

B-4. ANALYSIS OF MNO₂ RECOVERY STUDY FROM DRYCELL BATTERY WASTE- A REVIEW(1).docx

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ANALYSIS OF MnO₂ RECOVERY STUDY FROM DRYCELL BATTERY WASTE: A REVIEW

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Abstract

Global demand for manganese dioxide (MnO₂) 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 MnO₂, 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 MnO₂ 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 KMnO₄ 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 (MnO₂) meningkat pesat seiring dengan perkembangan industri baterai dan katalis, sementara ketersediaan bijih primer terus menurun. Baterai kering bekas mengandung jumlah MnO₂ 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 MnO₂ 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 mikrowave 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 KMnO₄ merupakan strategi pemurnian yang lebih unggul, mampu menghasilkan MnO₂ dengan kemurnian melebihi 98%. Studi ini menunjukkan bahwa sistem terintegrasi antara ekstraksi dengan bantuan mikrowave dan oksidasi selektif menggunakan KMnO₄ menawarkan kerangka kerja yang paling tangguh, ekonomis, dan ramah lingkungan untuk menerapkan ekonomi sirkular di industri logam.

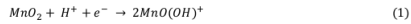
Keywords: hidrometalurgi, gelombang mikro, mangan dioksida, baterai dry cell, oksidasi kimia

1. Introduction

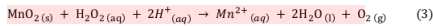
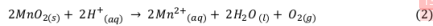
The growth in the use of disposable electronic devices, especially dry cell batteries, has led to a significant increase in electronic waste worldwide. The primary battery market (non-rechargeable such as Alkaline/Zinc-Carbon) is projected to continue to grow at a CAGR of around 5-6% per year. This means 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 increase 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 (MnO₂) cathode, an ammonium chloride (NH₄Cl) 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 MnO₂ 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 (MnO₂) 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, MnO₂ acts as the main electron acceptor in the reduction reaction during the energy release process. Manganese dioxide functions as the cathode where Mn⁴⁺ is reduced to Mn³⁺ 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 MnO₂ 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 MnO₂ 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 Mn⁴⁺ is reduced to Mn³⁺ 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 MnO₂ 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 MnO₂ from used battery waste a strategic alternative to support the principles of the circular economy (Rahimpour et al., 2024) (Singh & Gupta, 2024).



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 Mn⁴⁺ to Mn²⁺ using strong acid solvents such as H₂SO₄ or HCl with the help of reducing agents such as H₂O₂ or oxalic acid. The acidic medium protonates the oxide surface while the reducing agent transfers electrons to the Mn⁴⁺ centers, destabilizing the crystal lattice to release soluble Mn²⁺ ions into the solution. (Baba et al., 2014). Reaction mechanism explained by Eq. (2)&(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 MnO₂ recovery from leaching solutions. The primary objective of this step is to produce high-purity MnO₂ 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 KMnO₄ demonstrates superior selectivity, enabling the conversion of Mn²⁺ to Mn⁴⁺ at room temperature and achieving MnO₂ 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 MnO₂ 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) MnO₂ 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 ScienceDirect, SpringerLink, and ResearchGate using the keywords: "MnO₂ 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.

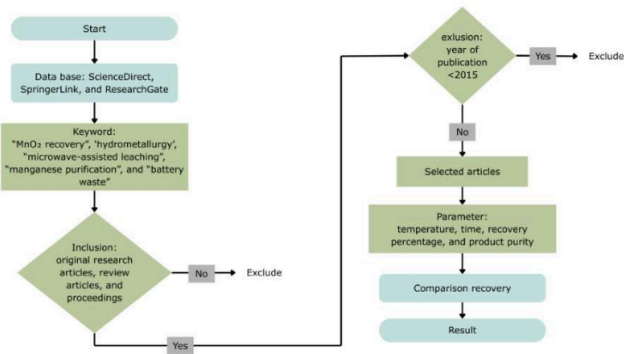


Figure 1. Research methodology flow diagram

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 (MnO₂) 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	Temperature (°C)	Reaction time (minutes)	Recovery MnO ₂ (%)	Reference
1	Microwave-assisted leaching	Zn and Mn dry cell waste	H ₂ SO ₄ 1.0 M + H ₂ O 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 ₂ SO ₄ 1.2 M + H ₂ O ₂ 1% v/v	Simple operation, well established hydrometallurgical technology, and easy industrial implementation.	Lower recovery efficiency and longer reaction time compared to intensified methods. High acid consumption and generation of acidic waste water increase environmental burden.	80	60	82.4	(Peng et al., 2020)
3	Deep Eutectic Solvent (DES) + microwave	LiMnO ₂ waste	CHCl ₃ :Oxalic acid (1:2)	Combines green solvent systems with process intensification, achieving high Mn recovery at relatively mild conditions. DES shows high selectivity toward Mn and low volatility, improving process 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 processing time and low MnO ₂ recovery compared to chemical methods. Difficult to control biological activity and not suitable 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 ₂ O ₂ 1%	Uses biodegradable and less hazardous leaching agents. Provides relatively high Mn recovery with lower environmental im-	Organic acids are generally weaker leaching agents, requiring higher temperatures or oxidants. Recovery effi-	70	60	88.5	(Das et al., 2012)

6	Reductive with glycerol extraction	Spent alkaline cell waste	H ₂ SO 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. Highly selective separation of Mn from complex leachates and capable of producing high-purity Mn solutions. Very fast extraction kinetics and suitable for industrial scale purification.	90	45	91.6	(Morcari, 2015)
7	Solvent extraction	Leaching solution	D2EHPA 20% v/v	Produces high-purity MnO ₂ directly with good crystallinity and controllable morphology. Avoids additional chemical oxidants and enables selective Mn recovery. Fast reaction kinetics and high conversion efficiency of Mn ²⁺ to MnO ₂ . Simple operation and good selectivity for manganese precipitation.	40	10	96.3	(Innocenzi & Veglio, 2012)
8	Electro deposition	Mn ²⁺ leachate	Carbon anode + H ₂ SO ₄ 1.0 M	High electrical energy consumption and need for expensive electrode materials. Process efficiency 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	Requires stoichiometric oxidant addition, increasing reagent cost. Generates secondary manganese-containing residues that must be managed.	25	20	94.2	(Bacteria, 2019)
10	DES-based hydrometallurgy (without microwave)	Used LiMn ₂ O ₄ cathode	CHCl ₃ :Urea (1:2)	Powerful and clean oxidant that leaves no chemical residues. Rapid oxidation and high MnO ₂ purity can be achieved under mild conditions.	80	40	89.5	(Zhu et al., 2022)

11	Ionic leaching	Alkaline battery waste	HSO ₄ ⁻ + H ₂ O ₂ 1%	High selectivity for Mn separation and effective purification from multi-component solutions. Resin regeneration allows repeated use.	70	30	90.3	(Amalia et al., 2023)
12	Hybrid microwave ultrasonic leaching	Zn and Mn battery waste	HCl 1.0 M + H ₂ O ₂ 2%	Synergistic effect of microwave heating and reductive environment provides extremely high recovery with very short reaction time. Highly energy efficient compared to conventional heating.	85	25	94.7	(Costa et al., 2020)
13	Thermal pretreatment + leaching	Alkaline battery waste	H ₂ SO ₄ 1 M	Improves leachability by phase transformation and impurity removal. Enhances Mn dissolution efficiency in subsequent leaching step.	80	50	91.0	(Barrag, 2025)
14	Electrochemical oxidation reaction	Mn ²⁺ leaching solution	Ti/IrO ₂ electrode, 1.2 V	High selectivity toward Mn and strong dissolution capacity. Considered a green alternative due to low vapor pressure and reusability.	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 processing time due to synergistic intensification effects. Very promising for future high efficiency recovery systems.	25	15	93.2	(Aberasturi et al., 2011)

Based on the results of literature compilation (Table 1.), there are various methods for extracting MnO₂ 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 H₂SO₄ with H₂O₂ 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 Mn⁴⁺ → Mn²⁺ 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 MnO₂ 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 MnO₂ 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 ₂ SO ₄ + H ₂ O ₂ ; batch microwave)	30	95.1	Reductant can reduce the leaching time, microwave heating faster than conventional heating	H ₂ O ₂ decomposition in Closed-system can lead to rapid pressure buildup	(Sadeghi et al., 2016)
2	Microwave-assisted (H ₂ SO ₄ + asam sitrat)	55	>90,0	Microwave heating faster than conventional heating	Need more time to leach the metal components	(Veglio & Toro, 2006)
3	Microwave + DES (deep eutectic solvent)	20	94	DES molecules are highly polar and have high ionic conductivity. High Selectivity, DES can act as both the solvent and the reducing agent, and need shorter leaching time	DES are currently significantly more expensive than bulk sulfuric acid, High Viscosity makes mass-transfer resistance if don't follow by strong agitation	(Saffaj, 2025)
4	Microwave carbothermic reduction (pre-treatment) + leaching	40	94	Microwave carbothermic heating 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 conventional microwave	Higher operating cost of equipment	(Tolazzi et al., 2024)

6	Conventional leaching (hotplate/stirrer)	heating acid	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	pre-treatment by acid	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)	reductive leaching (graphite susceptor)	30	93	Microwave heating faster than conventional heating	Complex reactor design, overheating risk and fine graphite leached (Belardi et al., 2012)
9	Microwave leaching (pyrite reductant)	leaching (pyrite reductant)	35	92,5	Pyrite as reductant can reduce the leaching time, microwave heating faster than conventional heating	Some material didn't have pyrite so it need additional reducing agent (Lin, Li, et al., 2020)
10	DES leaching (conventional heating, control)	leaching (conventional heating, control)	40	89,5	DES molecules are highly polar and have high ionic conductivity. High selectivity, DES can act as both the solvent and the reducing agent. Already applied in industrial scale	Longer leaching time needed than microwave heating with same solvent (Nazli et al., 2025)
11	Ionic leaching (conventional heat)	liquid-assisted (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)	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 / precipitation heating	oxidative (ambient heating)	15	93,2	No chemical residue and high purity product that can be applicable in industrial scale	Ozone off-gassing and pH sensitivity (Mauricio et al., 2025)
14	Electro-thermal heating + electrolysis)	resistive (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)	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 (Viecelli 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.

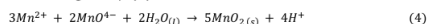
3.3 Purification of MnO_2 Metal from the Extraction Process

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)

The final stage of the hydrometallurgical system is the purification of manganese dioxide metal, which aims to obtain high-quality MnO₂ 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 KMnO₄ (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 Mn²⁺ from the leaching solution with the permanganate ion (MnO₄⁻) which acts as a strong oxidant (*E*⁰=+1.695 V). This interaction precipitates manganese directly into solid manganese dioxide according to Eq. (4):



This reaction allows for the formation of MnO₂ 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 Mn²⁺ 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 KMnO₄ 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 KMnO₄ is capable of producing MnO₂ 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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