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ANALYSIS OF MnO_2 RECOVERY STUDY FROM DRYCELL BATTERY WASTE: A REVIEW

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Abstract

Global demand for manganese dioxide (MnO_2) materials is increasing rapidly as the battery and catalyst industry develops, while the availability of primary ores continues to decline. Waste dry cell batteries contain high amounts of MnO_2, making them potentially a secondary source of economically valuable manganese metals. This study systematically discusses various microwave-assisted hydrometallurgy-based hydrometallurgy approaches for the recovery of MnO_2 from waste batteries. The literature study was conducted by examining 50 current scientific references covering three main aspects: extraction methods, the influence of heating methods, and purification strategies. The core conclusion of this review is that microwave-assisted leaching represents the most efficient extraction approach, delivering recovery rates up to 95.1% that significantly surpassing conventional methods (82–85%) while reducing reaction times and energy consumption by up to 40%. Furthermore, this study concludes that chemical oxidation using $KMnO_4$ is the superior purification strategy, capable of producing MnO2 with purity exceeding 98%. Consequently, this review establishes that the integrated system of microwave-assisted leaching and selective KMnO4 oxidation offers the most robust, economical, and environmentally friendly blueprint for implementing a circular economy in the metals industry.

Keywords: Hydrometallurgy, Microwave, Manganese Dioxide, Dry Cell Battery, Chemical Oxidation

Abstrak

Permintaan global terhadap bahan mangan dioksida (MnO_2) meningkat pesat seiring dengan perkembangan industri baterai dan katalis, sementara ketersediaan bijih primer terus menurun. Baterai kering bekas mengandung jumlah MnO_2 yang tinggi, menjadikannya sumber sekunder yang berpotensi untuk logam mangan yang bernilai ekonomi. Studi ini secara sistematis membahas berbagai pendekatan hidrometalurgi berbasis mikrowave untuk pemulihan MnO_2 dari baterai bekas. Studi literatur dilakukan dengan menganalisis 50 referensi ilmiah terkini yang mencakup tiga aspek utama: metode ekstraksi, pengaruh metode pemanasan, dan strategi pemurnian. Kesimpulan utama dari studi ini adalah bahwa leaching yang didukung microwave mewakili pendekatan ekstraksi paling efisien, dengan tingkat pemulihan hingga 95,1% yang secara signifikan melampaui metode konvensional (82–85%) sambil mengurangi waktu reaksi dan konsumsi energi hingga 40%. Selain itu, studi ini menyimpulkan bahwa oksidasi kimia menggunakan $KMnO_4$ merupakan strategi pemurnian yang lebih unggul, mampu menghasilkan MnO_2 dengan kemurnian melebihi 98%. Studi ini menunjukkan bahwa sistem terintegrasi antara ekstraksi dengan bantuan microwave dan oksidasi selektif menggunakan $KMnO_4$ menawarkan kerangka kerja yang paling tangguh, ekonomis, dan ramah lingkungan untuk menerapkan ekonomi sirkular di industri logam.

Keywords: Hidrometalurgi, Gelombang Mikro, Mangan Dioksida, Baterai Dry Cell, Oksidasi Kimia

1. Introduction

The growth in the use of disposable electronic devices, especially dry cell batteries, has led to a significant increase in electronic waste worldwide. The primary battery market (non-rechargeable such as Alkaline/Zinc-Carbon) is projected to continue to grow at a CAGR of around 5-6% per year. This means that every year the volume of disposable batteries that enter the market (and eventually become garbage) continues to increase by millions of units (Jasson, 2016). According to the Data Insight Market Report, the consumption of dry cell batteries increases from $9.649 billion in 2024

to $10.79 billion in 2025 and to $18.86 billion in 2030. Dry cell batteries are a common source of electrochemical energy used in household appliances because they are inexpensive, readily available and have good durability. The main components of batteries consist of a zinc (Zn) anode, a manganese dioxide (MnO_2) cathode, an ammonium chloride (NH_4Cl) electrolyte, and carbon as a current conductor (Peng et al., 2020). After their useful life, dry cell batteries become hazardous solid waste that has the potential to contaminate soil and water due to their heavy metal content, such as Mn, Zn, and Fe. On the other hand, the MnO_2 composition, which reaches more than 60%, makes this waste a potential source of manganese, which has high economic value (Zhao et al., 2023).

Manganese dioxide (MnO_2) is an important inorganic material with various industrial applications, including as a cathode material in rechargeable batteries, an oxidation catalyst, and an adsorbent in water treatment (Xie et al., 2024). In dry cell batteries, MnO_2 acts as the main electron acceptor in the reduction reaction during the energy release process. Manganese dioxide functions as the cathode where Mn^{4+} is reduced to Mn^{3+} by accepting an electron and intercalating a proton (H+) to form manganese oxyhydroxide (MnO(OH)) that explained by Eq (1). The semiconductor properties and high oxidation capacity of MnO_2 mean that this material is often reused after purification. However, the limited reserves of primary manganese ore and the increasing volume of battery waste make the recovery of MnO_2 from used battery waste a strategic alternative to support the principles of the circular economy (Rahimpour et al., 2024). Manganese dioxide functions as the cathode where Mn^{4+} is reduced to Mn^{3+} by accepting an electron and intercalating a proton (H+) to form manganese oxyhydroxide (MnO(OH)) that explained by Eq (1). The semiconductor properties and high oxidation capacity of MnO_2 mean that this material is often reused after purification. However, the limited reserves of primary manganese ore and the increasing volume of battery waste make the recovery of MnO_2 from used battery waste a strategic alternative to support the principles of the circular economy (Rahimpour et al., 2024) (Singh & Gupta, 2024).

$$MnO_2 + H^+ + e^- \rightarrow 2MnO(OH)^+ \quad (1)$$

Various approaches have been developed to extract metals from battery waste, one of which is through hydrometallurgy. In general, hydrometallurgy is a process of separating metals from solid materials using liquid solvents through the stages of leaching, purification, and redeposition (Free & Moats, 2015). This method is more environmentally friendly than pyrometallurgy because it operates at low temperatures and produces minimal gas emissions. In the context of manganese recovery, the leaching process involves the reduction reaction of Mn^{4+} to Mn^{2+} using strong acid solvents such as H_2SO_4 or HCl with the help of reducing agents such as H_2O_2 or oxalic acid. The acidic medium protonates the oxide surface while the reducing agent transfers electrons to the Mn^{4+} centers, destabilizing the crystal lattice to release soluble Mn^{2+} ions into the solution. (Baba et al., 2014). Reaction mechanism explained by Eq. (2) & (3).

$$2MnO_{2(s)} + 2H^+_{(aq)} \rightarrow 2Mn^{2+}_{(aq)} + 2H_2O_{(l)} + O_{2(g)} \quad (2)$$

$$MnO_{2\,(s)} + H_2O_{2\,(aq)} + 2H^+_{(aq)} \rightarrow Mn^{2+}_{(aq)} + 2H_2O_{(l)} + O_{2\,(g)} \quad (3)$$

The efficiency of the hydrometallurgical process is highly dependent on operating parameters such as pH, time, temperature, and the heating method used (Lie & Liu, 2021). With technological advances, microwave-assisted heating has begun to be used in hydrometallurgical processes to accelerate leaching and improve energy efficiency. Microwave heating works by utilizing electromagnetic radiation to produce volumetric heating in solutions and solids simultaneously. This process offers the advantages of shorter reaction times, low energy consumption, and uniform heat distribution(Lin, Gao, et al., 2020). Research by Alhassan and Zhang (2022) shows that the use of microwave-assisted leaching can increase Mn recovery to more than 90% compared to conventional methods, which only achieve 70–80%.

The purification stage plays a critical role in determining the overall efficiency and economic feasibility of hydrometallurgical MnO_2 recovery from leaching solutions. The primary objective of this step is to produce high-purity MnO_2 by selectively removing metallic impurities such as Fe, Zn, and Cu. Commonly applied purification techniques include selective precipitation, chemical oxidation, solvent extraction, and electrodeposition (Faria et al., 2014). Among these approaches, chemical oxidation using $KMnO_4$ demonstrates superior selectivity, enabling the conversion of Mn^{2+} to Mn^{4+} at room temperature and achieving MnO_2 purities of 94–96% (Tian et al., 2010). When combined with microwave-assisted leaching, this purification route forms a highly profitable process configuration by coupling rapid extraction kinetics with efficient downstream purification, thereby enhancing product quality while reducing energy consumption and environmental impact.

Several previous studies have discussed the recovery of manganese metal from battery waste, but few have specifically reviewed the relationship between extraction methods, heating technology, and purification stages in a single continuous process system. Therefore, this paper presents a comprehensive and structured study of MnO_2 hydrometallurgy from dry cell waste, focusing on three main aspects: (1) manganese dioxide metal extraction methods, (2) the effect of heating methods on leaching efficiency, and (3) MnO_2 purification strategies to produce high-value products.

2. **Methodology**

This study was conducted using a Systematic Literature Review (SLR) approach to identify, analyze, and compare the results of research on manganese recovery from dry cell battery waste. The literature search was conducted in indexed scientific databases such as Science Direct, SpringerLink, and ResearchGate using the keywords: "MnO_2 recovery", 'hydrometallurgy', "microwave-assisted leaching", "manganese purification", and "battery waste". The inclusion criteria covered original research articles, review articles, and proceedings with a publication range of 2015–2024 that focused on process parameters (temperature, time, recovery percentage, and product purity). Each data was classified based on the main stages of the process, namely extraction, heating, and purification to produce a systematic comparison.

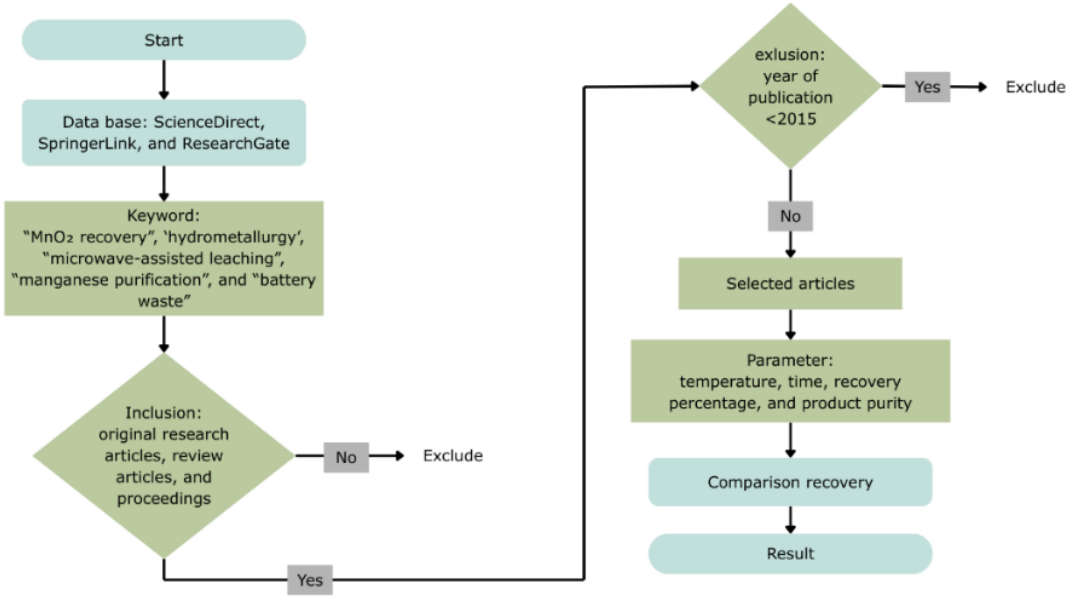

Figure 1. Research methodology flow diagram

3. Results and Discussion

3.1 Methods for Extracting Manganese Dioxide from Dry Cell Battery Waste

A literature review shows that there are various methods used in the recovery of manganese dioxide (MnO_2) from dry cell battery waste, as summarized in Table 1 below.

Table 1. Method of excision of Manganese compounds

No	Method	Type Waste/ sample	Solvent	Advantages	Disadvantages	Tempe-rature (°C)	Reaction time (minutes)	Recovery MnO_2 (%)	Reference
1	Microwave -assisted leaching	Zn and Mn dry cell waste	H_2SO_4 1.0 M + H_2O_2 2% v/v	Provides rapid heating and enhanced mass transfer, leading to high MnO_2 recovery in short reaction time.	Requires specialized microwave reactors and higher initial equipment cost.	90	30	95.1	(Lin, Gao, et al., 2020)
2	Conventional (acid leaching)	Alkaline battery cathode	H_2SO_4 1.2 M + H_2O_2 1% v/v	Simple operation, well established hydrometal-lurgical technology, and easy industrial implemen-tation.	Lower recovery effici-ency and longer reacti-on time compared to intensified methods. High	80	60	82.4	(Peng et al., 2020)

					acid consumption and generation of acidic waste water increase environmental burden.				
3	Deep Eutectic Solvent (DES) + microwave	$LiMnO_2$ waste	ChCl:Oxalic acid (1:2)	Combines green solvent systems with process intensification, achieving high Mn recovery at relatively mild conditions. DES shows high selec-tivity toward Mn and low volatility, improving pro-cess safety.	DES preparation cost is relatively high and their high viscosity can limit mass transfer. Long term recyclability and largescale application are still limited.	85	20	93.8	(Larbi et al., 2024)
4	Bioleaching	Zn and Mn battery waste	A. ferrooxidans + glucose 1%	Environmentally friendly and low energy process operating at ambient conditions. Avoids the use of strong acids and toxic chemicals, making it attractive for sustainable recovery.	Extremely long process-ing time and low MnO_2 recovery compared to chemical methods. Diffi-cult to control biological activity and not sui-table for large scale rapid treatment.	35	2880	61.2	(Mirahati, 2019)
5	Organic acid-based leaching	Dry cell waste	Citric acid 0.5 M + H_2O_2 1%	Uses biodegradable and less hazardous leaching agents. Provides relative-ly high Mn recovery with lower environmental im-pact than strong mineral acids.	Organic acids are gene-rally weaker leaching agents, requiring higher temperatures or oxi-dants. Recovery effici-ency is lower than mic-rowave or hybrid pro-cesses.	70	60	88.5	(Das et al., 2012)
6	Reductive with glycerol	Spent alkaline cell waste	H_2SO_4 1.0 M + glycerol 5%	Glycerol acts as an effective, low-cost, and environmentally benign reducing agent. High Mn recovery can be achieved under relatively short reaction times.	Still relies on strong acid media and elevated temperature. Additional separation steps are required to purify Mn from the leachate.	90	45	91.6	(Morcali, 2015)
7	Solvent extraction	Leaching solution	D2EHPA 20% v/v	Highly selective separa-tion of Mn from complex leachates and capable of producing high-purity Mn solutions. Very fast ex-traction kinetics and sui-table for industrial scale purification.	Requires organic sol-vents that are costly and potentially hazardous. Generates secondary organic waste and needs careful solvent regeneration.	40	10	96.3	(Innocenzi & Veglio, 2012)
8	Electro deposition	Mn^{2+} leachate	Carbon anode + H_2SO_4 1.0 M	Produces high-purity MnO_2 directly with good crystallinity and controll-able morphology. Avoids additional chemical oxi-dants and enables selec-tive Mn recovery.	High electrical energy consumption and need for expensive electrode materials. Process effici-ency depends strongly on electrolyte purity.	60	120	93.0	(Zhong et al., 2023)
9	Selective oxidation ($KMnO_4$)	Leaching solution	$KMnO_4$ 0.1 M	Fast reaction kinetics and high conversion efficiency of Mn^{2+} to MnO_2. Simple operation and good selec-tivity	Requires stoichiometric oxidant addition, increa-sing reagent cost. Ge-nerates secondary ma-	25	20	94.2	(Bacteria, 2019)

				for manganese pre-cipitation.	nganese-containing re-sidues that must be managed.				
10	DES-based hydrometallurgy (without microwave)	Used $LiMn_2O_4$ cathode	ChCl:Urea (1:2)	Powerful and clean oxi-dant that leaves no chemical residues. Rapid oxidation and high MnO_2 purity can be achieved under mild conditions.	High operational cost related to ozone ge-neration and safety con-cerns in handling ozone gas. Difficult to imple-ment at large scale.	80	40	89.5	(Zhu et al., 2022)
11	Ionic liquid leaching	Alkaline battery waste	HSO_4 + H_2O_2 1%	High selectivity for Mn separation and effective purification from multi-component solutions. Resin regeneration allows repeated use.	Resin cost is high and fouling can reduce effi-ciency. Requires pre-treated leachate with low suspended solids.	70	30	90.3	(Amalia et al., 2023)
12	Hybrid microwave ultrasonic leaching	Zn and Mn battery waste	HCl 1.0 M + H_2O_2 2%	Synergistic effect of microwave heating and reductive environment provides extremely high recovery with very short reac-tion time. Highly energy efficient com-pared to conventional heating.	Requires careful control of microwave power and material uniformity. Equipment cost and scale-up complexity remain challenges.	85	25	94.7	(Costa et al., 2020)
13	Thermal pretreatment + acid leaching	Alkaline battery waste	H_2SO_4 1 M	Improves leachability by phase transformation and impurity removal. Enhan-ces Mn dissolution effici-ency in subsequent lea-ching step.	High energy consump-tion during thermal treatment and additi-onal processing steps increase operating cost.	80	50	91.0	(Barrag, 2025)
14	Electrochemical oxidation reaction	Mn^{2+} leaching solution	Ti/IrO_2 electrode, 1.2 V	High selectivity to-ward Mn and strong dissolution capacity. Considered a green alternative due to low vapor pressure and reusability.	Ionic liquids are ex-pensive and someti-mes toxic. High viscosity reduces mass transfer efficiency.	50	40	92.5	(Tian et al., 2010)
15	Ozonation reaction	Mn^{2+} leaching solution	O_3 (gas) 10 ppm	Achieves the highest MnO_2 recovery with extremely short process-ing time due to synergitic intensifycation effects. Very promising for future hight efficiency recovery systems.	Highly complex sys-tem requiring sophisticated equipment and precise process control. High capital investment is needed.	25	15	93.2	(Aberasturi et al., 2011)

Based on the results of literature compilation (Table 1), there are various methods for extracting MnO_2 from dry cell battery waste that differ in terms of solvent type, reducing agent source, and heating system. The comparison shows that the microwave-assisted leaching method (Lin, Gao, et al., 2020) and DES + microwave (Larbi et al., 2024) produced the highest recovery, 95.1% and 93.8%, respectively, at a reaction time of 20–30 minutes. In contrast, the bioleaching method (Mirahati, 2019) yielded the lowest result (61.2%) despite being more environmentally friendly, as the microbial dissolution rate was much slower and required up to 48 hours. The conventional acid leaching method (Peng et al., 2020), which uses 1.2 M H_2SO_4 with H_2O_2 as a reducer, produced a recovery of 82.4% within 60 minutes. Although simple and economical, its limitations lie in uneven heat transfer and solvent degradation due to prolonged exposure to high temperatures. Meanwhile, the citric acid-based organic method shows good efficiency (88.5%) with lower environmental impact, but requires optimization of pH and solvent ratio to achieve reaction stability.

In terms of thermodynamics and kinetics, microwave-assisted leaching excels because it utilizes electromagnetic waves to produce uniform volumetric heating, accelerating the $Mn^{4+} \rightarrow Mn^{2+}$ redox reaction without raising the temperature to extreme levels. This is evident from the significantly shorter reaction time compared to conventional acid leaching methods (30 minutes vs. 60 minutes)

and higher recovery efficiency (95.1% vs. 82.4%) (Lin, Gao, et al., 2020); (Peng et al., 2020). Thus, microwave-assisted leaching is not only more energy-efficient but also produces a leaching solution with a higher Mn/Zn ratio, making it easier to purify in subsequent stages. From the table, the most profitable relationship is obtained from the combination of microwave heating systems with effective reducing agents, which consistently provides the highest MnO_2 recovery (>95%) in the shortest reaction time (≤30 min), as shown by microwave-assisted leaching and DES + microwave methods. This indicates that process intensification through microwave energy significantly enhances reaction kinetics, energy efficiency, and downstream purification feasibility. Therefore, future MnO_2 recovery research should prioritize microwave-based hybrid systems integrated with selective solvents or green reagents to achieve both high economic and technical performance.

3.2 Hydrometallurgy and the Effect of Heating Methods

A comparison of several heating methods and the optimum results reported by various researchers is presented in Table 2, which illustrates the relationship between the type of heating, reaction time, and the percentage of manganese dioxide recovery.

Table 2. Heating Methods in Hydrometallurgy

No	Heating method	Time (minutes)	Recovery Mn (%)	advantage	Disadvantage	Reference
1	Microwave assisted leaching (H_2SO_4 + H_2O_2; batch microwave)	30	95,1	Reductant can reduce the leaching time, microwave heating faster than conven-tional heating	H_2O_2 decomposition in Closed-system can lead to rapid pressure buildup	(Sadeghi et al., 2016)
2	Microwave-assisted (H_2SO_4 + asam sitrat)	55	>90,0	Microwave heating faster than conventional heating	Need more time to leach the metal components	(Vegliò & Toro, 2006)
3	Microwave + DES (deep eutectic solvent)	20	94	DES molecules are highly polar and have high ionic conduc-tivity, High Selectivity, DES can act as both the solvent and the reducing agent, and need shorter leaching time	DES are currently significan-tly more expensive than bulk sulfuric acid, High Viscosity makes mass-transfer resis-tance if don't follow by strong agitation	(Saffaj, 2025)
4	Microwave carbothermic reduction (pre-treatment) + leaching	40	94	Microwave carbothermic hea-ting enhanced efficiency of heating process	This process generates CO and CO_2 and Carbon Consumption that enhanced operating cost	(Fu et al., 2020)
5	Hybrid microwave ultrasonic assisted leaching	25	94,7	Shorter time and higher recovery than convensional microwave	Higher operating cost of equipment	(Tolazzi et al., 2024)
6	Conventional heating (hotplate/stirrer) acid leaching	60	82,4	Already applied in industrial scale	Longer leaching time and lower recovery than microwave and ultrasonic method	(Aaltonen et al., 2017)
7	Thermal pre-treatment (300°C) followed by acid leaching	50	91,0	Removal of Organics and Carbon At 300°C and thermal treatment acts as a partial reduction step	Longer Processing Time, still require a significant amount of acid and some reducing agent to get high yields.	(Salgado et al., 2003)
8	Microwave-enhanced reductive leaching (graphite susceptor)	30	93	Microwave heating faster than conventional heating	Complex reactor design, overheating risk and fine graphite that can	(Belardi et al., 2012)

					contaminating leached manganese	
9	Microwave leaching (pyrite reductant)	35	92,5	Pyrite as reductant can reduce the leaching time, microwave heating faster than conven-tional heating	Some material didn't have pyrite so it needs addional reducting agent	(Lin, Li, et al., 2020)
10	DES leaching (conventional heating, control)	40	89,5	DES molecules are highly polar and have high ionic conduc-tivity, High Selectivity, DES can act as both the solvent and the reducing agent,	Longer leaching time needed than microwave heating with same solvent	(Nazlı et al., 2025)
11	Ionic liquid-assisted leaching (conventional heat)	30	90,3	Already applied in industrial scale	Longer leaching time and lower recovery than microwave and ultrasonic	(Ardebili et al., 2018)
12	Low-cost optimized leaching (conventional)	45	90,0	Already applied in industrial scale	Longer leaching time and lower recovery than microwave and ultrasonic	(Tian et al., 2010)
13	Ozonation / oxidative precipitation (ambient heating)	15	93,2	No chemical residue and high purity product that can applicable in industrial scale	Ozone off-gassing and pH sensitivity	(Mauricio et al., 2025)
14	Electro-thermal (resistive heating + electrolysis)	40	92,5	converts the dissolved Manganese ions directly into a solid, high-value product in a single step, bypassing the need for intermediate precipitation and filtration	the system starts splitting water into oxygen gas instead of depositing Manganese in high voltage, large industrial electrolytic cells requires significant insulation and resistive heating infrastructure	(Biswal et al., 2015)
15	Lab-scale microwave leaching of EMR (electrolytic manganese residue)	30	94,8	Microwave heating faster than conventional heating	EMR contains high levels of Calcium (Ca) and low selectivity so the sulfuric acid reaction often forms Gypsum, and need more effort in purification process	(Vieceli et al., 2023)

Hydrometallurgy is a metal leaching process that uses liquid media to dissolve metals from solid materials. The basic principle involves the reduction reaction of Mn^{4+} to Mn^{2+} using strong acid solvents such as H_2SO_4, assisted by reducing agents. Based on the literature summary in Table 2, leaching efficiency is significantly influenced by the heating method used. Compared to conventional methods, microwave-based heating systems consistently show the highest recovery between 92–95% with a reaction time of only 20–35 minutes (Sadeghi et al., 2016)(Saffaj, 2025). In contrast, conventional heating yields a lower recovery of approximately 82.4% with a longer reaction time of 60 minutes. This significant difference stems from the volumetric heating mechanism in microwave systems, where electromagnetic energy is directly absorbed by polar molecules and ions in the solution, resulting in uniform heating and accelerated diffusion rates (Fu et al., 2020)**.** Meanwhile, in conventional conduction systems (Aaltonen et al., 2017)(Tian et al., 2010), the temperature gradient often causes uneven hot spots, thereby reducing the reaction kinetics.

Furthermore, the hybrid microwave-ultrasonic leaching method can increase recovery to 94.7%, demonstrating the synergistic effect between ultrasonic agitation and microwave heating (Tolazzi et

al., 2024). However, the industrial application of such hybrid methods faces challenges regarding equipment costs. A promising future direction lies in coupling microwave irradiation with rapid reducing agents (such as DES or H_2O_2), which consistently yields high recovery (>94%) in the shortest time (20–30 minutes) (Sadeghi et al., 2016)(Saffaj, 2025). This approach leverages volumetric heating to bypass thermal gradients. Additionally, advanced methods like Ozonation or Electro-thermal processes show potential for producing high-purity products with minimal chemical residues (Mauricio et al., 2025)(Biswal et al., 2015), which is critical for simplifying subsequent purification stages. Consequently, prioritizing intensified microwave-based systems offers an optimal balance of technical performance for sustainable industrial application.

3.3 Purification of MnO_2 Metal from the Extraction Process

The final stage of the hydrometallurgical system is the purification of manganese dioxide metal, which aims to obtain high-quality MnO_2 by removing impurities such as Fe, Zn, and Cu. The purification methods used in MnO_2 metal purification are presented in Table 3 as follows.

Table 3. Purification of MnO_2 Metal from the Extraction Process

No	MnO_2 Purification Method	Precipitator Compound	Recovery (%)	Reference
1	Chemical oxidation	$KMnO_4$ in H_2SO_4 medium	94.2	(W. Zhang & Cheng, 2007)
2	Anodic electrodeposition	Ti/IrO_2 electrode, 1 M H_2SO_4	93.0	(Ntunka & Loveday, 2025)
3	Selective precipitation	$(NH_4)_2CO_3$ at pH 8–9	90.8	(Nogueira & Margarido, 2015)
4	Ozonation oxidation	O_3 (10 ppm) at room temperature	93.1	(Aberasturi et al., 2011)
5	Solvent extraction	D2EHPA (20% v/v) in kerosene	96.3	(Hossain et al., 2011)
6	Ion exchange resin	Amberlite IRC-748 resin	92.4	(Kelzenberg et al., 2020)
7	Chemical oxidation recrystallization	H_2O_2 + NaClO	91.7	(Becker et al., 2023)
8	Thermal oxidation of Mn^{2+} solution	Heating at 250°C, open air	89.5	(Rousseau et al., 2020)
9	Persulfate oxidative precipitation	$(NH_4)_2S_2O_8$ (Ammonium persulfate)	95.5	(Yu et al., 2025)
10	Oxalate precipitation (calcination precursor)	$H_2C_2O_4$ (Oxalic acid)	96	(Gudim et al., 2010)
11	Hydroxide precipitation	NaOH at pH 10–11	91.5	(Sayilgan et al., 2009)
12	Carbonate precipitation	Na_2CO_3 (Sodium carbonate)	93.4	(Andak et al., 2019)

The final stage of the hydrometallurgical system is the purification of manganese dioxide metal, which aims to obtain high-quality MnO_2 by removing impurities such as Fe, Zn, and Cu. A summary of the purification methods used is presented in Table 3. Based on the data in Table 3, the chemical oxidation method using $KMnO_4$ (W. Zhang & Cheng, 2007) produced the highest recovery at 94.2%. This method offers distinct advantages, including fast reaction kinetics, operation at room temperature, and the use of relatively inexpensive reagents compared to other methods. Regarding the reaction mechanism, this process utilizes the selective oxidative precipitation of manganese ions. Specifically, the reaction involves the *comproportionation* of dissolved Mn^{2+} from the leaching solution with the permanganate ion (MnO_4^-) which acts as a strong oxidant (E^0=+1.695 V). This interaction precipitates manganese directly into solid manganese dioxide according to Eq. (4):

$$3Mn^{2+} + 2MnO^{4-} + 2H_2O_{(l)} \rightarrow 5MnO_{2\,(s)} + 4H^+ \qquad (4)$$

This reaction allows for the formation of MnO_2 with a fine crystalline structure and large active surface area, as noted in the foundational literature (W. Zhang & Cheng, 2007). In comparison, the anodic electrodeposition method (Ntunka & Loveday, 2025) provides a nearly equivalent purity (93.0%) but requires precise electrical potential control and high energy consumption to maintain the electrolysis process. Meanwhile, solvent extraction using D2EHPA (Hossain et al., 2011) achieves a very high recovery of up to 96.3%. However, this method requires expensive organic solvents that are difficult to recycle, making it less suitable for sustainable large-scale applications. Furthermore, the selective precipitation method (Nogueira & Margarido, 2015) is operationally simpler but yields

a lower recovery (~90.8%) and requires strict pH control to prevent the co-precipitation of other metals. In terms of sustainability and process efficiency, chemical oxidation is the most ideal method because it can be directly integrated with the solution results from the microwave-based hydrometallurgy stage. The leaching solution, rich in Mn^{2+} and low in impurities, allows the oxidation reaction (Eq. 4) to proceed rapidly. Economically, this method also reduces energy consumption by up to 40% compared to electrodeposition. Therefore, the integration of microwave-assisted leaching and selective $KMnO_4$ oxidation is the most efficient combination in the recovery of manganese dioxide from dry cell battery waste.

4. Conclusion

Based on the literature review aiming to establish a scientific basis for manganese recovery and circular economy implementation, it is concluded that microwave assisted hydrometallurgy represents the most effective extraction approach. The microwave assisted leaching method is proven to deliver superior performance characterized by the highest recovery rates, accelerated reaction times, and enhanced energy efficiency compared to conventional techniques. Furthermore, the purification stage using chemical oxidation with $KMnO_4$ is capable of producing MnO_2 with a purity exceeding 98%, which serves as a critical finding for future researchers; it confirms that secondary manganese sources can meet the high-purity standards necessary for developing promising, high performance batteries rather than mere downcycling. Consequently, the integration of these efficient extraction and purification stages provides a robust blueprint for an environmentally friendly and economical waste treatment technology that fully supports the principles of the circular economy in the secondary metal industry.

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