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RESEARCH ARTICLE

Reductive leaching of low-grade manganese ores from Way Kanan using corncob as reductant

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OBJECTIVES The processing of mining products in Indonesia has not been utilized optimally. One of them is manganese ore. Way Kanan is one of Indonesia's potential manganese ore sites. METHODS The manganese leaching study used a -200 mesh Way Kanan manganese ore that was reacted with sulfuric acid at concentrations of 0.1 M, 0.5 M, and 1 M, as well as corncob as a reductant. To separate the dissolved iron in the leaching process, the manganese sulfate solution was purified with sodium hydroxide and then filtered to have a manganese sulfate solution free of iron. Manganese was precipitated using oxalic acid. The manganese oxalate precipitation was calcined at a temperature of 350 °C for two hours. RESULTS The best manganese extraction obtained at 92.3% was at a sulfuric acid concentration of 1 M, a temperature of 80 °C, and a solution volume of 400 ml. CONCLUSIONS Calcination of manganese oxalate converted the material into hausmannite (Mn_3O_4).

KEYWORDS corncob; leaching; manganese; manganese ores; sulfuric acid

1. INTRODUCTION

Indonesia has a large variety of mineral resources, one of which is manganese ores(Sujoto et al. 2022). Manganese ores in Indonesia are distributed in many areas such as West Sumatera, Lampung, Yogyakarta, East Java, Kalimantan, and East Nusa Tenggara (Kisman and Edya 2016). However, despite having so many resources, manganese ore in Indonesia has not been utilized and processed optimally. Even to fulfill Indonesia's manganese demands, it needs imports. Manganese is a valuable metal widely utilized in metallurgy, the chemical industry, batteries, electronics, and various other industries (Sun et al. 2017).

Manganese ores can be categorized into two, namely

TABLE 1. Chemical composition of manganese ore from Way Kanan Regency using XRF.

Elements	Concentration, %
Mn	36.775
Fe	6.598
Si	4.132
Pb	1.143
Zn	0.548
Al	0.455
S	0.312
Cu	0.108
Ni	0.104
other	49.825

TABLE 2. Chemical analysis of corncob.

Biomass constituent	Concentration	Unit
Hemicellulose	36.9262	%
Cellulose	28.5673	%
Lignin	9.0092	%
Other	25.4973	%

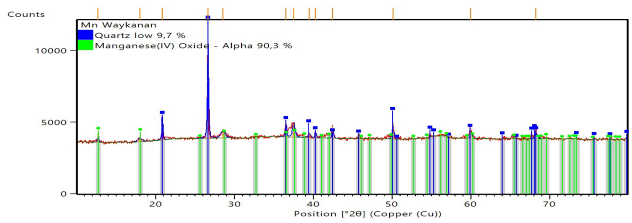

FIGURE 1. XRD pattern of manganese ore from Way Kanan Regency, Lampung Province.

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TABLE 3. The 3^3 factorial design for Mn-leaching: the size of ore -200 mesh.

Variables	Low level	Base level	High level
X1 Temperature (°C)	30	55	80
X2 Concentration of sulfuric acid (M)	0.1	0.5	1
X3 Volume of sulfuric acid (mL)	100	200	400
L/S Ratio (mL/g)	3.34	6.68	13.36

high-grade manganese ore and low-grade manganese ore. The processing of manganese ores is dependent upon the Mn content of the ore where high-grade manganese ores are processed into suitable metallic alloy formed by pyrometallurgical processes, the hydrometallurgical processing of low-grade manganese ores is performed after conventional pyrometallurgical reductive roasting for the manufacturing of chemical manganese dioxide (CMD) or electrolytic manganese dioxide (EMD) (Jing-sheng 2007). Manganese ore which was found in Way Kanan Regency, Lampung Province, is a low-grade manganese ore (Mufakhir and Sumardi 2013). The manganese ores with low manganese levels can be processed by hydrometallurgy (Liu et al. 2014). To recover and extracts manganese from manganese ores, it can be extracted by adding a reducing agent and followed by acid leaching (Ismail et al. 2004; Sahoo and Rao 1989). Ismail et al. (2004) used sulfuric acid (H_2SO_4) as the leaching agent or solvent and obtained 90.5% manganese from manganese ores.

Most manganese in nature is a pyrolusite mineral known as MnO_2, which is stable in acid and alkali leaching. Therefore, manganese is leached from manganese ore in a reduced state. Previously, many reducing agents, such as coal, pyrite, iron sulfate, sulfur dioxide, and peroxide were utilized (Zhang and Cheng 2007). The reducing agents like iron sulfate, sulfur dioxide, and peroxide are harmful to the environment. Thus, many researchers currently use organic reductants as reducing agents. Instead of coal and pyrite, corncob is more effective as a reduction agent in this process because corncob has a lesser number of impurities than coal such as volatile matter (Putra et al. 2015).

Many researchers also use carbohydrates-based materials as reductants such as glucose, sucrose, lactose, and cellulose and utilize organic acid reductants such as oxalic acid, citric acid, and tannic acid (Astuti et al. 2019b). Carbohydrates are harmless, low-cost materials and easy to be obtained, both in pure and waste forms. Carbohydrates are reductants or reducing agents that effectively work at temperatures lower than 90 °C.

TABLE 4. Results of 3^3 full factorial experiments.

N	X1	X2	X3	Leaching efficiency of Mn (%)
1	30	0.1	400	7.28
2	30	0.5	400	11.99
3	30	1	400	21.44
4	55	0.1	400	8.65
5	55	0.5	400	37.77
6	55	1	400	64.6
7	80	0.1	400	49.16
8	80	0.5	400	75.23
9	80	1	400	92.3
10	30	0.1	200	0.54
11	30	0.5	200	2.65
12	30	1	200	3.95
13	55	0.1	200	4.27
14	55	0.5	200	20.5
15	55	1	200	43.09
16	80	0.1	200	13.96
17	80	0.5	200	44.19
18	80	1	200	64.32
19	30	0.1	100	0.42
20	30	0.5	100	1.64
21	30	1	100	2.66
22	55	0.1	100	1.35
23	55	0.5	100	6.95
24	55	1	100	9.69
25	80	0.1	100	4.01
26	80	0.5	100	15.96
27	80	1	100	49.58

X_1: Temperature (°C); X_2 : Sulfuric acid Concentration (M); X_3 : Volume of Sulfuric acid (mL); Extraction of Mn (%) obtained from the results of XRF Analysis.

TABLE 5. RSM summary.

S	R-sq	R-sq(adj)	R-sq(pred)
11.8186	82.51%	80.23%	74.74%

TABLE 6. Coefficients.

Term	Coef
Constant	-59.97
Sulfuric acid Concentration (M)	32.25
Volume of Sulfuric acid (mL)	0.1012
Temperature (°C)	0.791

Corn (*Zea mays* L.) is one of the agricultural products widely produced and consumed by the society of Indonesia. After East Java and Central Java, Lampung Province is the third-largest corn producer in Indonesia. Lampung's corn production in 2018 reached 2,582,224 tons (Badan Pusat Statistik Lampung 2019). Corn crops generate solid waste,

Different mineral content from each location has different maximum operating conditions. The researchers chose to extract manganese ore from Way right because it has a fairly high manganese content, which reaches almost 40%. Thus, researchers are interested in the reductive leaching of manganese ore found in Way Kanan Regency (Lampung Province) by utilizing corncob as a reductant in sulfuric acid leaching solution and investigating the effect of temperature, acid concentration, and solution volume on the percent of manganese extraction in this study.

2. MATERIALS AND METHOD

2.1 Materials

Manganese ore used in this study was obtained from Way Kanan Regency, Lampung Province (Indonesia). The raw material was characterized using X-ray Fluorescence (XRF, PANalytical, Epsilon 3XLE) and X-ray Diffraction (XRD, PANalytical, X'pert 3 Powder). Table 1 shows that the manganese content in the manganese ore used was around 36%. XRD pattern of raw ore (Figure 1) show that the manganese compound in raw ore was in the form of MnO_2 (Pyrolusite type). Corncob as a reducing agent was obtained from a corn plantation in Lampung. The dried corncob was analyzed using X-ray fluorescence (XRF, Epsilon 3XLE, PANalaytical, Netherland) and Atomic absorption spectroscopy (AAS, AA 7000, Shimadzu, Japan). to calculate the cellulose content in the corncob (see Table 2).

TABLE 7. XRF analysis of precipitated manganese oxalate.

Component	Concentration	Unit
S	0.312	%
Ca	0.127	%
Ti	47.4	ppm
Mn	98.233	%
Fe	0.495	%
Ni	295.5	ppm
Cu	0.284	%
Zn	0.210	%

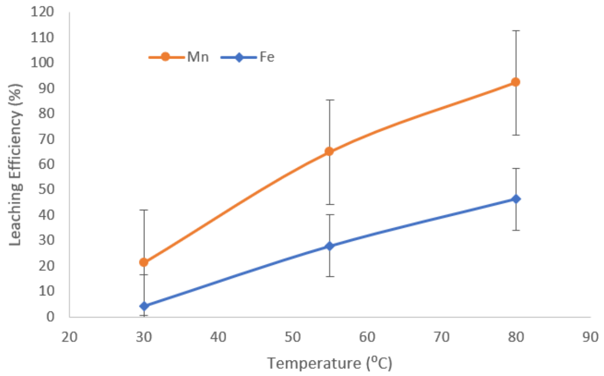

FIGURE 2. Effect of temperature upon the leaching efficiencies of Mn with sulfuric acid concentration at 1 M and 400 mL volume of sulfuric acid.

2.2 Methods

The experiments used manganese ore from Way Kanan, Lampung. Manganese ore and corncob were prepared through sampling and milling. The sampling process was carried out directly from Way Kanan, Lampung. Meanwhile, the milling process goes through several stages. The first stage is the crushing process using a crusher. The next stage is the refining process using a ball mill. The last stage is the shieving process to get a more uniform particle size by using a size of -200 mesh. 20 g of manganese ores and 9.94 g of corncobs (The use of ore and reductant compositions is based on previous research conducted by Astuti et al. (2019a). were then reacted with sulfuric acid. Various sulfuric acid concentrations (0.1; 0.5; 1 M), various sulfuric acid volumes (100; 200; 400 mL) at different temperatures (30; 55; 80 °C) stirring speed of 200 rpm was used. After four hours, the slurry was filtered. Then, the leaching filtrate was analyzed using an Atomic Absorption Spectrophotometer (AAS, AA 7000, Shimadzu, Japan). To precipitate the ferrous hydroxide, the leachate from the filtered leaching solution is heated at 60 °C along with 10% NaOH until pH 6. Therefore, the solution was filtered to separate ferrous hydroxide. The remained solution was heated to 60 °C and added with oxalic acid 1 M, ratio (1 filtrate from leaching (mL): 2 oxalic acids (mL)) for four hours with a stirring speed of 200 rpm to get precipitated manganese (II) oxalate dihydrate. Then, manganese (II) oxalate dihydrate was calcined in a furnace (Nabertherm Muffle Furnace LT 9/14) at 350 °C for two hours.

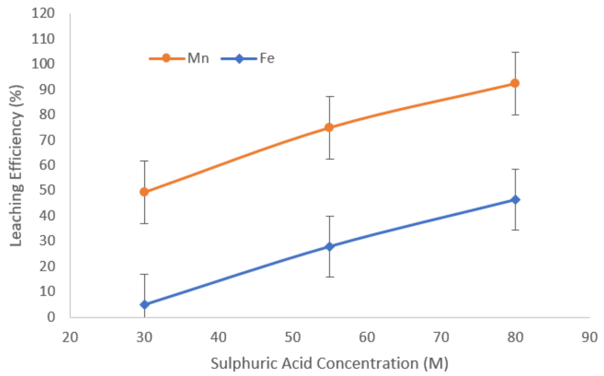

FIGURE 3. Effect of sulfuric acid concentration upon the leaching efficiencies of Mn with the volume of sulfuric acid of 400 mL and a temperature of 80 °C.

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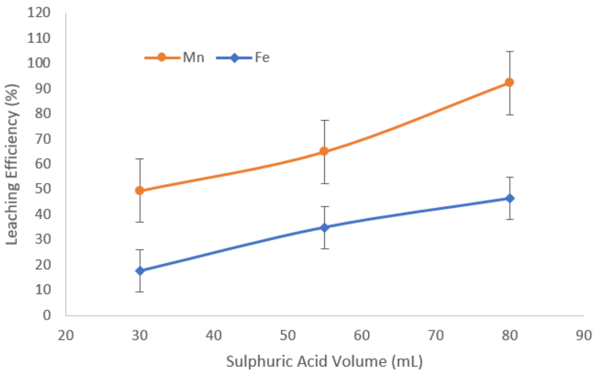

FIGURE 4. Effect of sulfuric acid volume upon the leaching efficiencies of Mn at 1 M of sulfuric acid concentration and a temperature of 80 °C.

In the present work, a 3^3 full factorial design was selected for conducting the leaching experiments. The variables selected were temperature, sulfuric acid concentration, and volume of sulfuric acid. The analysis was carried out using the response surface method (RSM) with the help of Minitab software. The levels of variables are given in Table 3.

3. RESULTS AND DISCUSSION

The use of corncob as a reductant is the novelty of this research. However, the reaction that occurs can be approximated by using the reaction of leaching of low-grade manganese ore in sulfuric acid media that can be explained by the following reaction (Unal and Mahmut 1988):

$$12MnO_2 + C_6H_{10}O_5 + 12H_2SO_4 \rightarrow 12MnSO_4 + 17H_2O + 6CO_2 \quad (1)$$

$$Fe_2O_{3(s)} + 3H_2SO_{4)} \rightarrow Fe_2(SO_4)_3 + 3H_2O \quad (2)$$

After conducting a regression analysis on the effect of experimental variations on manganese ore extraction results using Minitab applications, the regression analysis results in this study are as Table 5.

Which, R squared (R-sq) is a number that ranges from 0 to 1 which indicates the magnitude of the combination of independent variables that together affect the value of the dependent variable. Adjusted R-Square (R-sq(adj)) only measures R-Square with significant independent variables. Predicted R-squared (R-sq(pred)) is used to determine how well a regression model makes predictions. The R-sq in Table 5 showed that the effect values of the three variations in the experiment on the percentage of manganese ore *leaching* results.

By using Minitab, it can be drawn an equation that relates the % of Mn leaching results with the independent variables and the equation applies effectively to variables between low-level and high-level variables, as follows:

$$\begin{aligned}\text{Leaching efficiency of Mn} = & -59.97 + 0.791.\text{Temperature (°C)} \\ & +32.25.\text{Sulfuric acid concentration (M)} \\ & +0.1012.\text{Sulfuric acid volume (mL)}\end{aligned} \quad (3)$$

3.1 Effect of temperature

Sulfuric acid concentration at 1 M, 400 mL volume of sulfuric acid, and leaching time of four hours. Figure 2 presents the effect of temperature on manganese and iron leaching efficiency. As a result, when temperatures were increased from 30 °C to 80 °C, the efficiency of manganese increased from 21.44% to 92.3%. Accordingly, the extraction of iron increased from 4.47% to 46.49%. Based on the analysis data, it can be concluded that the higher the temperature, the faster the leaching reaction will occur. This is in line with the theory of the effect of temperature on the reaction rate (Levenspiel 1999).

3.2 Effect of sulfuric acid concentration

Leaching experiments were performed at different sulfuric acid concentrations of 0.1 – 1 M, and the other conditions were fixed at a corncob of 9.94 g (stoichiometric ratio). The volume of sulfuric acid was 400 mL, with a stirring speed of 200 rpm, and a temperature of 80 °C. Figure 3 showed that the leaching efficiency of manganese increased with the sulfuric acid concentration. With an acid concentration of 1 M and a leaching time of four hours, approximately 92.3% of manganese was extracted. However, iron dissolution rose from 4.94% to 46.49%. The higher the concentration of the reactants, the closer the distance between the particles, as a result, the probability of the particles colliding will be greater. The reaction rate will be faster if the effective collisions that occur are also getting bigger (Levenspiel 1999).

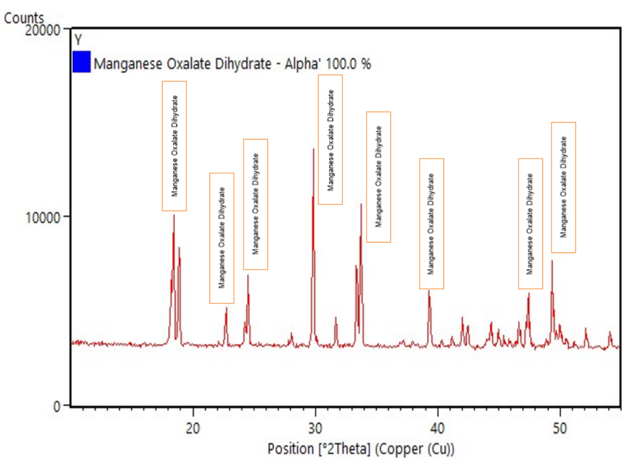

FIGURE 5. XRD analysis of precipitated manganese oxalate.

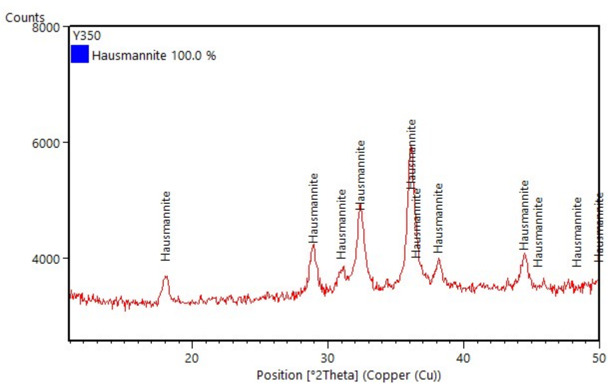

FIGURE 6. XRD analysis of calcined manganese oxalate.

3.3 Effect of sulfuric acid volume

The effect of sulfuric acid volume on manganese's leaching efficiency was investigated in the range of 100 mL – 400 mL. The other leaching conditions were fixed at 1 M of sulfuric acid concentration, a corncob of 9.94 g (stoichiometric ratio), a stirring speed of 200 rpm, and a temperature of 80 °C. Leaching experiments at the different volumes of sulfuric acid were carried out, as shown in Figure 4. The result demonstrates that the leaching efficiency of manganese and iron increases as the volume of sulfuric acid increases. The leaching efficiency of manganese increased from 49.54% to 92.3% for four hours, while iron increased from 17.62% to 46.49%. Leaching using several other reducing agents has been carried out as was done with sawdust as a reducing agent where the efficiency is only 90.50% (Ismail et al. 2004). In addition, using molasses as a reducing agent only produces an efficiency of 86.26% (Sumardi 2014). This shows that corncob is a good reducing agent.

3.4 Precipitation and calcination

The best Mn extraction used 1 M of sulfuric acid concentration was 400 mL of sulfuric acid volume and 80˚C of temperature. The leachate was purified from a ferrous ion with sodium hydroxide (NaOH) and precipitated ferrous. The remained solution was heated to 60˚C and added with oxalic acid 1 M for four hours with a stirring speed of 200 rpm to get 6.789 grams of precipitated manganese oxalate. Figure 5 showed an XRD analysis of the precipitated mineral composition. Analysis of XRD affirmed the precipitate was manganese (II) oxalate dihydrate. Chemical composition of manganese oxalate is presented in Table 7.

The manganese (II) oxalate dehydrate was calcined in a furnace at 350 ˚C for two hours. In this process, manganese (II) oxalate dehydrate was oxidized to hausmannite (Mn_3O_4). The product is shown in Figure 6.

4. CONCLUSIONS

Corncob has a good ability as a reducing agent when compared to some other reducing agents such as molasses and sawdust. In this leaching experiment, the maximum manganese extracted was 92.3% for 1 M of sulfuric acid concentration and 400 mL of sulfuric acid volume at 80 ˚C of temperature for four hours. Precipitation of Mn from manganese sulfate leachate can be conducted using oxalic acid. Calcination at 350 ˚C for two hours can oxidize manganese (II) oxalate dehydrate to haussmannite (Mn_3O_4).

5. ACKNOWLEDGEMENTS

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REFERENCES

Astuti W, Mufakhir FR, Prasetyo E, Sumardi S, Yuda APT, Nurjaman F, Supriyatna YI, Handoko AS. 2019a. Reductive-atmospheric leaching of manganese from pyrolusite ore using various reducing agents. p. 030117. doi:10.1063/1.5098292.

Astuti W, Mufakhir FR, Prasetyo E, Yuda APT, Sumardi S, Nurjaman F, Supriyatna YI, Handoko AS, Suharto. 2019b. Effect of ore mineralogy on the reductive-leaching of manganese ores. IOP Conference Series: Materials Science and Engineering. 478:012014. doi:10.1088/1757-899X/478/1/012014.

Badan Pusat Statistik Lampung. 2019. Luas Panen, Produksi, dan Produktivitas Tanaman Jagung. https://lampung.bps.go.id/linkTableDinamis/view/id/191.

Ismail AA, Ali EA, Ibrahim IA, Ahmed MS. 2004. A comparative study on acid leaching of low grade manganese ore using some industrial wastes as reductants. Canadian Journal of Chemical Engineering. 82(6):1296–1300. doi: 10.1002/cjce.5450820618.

Jing-sheng Z. 2007. Current Challenge and Chance in China's Mn-Industry. https://www.semanticscholar.org/paper/Current-Challenge-and-Chance-in-China's-Mn-Industry-Jing-sheng/aa455629560c1d190ff081ef44b93b1e6d19e7dd.

Kisman BP, Edya P. 2016. Prospeksi Mangan Di Kecamatan Timpeh, Kabupaten Dharmasraya, Provinsi Sumatera Barat. Prosiding Kelompok Penyelidikan Mineral .... http://203.189.89.148/kolokium/2015_2/min/08.ProsedingDharmasraya_Kisman.pdf.

Levenspiel O. 1999. Chemical Reaction Engineering. Industrial & Engineering Chemistry Research. 38(11):4140–4143. doi:10.1021/ie990488g.

Liu Y, Lin Q, Li L, Fu J, Zhu Z, Wang C, Qian D. 2014. Study on hydrometallurgical process and kinetics of manganese extraction from low-grade manganese carbonate ores. International Journal of Mining Science and Technology. 24(4):567–571. doi:10.1016/j.ijmst.2014.05.022.

Mufakhir FR, Sumardi S. 2013. Karakterisasi Bijih Mangan Daerah Kabupaten Tanggamus dan Way Kanan Provinsi Lampung dan Prosfektif Pengolahannya. Unit Pelaksanaan Teknis Balai Pengolahan Mineral Lampung LIPI. Lampung. https://nanopdf.com/download/karakterisasi-bijih-mangan-daerah-kabupaten_pdf.

Putra AA, Suharno B, Ferdian D, Nurjaman F. 2015. Pengaruh campuran reduktor coal-coke dalam proses reduksi biji mangan lokal pada submerged arc furnace = Effect of mix reductant coal-coke in process reductin local manganese ore in the submerged arc furnace. https://lib.ui.ac.id/detail?id=20421581&lokasi=lokal.

Sahoo P, Rao K. 1989. Sulphation-roasting of low-grade manganese ores — Optimisation by factorial design. International Journal of Mineral Processing. 25(1-2):147–152. doi: 10.1016/0301-7516(89)90061-6.

Sujoto VSH, Sutijan, Astuti W, Sumardi S, Louis ISY, Petrus HTBM. 2022. Effect of Operating Conditions on Lithium Recovery from Synthetic Geothermal Brine Using Electrodialysis Method. Journal of Sustainable Metallurgy. doi:10.1007/s40831-021-00488-3.

Sumardi S. 2014. Leaching of manganese ores from east nusa tenggara using oxalic acid and molasses as reducing agents and synthesis of manganese dioxide powder by hydrothermal method. Publikasi LIPI. http://lipi.go.id/publikasi/leaching-of-manganese-ores-from-east-nusa-tenggara-using-oxalic-acid-and-molasses-as-reducing-agents-and-synthesis-of-manganese-dioxide-powder-by-hydrothermal-method/18684.

Sun Y, Fu G, Jiang L. 2017. Kinetic Study of the Leaching of Low-Grade Manganese Ores by Using Pretreated Sawdust as Reductant. Minerals. 7(5):83. doi:10.3390/min7050083.

Unal S, Mahmut B. 1988. Bench-Scale Manganese Sulfate Production from Low-grade Pyrolusite. Chimica Acta Turcica. 16(1):9–20.

Zhang W, Cheng CY. 2007. Manganese metallurgy review. Part I: Leaching of ores/secondary materials and recovery of electrolytic/chemical manganese dioxide. Hydrometallurgy. 89(3-4):137–159. doi:10.1016/j.hydromet.2007.08.010.