice of 2.5V, 3.0V and 4.0V as the driving potentials for the electrolytic decomposition of the leach filtrates to get manganese dioxide deposited at the anode (Norman *et al*, 2010). Three portions of 1200ml each from sample (A) were electrolyzed at 2.5V, 3.0V and 4.0V driving potentials respectively using ISO-Tech IPS – 3303, 0 – 30V, 3A DC power supply. Graphite electrodes with average dimensions of 9 × 37 × 124mm (cathode) and 10 × 37 × 124mm (anode), suspended in the electrolytes by polystyrene material were used. The electrolytes were

maintained at 90 – 95^{0}C temperature range for five hours each to get it decompose according to equation (13). The same procedures were repeated each with samples (B) and (C), while sample (D) was electrolyzed in a single run at 2.5V but with other parameters being the same. The electrodes were oven-dried at the end of each run and weighed to determine the quantity of EMD deposited on the anode (George,1952). The spent electrolytes were analysed and the deposited EMD were recovered and tested for its elemental and mineralogical compositions. Current efficiency, ξ_C was calculated from equations (14) and (15) while the energy requirement per kilogram of EMD deposited was calculated from equation (16) (Edward, 1950).

At anode: $Mn^{2+}(aq) + H_2O(l) \rightarrow MnO_2(s) + 4H^+(aq) + 2e^-$
E^0_{oxi} = -1.21V   (11)

At the Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$,
E^0_{red} = - 0.83V   (12)

Cell Potential, E^0_{cell} = - 2.04V

Overall Reaction: $Mn^{2+}(aq) + 2H_2O(l) \rightarrow MnO_2(s) + 2H^+(aq) + H_2(g)$ (13)

The theoretical EMD yield (mass deposited by Faraday), M_F for each electrolytic process according to Edward (1950) was calculated from:

$M_F = AIt [F \times n]^{-1}$ (14)

According to Walter (1952), current efficiency, ξ_C was calculated from:
$\xi_C = M_a \times M_F^{-1} \times 100$ (15)

Where A = molar mass of MnO_2 (87g/mol)
   I = average current flowing in Ampere
   t = time of run in seconds
   F = Faraday's constant (96500C)
   n = number of moles of electrons transferred (2)
   M_a = actual mass of MnO_2 deposited during the electrolytic process in (g)

The energy requirement, E in kWhkg^{-1} of EMD deposited was calculated from:

$E = IVt [M_A \times 1000]^{-1}$ (16)

Where I = average current flowing in Ampere
   V = average driving potential in Volts
   t = time of run in hours
   M_A = mass of MnO_2 deposited in kg

3   RESULTS AND DISCUSSION
3.1   ORE CARBOTHERMIC REDUCTION
With the XY 1000C electronic weighing balance, 2959.96g of untreated ore-charcoal mix lost 188.69g weight after reduction. Some 1864.47g of treated ore and 906.80g of unreacted charcoal were recovered, which meant an ore loss in weight of 108.84g and charcoal loss in weight of 79.85g from their initial weights before treatment.

Neglecting loss through dust escape during separation of reduced ore and unreacted charcoal, the ore loss in weight after reduction affirmed the reduction of heavier MnO_2 to a lighter MnO. During the reduction process, MnO_2 lost one atom of oxygen to the carbon in charcoal oxidising it to carbon (II) oxide whose diffusion through the ore particles was the driving force of the reduction process. This loss of carbon through oxidation was the architect of charcoal loss in weight.

3.2   ANALYSIS OF TREATED ORE
The XRF results shown in Table 1 shows that the treated ore contains 38.90% manganese, 20.14% iron and 14.94% silicon. Aluminium and calcium appeared as minor elements while other elements are in traces.

Figure (1) shows the generated XRD patterns of the treated ore which indicates the presence of three minerals namely: Spessartine [$Mn_3Al_2(SiO_4)_3$], Magnetite (Fe_3O_4) and Quartz (SiO_2). The iron mineral contained as hematite (Fe_2O_3) in the untreated ore got reduced to magnetite while spessartine became richer in manganese as pyrolusite got reduced to a lower oxide.
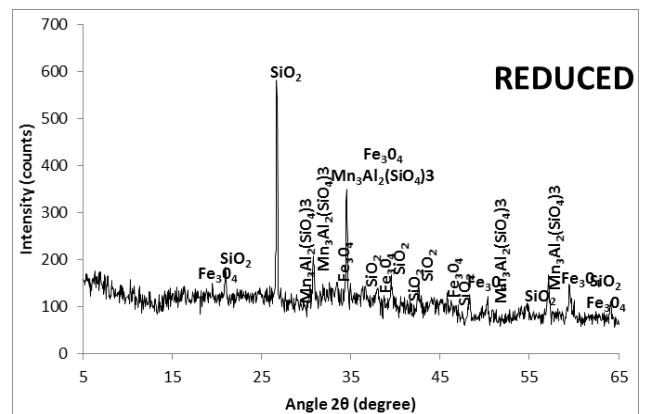

Figure 1: XRD Pattern of Treated Ore

3.3 LEACH FILTRATE AND RESIDUE ANALYSIS
Equations (4) through (8) explain the single-step purification of the leach liquors. Some 4608, 4612 and 4025mls labelled samples A, B and C were recovered after purification of filtrates of 1.0M, 1.5M and 2.0M acid leachings respectively. Meanwhile, some 600ml of

unpurified liquor extracted with 2.0M acid represents sample D.

Leaching with 2.0M sulphuric acid was the most efficient and hence, was used as representative. In comparison, the XRF results of the leach residue from 2.0M sulphuric acid and that of the treated ore (Table 1) shows depletion in the percentages of major elements (manganese and iron) from 38.90% to 22.42% and 20.14% to 17.87% respectively. This translates to 42.36% manganese leaching efficiency. Iron was the major element that dissolved along with manganese as shown in Table 2. The liquor also contains traces of aluminium but silicon and calcium did not dissolve as evident even in the XRF analysis of the EMD products (Table 4).

Generated XRD patterns of the residue (figure 2) were identified as those of Quartz, Magnetite and Spessartine. The diffraction intensity of spessartine decreased from 350 to about 80 counts as manganese dissolved in sulphuric acid. Iron equally dissolved as the intensity of magnetite decreased from about 350 to 170 counts per second.
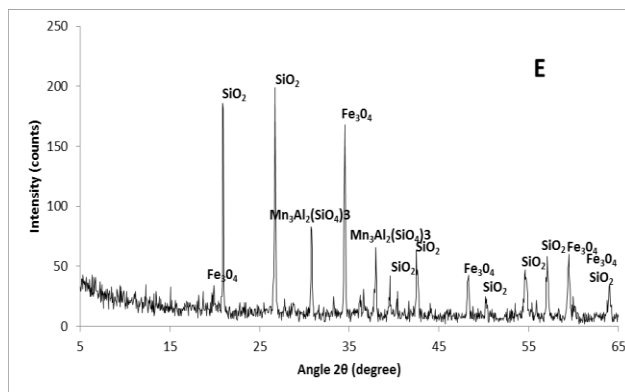

Figure 2: XRD Pattern of the Residue

Table 1: XRF Analysis of Treated Ore and Leach Residue

S/N	Element	Composition (%)	
		Treated Ore	Leach Residue
1	Al	5.2015	3.9776
2	Si	14.9380	20.9813
3	P	0.2443	0.3228
4	S	0.4661	9.7076
5	K	0.3792	0.2248
6	Ca	4.5054	5.1498
7	Ti	0.2070	0.1693
8	V	0.0544	0.0330
9	Cr	0.0533	0.0289
10	Mn	38.9035	22.4246
11	Fe	20.1367	17.8692
12	Ni	0.0865	0.0633
13	Cu	0.0276	0.0215
14	Zn	0.1013	0.0740
15	As	0.0069	0.0059
16	W	0.0662	0.1028
17	Au	0.3957	0.1670
18	Ag	0.0015	0.0040
19	Nb	0.0068	0.0030
20	Mo	0.1353	0.2323
21	Sn	0.3788	0.4769
22	Sb	0.3818	0.4858

Table 2: Elemental composition of the leach liquor

S/N	Element	% in Treated Ore ($M_{Treated}$)	% in Leach Residue ($M_{Residue}$)	% in Leach Liquor (M_{Liquor})	Mass of Element in the Liquor (M_E) (g)
1	Mn	38.9035	22.4246	16.4789	100.52
2	Si	14.9380	20.9813	-	-
3	Fe	20.1367	17.8692	2.2675	13.83
4	Al	5.2015	3.9776	1.2239	7.47
5	Ca	4.5054	5.1498	-	-

3.4 ELECTRO-DEPOSITION OF MANGANESE DIOXIDE

Electrolytic manganese dioxide got deposited according to equation (17) at the anode as the samples of the electrolytes got decomposed electrolytically at driving potentials of 2.5V, 3.0V and 4.0V respectively (Ramesh and Shri, 2014). During the process, the concentrations of the electrolyte got depleted in manganese and the solution became more acidic.

$$MnSO_4(aq) + 2H_2O(l) \rightarrow MnO_2(s) + H_2SO_4(aq) + H_2(g)$$
(17)
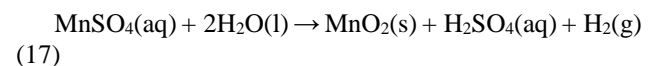
3.5 EFFECTS OF DRIVING POTENTIAL ON EMD DEPOSITION

Results show that the effects of driving potential on EMD deposition depends on the concentration of the leachant and in extension the concentration of the electrolyte. Highest quantity of EMD (6.50g) was deposited with liquor obtained from 2.0M sulphuric acid and electrolysed at 4.0V driving potential as shown in Figure 3 below. On the other hand, the least quantity (3.26g) was deposited by liquor obtained from 1.0M sulphuric acid and electrolysed at 4.0V, a result unconnected with the adverse effects posed by over-potential when the concentration of the electrolyte is very low.
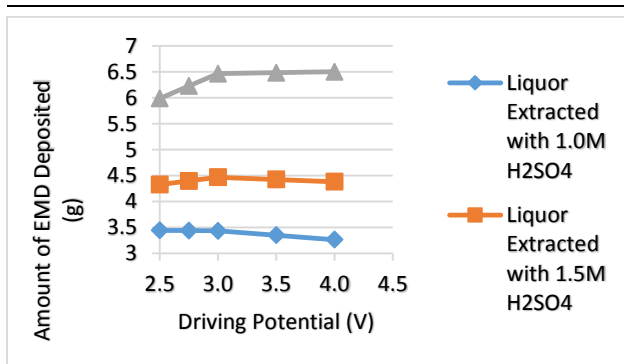
Figure 3: Amount of EMD Deposited Against Driving Potential

3.6 EFFECT OF LEACHANT CONCENTRATION ON QUANTITY OF EMD DEPOSITED

From the results obtained it is seen that on average, the quantity of EMD deposited increased with leachant concentration. Higher leachant concentration meant higher manganese extraction efficiency and this translated to higher concentration of the electrolyte. This in extension means a good quantity of dischargeable manganese ions in the electrolyte that would lead to greater quantity of EMD to be deposited at the anode. Highest quantity of EMD (6.50g) was deposited from 2.0M acid leach liquor while least quantity (3.26g) was deposited from 1.0M as shown in figure 4 below.
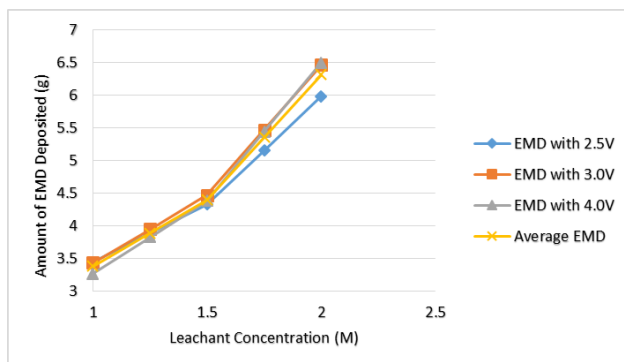

Figure 4: Quantity of EMD Deposited Against Leachant Concentration

3.7 ANALYSIS OF EMD PRODUCTS

The EMD deposits from liquor obtained with 2.0M sulphuric acid leaching and electrolyzed at 2.5V, 3.0V and 4.0V driving potentials were analysed using XRD and XRF. In this order of driving potential used for the electrolytic deposition, the EMD deposits are labelled samples G, H, F respectively. Table (3) shows the XRF results while the XRD diffraction patterns are shown in figures 5, 6 and 7. The XRF result of the EMD product of

unpurified liquor, labelled sample D^1, is also contained in Table 4 for comparison.

On average, the XRF results show similar chemical composition with little variation, iron being the major impurity. However, the product obtained with 4.0V driving potential has the highest percentage of manganese (61.95%) and the least iron content of 0.69%. In comparison, the unpurified pregnant liquor deposited EMD with the lowest manganese content of 54.68% and highest iron content of 7.07%.

The XRD results also show similar diffraction patterns, each with outstanding sharp narrow peak identified as manganese dioxide. This indicates the crystalline nature of EMD. However, the diffraction intensities favour the product of 4.0V driving potential with about 2250 counts while that with 2.5V has the least of about 1350 counts.

Table 3: XRF Analysis of EMD

| S/N	Element	Composition (%)			
		Sample G	Sample H	Sample F	Sample D^1
1	Mg	0.0000	0.0000	0.0421	0.0432
2	Al	0.0902	0.1026	0.1127	0.0602
3	Si	0.0000	0.0000	0.0000	0.0000
4	P	0.0381	0.0398	0.0362	0.0162
5	S	0.0326	0.0539	0.0381	0.0635
6	K	0.0000	0.0140	0.0000	0.2252
7	Ca	0.0324	0.0372	0.0382	0.0414
8	Ti	0.0000	0.0000	0.0000	0.0000
9	V	0.0598	0.0543	0.0423	0.0621
10	Cr	0.0524	0.0532	0.0498	0.0672
11	Mn	60.2179	59.8442	61.9515	54.6827
12	Fe	1.2610	0.8743	0.6863	7.0719
13	Ni	0.0326	0.0331	0.0320	0.0652
14	Cu	0.0219	0.0224	0.0201	0.0379
15	Zn	0.0528	0.0593	0.0412	0.0661
16	As	0.0032	0.0020	0.0029	0.0000
17	W	0.0000	0.0154	0.0263	0.0524
18	Au	0.6015	0.6001	0.6109	0.7482
19	Mo	0.2122	0.2017	0.1517	0.1842
20	Sn	0.3528	0.3624	0.3510	0.3105
21	Sb	0.2501	0.2918	0.2901	0.2218
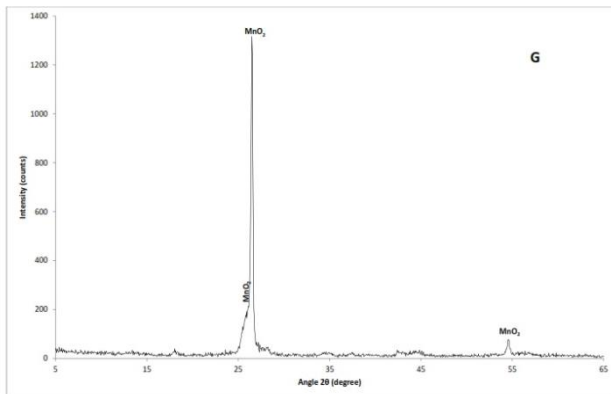
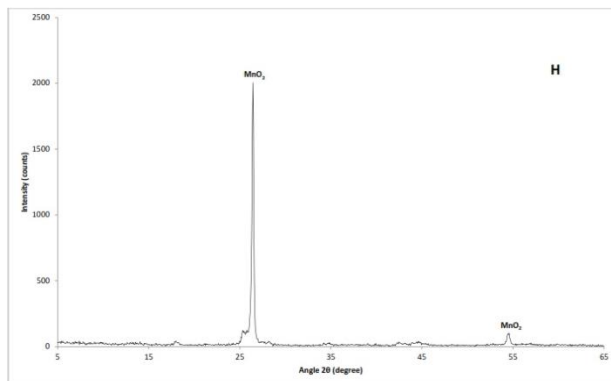Figure 5: XRD Pattern of EMD from Purified Sample Electrolysed at 2.5V Driving Potential

Figure 6: XRD Pattern of EMD from Purified Sample Electrolysed at 3.0V Driving Potential
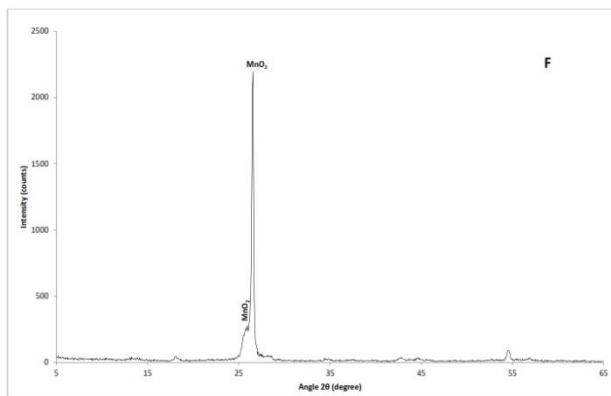
Figure 7: XRD Pattern of EMD from Purfied Sample Electrolysed at 4.0V Driving Potential

4   CONCLUSION

Manganese dioxide got deposited at the anode as Electrolytic Manganese Dioxide when manganese sulphate obtained by leaching treated Ka'oje manganese ore was electrolytically decomposed. The ore is a metallurgical manganese ore high in pyrolusite. It is therefore a usable raw material in the production of electrolytic manganese dioxide for electrochemical cells and other allied manganese-based chemicals, as high quality EMD needed in such areas can be produced from the ore. Current efficiency of 26.82% was achieved when 6.50g of EMD containing 98% MnO_2 was deposited at 4.0V driving potential.

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