INDONESIAN MINING JOURNAL Vol. 26, No. 1, April 2023 : 19 - 27

LEACHING OPTIMIZATION OF MANGANESE ORE FROM NORTH CENTRAL TIMOR USING H_2O_2 AS A REDUCING AGENT

OPTIMALISASI PELINDIAN BIJIH MANGAN ASAL TIMOR TENGAH UTARA MENGGUNAKAN H_2O_2 SEBAGAI PEREDUKSI

FAUSTINA D.Y.P. ABI*, RACHMAT T. TJAHJANTO and YUNIAR P. PRANANTO
Department of Chemistry, Faculty of Mathematics and Natural Sciences,
Brawijaya University, Malang, Indonesia
*Corresponding author's email: faustinaabi82@gmail.com

ABSTRACT

Optimization of manganese ore leaching process from North Central Timor, Indonesia has been investigated. The final product of the leaching process was $MnSO_4$. Variables that were optimized during the process were volume of H_2O_2, reaction temperature, and reaction time. The final products were characterized by FTIR, powder-XRD, XRF, and AAS. Experimental data shows that the optimum conditions for the leaching process were 50 mL H_2SO_4 4 M, 25 mL H_2O_2 2 M, in which the reaction was done at room temperature for two hours. This optimum condition resulting in 38.2% of Mn extraction with 96.88% purity. Based on powder-XRD, the products were a mixture of crystalline $MnSO_4.4H_2O$, $MnSO_4.5H_2O$ and $[NH_4]_8[Mn_8(SO_4)_{12}]$.

Keywords: hydrometallurgy, leaching, manganese ore, peroxide, sulfuric acid.

ABSTRAK

Penelitian optimalisasi proses pelindian bijih mangan dari Timor Tengah Utara, Indonesia telah dilakukan. Produk akhir proses pelindian berupa $MnSO_4$*. Variabel yang dioptimalkan selama proses pelindian adalah volume* H_2O_2*, suhu reaksi, dan waktu reaksi. Produk akhir dikarakterisasi dengan FTIR, powder-XRD, XRF dan AAS. Data hasil penelitian menunjukkan bahwa kondisi optimum proses pelindian untuk mendapatkan* $MnSO_4$ *adalah 50 mL* H_2SO_4 *4 M, 25 mL* H_2O_2 *2 M, dan reaksi dilakukan pada suhu ruang selama dua jam. Kondisi optimum ini menghasilkan ekstrasi Mn sebesar 38,2% dengan kemurnian 96,88%. Berdasarkan analisis powder-XRD, produk yang dihasilkan adalah campuran kristal* $MnSO_4.4H_2O$*,* $MnSO_4.5H_2O$ *and* $[NH_4]_8[Mn_8(SO_4)_{12}]$*.*

Kata kunci: hidrometalurgi, pelindian, bijih mangan, peroksida, asam sulfat.

INTRODUCTION

East Nusa Tenggara (ENT) Province is one of the manganese-producing provinces in Indonesia with total manganese ore resources around 36,207,271 tons and manganese ore reserves approximately 79,712,386 tons (Supriadi *et al*., 2017). Manganese resources in ENT are naturally distributed in several areas particularly in the Districts of Manggarai, Kupang, South Central Timor, Belu, and North Central Timor (NCT). The most abundant distribution of the ore is in the Central District of NCT (Leto, 2017). To this date, this natural resource has not been optimally explored. The people of ENT, especially in the NCT Regency, only mine the ore traditionally, collect, and then sell them to the collectors at low prices. In the form of oxide, manganese can be used as catalysts and sensors (Paulose and Mohan, 2019), supercapacitors (Singu and Yoon, 2019), and as photocatalysts for degradation of rhodamine B (Hao *et al*., 2017), or image improvement from MRI (Sun *et al*., 2018). In the form of salt and other derivative products, manganese can be

Received: 09-05-2022, first revision: 20-12-2022, second revision: 24-03-2023, accepted: 27-04-2023.
DOI: 10.30556/imj.Vol26.No1.2023.1301

used as fertilizer and livestock supplements (Šaric and Lucchini, 2007), as a regulator for immune responses, immune function, cellular energy, blood sugar, digestion, reproduction, blood clotting, growth of bone and antioxidant defense (Ali and Iqbal, 2017; Zhang *et al.*, 2021).

Manganese ore is classified into several mineral types, namely pyrolusite, manganese, psilomelane, hausmannite, rhodochrosite, rhodonite, and bementite (Sukandarrumidi, 2007). Pyrolusite (MnO_2) is a metallic luster gray oxide mineral with a manganese content of 63%, while manganese ($Mn_2O_3.H_2O$) is a hydrated mineral that is iron black or steel gray, with a manganese content of 62.4%. The psilomelane ($MnO.MnO_2.2H_2O$) is a gray hydrated secondary mineral deposited and its manganese content is 45-60%. Hausmannite (Mn_3O_4) is a blackish-brown manganese mineral with a sub-metallic luster and retains a manganese content of about 72.5%, meanwhile rhodochrosite ($MnCO_3$) is a pink to brown manganese mineral containing manganese of 47.6%. Rhodonite ($MnSiO_3$) is a manganese mineral containing about 41.9% manganese, whereas bementite ($2MnSiO_3.H_2O$) is a mineral that contains about 39.1% manganese (Sukandarrumidi, 2007). In addition, based on the quality, manganese is categorized as a high grade if the percentage of the manganese within the ore is greater than 44%; while the medium-grade contains Mn as much as 40-44%, and the low grade has as much as 35-40% of Mn; and steel mill grade has Mn as much as 28-35% (Gao *et al.*, 2012).

Manganese can be obtained from the manganese ore using various leaching methods, one of which is hydrometallurgy namely a technique for extracting metals or compounds from ores using liquid phase chemicals at temperatures below 100 °C to about 300 °C. The main procedure in hydrometallurgical process is leaching (using acids, bases, cyanides, and an organic solvent), separation, enrichment, and extraction. Meanwhile, the reactions involved in this process are oxidation, reduction, neutralization, hydrolysis, and complexation (Haldar, 2018). The recent development of the hydrometallurgy process of manganese ore is reported by Li *et al.* (2017). In their study, low-grade manganese-zinc ore components were leached using 2.16 mol/L H_2SO_4 and 1.48 mol/L H_2O_2 (added 30 minutes after) as a reducing agent for two hours at room temperature (25 °C) and stirred at 120 rpm. The solid-liquid ratio used was 1:5 and the yield obtained by this method was 95.73% which had a sharp increase compared to that of leaching without H_2O_2, which was only 40.64% (Li *et al.*, 2017). Moreover, Hazek *et al.* (2006) reported that his method resulted in a leaching efficiency of higher than 97%. The leaching method was done by reacting the manganese ore with 2 M HCl and 0.4 M H_2O_2 with an S/L ratio of 1:12 for 1 hour at a temperature of 60–90 °C (El Hazek, Lasheen and Helal, 2006).

In this research, manganese ore was taken from North Central Timor was firstly grounded into 200 mesh which then characterized by powder-XRD and XRF to determine the type of mineral and composition of the ore. The ore sample was then leached using sulfuric acid and hydrogen peroxide in various parameters, namely peroxide volume, various leaching temperature, and various leaching time.

METHOD

Chemicals and Instrumentation

Chemicals and materials used in this study include the manganese ore from Luniup village, North Central Timor (East Nusa Tenggara – Indonesia), sulphuric acid (Merk), ammonium hydroxide (Merck), hydrogen peroxide (Merck).

General laboratory wares were used in this work, such as standard glassware, Whatman filter paper no.42, pH paper, hot plate, magnetic stirrer (and the bar), 200 mesh and 300 mesh sieves, XRF spectrometer (PANalytical Minipal 4), powder-XRD (PANalytical X'Pert PRO), UV-Vis spectrophotometer (Shimadzu 1601), and Atomic Absorption Spectrophotometer (Shimadzu AA-6200).

Sample Preparation

The manganese ore was separated from the soil and other impurities physically, then it was crushed with a hammer into powder and passed through the sieves. Fine powder that passed the 200-mesh sieve but unpassed the 300-mesh sieve were used on the next stage. At this point, XRF and powder XRD characterizations were carried out to determine the composition and the type of manganese ore from North Central Timor, respectively.

Optimization of Manganese Ore Leaching

The leaching of manganese ore was conducted in three optimization stages, namely (1) leaching volume of H_2O_2, (2) leaching temperature, and (3) leaching reaction time. The final product obtained from the third stage was then selected for characterization using FTIR spectrometer, XRF spectrometer, powder X-Ray diffractometer and atomic absorption spectrometer (AAS), then compared with the results of the initial manganese ore.

At the first optimization stage, a total of 10 grams of ore powder were added to 50 mL of 4M H_2SO_4. The mixture was stirred at room temperature for 30 minutes. Next, 5 mL of 2M H_2O_2 was added to the mixture and the mixture was kept stirred for 1.5 hours (in total was two hours of leaching time). After cooling it to room temperature, the mixture was filtered off using a filter paper. The filtrate, in a red purplish color solution, was then added with 25% of NH_4OH dropwise until the pH of the solution turned into 7. The solution was then stood at room temperature overnight and resulting in brown precipitation. A clear solution was obtained after the brown precipitate was separated by a filter paper. Next, the clear solution was fully evaporated and resulting in a white crystalline solid. The solid was then dried in an oven at 100 °C for two hours, followed by saving it in a desiccator for several days, in which silica gels beads were used as a drying agent. The yield was measured using an analytical balance. This treatment was repeated using different compared volumes of H_2O_2, namely 10, 15, 20, and 25 mL. The optimum condition was selected based on the volume of H_2O_2 that gives the highest yield of dry solid.

In the second optimization stage, the optimum volume of H_2O_2 selected from the previous stage was used. An identical procedure was used as in the first stage but the temperature for the leaching process was 70 °C. The result was then compared to that of the first stage at the optimum volume of H_2O_2. Similarly, the optimum condition was selected based on the leaching temperature that gives the highest yield of dry solid. In the last stage, both optimum volumes of H_2O_2 and leaching temperature were used. At this stage, an identical procedure was used but the leaching time was varied, namely two, three and four hours. Similarly, the optimum condition was selected based on the leaching temperature that gives the highest yield of dry solid.

After the last stage was finished and the optimum leaching time was obtained, the product, which is expected to be in the form of manganese (II) sulfate, was characterized. The results were then compared to that of the initial manganese ore.

RESULTS AND DISCUSSION

Sample Preparation

The XRF measurement results are presented in Table 1, whereas the XRD diffraction pattern of the ore is presented in Figure 1. Based on Table 1, the content of Mn in the ore, supplied from the Luniup Village in the North Central Timor, is 77.5%, which indicates that the manganese ore sample was classified as a high-grade (Gao *et al.*, 2012). There are several other major and minor elements within the ore, in which the three major elements were Ca (8.57%), Fe (6.58%), and Si (4.1%). Hence, enrichment of the ore was mainly focused on the elimination of those major elements.

Meanwhile, X-ray diffraction pattern of the ore was quantitatively analyzed using a High Score Plus software using the Rietveld method and compared to the COD standard database. The analysis result confirms that the manganese ore is pyrolusite (MnO_2) in a space group of P_{42}/MNM, with the four high intense peaks at angles of 28.67°, 37.37°, 56.64° and 72.47°(Kusumaningrum *et al.*, 2018). Those peaks, along with other peaks, match with that of the ID number of 1514110 and give GoF value of 2. This GoF value indicates that the refinement Rietveld is acceptable because the value of the requirement of GoF is lower than 4% (Mukminin, 2019). Other peaks that were observed and mixed with the main peaks (around 26°, 30°, 39°, and 48°) indicate the presence of minor elements and/or other types of minerals within the ore.

Table 1. XRF analysis of the manganese ore from the Luniup village

Element	Percentage (%)	Compound	Percentage (%)
Mn	77.5	MnO_2	78.29
Ca	8.57	CaO	7.66
Fe	6.58	Fe_2O_3	6.00
Si	4.1	SiO_2	5.61
Ba	1.9	BaO	1.36
Re	0.29	Re_2O_7	0.24
Sr	0.27	SrO	0.199
P	0.20	P_2O_5	0.29
K	0.20	K_2O	0.15
Cu	0.17	CuO	0.14
Ti	0.06	TiO_2	0.04
Zn	0.01	ZnO	0.008

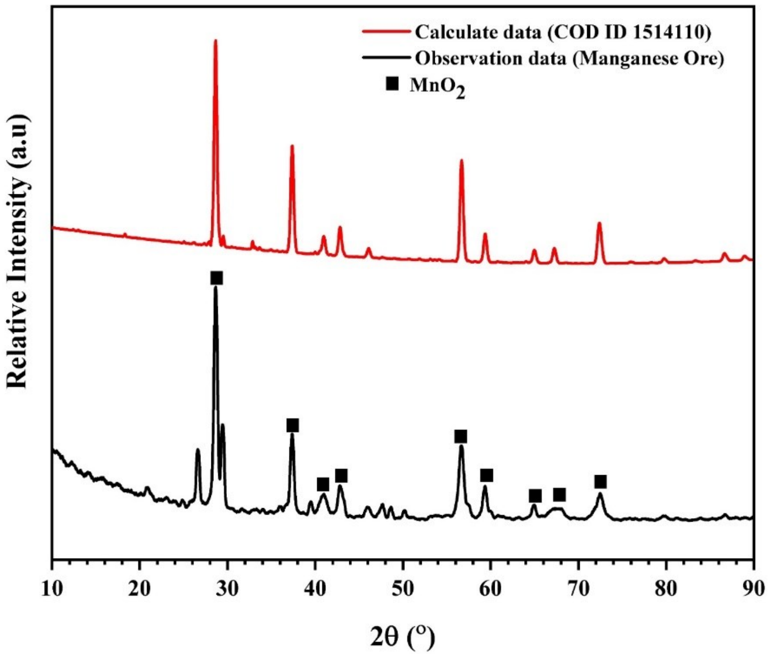


Figure 1. X-ray diffraction pattern of the manganese ore supplied from the Luniup village compared to that of pyrolusite (MnO_2) standard (COD ID: 1514110).

Optimization of Manganese Ore Leaching

The leaching of manganese ore was conducted using hydrogen peroxide as the reducing agent. The ore was dissolved in sulfuric acid and then was added with the peroxide to reduce Mn(IV) to Mn(II), in which the latter is more soluble in an acid solvent (Li *et al.*, 2017; Royani *et al.*, 2017), thus, more manganese can be extracted from the ore. Next, the solution resulting from the leaching was neutralized with NH_4OH 25% solution to precipitate other dissolved substances, such as iron, since the iron was easily deposited in the pH range of 6.9–7.2. However, manganese precipitation can also occur at pH below 9.5 but very slowly (Makhmudah and Notodarmojo, 2010), thus direct filtration was conducted to avoid this. In general, the main reactions that occur during the leaching and purification process are (Kusumaningrum *et al.*, 2018):

$$MnO_{2\,(s)} + H_2SO_{4\,(aq)} + H_2O_{2\,(aq)} \rightarrow MnSO_{4\,(aq)} + 2H_2O_{(l)} + O_{2\,(g)} \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$Fe_2O_{3\,(s)} + 2H_2SO_{4\,(aq)} + H_2O_{2\,(aq)} \rightarrow 2FeSO_{4\,(aq)} + 3H_2O_{(l)} + O_{2\,(g)} \ldots\ldots\ldots\ldots\ldots (2)$$

$$MnSO_{4\,(aq)} + 2NH_4OH_{(aq)} \rightarrow Mn(OH)_{2\,(s)} + (NH_4)_2SO_{4\,(aq)}\ (\textit{if pH = 9}) .\ (3)$$

$$FeSO_{4\,(aq)} + 2NH_4OH_{(aq)} \rightarrow Fe(OH)_{2\,(s)} + (NH_4)_2SO_{4\,(aq)} \ldots\ldots\ldots\ldots\ldots\ldots (4)$$

The reaction for producing $MnSO_4$ crystal are:

$$MnSO_{4(aq)} + 2H_2O_{(l)} \xrightarrow{heating} MnSO_{4(s)} + 2H_2O_{(g)} \text{ ....(5)}$$

$$MnSO_{4(aq)} + 4H_2O_{(l)} \xrightarrow{heating} MnSO_4.4H_2O_{(s)} \text{ .....(6)}$$

$$MnSO_{4(aq)} + 5H_2O_{(l)} \xrightarrow{heating} MnSO_4.5H_2O_{(s)} \text{ .....(7)}$$

Optimization of H_2O_2 Addition

In this stage, the H_2O_2 was added gradually every 5 ml (up to 25 mL). Multistep addition of H_2O_2 affects the number of moles of H_2O_2 that reacts with manganese in the ore. The addition of more H_2O_2 will enhance the reduction of Mn(IV) to water-soluble Mn(II) (Li *et al.*, 2017). The more volume of H_2O_2 used, the higher the number of moles involved in the leaching process. This is in accordance to general chemical equation, which a number of mol is equal to multiplication of molarity and volume ($n = M \times V$). An increase in manganese concentration was also observed within the XRF results of the obtained $MnSO_4$ (Table 2), in which at the first 5 mL addition, the percentage of Mn in the product was only 19.4%, and it was increased to 50.3% at the 25 mL- total addition. Moreover, the content of other elements was also reduced, namely Mo and Ca, due to the oxidation of Mo and Ca by H_2O_2 to form soluble Mo and Ca compounds. This reduction of concentration shows that the more volume of H_2O_2 used, the higher purity of $MnSO_4$ produced. The $MnSO_4$ obtained from every 5 mL addition was also analyzed using the UV Vis spectrophotometry to measure the Mn concentrations. The result is shown in Figure 2. The more volume of H_2O_2 added, the higher Mn concentration in the sample obtained. This increase indicates that the purity of the $MnSO_4$ is getting higher, which is also in accordance with the XRF result. The concentration level of Mn is raised from 3.42×10^4 mg/kg to 6.41×10^4 mg/kg. It is predicted that the addition of more H_2O_2 volume may or may not increase the Mn due to the result having nearly reach a flat curve.

Table 2. XRF results of $MnSO_4$ in the lowest and the highest H_2O_2 addition

Elements (%)	Mn	S	Mo	Ca	Yb
H_2O_2 = 5 mL	19.4	64.2	15	1.3	0.2
H_2O_2 = 25 mL	50.3	45.1	3	0.85	0.2

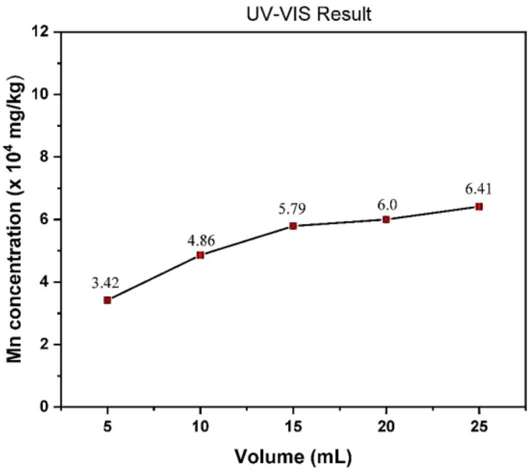


Figure 2. UV-Vis results for Mn concentration after H_2O_2 addition

Optimization of Leaching Temperature

In this stage, the manganese ore leaching was carried out by dissolving 10 grams of manganese ore into 50 mL of 4 M H_2SO_4 and adding directly 25 mL of 2 M H_2O_2. The leaching was carried out for two hours at room temperature and 70°C. At lower temperatures (20–40°C), the leaching kinetics on the surface was controlled chemically while at higher temperatures, the leaching kinetics was controlled by diffusion, in which in this process also occurs the formation of metal oxides in the matrix (Nayl, Ismail and Aly, 2011).

The result shows that at 70°C, the content of manganese in the product decreased about 17% from 6.41×10^4 mg/kg to 5.32×10^4 mg/kg. This might be due to at high temperatures, not only H_2O_2 easily decomposed into H_2O and O_2 (Li *et al.*, 2017), but also diffusion-reaction occurs (Nayl, Ismail and Aly, 2011). When the temperature is high, more H_2SO_4 diffuses into manganese ore, thus substances other than Mn that can dissolve in acid solvents will also dissolve easily and reduces the ability of the acid to dissolve the Mn. This result is also supported by the fact that the residual mass obtained after purification at room temperature is lower (0.13 grams) than that of at 70°C (1.24 grams).

Optimization of Leaching Time

In this study, the leaching process was carried out based on the previous optimum condition by dissolving 10 grams of manganese ore in 50 mL of 4 M H_2SO_4 and adding 25 mL of 2 M H_2O_2. This leaching was carried out at room temperature with time variations of two, three, and four hours.

The result shows that the time variation gives fluctuated results of Mn concentrations, namely 6.41 x 10^4 mg/kg (2 hrs), 5.39 x 10^4 mg/kg (3 hrs), and 6.15 x 10^4 mg/kg (4 hrs). The difference between the lowest and the highest concentrations is 1.02 x 10^4 mg/kg. There is a slight decline between the 2-hr and the 4-hr reaction (0.26 x 10^4 mg/kg). This trend indicates that if longer time was applied (i.e 5 or 6 hrs and so on), the result might not be insignificantly different. Therefore, the 2-hour reaction time was decided to be the optimum reaction time.

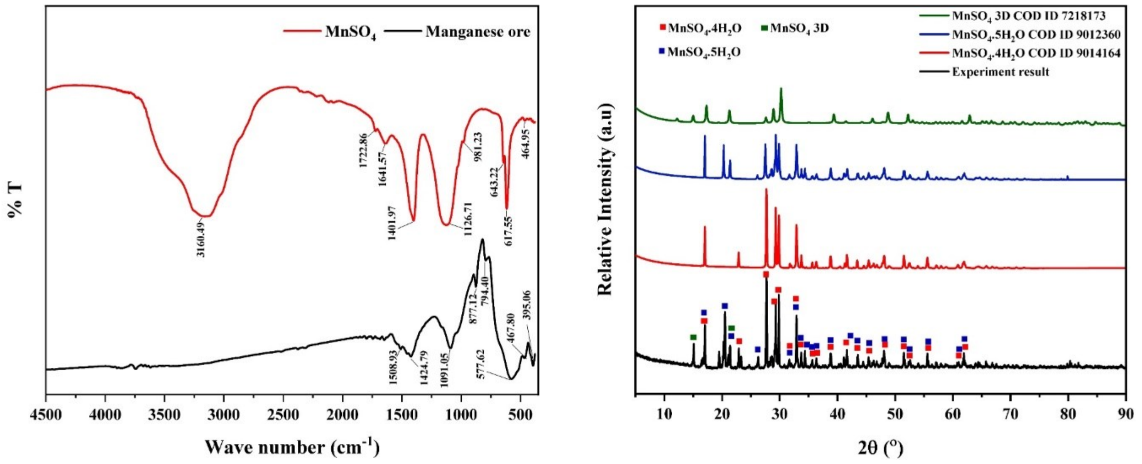
During the leaching of manganese ore, the ore went through several stages, namely hydrolysis, the reductant diffusion from the solution through the boundary layer to the manganese ore active site, product nucleation to the active site, and product hydration and diffusion into the leach solution (Nayl, Ismail and Aly, 2011).

Characterization of the Product

From 10 grams of manganese ore, as much as 17.48 grams of $MnSO_4$ with percent recovery after purification of 113.38% were obtained using the optimized procedures. It is an increase of 62% from percent recovery before refining.

The $MnSO_4$ was then characterized by infrared spectroscopy, powder-XRD, XRF, and AAS. The infrared data and diffraction pattern of the $MnSO_4$ product were presented in Figure 3.

Infrared analysis shows that the $MnSO_4$ sample has absorption at 1401.97 cm^{-1} and 1126.71 cm^{-1}, which corresponds to S=O stretching of the sulphate (OChemOnline, 2011). Absorption at 981.23 cm^{-1} relates to the symmetrical vibration of SO_4^{2-} ion. Absorptions at 643.22 cm^{-1} and 617.55 cm^{-1} indicate the out-of-plane bending vibration of SO_4^{2-} (Lane, 2007; Guo *et al.*, 2010; Ramaswamy, Vimalathithan and Ponnusamy, 2010). Absorption at 464.95 cm^{-1} indicates the presence of Mn-O bonds (Sagunthala, Yasotha and Vijaya, 2013). A broadband around 3200 cm^{-1} indicates the O-H stretching of the water (Guo *et al.*, 2010). Meanwhile for powder-XRD analysis, the $MnSO_4$ product is confirmed to be a mixture of $MnSO_4.4H_2O$ and $MnSO_4.5H_2O$ with the high intensity peaks observed at 2-theta angles of 27.72°, 29.32°, 29.86° for $MnSO_4.4H_2O$ and at 2-theta angles of 17.02°, 20.50°, 32.90° for $MnSO_4.5H_2O$. Other peak at theta angles of 15,12° is $MnSO_4$ three dimensional (3D) ($[NH_4]_8[Mn_8(SO_4)_{12}]$) (Behera *et al.*, 2014).



(a) (b)

Figure 3. FTIR pattern of manganese ore and optimum product ($MnSO_4$, $V_{H_2O_2}$= 25 mL, t = two hours, T = room temperature (a); XRD pattern of optimum product (b)

Table 3. XRF result of the product in optimum conditions

Compound	Percentage (%)	Element	Percentage (%)
MnO	30.08	Mn	50.27
SO_3	66.8	S	45.1
CaO	0.62	Ca	0.85
CuO	0.16	Cu	0.3
MoO_3	2	Mo	3
Yb_2O_3	0.08	Yb	0.2
Re_2O_7	0.1	Re	0.2

Table 4. AAS results of manganese ore and product in optimum conditions

Sample	Concentration (mg/kg)
Manganese ore	3.081×10^5
$MnSO_4$	1.177×10^5

Furthermore, based on the XRF analysis (Table 3), the $MnSO_4$ product has a purity of 96.88% with the percentages of MnO and Mn in the sample being 30.08% and 50.27% respectively. This result is higher than that of the previous studies that reported the purity of $MnSO_4$ of 79.11% with an MnO percentage of 27.56% (Sumardi, Mubarok and Saleh, 2013). Meanwhile, based on AAS analysis (Table 4), the concentration of Mn in the $MnSO_4$ product is only 1.177×10^5 mg/kg. This result shows that the ability of H_2O_2 as a reducing agent in the extraction of Mn from manganese ore is on medium level (38.2%), as compared to the initial Mn content in the ore (3.081×10^5 mg/kg). However, although this result is lower than 50%, the purity of the obtained $MnSO_4$ is much higher than that of the previous study.

CONCLUSIONS

Manganese ore from North Central Timor is categorized as pyrolusite mineral which contains 77.50% Mn and is classified as high-grade manganese ore. The optimum leaching conditions of the manganese ore in this work are 50 mL H_2SO_4 4 M, 25 mL H_2O_2, and at room temperature for two hours. This optimum condition results in 38.2% Mn extraction with 96.88% purity. In addition, the products were a mixture of crystalline $MnSO_4.4H_2O$, $MnSO_4.5H_2O$ and $[NH_4]_8[Mn_8(SO_4)_{12}]$. The percentage of Mn extraction was moderate. It was probably due to the insufficient amount H_2O_2 added, so not all of the Mn was dissolved. Therefore, recommended being able to vary the addition of H_2O_2 in large quantities or volume or by variant the concentration of H_2O_2.

ACKNOWLEDGEMENTS

The authors wish to thankti the Universitas Katolik Widya Mandira, Kupang and the Brawijaya University, Malang (Master Degree Program of Chemistry) for the research support. The acknowledgement is also addressed to the XRD facility (PANalytical X'Pert3 Powder) at the Central Laboratory of Life Science - Brawijaya University (LSIH-UB).

REFERENCES

Ali, B. and Iqbal, M.A. (2017) 'Coordination complexes of manganese and their biomedical applications', *ChemistrySelect*, 2(4), pp. 1586–1604. Available at: https://doi.org/10.1002/slct.201601909.

Behera, J.N., Bhattacharjee, J., Horike, S., Marri, S.R. and Dahiya, P.P. (2014) 'Synthesis and characterization of robust three-dimensional chiral metal sulfates', *RSC Advances*, 4(92), pp. 50435–50442. Available at: https://doi.org/10.1039/c4ra09471a.

Gao, Y., Olivas-Martinez, M., Sohn, H.Y., Kim, H.G. and Kim, C.W. (2012) 'Upgrading of Low-Grade Manganese Ore by Selective Reduction of Iron Oxide and Magnetic Separation', *Metallurgical and Materials Transactions B*, 43(6), pp. 1465–1475. Available at: https://doi.org/10.1007/s11663-012-9731-6.

Guo, X., Xiao, H.S., Wang, F. and Zhang, Y.H. (2010) 'Micro-Raman and FTIR spectroscopic observation on the phase transitions of MnSO4 droplets and ionic interactions between Mn2+ and SO42-', *Journal of Physical Chemistry A*, 114(23), pp. 6480–6486. Available at: https://doi.org/10.1021/jp9104147.

Haldar, S.K. (2018) 'Chapter 13 - Mineral Processing', in S.K.B.T.-M.E. (Second E. Haldar (ed.). Elsevier, pp. 259–290. Available at: https://doi.org/https://doi.org/10.1016/B978-0-12-814022-2.00013-7.

Hao, X.L., Zhao, J.Z., Song, Y.H. and Huang, Z.F. (2017) ‘Synthesis and Oxidizability Study on Mn3O4 Nanoparticles’, *Journal of Nano Research*, 48, pp. 138–147. Available at: https://doi.org/10.4028/www.scientific.net/JNanoR.48.138.

El Hazek, M.N., Lasheen, T.A. and Helal, A.S. (2006) ‘Reductive leaching of manganese from low grade Sinai ore in HCl using H2O2 as reductant’, *Hydrometallurgy*, 84(3–4), pp. 187–191. Available at: https://doi.org/10.1016/j.hydromet.2006.05.006.

Kusumaningrum, R., Rahmani, S.A., Widayatno, W.B., Wismogroho, A.S., Nugroho, D.W., Maulana, S., Rochman, N.T. and Amal, M.I. (2018) ‘Characterization of Sumbawa manganese ore and recovery of manganese sulfate as leaching products’, in *AIP Conference Proceedings*. American Institute of Physics, p. 020042. Available at: https://doi.org/10.1063/1.5038324.

Lane, M.D. (2007) ‘Mid-infrared emission spectroscopy of sulfate and sulfate-bearing minerals’, *American Mineralogist*, 92(1), pp. 1–18. Available at: https://doi.org/10.2138/am.2007.2170.

Leto, K.T. (2017) *Pelindian bijih mangan dari Nusa Tenggara Timur menggunakan serbuk kayu hasil hidrolisi sebagai reduktor dengan pelarut asam sulfat*. Institut Teknologi Sepuluh Nopember.

Li, Q., Rao, X., Xu, B., Yang, Y., Liu, T., Jiang, T. and Hu, L. (2017) ‘Extraction of manganese and zinc from their compound ore by reductive acid leaching’, *Transactions of Nonferrous Metals Society of China*, 27(5), pp. 1172–1179. Available at: https://doi.org/10.1016/S1003-6326(17)60137-7.

Makhmudah, N. and Notodarmojo, S. (2010) ‘Penyisihan besi-mangan, kekeruhan dan warna menggunakan saringan pasir lambat dua tingkat pada kondisi aliran tak jenuh studi kasus: Air Sungai Cikapundung’, *Jurnal Tehnik Lingkungan*, 16(2), pp. 150–159. Available at: https://doi.org/10.5614/jtl.2010.16.2.5.

Mukminin, A. (2019) ‘Analisis komposisi fasa dan parameter unit sel kristal hasil kalsinasi suhu tinggi abu cangkang (Paguroidea) dengan metode rietveld’, *JST (Jurnal Sains Terapan)*, 5(1), pp. 1–5. Available at: https://doi.org/10.32487/jst.v5i1.635.

Nayl, A.A., Ismail, I.M. and Aly, H.F. (2011) ‘Recovery of pure MnSO4·H2O by reductive leaching of manganese from pyrolusite ore by sulfuric acid and hydrogen peroxide’, *International Journal of Mineral Processing*, 100(3–4), pp. 116–123. Available at: https://doi.org/10.1016/j.minpro.2011.05.003.

OChemOnline (2011) *Infrared spectroscopy absorption table*, *LibreTexts Chemistry*. Available at: https://chem.libretexts.org/Ancillary_Materials/Reference/Reference_Tables/Spectroscopic_Reference_Tables/Infrared_Spectroscopy_Absorption_Table.

Paulose, R. and Mohan, R. (2019) ‘Hausmannite (Mn3O4) – Synthesis and its electrochemical, catalytic and sensor application’, in *Photoenergy and Thin Film Materials*. Wiley, pp. 283–320. Available at: https://doi.org/10.1002/9781119580546.ch7.

Ramaswamy, V., Vimalathithan, R.M. and Ponnusamy, V. (2010) ‘Synthesis and characterization of BaSO 4 nano particles using micro emulsion technique’, *Advances in Applied Science Research*, 1(3), pp. 197–204.

Royani, A., Subagja, R. and Manaf, A. (2017) ‘Studi pelindian mangan secara reduksi dengan menggunakan larutan asam sulfat’, *Jurnal Riset Teknologi Industri*, 11(1), pp. 1–9. Available at: https://doi.org/10.26578/jrti.v11i1.1724.

Sagunthala, P., Yasotha, P. and Vijaya, L. (2013) ‘Growth and characterization of manganese (II) sulphate and L-Lysine doped manganese (II) sulphate (LMnSO4) crystals’, *International Journal of Science and Engineering Applications*, 7560(Special Issue NCRTAM), pp. 46–52. Available at: https://doi.org/10.7753/IJSEANCRTAM.1012.

Šarić, M. and Lucchini, R. (2007) ‘Manganese’, in G.F. Nordberg, B.A. Fowler, M. Nordberg, and L.T. Friberg (eds) *Handbook on the Toxicology of Metals (Third Edition)*. Third Edit. Burlington: Academic Press, pp. 645–674. Available at: https://doi.org/https://doi.org/10.1016/B978-012369413-3/50087-2.

Singu, B.S. and Yoon, K.R. (2019) ‘Exfoliated graphene-manganese oxide nanocomposite electrode materials for supercapacitor', *Journal of Alloys and Compounds*, 770, pp. 1189–1199. Available at: https://doi.org/10.1016/j.jallcom.2018.08.145.

Sukandarrumidi (2007) *Geologi mineral logam*. Yogyakarta: Gadjah Mada University Press.

Sumardi, S., Mubarok, M.Z. and Saleh, N. (2013) 'Pengolahan bijih mangan menjadi mangan sulfat melalui pelindian reduktif menggunakan asam oksalat dalam suasana asam', in *Semirata FMIPA Universitas Lampung*. Lampung: FMIPA Universitas Lampung, pp. 123–130.

Sun, W., Zhang, J., Zhang, C., Wang, P., Peng, C., Shen, M. and Shi, X. (2018) 'Construction of hybrid alginate nanogels loaded with manganese oxide nanoparticles for enhanced Tumor Magnetic Resonance Imaging', *ACS Macro Letters*, 7(2), pp. 137–142. Available at: https://doi.org/10.1021/acsmacrolett.7b00999.

Supriadi, A., Sunarti, Kencono, A.W., Kurniasih, T.N., Prasetyo, B.E., Kurniawan, F., Kurniadi, C.B., Alwendra, Y., Aprilia, R., Rabbani, Q., Setiadi, I. and Anggraeni, D. (2017) *Kajian dampak hilirisasi mineral mangan terhadap perekonomian regional*. Jakarta: Pusat Data dan Teknologi Informasi Energi dan Sumber Daya Mineral.

Zhang, R., Wang, C., Guan, Y., Wei, X., Sha, M., Yi, M., Jing, M., Lv, M., Guo, W., Xu, J., Wan, Y., Jia, X.-M. and Jiang, Z. (2021) 'Manganese salts function as potent adjuvants', *Cellular & Molecular Immunology*, 18(5), pp. 1222–1234. Available at: https://doi.org/10.1038/s41423-021-00669-w.