Enhancing the Efficiency of Manganese Recovery from Pyrolusite Ore through Hydrometallurgical Techniques Utilizing Nitric Acid and Distilled Water

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Abstract:- The efficient extraction of manganese from pyrolusite ore holds significant importance in meeting the global demand for this essential metal. This study focuses on optimizing the hydrometallurgical process for manganese recovery, utilizing nitric acid and distilled water as solvents. The investigation delves into the effects of varying nitric acid concentrations, reaction temperatures, agitation rates, and reaction times on the extraction efficiency of manganese, while simultaneously minimizing impurity co-dissolution. Through systematic experimentation, a comprehensive understanding of the interplay between process parameters and their impact on manganese extraction and impurity contamination is achieved. The research not only contributes to enhancing the fundamental knowledge of manganese extraction mechanisms but also aims to provide practical insights for industrial applications. Recommendations are made for advanced parameter optimization using modelling techniques, improved impurity control strategies, and exploration of environmentally sustainable alternatives. Additionally, the study emphasizes the importance of scaling up the optimized conditions to pilot-scale operations and conducting thorough economic analyses to evaluate the feasibility and cost-effectiveness of the proposed hydrometallurgical approach.

Keywords:- *Manganese, Pyrolusite Ore, Hydrometallurgical, Nitric Acid and Distilled Water.*

I. BACKGROUND OF THE STUDY

Metals, crucial to many aspects of modern life and historically essential since the Bronze Age, play a vital role in tools, food production, construction, medical devices, energy generation, transportation, and communication. With the growing use of metals in everyday items like electronics, household goods, jewelry, and accessories, the demand for metals has surged significantly. This heightened demand, coupled with rapid industrialization, has led to the depletion of high-grade primary metal sources. Consequently, metal-producing industries are seeking alternative sources for extraction.

Metals can be found in nature as deposits on the Earth's crust and seabed due to their reactivity with other elements in their surroundings, particularly oxygen, sulfur, and carbon dioxide. While some metals like gold and platinum are primarily found in metallic form, others like silver, mercury, and copper can exist both as metals and in compounds like sulfides, carbonates, and chlorides. Highly reactive metals are typically found in compound forms, such as oxides and silicates of aluminum and beryllium. These naturally occurring compounds are generally referred to as minerals, with names based on their composition, such as lead sulfide (Galena), tin oxide (cassiterite), iron (II) carbonate (Siderite), and manganese dioxide (pyrolusite).

Most metals are too reactive to exist independently in the ground and are found in combination with other elements as ores. Ores are the materials from which metals are extracted. Two key factors determine if a mineral can be considered an ore mineral: its ease of separation from the surrounding waste material (gangue) and its ability to be smelted to release the metal from chemical bonds within the mineral.

Ore minerals are often found concentrated in specific rock formations resulting from unique geological processes, and these concentrated areas are known as mineral deposits. Prospectors seek mineral deposits, and the terms "ore mineral" and "mineral deposit" have expanded to include a few non-metallic minerals found in similar types of deposits as metallic minerals, such as barite and fluorite.

It's important to note that ore deposits are not composed solely of a single ore mineral; they contain a mixture of valueless minerals, collectively known as gangue. The higher the concentration of the ore mineral, the more valuable the mineral deposit. To be economically viable, a mineral deposit must meet certain conditions, including concentration levels and deposit size, and is then referred to as an ore deposit, with the combination of ore minerals and gangue called the ore.

All ore deposits are mineral deposits, but the reverse is not true. "Ore deposit" is an economic term, while "mineral deposit" is a geological term. Whether a mineral deposit is considered an ore deposit depends on various factors beyond concentration levels and deposit size, including factors related to mining, processing, transportation, political stability, market prices, and financing costs. Market dynamics can shift, causing a mineral deposit to be considered an ore deposit at one time and uneconomic at another.

Mineral deposits have been discovered in both oceanic and continental rocks, but mining operations have so far been limited to continental rocks, with the potential for mining oceanic deposits in the future.

Manganese, a chemical element with the symbol Mn and atomic number 25, is a hard, silvery metal often found in minerals in combination with iron. It is classified as a transition metal and has a wide range of industrial uses, especially in stainless steel production, due to its ability to enhance strength, workability, and resistance to wear. Manganese oxide serves various purposes, including as an oxidizing agent, rubber additive, and in glassmaking, fertilizers, and ceramics. Manganese sulfate is utilized as a fungicide.

This element occurs naturally in rocks, soil, and water, comprising about 0.1% of the Earth's crust, primarily sourced from crustal rock. Manganese rarely occurs in its pure form and is usually combined with other elements in nearly 300 different minerals. It is extracted from various economically significant oxide minerals, such as pyrolusite, psilomelane, manganite, and wad.

Historically, the use of manganese oxide, specifically pyrolusite, dates back to the time of the Egyptian pharaohs, who employed it in glassmaking. In 1774, the Swedish chemist Carl Wilhelm Scheele identified manganese as an element while working with pyrolusite, and later that same year, his colleague, Johan Gottlieb Gahn, isolated it by heating pyrolusite with charcoal. Manganese had no practical applications until 1839 when it was introduced as an additive in the production of crucible steel. The real turning point came in 1856 with the utilization of ferromanganese in the Bessemer steelmaking process, which proved highly successful.

The primary sources of commercial-grade manganese ore for global use are located in Australia, Brazil, China, Gabon, India, South Africa, and Ukraine. The key minerals containing manganese include pyrolusite (MnO2), romanechite (BaMnMn5O16(OH)4), manganite (Mn2O3H2O), and haussmannite (Mn3O4). It's important to note that "wad" is not a specific mineral but rather a term used to describe amorphous manganese-bearing material with high moisture content.

Manganese is a strategically vital nonferrous element used in the manufacturing of steel, ferromanganese, non-ferrous alloys, dry cell batteries, paints, and various chemicals. The growing demand for this metal is depleting its sources rapidly, prompting significant attention towards improving its extraction from ore and slag (Elsherief, 2019).

Manganese steel, containing approximately 13% manganese, possesses exceptional strength and finds application in products like railway tracks, safes, rifle barrels, and prison bars. Manganese (IV) oxide serves as a catalyst, a rubber enhancer, and is employed to remove green coloration caused by iron impurities in glass. Manganese sulfate, the most extensively produced manganese compound, serves as a crucial raw material for manufacturing various manganese-based products in industries such as dyes, pharmaceuticals, textiles, and others, making the leaching of manganese ore for manganese sulfate production economically significant (Abali et al., 2017).

In the periodic table, manganese is ranked as the twelfth most abundant element overall, the third most prevalent transition metal, trailing only iron and titanium, and the fifth most abundant metal in the Earth's crust. It exists in the Earth's crust at a concentration of 1000 ppm and is found in various minerals, including pyrolusite (MnO2), Hausmannite, Braunite, and manganese spar (MnCO), primarily in countries like Chile, South Africa, Ghana, India, and Russia. Notably, manganese nodules, containing 15 to 30 percent metal on a dry basis and accompanied by copper, nickel, and cobalt, are located on the ocean floor as dense manganese particles. In fact, these nodules have already been harvested from the ocean floor in quantities exceeding 10 tons, with the potential for substantial future commercial significance.

Manganese plays a vital role in biological processes, being an essential element found in food, plants, and the bodies of animals. In its natural state, manganese possesses a single stable isotope with an atomic mass of 55 and several radioactive isotopes with atomic masses ranging from 44 to 69. These radioactive isotopes of manganese are produced through various nuclear reactions, with the most stable ones being Mn (half-life = 3.7 million years) and Mn (half-life = 312.2 days).

Numerous methods have been documented for the leaching and recovery of manganese from its ores. When manganese exists in a soluble divalent form (Mn+2), manganese salts are typically obtained through direct acid leaching. However, when it is present in an insoluble Mn+4 form, the extraction of soluble Mn+2 compounds into solution requires the use of reducing agents (De Michelis et al., 2009). One well-known approach for manganese leaching from its ores involves the use of sulfuric acid (Belyi et al., 2016). Various studies have explored the utilization of different reducing agents, such as natural gases, oxalic acid, methanol, carbohydrates, coal, graphite, sulfur dioxide, hydrogen, cornstalk, and more. After treatment with these agents, the resulting product is then subjected to sulfuric acid leaching (Misra and Khangaonkar, 2015; Guven and Hurman, 2015).

South Africa and Ukraine collectively host over 80% of the world's known manganese resources. Other significant manganese deposits can be found in China, Australia, Brazil, Gabon, India, and Mexico. Economically viable manganese deposits exhibit concentrations that are 150 to 500 times the average abundance in the Earth's crust. Manganese is a mobile element, and various geological processes have led to the creation of naturally occurring concentrations suitable for mining. These deposits of current and future economic importance fall into five categories, each formed by distinct geological processes. These deposits arise from chemical processes that separated manganese during the deposition of marine sediments. Certain sedimentary deposits are particularly extensive, containing substantial quantities of ore. The world's largest manganese deposits fall under the category of sedimentary deposits, which includes those found in the Nikopol District in Ukraine, the Chiatura District in Georgia, and the Kalahari District in South Africa.

Manganese ore, known as Pyrolusite, can be transformed into manganese by two distinct methods. The first involves heating concentrated sulfuric acid to 150°C, and the second employs the electrolysis of an aqueous solution of Manganese (II) sulfate. Alternatively, Pyrolusite can be subjected to heating with dried green vitriol at temperatures below 800°C. In both processes, residual impurities, such as iron oxide and other silicate compounds, are left behind, enabling the leaching of manganese sulfate (MnSO) from the remaining material. After further refinement through crystallization, the Mn (II) sulfate undergoes electrolysis.

Pyrolusite ore is typically formed under conditions of high oxidation and alkaline pH. It is found in various environments, including shallow marine settings, bogs, lacustrine areas, as well as in oxidized zones within manganese-rich deposits and in deposits created through the influence of circulating meteoric water. The formation of Pyrolusite involves both bacterial activity and colloidal processes.The primary producers of Pyrolusite are countries such as India, Brazil, China, Russia, South Africa, and Gabon.

➢ *Problem statement*

Due to the depleting reserves of high-grade hematite iron ores (direct shipping ore (DSO)) and increasing development of low-grade pyrolusite deposits, the need for Manganese ore beneficiation is increasing (Liming, 2015).

Even the DSO ores are requiring a higher level of processing as the depth of existing mines are increasing (below water table) where ores are wet and stickier, which creates challenges for conventional crushing and screening. It is against this background that this work seeks to maximize the amount of Manganese that can be obtained from an ore of Manganese by determining the conditions needed as well as the optimum solution ratio that will cause the maximum amount of Manganese to be obtained.

➢ *Objectives of Study*

The objective of this study is to investigate the optimization of Manganese Extraction from Pyrolusite Using Hydrometallurgical Process with Nitric Acid and Distilled Water as Solvents. Its specific objectives are to:

- Explore the effects of varying nitric acid concentrations, reaction temperatures, agitation rates, and reaction times on the extraction efficiency of manganese from pyrolusite.
- Determine the optimal conditions that yield the highest manganese extraction while minimizing impurity co-dissolution.

II. LITERATURE REVIEW

A. Pyrolusite

Pyrolusite is a mineral primarily composed of manganese dioxide (MnO2) and holds significant importance as a manganese ore source (Reidies, 2002). It typically appears as a black, amorphous mineral with a granular, fibrous, or columnar structure, and it can sometimes form reniform (kidney-shaped) crusts. Pyrolusite displays a metallic sheen, exhibits a black or bluish-black streak, and is readily smudge-inducing. Its specific gravity is approximately 4.8. The name "Pyrolusite" originates from the Greek words denoting "fire" and "to wash," alluding to its historical use in removing impurities from glass (Anthony et al., 2022).

Pyrolusite is one of the most prevalent manganese minerals. It often coexists with minerals like manganite, hollandite, hausmannite, braunite, chalcophanite, goethite, and hematite in oxidizing hydrothermal deposits. Furthermore, it can be found in bogs and frequently results from the transformation of other manganese ores, such as rhodochrosite (Anthony et al., 2022).

Pyrolusite, a widely encountered manganese mineral primarily composed of manganese dioxide (MnO2), is a crucial ore source. This mineral forms in highly oxidizing conditions and manifests as light-gray to black, metallic coatings, crusts, or fibers. These forms represent alteration products of other manganese ores like rhodochrosite, originate in environments like bogs, lakes, or shallow marine areas, and are also found in deposits left behind by circulating waters. Pyrolusite is extracted in various regions, including Germany, Brazil, India, the United States, Cuba, Morocco, Ghana, and South Africa. It serves diverse applications in the manufacturing of steel and manganese bronze, as well as in dry cells, and is employed as a decolorizing agent in the glass industry.

Pyrolusite takes shape in environments characterized by high oxidation levels, influenced by atmospheric oxygen, and elevated pH levels. Consequently, it primarily occurs within the sedimentary cycle, arising as a result of weathering processes affecting other manganese minerals, particularly manganite, which it often replaces in a pseudomorphous manner. It develops in oxidation zones that form over rocks and hydrothermal deposits containing manganese. Additionally, Pyrolusite is found in deposits formed through the influence of meteoric waters. The formation of Pyrolusite is greatly influenced by colloidal processes and the activity of bacteria.

This mineral predominantly originates in environments like swamps and lakes and can also be found in shallow marine conditions, often displaying an oolitic texture. In its occurrences, Pyrolusite is commonly associated with typical gangue minerals such as quartz (including chalcedony), calcite, and barite. It coexists with a variety of other manganese minerals, including manganite, hollandite, jacobsite, psilomelane, cryptomelane, hausmannite, braunite, todorokite, chalcophanite, alabandite, bixbyite, and rhodonite. Furthermore, it can be found alongside minerals like goethite, hematite, magnetite, malachite, vanadinite, and gold.

- *Characteristics of Pyrolusite*

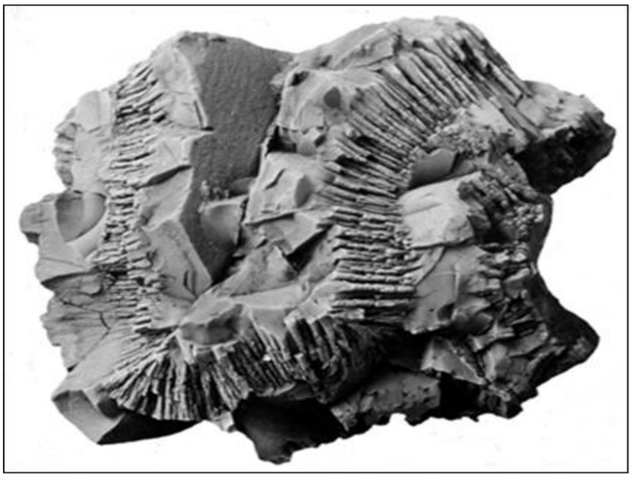

Fig 1 Pyrolusite Ore

- **Color** is steel gray to a solid black in earthy specimens.
- **Luster** is metallic to dull in weather or thinly crusted specimens.
- **Transparency** crystals are opaque, translucent in only thin splinters.
- **Crystal System** is tetragonal; 4/m 2/m 2/m
- Crystal Structure: Pyrolusite typically presents itself in massive and compact forms. However, it can also take on various other structures, including fibrous, acicular, columnar, concretionary, scaly, and earthy forms. In particular, a thin dendritic structure is often observed encrusting sandstones and siltstones, forming intricate patterns resembling ferns or trees, which can be mistakenly identified as fossil plants. A variation featuring large, easily visible crystals is known as "polianite," characterized by minute prismatic crystals with a square or rectangular cross-section and wedge-shaped terminations.
- Cleavage: Although pyrolusite can exhibit good cleavage in two directions, this feature is rarely observed, especially in large crystals.
- Fracture: The mineral generally displays conchoidal to uneven fracture patterns.
- Hardness: Individual pyrolusite crystals possess a hardness rating of 6 on the Mohs scale. However, aggregates can be softer, with hardness levels ranging from 4 to 5. In its massive or earthy forms, pyrolusite is even softer, marking paper and leaving a powdery residue on fingers (indicating a hardness below 2).
- Specific Gravity: Pyrolusite has a specific gravity that typically falls within the range of 4.4 to 5.1, which is an average value for metallic minerals.
- Streak: The streak of pyrolusite is black.
- Associated Minerals: Pyrolusite is often found in association with minerals such as limonite, hematite, quartz, manganite, psilomelane, and other manganese and iron oxide minerals.
- Notable Occurrences: Notable occurrences of pyrolusite include Germany, iron mines in Minnesota and Michigan, and Lake County, New Mexico, USA. This mineral is mined in various countries worldwide, with the most productive ones being Georgia and Ukraine (formerly part of the USSR), India, China, South Africa, Brazil, Australia, and Gabon. Polianite is abundant at the Kisenge Mine in Zaire.
- Best Field Indicators: Identification of pyrolusite is aided by its distinctive habits, luster, softness, color, and streak

- *Chemical Composition of Pyrolusite*

Pyrolusite is a mineral with the chemical formula MnO_2. The pyrolusite ore contains the following minerals;

- Manganese
- Manganese (IV) Oxide
- Manganese (II) Oxide
- Iron
- Silica
- Aluminium Oxide
- Calcium Oxide
- Sulphur
- Phosphorus

B. *Uses of Pyrolusite*

- It is used in the manufacture of green and violet paints.
- It is used to prepare disinfectant and for decolorizing glass.
- As a coloring material, pyrolusite is used in calico printing and dyeing.
- It is used for imparting black, violet, and amber colors to glass, pottery, and bricks.
- It is extensively used in the preparation of various alloys such as manganese-bronze.
- As an oxidizing agent, pyrolusite is used in the preparation of chlorine.
- Pyrolusite is extensively used for the manufacture of spiegeleisen and ferro-manganese and of various alloys such as manganese-bronze.
- When mixed with molten glass it oxidizes the ferrous iron to ferric iron, and so discharges the green and brown tints.

- *Pyrolusite is the primary source of manganese, and its extraction is crucial for the supply of this critical element. However, the extraction of manganese from pyrolusite is a complex process that requires the optimization of various parameters. These parameters include:*

- Beneficiation of Pyrolusite
- Leaching
- Purification
- Electrolysis

C. Beneficiation of Pyrolusite

Pyrolusite ore typically contains various minerals and impurities, including elements like iron and silica, which can have a detrimental impact on the efficiency of the extraction process. Hence, it is often necessary to carry out beneficiation procedures to eliminate these impurities and enhance the ore's quality before the leaching process.

In a study conducted by Zhang and colleagues in 2018, they explored the application of reduction roasting and magnetic separation as a beneficiation method to facilitate the extraction of manganese from pyrolusite ore rich in iron. The researchers observed that this technique proved effective in eliminating iron impurities from the ore and augmenting the manganese content in the resulting concentrate. The optimized procedure entailed subjecting the ore to roasting at 600°C for 30 minutes, followed by magnetic separation utilizing a magnetic intensity of 0.3 T. This investigation illustrated the efficiency of this approach in enhancing the quality of pyrolusite ore, making it more suitable for subsequent leaching processes.

D. Leaching

The initial stage in extracting manganese from pyrolusite involves a process known as leaching. In the quest to optimize manganese extraction from pyrolusite, leaching is a commonly employed method. Among the various techniques, sulfuric acid leaching stands out as one of the most widely utilized methods for extracting manganese from pyrolusite. In this procedure, finely ground pyrolusite ore is blended with sulfuric acid and heated to facilitate the dissolution of manganese into the solution. Subsequently, further processing steps are applied to isolate the manganese and eliminate any impurities. Additional leaching techniques employed for extracting manganese from pyrolusite encompass acid leaching using citric acid, hydrochloric acid, or hydrofluoric acid, as well as alkali leaching with sodium hydroxide or ammonium hydroxide. The efficiency of the leaching process hinges on various factors, including acid concentration, temperature, and duration, with the aim of optimizing extraction while minimizing the consumption of chemicals and energy.

Numerous studies have delved into enhancing leaching conditions for manganese extraction from pyrolusite. For instance, Chen and colleagues (2017) conducted research examining the impact of sulfuric acid concentration, temperature, and reaction time on the efficiency of manganese leaching from pyrolusite. Their findings revealed that augmenting acid concentration and temperature could enhance leaching efficiency, although the effect of reaction time was somewhat limited.

Li and their team (2019) also explored the enhancement of leaching conditions and determined that as the acid concentration and temperature increased, the leaching efficiency likewise improved. They further noted that the introduction of an oxidizing agent, such as hydrogen peroxide, had the capacity to further boost leaching efficiency. Additionally, Kao and associates (2018) delved into the application of microwave-assisted leaching for the extraction of manganese from low-grade pyrolusite ore. Their research revealed that this method effectively amplified leaching efficiency and shortened the required leaching duration in comparison to conventional leaching techniques. The optimized process entailed utilizing an aqueous SO2 solution as the leaching agent and subjecting the ore to microwave irradiation at a power level of 900 W for a duration of 30 minutes. This study underscored the potential of microwave-assisted leaching as a technique to refine the leaching process for extracting manganese from pyrolusite.

E. Purification of Manganese

Following the leaching process, it is essential to purify the solution containing soluble manganese salts by eliminating impurities like iron, aluminum, and calcium, and to isolate the desired metal. The presence of these impurities can negatively impact the quality of the final product and reduce the efficiency of the extraction process. Various purification techniques have been developed for the extraction of manganese from pyrolusite. These methods encompass solvent extraction, precipitation, and electro-winning.

For instance, Kao and colleagues (2012) explored the application of solvent extraction to eliminate iron from a solution containing both manganese and iron. They determined that the introduction of an extractant, such as D2EHPA, proved effective in removing iron from the solution. In a separate study, Cheng and their team (2015) investigated the use of precipitation and adsorption methods to eliminate impurities from a manganese solution. Their findings revealed that the addition of a precipitant, like sodium hydroxide, was efficient in removing aluminum and calcium from the solution, while employing an adsorbent, such as activated carbon, effectively eliminated organic impurities

Li and colleagues (2020) conducted a study to examine the utility of solvent extraction as a purification method for extracting manganese from pyrolusite. They employed a mixed extractant consisting of di(2-ethylhexyl) phosphoric acid (D2EHPA) and tributyl phosphate (TBP) to facilitate the extraction of manganese from the leach solution. Their investigation determined that the ideal extraction conditions included maintaining a pH level of 2, employing an organic-to-aqueous phase ratio of 1:1, and conducting the extraction for a period of 5 minutes. This study underscored the efficiency of solvent extraction in the purification of manganese extracts from pyrolusite.

In a separate study, Hwang and their team (2019) explored the use of precipitation as a purification technique for extracting manganese from pyrolusite. They observed that the introduction of ammonium carbonate to the leach solution effectively caused the precipitation of impurities such as aluminum and calcium. This, in turn, enabled the selective precipitation of manganese in the form of manganese carbonate. The research demonstrated the potential of precipitation as a method for purifying manganese extracts from pyrolusite

- *Electrolysis*

Electrolysis serves as the concluding phase in the process of extracting manganese from pyrolusite, involving the conversion of soluble manganese salts into metallic manganese. The efficacy of this electrolysis process is contingent upon a range of factors, including current density, temperature, and the composition of the electrolyte. Electrolysis, as a method, employs electrical energy to facilitate a chemical reaction. In the context of manganese extraction, it is harnessed to further refine the purified manganese solution derived from preceding stages.

This electrolysis process entails the utilization of an electrolytic cell, housing both an anode and a cathode submerged in the manganese solution. When an electric current course through the cell, manganese ions within the solution undergo reduction at the cathode, concurrently leading to the liberation of oxygen gas at the anode. This reduction of manganese ions results in the deposition of metallic manganese on the cathode's surface, subsequently amenable to further processing to acquire high-purity manganese products.

Numerous factors bear influence on the efficiency and effectiveness of the electrolysis process when it comes to extracting manganese from pyrolusite. These influential factors encompass the constitution of the electrolyte solution, the magnitude of current density, the prevailing temperature, and the material comprising the electrodes. The electrolyte solution's composition stands out as a pivotal factor as it dictates the concentration of manganese ions and other impurities within the solution. A higher concentration of manganese ions in the electrolyte solution translates to a heightened deposition rate of metallic manganese on the cathode surface. However, the presence of impurities, such as iron and calcium ions, can disrupt the electrodeposition process and impact the quality of the final manganese product.

The magnitude of current density is another pivotal factor in the electrolysis process, carrying a dual impact on both the rate of electrodeposition and the ultimate quality of the resulting product. A heightened current density may expedite the deposition of manganese on the cathode surface; however, it can also give rise to the formation of dendritic structures and the production of subpar manganese products. The temperature of the electrolyte solution plays a significant role in influencing the electrodeposition process, with elevated temperatures augmenting the solubility of manganese ions and facilitating the deposition of metallic manganese on the cathode surface. The choice of electrode material stands as another vital determinant in the efficacy and efficiency of the electrolysis process. Common electrode materials employed in the extraction of manganese from pyrolusite encompass graphite, lead, and stainless steel. Graphite is often favored due to its excellent electrical conductivity and resistance to corrosion. Conversely, lead and stainless steel are employed for specialized applications owing to their distinct properties.

Numerous studies have delved into the optimization of electrolysis conditions for manganese extraction from pyrolusite. For instance, Zhang and colleagues (2017) explored the influence of current density and temperature on the electrolysis efficiency of manganese, affirming that heightened current density and temperature could enhance the efficiency of the electrolysis process. However, the impact of electrolyte composition was found to be limited. Furthermore, Li and their team (2016) undertook investigations into the optimization of electrolysis conditions and observed that the introduction of a complexing agent, such as EDTA, had the potential to amplify the efficiency of the electrolysis process.

- *Overall Optimization*

Efficiently optimizing each facet of the manganese extraction process is of paramount importance to attain the highest extraction efficiency while curbing costs. Multiple research studies have delved into the comprehensive optimization of the extraction process from pyrolusite. For instance, Peng and their colleagues (2018) harnessed response surface methodology to fine-tune the leaching and purification conditions for extracting manganese from pyrolusite. Their investigations pinpointed that the most favorable leaching conditions entailed an acid concentration of 1.5 M, a temperature of 70°C, and a reaction time of 3 hours. Likewise, the optimal purification conditions were characterized by a pH of 6.5 and a D2EHPA concentration of 20% (v/v). Remarkably, they achieved a remarkable extraction efficiency of 97.6% under these circumstances.

Similarly, Wang and their team (2020) undertook a study to optimize the entire extraction process, encompassing leaching, solvent extraction, and electrolysis. They established that the prime leaching conditions involved an acid concentration of 1.5M, a temperature of 70°C, and a reaction time of 4 hours. Concurrently, the most advantageous purification conditions featured a pH of 6.5 and a D2EHPA concentration of 20% (v/v). Their study also extended to the optimization of electrolysis conditions, culminating in the achievement of an impressive extraction efficiency of 98.7% under these particular parameters.

- *Green Extraction*

The process of extracting manganese from pyrolusite is resource-intensive, demanding substantial energy and chemical inputs. As a result, there is a growing interest in the development of eco-friendly extraction methods aimed at mitigating the environmental footprint and cost associated with the extraction process. Numerous studies have explored the application of environmentally friendly extraction techniques for manganese extraction from pyrolusite.

For instance, Li and their team (2021) investigated the use of ultrasound-assisted leaching to boost the leaching efficiency of manganese from pyrolusite. Their research revealed that ultrasound had the capacity to enhance leaching efficiency by augmenting the surface area of the pyrolusite particles and diminishing diffusion resistance.

Likewise, Wang and their colleagues (2019) delved into the potential of bioleaching for extracting manganese from pyrolusite. They discovered that the introduction of acidophilic bacteria, such as Acidithiobacillus ferrooxidans, could heighten the leaching efficiency of manganese by facilitating the oxidation of pyrolusite and the generation of soluble manganese salts.

F. *Methods of Leaching*

There are two main methods of carrying the leaching process;

- *Simple Leaching:* This is carried out at ambient temperature and atmospheric pressure.
- *Pressure Leaching:* this method is carried out at increased temperature and pressure in order to accelerate the operation.

G. *Types of Leaching*

There are four types of leaching namely;

➢ *Cyanide Leaching (Gold Ore)*

Cyanide leaching has been the industry standard for gold processing for more than 100 years. During the cyanide leach process, a cyanide solution, or lixiviant, is percolated through ore contained in vats, columns or heaps. Gold is dissolved by the cyanide and then removed from the heap or columns.

➢ *Ammonia Leaching*

Ammonia leaching primarily relies on the complexation of NH_3 with Ni^{2+} and Co^{2+} to generate stable ammonia complexes $Ni\ (NH_3)_6^{2+}$ and $Co\ (NH_3)_6^{3+}$. Therefore, it is commonly used as a powerful reagent for the selective leaching of Ni and Co from materials that contain those metals.

➢ *Alkali Leaching*

Alkali leaching is an effective method used to purify graphite and remove silicate minerals.

➢ *Acid Leaching*

It is a metallurgical process for dissolution of metals by means of acid solution. Examples include extraction of copper from oxide- or sulfide-bearing ore and dissolution of uranium from sandstone ores.

➢ *Factors Affecting the Process of Leaching*

- *Particle Size*

The rate of leaching can be greatly improved by the grinding process which reduces the particle size. The smaller the particle size the faster the rate of leaching.

- *Temperature*

The leaching rate of heavy metals is directly related to the ambient temperature, so an increase in temperature can accelerate the leaching process of heavy metals.

- *Solvent Concentration*

The rate of leaching is proportional to the concentration of solvent. Therefore, increasing the solvent concentration is conductive to the improvement of the leaching reaction rate.

- *Agitation Rate*

As the diffusion thickness decreases, the leaching reaction kinetics will increase with the suspension agitation. Therefore, the leaching process will be faster as well as the metal recovery.

- *Surface Area*

Through increasing its specific surface area and causing its lattice defects, the activity of mineral is extremely increased to improve the leaching rate of rare-earth elements without adding a reducing agent and introducing impurities.

- *Microorganism Activity*

This plays an important role in bioleaching which is the use of microorganisms and their microbial activity to leach the desired components. The effectiveness of the microorganism will determine the rate of leaching.

➢ *Limitations of leaching process*

- Leaching can be a slow process, taking many hours or even days to complete
- The leaching process can be expensive, depending on the type of leaching process used
- Leaching can produce hazardous waste products that must be handled and disposed of safely
- Leaching removes vital nutrients and micronutrients, such as water-soluble boron, from the soil, causing potential deficiencies in crops

➢ *Applications of Leaching*

The various applications of leaching are as follows:

- The food processing industries make use of leaching. One of the examples is the extraction of sugar from sugar beets.
- This technique is also used in metal processing industries where metals are removed from its ores. Like in order to extract gold from its ore, sodium cyanide solution is used.
- Pharmaceutical industries also make use of leaching where we get various products by performing leaching of roots, leaves, stems of plants.
- The extraction of oils from peanuts, soybeans, sunflower seeds, cotton seeds, and halibut livers.

III. MATERIALS AND METHODS

A. *Materials*

To achieve the aim of obtaining the optimum conditions necessary for leaching of manganese to happen, some materials and equipment’s were put to use, The main raw material used is pyrolusite ore gotten from Jos, Plateau State, Nigeria.

Fig 2 Grounded Ore of Pyrolusite

➢ *Reagents*

- Nitric acid
- Manganese
- Distilled water

➢ *Apparatus*

- Magnetic stirrer
- Reflux condenser
- Mechanical shaker
- 500ml flat bottom flask
- Condenser
- Digital analytical balance
- Mortar and pestle
- Volumetric flask
- Measuring cylinder
- Whatman filter paper
- Conical flask
- Beaker
- Sieve
- Atomic Adsorption Spectrophotometer (AAS)

Fig 3 (a)Atomic Adsorption (b)Sample on a Hot magnetic Spectrophotometer (AAS) Stirrer

B. *Methods*

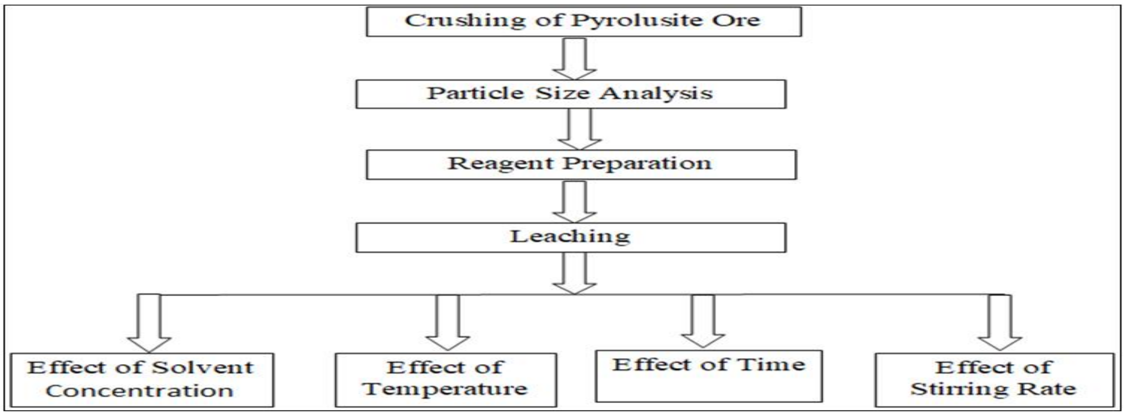

Fig 4 Process Flow Diagram for the Leaching Process

- *Raw Material Preparation*

Pyrulosite ore used in this study was crushed with the mortar and pestle and subjected to particle size analysis with the aid of a mechanical shaker. The crushed ore was placed on the sieve with a mesh size of 0.4mm. The mechanical shaker was set tightly by adjusting the knobs, and was turned on for 30minutes in order to get the required particle size of 0.4mm. Particle size of 0.4mm was used for the analysis.

- *Adsorption Studies*

- *Effect of Solvent Concentration*

Different concentration of nitric acid (2M, 4M, 6M, 8M & 10M) were prepared with 50ml of distilled water. 50ml of the acid solution was emptied into a flat bottom flask containing 0.9g of 0.4mm particle size of the pyrulosite ore. The solution was then plugged with a reflux condenser of soxhlet apparatus on a magnetic stirrer with stirring speed of 300rpm at temperature of 60^0C for 60, 90 & 120minutes respectively until equilibrium was reached. The samples were filtered using whatman filter and the filtrate stored in sample bottle for manganese assay with Atomic Adsorption Spectrophotometer (AAS)

- *Effect of Temperature*

Temperature effect of 30, 45, 60, 70 & 80^0C were observed with varying time of 60, 90 and 120 minutes at constant weigh of 0.9g adsorbent with stirring speed of 400rpm to vary temperatures until equilibrium was reached. The samples were filtered using Whatman filter and the filtrate stored in sample bottle for manganese assay with Atomic Adsorption Spectrophotometer (AAS).

- *Effect of Time*

Time effect of 30, 60, 90, 120 & 150 minutes were observed with varying temperature of 60, 70 and 80^0C at constant weigh of 0.9g adsorbent with stirring speed of 400rpm to vary time until equilibrium was reached. The samples were filtered using Whatman filter and the filtrate stored in sample bottle for manganese assay with Atomic Adsorption Spectrophotometer (AAS).

- *Effect of Stirring Speed*

Stirring rate of 200, 300, 400, 500 & 600rpm were observed with varying time of 60, 90 and 120 minutes at constant weigh of 0.9g adsorbent with stirring speed of 400rpm to vary stirring speed until equilibrium was reached. The samples were filtered using Whatman filter and the filtrate stored in sample bottle for manganese assay with Atomic Adsorption Spectrophotometer (AAS).

IV. PRESENTATION AND DISCUSSION OF RESULTS

Table 1 Effect of Solvent Concentration on the Leaching of Manganese from Pyrulosite

Time (minutes)	**Concentration of Manganese (mol/dm^3)**				
	2M	**3M**	**6M**	**8M**	**10M**
60	54.648	74.517	56.852	53.459	59.778
90	66.466	81.117	102.883	82.870	102.842
120	139.256	123.906	61.504	75.925	96.889

From table 1 above the highest concentration of manganese was obtain at 2M solvent concentration and at a time of 120 minutes while the lowest concentration was obtained at 8M solvent concentration and at a time of 60 minutes. The above results are presented in the fig below.

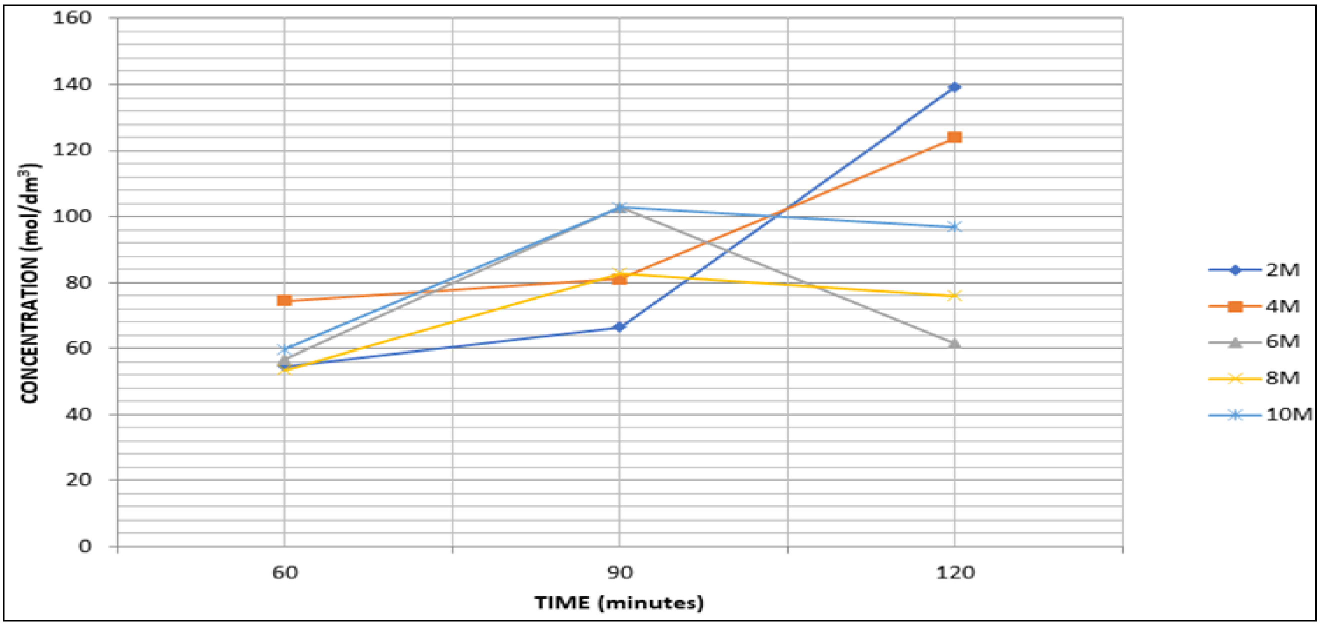

Fig 5 Graph of Concentration of Manganese against Time at Different Solvent Concentrations

From Fig 5 above it can be seen that for solvent concentration of 2M, the concentration of manganese increases as the time increases. Therefore, longer leaching time is required for very small solvent concentration. When the solvent concentration was 4M, the concentration of manganese also increases as the time for leaching increases as the solvent concentration is still low. When the solvent concentration was 6M, the concentration of manganese is seen to increase then it starts decreasing. The same trend occurs for solvents concentrations of 8M and 10M. This is as result of the fact that as solvent concentration increases the rate of leaching also increases but at prolonged time there is depletion of soluble substances in the solid matrix leading to a reduction of the leaching rate hence the reduction in the concentration of manganese.

Table 2 Effect of Temperature on the Leaching of Manganese from Pyrolusite Ore

Time (minutes)	**Concentration of Manganese (mol/dm^3)**				
	30°C	**45°C**	**60°C**	**70°C**	**80°C**
60	147.577	101.765	103.349	45.090	175.532
90	110.464	99.635	84.859	108.936	72.607
120	178.941	114.689	156.200	137.591	142.364

From table 2 above the highest concentration of manganese was obtained at a temperature of 30°C and at a time of 120 minutes while the lowest was obtained at a temperature of 70°C and at a time of 60 minutes. The above results are presented in Fig 6 below.

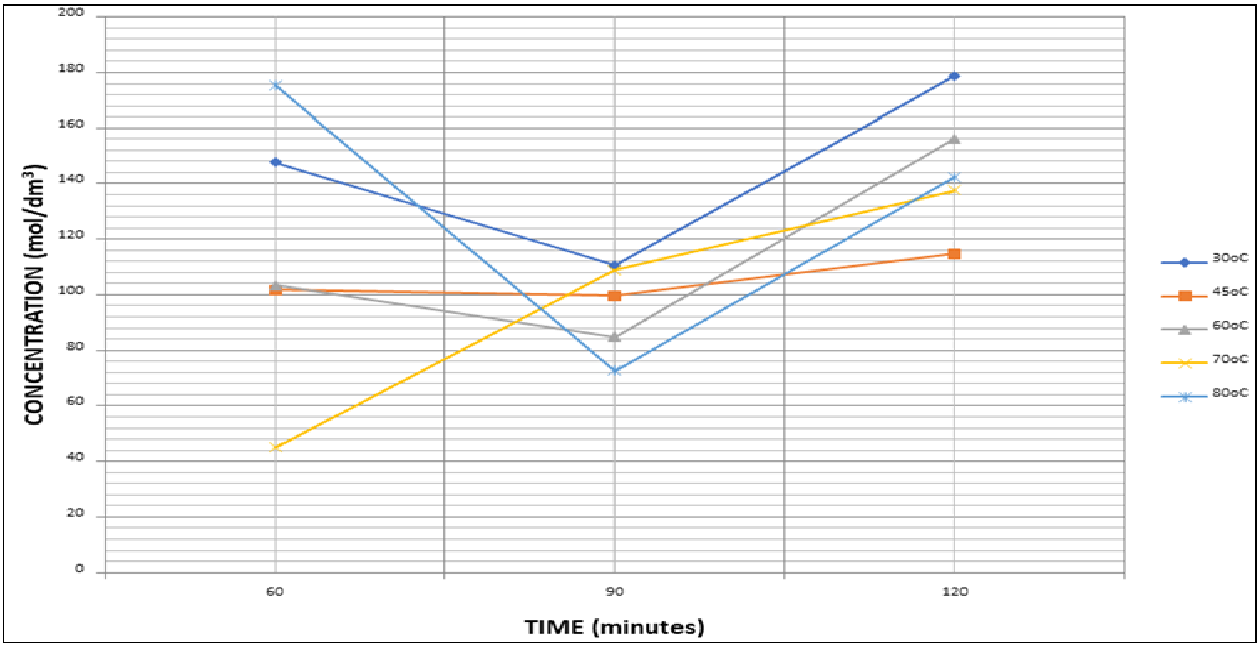

Fig 6 Graph of Concentration of Manganese against Time at Different Temperatures

From Fig 6 above for all the temperatures there is a general increase in the concentration of manganese as the leaching time increases for the various temperatures except at 80°C. This general increase in manganese concentration is as a result of the fact that as the leaching time increases there is enhanced dissolution of the solute in the solvent. But at 80°C there is a decrease due to the fact that prolong leaching at high temperatures results in the depletion of soluble substances in the solid matrix. The highest concentration of manganese was obtained at 30°C and at 120 minutes because low temperatures require prolong time for effective dissolution of the solute while the at the highest temperature which is 80°C, the highest manganese concentration was obtained at 60 minutes because high temperatures require small leaching time to avoid depletion of the soluble substances.

Table 3 Effect of Time on the Leaching of Manganese from Pyrolusite Ore at different Temperatures

Temperature (°C)	**Concentration of Manganese (mol/dm^3)**				
	30mins	**60mins**	**90mins**	**120mins**	**150mins**
60	172.796	189.369	175.218	163.142	138.252
70	142.091	191.928	170.218	152.153	77.167
80	131.835	142.364	101.901	89.929	49.180

From table 3 above the lowest concentrations of manganese for each of the temperatures were obtained at a leaching time of 150 minutes and the highest at 60 minutes. They results from the table above is presented in Fig 7 below.

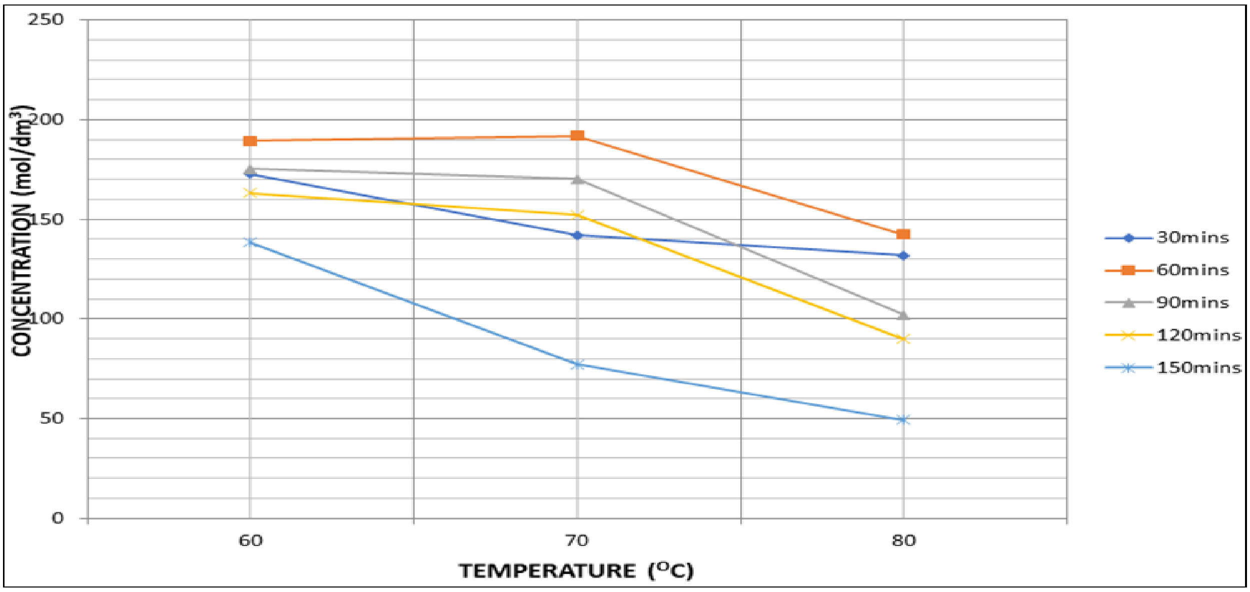

Fig 7 Graph of Concentration of Manganese against Temperature at Different Leaching Times

From Fig 7 the concentration of manganese decreases as the temperature for leaching increases for the different leaching times. This shows that an increment in temperature does not increase the rate of leaching but rather it reduces the leaching rate. Also, from the graph above it can be seen that as the leaching time increases for each temperature, there is a decrease in the concentration of manganese because leaching at a prolong time at high temperatures leads to depletion in the rate of dissolution. Therefore, moderate reaction times are required for leaching at high temperatures.

Table 4 Effect of Stirring Rate on the Leaching of Manganese from Pyrolusite Ore

Time (minutes)	**Concentration of Manganese (mol/dm^3)**				
	200rpm	**300rpm**	**400rpm**	**500rpm**	**600rpm**
60	168.180	160.035	135.656	189.351	172.568
90	130.237	16.389	18.494	7.862	0.000
120	0.000	0.000	95.768	92.766	74.149

From Table 4 above, the highest concentration of manganese was obtained at a stirring speed of 500rpm at 60 minutes, the highest concentration at 90 minutes was obtained at a stirring speed of 200rpm and at 120 minutes the highest concentration of manganese was obtained at a stirring speed of 400rpm. The maximum concentration of manganese from the study was obtained at 60 minutes and at a speed of 500rpm. They results from the above table is presented in Fig 8 below.

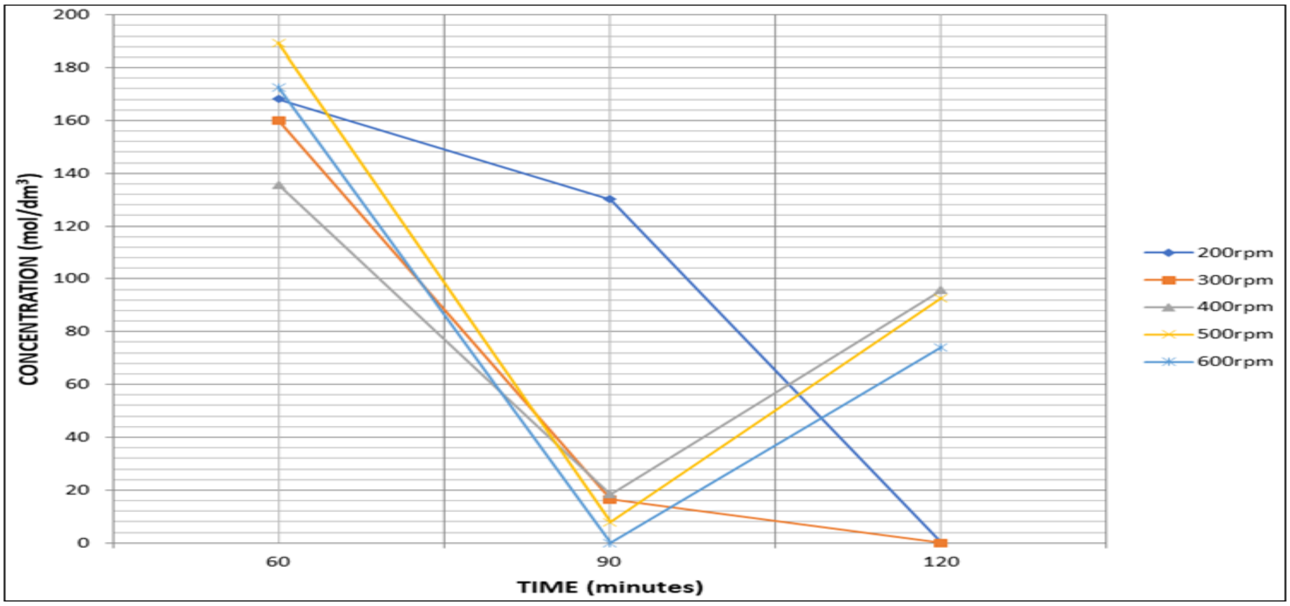

Fig 8 Graph of Concentration of Manganese against Time at Different Stirring Speeds

From Fig 8 above it can be seen that generally as the leaching time increases, the concentration of manganese decreases at the different stirring speeds. The highest concentration of manganese was obtained at a speed of 500rpm because as the stirring rate increases the rate of dissolution of solute also increases.

V. CONCLUSION

In conclusion, the investigation into the effects of varying nitric acid concentrations, reaction temperatures, agitation rates, and reaction times on manganese extraction from pyrolusite has provided valuable insights into the intricacies of the hydrometallurgical process. The systematic exploration of these parameters has highlighted the complex interplay between process variables and their impact on extraction efficiency and impurity co-dissolution. This research significantly contributes to our understanding of optimizing manganese recovery and refining processes from pyrolusite using nitric acid and distilled water.

RECOMMENDATIONS

➢ *Based on the findings of this study, several key recommendations can be made for further research and industrial application:*

- Solvent systems such as organic acids or chelating agents could potentially increase selectivity and facilitate higher extraction efficiencies. Rigorous solvent compatibility and optimization studies should be conducted to identify synergistic combinations that enhance both extraction rates and product purity.
- By understanding the thermodynamics and kinetics of impurity dissolution and co-precipitation, tailored mitigation strategies can be developed to minimize impurity co-dissolution. This approach will contribute to producing high-purity manganese products suitable for downstream applications.
- The integration of automation and feedback systems will enable rapid adjustments to optimize conditions based on real-time performance data. Continuous monitoring can lead to improved process stability, reduced variability, and enhanced overall efficiency.
- The proposed process should be compared against alternative extraction methods to quantify its potential environmental benefits, including reduced energy consumption, minimized waste generation, and lower greenhouse gas emissions. Based on LCA results, identify opportunities for further sustainability improvements and resource efficiency.

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