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Research Article

Effect of Sulfuric Acid Concentration on the Leaching Behavior of Manganese Ore from Palludda Barru Regency

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Abstract: Manganese is one of the minerals that constitute various rock formations found throughout Indonesia, particularly in the Sulawesi region. Therefore, research on the processing of manganese ore is essential to ensure its availability can be utilized efficiently and effectively. The objective of this study is to determine the effect of varying H_2SO_4 concentrations and identify the optimum concentration for achieving the highest recovery in manganese ore processing. One method to enhance manganese ore grade is by applying a leaching process using H_2SO_4 solution with concentration variations of 4%, 6%, 8%, and 10%, with a solid mass of 5 grams for each concentration. The leaching process was carried out for 6 hours at each concentration with a stirring speed of 200 rpm. The resulting filtrate was analyzed using Atomic Absorption Spectroscopy (AAS). The leaching results yielded dissolved Mn with 47.600% at 4% concentration, 52.585% at 6%, 50.141% at 8%, and 50.557% at 10%. Based on the results, the highest Mn extraction was achieved at a 6% concentration with a recovery of 52.585% after 6 hours of leaching.

Keywords: Manganese ore, sulfuric acid, Mn recovery, Palludda.

1. Introduction

Manganese (Mn) is one of the mineral resources in Indonesia that possesses substantial potential in terms of economic value, applications, and the abundance of its reserves [1]. To date, low-grade manganese ores in Indonesia have not been optimally utilized [2]. Manganese is a strategically important metal extensively used in steel production, battery technologies, chemical industries, and alloy manufacturing. Approximately 90% of global manganese consumption is attributed to the iron and steel industry, where it functions as a deoxidizer and alloying element to improve strength and hardness [3]. In recent years, the rapid development of lithium-ion batteries and renewable energy technologies has further increased the demand for high-purity manganese compounds, thereby encouraging the exploration of efficient extraction techniques from both high-grade and low-grade manganese ores [4][5].

Manganese ore deposits are found in various regions, including Sumatra, Riau, Java, Kalimantan, Sulawesi, Nusa Tenggara, Maluku, and Papua [6]. In Sulawesi Island, particularly in the Palludda area of Barru Regency, South Sulawesi, manganese ores are generally characterized by relatively low grades, thus requiring beneficiation processes prior to their economic utilization [7][8]. Manganese ores are often associated with gangue minerals such as silica, clay, and iron oxides [2][9]. The implementation of Government Regulation No. 7 of 2012, which prohibits the export of unprocessed mineral resources, underscores the necessity of processing raw minerals into semi-finished or final products to enhance their added value. Fourteen types of metallic ores, including manganese, are restricted from export in their raw form [6].

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Manganese ore primarily consists of oxide compounds containing various minerals such as pyrolusite, manganite, bixbyite, hausmannite, rhodochrosite, rhodonite, and others [10][11]. Minerals such as pyrolusite, bixbyite, and hausmannite are particularly important in the battery industry. Manganese ore also plays a significant role in iron and steel production, with additional applications in the manufacture of dry-cell batteries, glass, ceramics, and other chemical products [12]. Hence, manganese ore holds considerable industrial significance, and the global demand for manganese is expected to increase annually.

Manganese ore processing can generally be divided into two main categories: pyrometallurgical and hydrometallurgical methods. High-grade manganese ore (above 40% Mn), commonly referred to as metallurgical grade, is typically processed via pyrometallurgy to produce ferromanganese alloys [6]. In contrast, low-grade manganese ores are usually treated by hydrometallurgical methods, such as leaching. Hydrometallurgical processing has emerged as a promising alternative to conventional pyrometallurgical routes for manganese extraction due to its lower energy consumption, reduced greenhouse gas emissions, and better suitability for low-grade ores [5]. Among various hydrometallurgical techniques, acid leaching is widely applied owing to its operational simplicity and high metal recovery efficiency. Sulfuric acid (H_2SO_4) is one of the most commonly used leaching agents because of its strong acidity, wide availability, and relatively low cost [4]. In sulfuric acid leaching systems, hydrogen ions (H^+) play a dominant role in dissolving manganese-bearing minerals, particularly manganese oxides such as pyrolusite (MnO_2), manganite (MnOOH), and bixbyite (Mn_2O_3). The concentration of sulfuric acid directly affects the dissolution rate, leaching kinetics, and overall manganese recovery [13]. An increase in acid concentration generally enhances manganese extraction by increasing proton availability; however, excessive acid concentrations may lead to higher reagent consumption, dissolution of gangue minerals, and unfavorable process economics [14]. Manganese extraction can be achieved through reductive leaching, in which a reducing agent is introduced to facilitate acid dissolution. Ores containing less than 40% Mn are commonly used for the production of chemical compounds such as potassium permanganate, MnO_2, and other manganese-based chemicals. Selective dissolution of pyrolusite-type manganese ore can occur under acidic conditions. The leaching process is reductive in nature, requiring the addition of specific reducing agents to lower the oxidation state of manganese from Mn(IV) to Mn(II), thereby enhancing its solubility in acid media [15].

The primary objective of this study is to develop an efficient process for converting low-grade manganese ore from the Palludda area, Barru Regency, into economically valuable products. This research focuses on the hydrometallurgical treatment of manganese ore through acid leaching. Previous studies on this deposit primarily concentrated on upgrading the ore via beneficiation processes based on the magnetic properties of the associated minerals to separate manganese from its impurities [16]. The leaching behavior of manganese ores is strongly influenced by mineralogical composition, particle size, and the presence of associated impurities. Ores originating from different geological environments often exhibit distinct responses to identical leaching conditions [11]. Indonesia hosts several manganese deposits, including those located in Palludda, Barru Regency, which are predominantly composed of manganese oxide minerals. Despite the potential of these local resources, systematic studies focusing on their hydrometallurgical characteristics, particularly the influence of sulfuric acid concentration on manganese leaching behavior, remain limited. Therefore, this study aims to investigate the effect of sulfuric acid concentration on the leaching behavior of manganese ore from Palludda, Barru Regency. The research evaluates manganese recovery under varying sulfuric acid concentrations and analyzes the relationship between acid strength and leaching efficiency. The results of this study are expected to provide fundamental insights into the hydrometallurgical processing of Indonesian manganese ores and contribute to the optimization of leaching parameters for sustainable manganese extraction.

2. Research and Methodology

2.1 Materials (Heading two)

The manganese ore sample used in this study was collected from the Palludda area, Barru Regency, South Sulawesi, Indonesia. The experimental work began with sample preparation to ensure representative and homogeneous material for subsequent analyses, as shown in Figure 1. Initially, the ore was crushed using a jaw crusher and then ground in a ball mill until the particle size reached 200 mesh. The ground sample was subsequently homogenized through quartering and splitting techniques to obtain a uniform distribution and the desired sample mass.

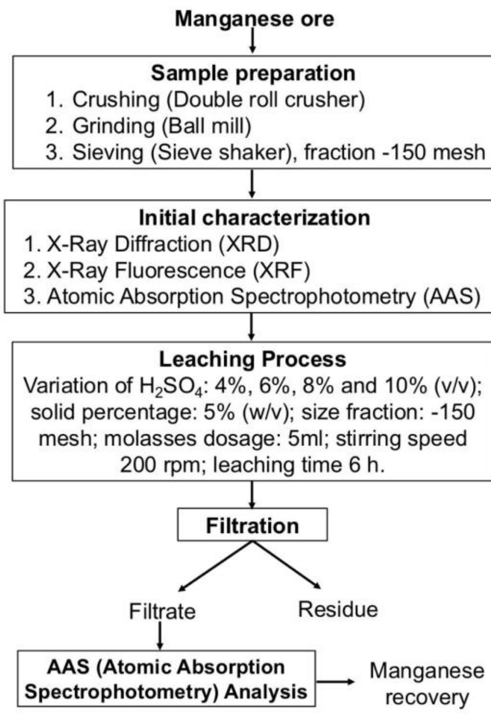

Figure 1. Experimental design

Preliminary characterization of the prepared sample was carried out using X-ray diffraction (XRD) and X-ray fluorescence (XRF) analyses to determine its mineralogical and elemental compositions, respectively. Table 1 summarizes the mineral phases identified from the XRD analysis, while Table 2 presents the elemental composition of the manganese ore as determined by XRF. These characterization results provided essential baseline information for the subsequent leaching experiments.

Table 1. Mineral composition of manganese ore based on XRD analysis

Minerals	Chemical composition	Presentation (%)
Manganite	MnO_2	13,99%
Hematite	Fe_2O_3	18,09%
Geothite	$FeO(OH)$	54,61%
Jarosite	$Kfe^{+3}3(OH)_6(SO_4)_2$	8,87%
Mordenite	Al_2O_3, Na_2O, H_2O	4,44%

Table 2. Chemical composition of manganese ore based on XRF analysis

No.	Element	Composition (%)
1	SiO_2	-0,19
2	Al_2O_3	0,425
3	TiO_2	0,077
4	Fe_2O_3	16,718
5	CaO	0,796
6	MgO	-0,106
7	K_2O	0,109
8	P_2O_5	0,591
9	**MnO**	**24,679**
10	Cr_2O_3	0,07

2.2 Experiments

The leaching experiments were conducted using sulfuric acid (H_2SO_4) solutions with varying concentrations of 4%, 6%, 8%, and 10% (v/v). For each concentration, the leaching process was performed for a duration of 6 hours at a constant stirring speed of 200 rpm under ambient temperature conditions. In addition to sulfuric acid, molasses was introduced into the leaching system as a reducing agent to enhance the dissolution of manganese.

After completion of the leaching process, the leach slurry was filtered through standard filter paper to separate the solid residue from the leachate (filtrate). The obtained filtrate was subsequently subjected to chemical analysis using Atomic Absorption Spectrophotometry (AAS) to determine the concentration of dissolved manganese ions (Mn^{2+}).

3. Results and Discussion

The leaching process was carried out using varying concentrations of sulfuric acid, specifically 4%, 6%, 8%, and 10%. In addition to sulfuric acid, molasses was added as a reducing agent within the leaching medium. The resulting leachates (pregnant leach solutions) were subsequently analysed using Atomic Absorption Spectrophotometry (AAS) to determine the concentration of dissolved manganese. The leaching operations and the corresponding AAS results for each filtrate are presented in Table 3.

Table 3. The operational variables of manganese ore leaching and the AAS analysis results of each filtrate

Sample mass (gr)	Molasses (ml)	Leaching time (hour)	Stirring speed (rpm)	Size fraction (Mesh)	H_2SO_4 Concentration (% v/v)	Dissolved Mn concentration (ppm)
AAS analysis of the initial sample						195.2336
5	5	6	200	-150	4	92.9327
					6	102.6636
					8	97.8932
					10	98.7056

The use of varying sulfuric acid concentrations in the manganese ore leaching process is of critical importance, as sulfuric acid plays a key role in dissolving minerals to enhance manganese metal recovery. Based on the calculated recoveries for each concentration variation, the average leaching recovery of manganese ore was obtained, as illustrated in Figure 2.

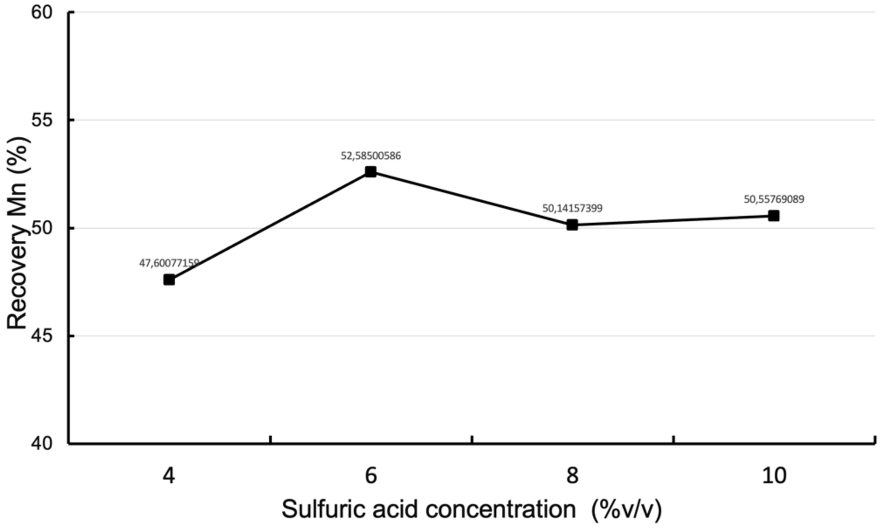

Figure 2. The effect of sulfuric acid concentration on Mn recovery

In the acid leaching process, H^+ ions supplied by the acid facilitate the dissolution of manganese minerals into the solution. An increase in H_2SO_4 concentration results in a higher availability of H^+ ions, which is expected to accelerate and enhance the effectiveness of the leaching reactions. Figure 4.3 illustrates that the leaching behavior of manganese ore varies with increasing sulfuric acid concentration, where the y-axis represents manganese recovery (%) and the x-axis denotes the variation in sulfuric acid concentration. As the sulfuric acid concentration increases, Mn recovery tends to rise, as evidenced by the highest recovery of 52.585% achieved at a concentration of 6% (v/v). Similar findings were reported by Slamet Sumardi et al. (2012), who investigated the leaching of NTT manganese ore using sulfuric acid and molasses, and observed that the maximum extraction occurred at a sulfuric acid concentration of 6%, with manganese extraction reaching approximately 50% [17]. These results are consistent with other studies indicating that increasing H_2SO_4 concentration generally enhances Mn extraction (recovery) [18]. However, further increases in sulfuric acid concentration to 8% (v/v) and 10% (v/v) led to a slight decline in Mn recovery. Previous studies have shown that Mn recovery does not always increase linearly with acid concentration, as an optimum point exists beyond which further increases result in marginal gains or even reduced yields due to factors such as excessive acid consumption and the dissolution of gangue minerals or impurities [19][20]. This phenomenon may be attributed to the increased solution viscosity at higher sulfuric acid concentrations, which reduces the mass transfer rate of H^+ ions. Additionally, high acid concentrations may promote the formation of solid phases or precipitates and the development of passive layers on the mineral surface, thereby hindering reactant contact and reducing selectivity through the concurrent dissolution of impurities [14].

4. Conclusion

Based on the experimental results, analysis, and discussion, it can be concluded that the recovery of Mn increases with increasing sulfuric acid concentration, although the improvement is not highly significant. The highest manganese extraction, reaching 52.5850%, was obtained in the reductive leaching experiment using molasses as a reducing agent at a sulfuric acid concentration of 6%, with the application of 5 g/L molasses, 5% solid content, a stirring speed of 200 rpm, and a leaching time of 6 hours; therefore, the optimum H_2SO_4 concentration for achieving the highest dissolved Mn recovery in this leaching process is 6% v/v.

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