A Sustainable Hydrometallurgical Route for Zinc and Manganese Recovery from Spent Dry-Cell Batteries Using Green Reductants

Submitted By

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A Thesis submitted in partial fulfilment of the requirement for the degree of Bachelor of Science in Industrial & Production Engineering (IPE)

Department of Mechanical and Production Engineering (MPE)

Islamic University of Technology (IUT)

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Candidate’s Declaration

This is to certify that the work presented in this thesis, titled, “**A Sustainable Hydrometallurgical Route for Zinc and Manganese Recovery from Spent Dry-Cell Batteries Using Green Reductants**”, is the outcome of the investigation and research carried out by me under the supervision of **Prof Dr. Shamsuddin Ahmed, PhD**.

It is also declared that neither this thesis nor any part of it has been submitted elsewhere for the award of any degree or diploma.

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Recommendation of the Thesis Supervisors

The thesis titled “**A Sustainable Hydrometallurgical Route for Zinc and Manganese Recovery from Spent Dry-Cell Batteries Using Green Reductants**” submitted by Fahim Muntasir Riyan & Sajjad Al Sajal, Student No: 200012114 and 200012142 has been accepted as satisfactory in partial fulfillment of the requirements for the degree of B Sc. in Mechanical Engineering **on 2nd October, 2025.**

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CO-PO Mapping of ME 4800 -Theis and Project

COs	Course Outcomes (CO) Statement	(PO)	Addressed by	
CO1	Discover and Locate research problems and illustrate them via figures/tables or projections/ideas through field visit and literature review and determine/Setting aim and objectives of the project/work/research in specific, measurable, achievable, realistic and timeframe manner.	**PO2** **Problem analysis**	Thesis Book	
			Performance by research	
			Presentation and soft skill	
CO2	Design research solutions of the problems towards achieving the objectives and its application. Design systems, components or processes that meets related needs in the field of mechanical engineering	**PO3** **Design/development of solutions**	Thesis Book	
			Performance by research	
			Presentation and soft skill	
CO3	Review, debate, compare and contrast the relevant literature contents. Relevance of this research/study. Methods, tools, and techniques used by past researchers and justification of use of them in this work.	**PO4** **Investigation**	Thesis Book	
			Performance by research	
			Presentation and soft skill	
CO4	Analyse data and exhibit results using tables, diagrams, graphs with their interpretation. Investigate the designed solutions to solve the problems through case study/survey study/experimentation/simulation using modern tools and techniques.	**PO5** **Modern tool usage**	Thesis Book	
			Performance by research	
			Presentation and soft skill	
CO5	Apply moral values and research/professional ethics throughout the work, and justify genuine referencing on sources, and demonstration of own contribution.	**PO8** **Ethics**	Thesis Book	
			Performance by research	
			Presentation and soft skill	
CO6	Perform own self and manage group activities from the beginning to the end of the research/work as a quality work.	**PO9** **Individual work and teamwork**	Thesis Book	
			Performance by research	
			Presentation and soft skill	
CO7	Compile and arrange the work outputs, write the report/thesis, a sample journal paper, and present the work to wider audience using modern communication tools and techniques.	**PO10** **Communication**	Thesis Book	
			Performance by research	
			Presentation and soft skill	
CO8	Recognize the necessity of life-long learning in career development in dynamic real-world situations from the experience of completing this project.	**PO12** **Life-long learning**	Thesis Book	
			Performance by research	
			Presentation and soft skill	

Student Name /ID:

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Signature of the Supervisor: …………………………

Name of the Supervisor: ……………………………..

K-P-A Mapping of ME 4800 -Theis and Project

CCs	PCs	Related Ks								Related Ps							Related As				
		K1	K2	K3	K4	K5	K6	K7	K8	P1	P2	P3	P4	P5	P6	P7	A1	A2	A3	A4	A5
CC1	PC2	√	√	√	√					√											
CC2	PC3					√				√	√	√				√	√	√	√		
CC3	PC4								√	√	√	√					√	√			
CC4	PC5						√			√				√							
CC5	PC8							√													
CC6	PC9																				
CC7	PC10																				
CC8	PC12																				

Student Name /ID:

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2. ……………………………………..

3. ……………………………………..

Signature of the Supervisor: …………………………

Name of the Supervisor: ……………………………..

List of Sustainable Development Goals (SDGs) Addressed in this Project

SDG No.	Goals	Targets	Relevance to the Thesis (put √ if valid)	Remarks
1	No Poverty	1.1 Eradicate extreme poverty (people living on less than $1.25/day).		
		1.2 Reduce poverty in all its forms by at least half.		
		1.3 Implement nationally appropriate social protection systems.		
		1.4 Ensure equal rights to economic resources, services, property, inheritance, technology, and financial services.		
		1.5 Build resilience of the poor and reduce exposure to climate-related and other shocks.		
		1.a Mobilize resources to end poverty.		
		1.b Create pro-poor policy frameworks.		
2	Zero Hunger	2.1 End hunger and ensure access to safe, nutritious food year-round.		
		2.2 End all forms of malnutrition.		
		2.3 Double agricultural productivity and incomes of small-scale producers.		
		2.4 Ensure sustainable food production systems and resilient agricultural practices.		
		2.5 Maintain genetic diversity of seeds, plants, and animals.		
		2.a Increase investment in rural infrastructure, research, and technology.		
		2.b Correct and prevent trade restrictions/distortions in global food markets.		
		2.c Adopt measures to ensure proper functioning of food commodity markets.		
3	Good Health and	3.1 Reduce global maternal mortality ratio.		

	Well-Being	3.2 End preventable deaths of newborns and under-5 children.		
		3.3 End epidemics of AIDS, tuberculosis, malaria, and neglected tropical diseases.		
		3.4 Reduce premature mortality from NCDs and promote mental health.		
		3.5 Strengthen prevention and treatment of substance abuse.		
		3.6 Halve global deaths/injuries from road traffic accidents.		
		3.7 Ensure universal access to sexual and reproductive healthcare.		
		3.8 Achieve universal health coverage.		
		3.9 Reduce deaths from hazardous chemicals, pollution, and contamination.		
		3.a Strengthen tobacco control (WHO FCTC).		
		3.b Support R&D of vaccines and medicines.		
		3.c Increase health financing and workforce.		
		3.d Strengthen capacity for early warning and risk management.		
4	Quality Education	4.1 Ensure all complete free, equitable, quality primary and secondary education.		
		4.2 Ensure access to quality early childhood development and pre-primary education.		
		4.3 Ensure equal access to affordable technical, vocational, and higher education.		
		4.4 Increase skills for employment and entrepreneurship.		
		4.5 Eliminate gender disparities in education.		
		4.6 Ensure literacy and numeracy for youth and adults.		

		4.7 Ensure learners acquire knowledge/skills for sustainable development.		
		4.a Build and upgrade education facilities that are inclusive and safe.		
		4.b Expand scholarships for developing countries.		
		4.c Increase supply of qualified teachers.		
5	Gender Equality	5.1 End all forms of discrimination against women and girls.		
		5.2 Eliminate violence against women and girls.		
		5.3 Eliminate harmful practices (child, early, forced marriage, FGM).		
		5.4 Recognize and value unpaid care and domestic work.		
		5.5 Ensure women's participation in leadership and decision-making.		
		5.6 Ensure universal access to reproductive health and rights.		
		5.a Undertake reforms to give women equal rights to resources.		
		5.b Enhance use of enabling technology to empower women.		
		5.c Adopt and strengthen policies and laws for gender equality.		
6	Clean Water and Sanitation	6.1 Achieve universal and equitable access to safe drinking water.		
		6.2 Achieve access to adequate sanitation and hygiene.		
		6.3 Improve water quality by reducing pollution.		
		6.4 Increase water-use efficiency and sustainable withdrawals.		
		6.5 Implement integrated water resources management.		

		6.6 Protect and restore water-related ecosystems.		
		6.a Expand international cooperation in water and sanitation.		
		6.b Support participation of local communities.		
7	Affordable and Clean Energy	7.1 Ensure universal access to affordable, reliable, modern energy services.		
		7.2 Increase substantially the share of renewable energy.		
		7.3 Double global rate of improvement in energy efficiency.		
		7.a Enhance international cooperation on clean energy research/technology.		
		7.b Expand infrastructure and upgrade technology for sustainable energy.		
8	Decent Work and Economic Growth	8.1 Sustain per capita economic growth.		
		8.2 Achieve higher levels of productivity through diversification, tech, and innovation.		
		8.3 Promote policies for decent job creation and entrepreneurship.		
		8.4 Improve resource efficiency in production and consumption.		
		8.5 Achieve full and productive employment for all.		
		8.6 Substantially reduce youth not in employment/education/training.		
		8.7 Eradicate forced labour, modern slavery, and child labour.		
		8.8 Protect labour rights and safe working environments.		
		8.9 Promote sustainable tourism.		
		8.a Increase aid for trade support.		
		8.b Develop a global youth employment strategy.		

9	Industry, Innovation, and Infrastructure	9.1 Develop quality, reliable, sustainable infrastructure.	✔	
		9.2 Promote inclusive and sustainable industrialization.	✔	
		9.3 Increase access of SMEs to financial services and integration into value chains.		
		9.4 Upgrade infrastructure for sustainability and resource efficiency.		
		9.5 Enhance scientific research and technology development.	✔	
		9.a Facilitate sustainable infrastructure in developing countries.	✔	
		9.b Support domestic tech development and value addition.		
		9.c Increase access to ICT and internet.	✔	
10	Reduced Inequalities	10.1 Achieve income growth of bottom 40%.		
		10.2 Empower and promote inclusion regardless of status.		
		10.3 Ensure equal opportunity and reduce inequalities of outcome.		
		10.4 Adopt policies for fiscal, wage, and social protection equality.		
		10.5 Improve regulation of global financial markets.		
		10.6 Ensure enhanced representation in global institutions.		
		10.7 Facilitate safe, regular, and responsible migration.		
		10.a Implement special treatment for developing countries.		
		10.b Encourage development assistance and investment in least developed areas.		
		10.c Reduce remittance costs.		
11	Sustainable Cities and	11.1 Ensure access to adequate, safe, and affordable housing.		

	Communities	11.2 Provide sustainable transport systems.		
		11.3 Enhance inclusive urbanization and capacity for planning.		
		11.4 Protect cultural and natural heritage.		
		11.5 Reduce disaster impact and losses.		
		11.6 Reduce environmental impact of cities (air quality, waste).		
		11.7 Provide access to safe, inclusive green/public spaces.		
		11.a Support positive links between urban, peri-urban, rural.		
		11.b Increase disaster risk reduction strategies.		
		11.c Support least developed countries in sustainable building.		
12	Responsible Consumption and Production	12.1 Implement 10-Year Framework on sustainable consumption/production.		
		12.2 Achieve sustainable management and use of resources.	✔	
		12.3 Halve per capita global food waste.		
		12.4 Manage chemicals and waste sustainably.		
		12.5 Substantially reduce waste generation.		
		12.6 Encourage companies to adopt sustainable practices.	✔	
		12.7 Promote sustainable public procurement.	✔	
		12.8 Ensure people have relevant information for sustainable development.		
		12.a Support developing countries' scientific and technological capacity.	✔	
		12.b Develop tools to monitor sustainable tourism impacts.		
		12.c Rationalize inefficient fossil-fuel subsidies.	✔	

13	Climate Action	13.1 Strengthen resilience and adaptive capacity to climate-related hazards.		
		13.2 Integrate climate measures into national policies.	✔	
		13.3 Improve education and awareness on climate change.	✔	
		13.a Implement UNFCCC commitments (mobilize $100 billion annually).		
		13.b Promote mechanisms for capacity-building in least developed countries.	✔	
14	Life Below Water	14.1 Reduce marine pollution.		
		14.2 Sustainably manage and protect marine ecosystems.		
		14.3 Minimize and address ocean acidification.		
		14.4 Regulate harvesting and end overfishing.		
		14.5 Conserve at least 10% of coastal and marine areas.		
		14.6 Prohibit harmful fisheries subsidies.		
		14.7 Increase economic benefits from sustainable marine resources.		
		14.a Increase scientific knowledge and marine technology transfer.		
		14.b Provide access for small-scale artisanal fishers.		
		14.c Implement international law for oceans.		
15	Life on Land	15.1 Conserve terrestrial and freshwater ecosystems.		
		15.2 Promote sustainable management of forests.	✔	
		15.3 Combat desertification and restore degraded land.		
		15.4 Ensure conservation of mountain ecosystems.	✔	

		15.5 Take urgent action to reduce biodiversity loss.	✔	
		15.6 Promote fair benefit-sharing from genetic resources.		
		15.7 End poaching and trafficking of protected species.		
		15.8 Prevent introduction of invasive alien species.		
		15.9 Integrate ecosystem values into policies/planning.	✔	
		15.a Mobilize resources for biodiversity.		
		15.b Finance sustainable forest management.		
		15.c Support local communities for forest and wildlife.	✔	
16	Peace, Justice and Strong Institutions	16.1 Reduce violence and related death rates.		
		16.2 End abuse, trafficking, and violence against children.		
		16.3 Promote rules of law and equal access to justice.		
		16.4 Reduce illicit financial/arms flows, organized crime.		
		16.5 Reduce corruption and bribery.		
		16.6 Develop effective, accountable institutions.		
		16.7 Ensure inclusive, participatory decision-making.		
		16.8 Broaden participation of developing countries in global governance.		
		16.9 Provide legal identity for all (including birth registration).		
		16.10 Ensure access to information and protect freedoms.		
		16.a Strengthen national institutions for prevention of violence.		

		16.b Promote/enforce non-discriminatory laws and policies.		
17	Partnerships for the Goals	17.1 Strengthen domestic resource mobilization.		
		17.2 Developed countries to implement ODA commitments.		
		17.3 Mobilize additional financial resources.		
		17.4 Assist developing countries with debt sustainability.		
		17.5 Invest in least developed countries.		
		17.6 Enhance access to science, technology, innovation.		
		17.7 Promote environmentally sound technologies.		
		17.8 Fully operationalize technology bank for LDCs.		
		17.9 Enhance international support for capacity-building.		
		17.10 Promote a universal, rules-based trading system (WTO).		
		17.11 Increase exports of developing countries.		
		17.12 Timely implementation of duty-free, quota-free market access.		
		17.13 Enhance global macroeconomic stability.		
		17.14 Enhance policy coherence for sustainable development.		
		17.15 Respect national policy space.		
		17.16 Enhance global partnerships.		
		17.17 Encourage multi-stakeholder partnerships.		
		17.18 Enhance data capacity of developing countries.		

Acknowledgment

At the very outset, we are profoundly grateful to **Almighty Allah (SWT)**, the Most Gracious and the Most Merciful, for granting us the health, patience, perseverance, and knowledge to complete this thesis work successfully. Without His countless blessings, this endeavor would not have been possible. We would like to place on record our sincere gratitude to our respected supervisor, **Prof. Dr. Shamsuddin Ahmed, PhD**, for his invaluable supervision, continuous encouragement, and insightful guidance throughout every stage of this project. His expertise, critical feedback, and inspiring advice have been instrumental in refining our ideas and improving the overall quality of our work. Our heartfelt thanks also go to all the **faculty members and staff of the Department of Mechanical and Production Engineering, Islamic University of Technology (IUT)**, for providing a supportive academic environment and access to necessary laboratory facilities that enabled us to carry out our experiments effectively. We are also indebted to the laboratory assistants and technical staff who extended their cooperation during the experimental phase. We gratefully acknowledge the help and suggestions received from our seniors, peers, and fellow researchers, who shared their experiences and offered constructive discussions that enriched our knowledge and helped us overcome several challenges during the course of this thesis. We also extend our deepest appreciation to our **families** for their unconditional love, constant support, patience, and encouragement. Their sacrifices, prayers, and belief in us have been a source of strength and motivation throughout our academic journey. Lastly, we acknowledge all those—whether mentioned by name or not—who have directly or indirectly contributed to the completion of this project. Each contribution, no matter how small, has played a part in helping us achieve this milestone.

Summary

(For non technical audience)

Every day in Bangladesh, millions of small batteries (like AA or AAA dry-cell batteries) are used in household items such as remote controls, toys, and flashlights. Once these batteries stop working, most families simply throw them away. However, inside these batteries are valuable materials like zinc and manganese, which can be reused. If they are left in the environment, these metals can also pollute soil and water, creating health risks for people and animals. Our research focused on finding a safe, affordable, and eco-friendly way to recycle these used batteries. Instead of using harsh chemicals that are harmful to the environment, we experimented with green alternatives such as glucose (sugar) and ascorbic acid (Vitamin C). These natural substances helped us recover zinc and manganese from the battery powder effectively. Through careful testing, we discovered that glucose performed the best, offering both higher recovery rates and lower costs. This shows that a greener recycling process can be developed for Bangladesh, turning waste into useful resources while protecting the environment. In the future, this method could be applied on a larger, industrial scale. If widely adopted, it would reduce battery waste, save valuable materials, protect health, and support Bangladesh's move toward a more sustainable and circular economy.

Table of Contents

Chapter 1: INTRODUCTION

As more people buy electronics, household gadgets, and portable devices, the demand for dry-cell batteries around the world has been steadily rising. In Bangladesh, millions of these batteries are used every year, and most of them are thrown away without being properly treated or recycled. Used dry-cell batteries are a major source of valuable metals, especially manganese (Mn) and zinc (Zn), which together make up a large part of the black mass content (Almeida et al., 2006; Chowdhury et al., 2022). Even though they are useful, throwing them away the wrong way can cause serious problems for the environment, such as heavy metals leaching into soil and water, which can harm both ecosystems and human health (Mantuano et al., 2006).

Hydrometallurgical recycling has become a useful and scalable way to get metals back from old batteries. This method uses acid leaching, which is when metals are dissolved with chemicals like sulfuric acid. People are more worried about the environment now, so they are looking for greener alternatives to traditional leaching systems that use harsh chemicals and non-sustainable reductants. Recent research has indicated the utilization of organic compounds such as citric acid, glucose, and ascorbic acid as efficient "green reductants," which not only attain elevated recovery rates but also mitigate environmental impact (Amaral et al., 2014; Almeida et al., 2006).

In light of this context, this thesis examines the recovery of zinc and manganese from spent dry-cell batteries utilizing sulfuric acid in conjunction with glucose and ascorbic acid as environmentally friendly reductants. The study also seeks to examine the efficacy of these reductants under diverse operational conditions and to evaluate the prospective implementation of this process in Bangladesh.

1.1 Goals of the Study

The goals of this study are as follows:

- To extract zinc and manganese from the black mass of spent dry-cell batteries via hydrometallurgical leaching, employing sulfuric acid with glucose and ascorbic acid as reducing agents.
- To examine the influence of various parameters—such as reagent concentration, temperature, and reaction duration—on recovery efficiency.
- To assess the efficacy of green reductants against traditional methods documented in literature and ascertain the optimal conditions for metal recovery.
- To examine the environmental and economic viability of implementing green reductant-based recycling within the Bangladeshi context.

1.2 Structure of the Thesis

There are six chapters in the thesis:

Chapter 1 gives an overview of the thesis's background, goals, and structure.

Chapter 2 reviews the literature on previous studies about getting metals back from used dry-cell batteries. It talks about the techniques that are already in use, their limits, and the areas where more research is needed.

Chapter 3 talks about the chemicals, materials, and experimental methods that were used in this study.

Chapter 4 talks about the computational and analytical methods, such as the governing equations and how to check them.

Chapter 5 shows the results of the experiments, how they were analyzed, and how they relate to other research.

Chapter 2: Literature Review

Recycling used dry-cell batteries has gotten a lot of attention lately because of both environmental concerns and the chance to get valuable metals back. Many studies have looked into hydrometallurgical leaching methods, how acids and reductants work, and how to use analytical techniques to describe black mass and materials that have been recovered. This chapter examines significant literature in these domains, concentrating on prior research pertinent to zinc (Zn) and manganese (Mn) recovery, the implementation of green reductants, and process optimization.

2.1 What Makes Up Spent Dry-Cell Batteries

Numerous studies have documented the elemental composition of dry-cell battery black mass.

Almeida et al. (2006) conducted XRF and chemical analyses, demonstrating that manganese (Mn) and zinc (Zn) are the predominant metals, constituting over 50% of the black mass.

Chowdhury et al. (2022) conducted XRF analysis on washed powder samples of spent zinc-carbon batteries in Bangladesh, verifying Mn at approximately 54% and Zn at approximately 21% as predominant components.

Mantuano et al. (2006) also looked at used batteries and talked about how dangerous it is to throw them away without any control, pointing out how heavy metals can get into the soil and water.

These studies show that Mn and Zn are the main things that need to be recovered, and they also show how important it is to recycle properly for the environment.

2.2 Traditional Hydrometallurgical Methods

Strong acids are a big part of traditional hydrometallurgical recovery.

Almeida et al. (2006) studied sulfuric acid leaching and showed that it could dissolve a lot of Zn at moderate temperatures.

Mantuano et al. (2006) investigated the application of hydrochloric acid and sulfuric acid, documenting effective recovery while acknowledging the corrosive and environmentally detrimental characteristics of these reagents.

Shin et al. (2009) investigated the kinetics of manganese leaching, demonstrating that temperature and acid molarity substantially affect recovery rates.

These processes work well, but they are bad for the environment and safety because they use harsh chemicals.

2.3 Using Green Reductants for Leaching

People are now looking at green and eco-friendly reductants as possible substitutes for regular chemicals.

Amaral et al. (2014) presented citric acid as a leaching agent, indicating moderate zinc recovery and a diminished environmental impact in comparison to strong acids.

Gharabaghi et al. (2016) assessed ascorbic acid (Vitamin C) as a reductant in sulfuric acid leaching, demonstrating substantial enhancement in manganese dissolution attributable to its potent reducing characteristics.

Sarma et al. (2019) examined glucose as a reductant and found that it offered sustainable recovery efficiencies while being cost-effective and biodegradable.

Chowdhury et al. (2022) built on this research in Bangladesh by comparing ascorbic acid and glucose in a lab setting. They found that ascorbic acid was better at extracting Mn, but glucose was cheaper.

These studies indicate that green reductants offer a more environmentally friendly option without compromising efficiency.

2.4 Factors that affect recovery in the process

Several factors have a big effect on how well leaching works:

Shin et al. (2009) found that higher temperatures led to better Mn recovery, but the gains started to level off after 80 °C.

Acid Concentration: Almeida et al. (2006) determined that elevating sulfuric acid concentration enhanced Zn recovery up to 1.0 M, after which the effect stabilized.

Gharabaghi et al. (2016) said that the right amount of ascorbic acid to black mass is very important. Too much of either one wastes reagents without adding any benefits.

Reaction Time: Sarma et al. (2019) noted that extended leaching enhances recovery while escalating operational expenses, thereby necessitating time optimization.

2.5 Methods for Characterization Analysis

It is very important to analyze raw materials and products correctly.

XRF Analysis: Almeida et al. (2006) and Chowdhury et al. (2022) utilized XRF to ascertain the metal composition in battery powder.

Shin et al. (2009) and Chowdhury et al. (2022) used AAS (Atomic Absorption Spectroscopy) to measure the amounts of Mn and Zn in leachates, which made it possible to figure out how well the recovery worked.

Amaral et al. (2014) employed scanning electron microscopy to examine alterations in surface morphology post-leaching, thereby validating dissolution behavior.

These methods make sure that the recycling process is being watched correctly.

2.6 Important Results and Areas for Further Research

Important Results:

Mn and Zn are always found to be the main metals that can be recovered from used dry-cell batteries.

Sulfuric acid leaching works well, but it needs to be better for the environment.

Citric acid, glucose, and ascorbic acid are examples of green reductants that could be very useful for long-term recycling.

The best way to recover depends on finding the right balance between the amount of acid, the amount of reductant, the temperature, and the time it takes for the reaction to happen.

Gaps in Research:

There have been few studies done in Bangladesh, where battery use is growing quickly.

There are still not many comparative studies of different green reductants under the same conditions.

There are not many studies that look at how practical it is to use glucose and ascorbic acid, even though they cost and work differently.

Scaling laboratory processes to industrial applications remains predominantly unexamined.

Chapter 3: The Model/System's Description

3.1 Materials and Blackmass Preparetion

We got used zinc-carbon dry-cell batteries from trash cans in homes. The outer casing was taken apart by hand, and the black mass inside was taken out. The main ingredients in this black mass are manganese dioxide (MnO_2), zinc oxide (ZnO), graphite, and a few other things.

To get the feedstock ready:

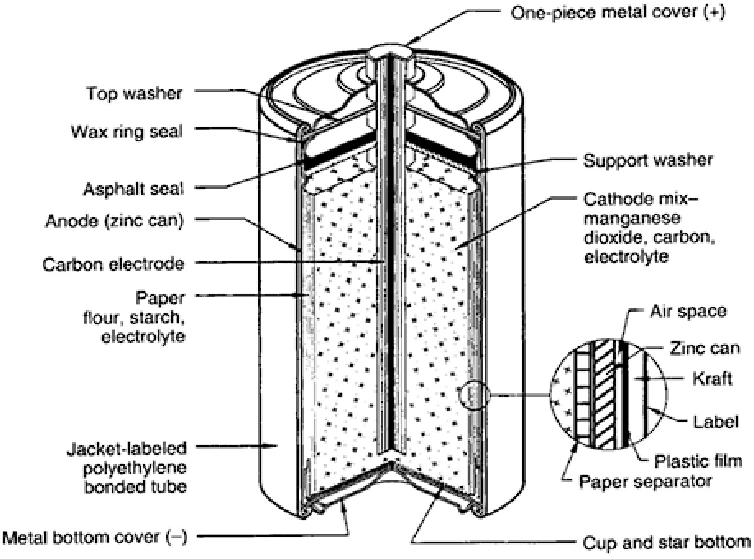
1.To get rid of soluble salts like ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$), the black mass was washed with distilled water over and over again.

2.To get rid of any leftover moisture, the washed material was dried in an oven at 80 °C for 6 to 8 hours.

We ground and sieved the dried powder (with particles smaller than 150 µm) so that it would be the same size for the next leaching experiments.

3.2 Black Mass Analysis

Characterizing the black mass is crucial for identifying the target metals and their concentrations.

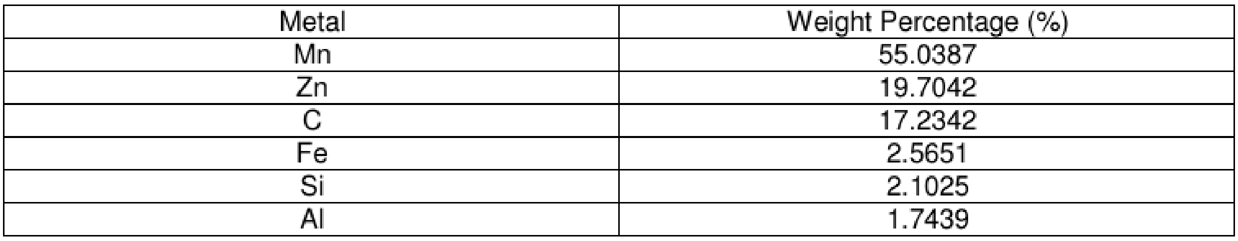


Referance: Mahbub, Hasib & Deb, Nandini & Abedin, Muhammad & Abedin, Shamsul & Khan, Mohidus Samad. (2015). Metal Recovery from Waste Dry Cell Batteries. 10.13140/RG.2.1.2890.4806

XRF Analysis: Earlier research (Almeida et al., 2006; Chowdhury et al., 2022) indicated that Mn comprised approximately 50–55% and Zn about 20–25% of the primary components, alongside trace amounts of Fe, K, and C.

AAS Baseline Analysis: The first AAS tests of the dissolved black mass showed that Mn^{2+} and Zn^{2+} were still in the solution after leaching.

Physical Properties: The black mass looked like a fine black powder with a bulk density of about 1.8 g/cm³.



Metal	Weight Percentage (%)
Mn	55.0387
Zn	19.7042
C	17.2342
Fe	2.5651
Si	2.1025
Al	1.7439

Reference: Mahbub, Hasib & Deb, Nandini & Abedin, Muhammad & Abedin, Shamsul & Khan, Mohidus Samad. (2015). Metal Recovery from Waste Dry Cell Batteries. 10.13140/RG.2.1.2890.4806

3.3 Reagents Used

The following chemicals were used:

Sulfuric Acid (H_2SO_4, 1.0 M): Main leaching agent.

Ascorbic Acid ($C_6H_8O_6$): A green reductant that helps change Mn^{4+}/Mn^{3+} into soluble Mn^{2+}.

Glucose ($C_6H_{12}O_6$): a different green reductant that is cheap and breaks down naturally.

Used in all reagent preparations and washing: **distilled water.**

All of the reagents were of **high quality** for analysis.

3.4 Specifications and Operating Parameters

We used a heating-stirring system that worked as the laboratory "boiler" to do leaching experiments.

Type: Magnetic stirrer with a hot plate

Glass reactor vessel with a capacity of 500 mL

Temperature range: 0 °C to 120 °C

Speed of stirring: 0–800 rpm

Power: 220 volts AC

Parameters for operation:

Temperature of the reaction: 80 °C (always)

Time for the reaction: 30 to 120 minutes (varied)

Volume of solution: 150 mL per batch

The ratio of solid to liquid is 15 g of black mass to 150 mL of acid solution.

Speed of stirring: 600 rpm

3.5 Experimental setup

The setup for the experiment was:

A **magnetic stirrer** with a **heating plate** holds a **250 mL** glass beaker (reactor).

Thermometer probe that lets you check the temperature in real time.

Magnetic stir bar to make sure the agitation is even.

Filtration unit (**Whatman filter paper and funnel)** to get rid of **solid waste.**

Flasks for collecting leachate before testing.

3.6 Analytical Methods

Different characterization and quantification methods were used:

- **XRF (X-ray Fluorescence):** To determine elemental composition of the black mass.
- **AAS (Atomic Absorption Spectroscopy):** To measure Mn and Zn concentration in filtrates and calculate recovery efficiency:

$$\text{Recovery Efficiency (\%)} = \frac{C_{leachate} \times V}{W_{BM} \times \%M_{BM}} \times 100$$

where $C_{leachate}$ = concentration in leachate (mg/L), V = solution volume (L), W_{BM} = weight of black mass (g), $\%M_{BM}$ = metal percentage in black mass.

Gravimetric Analysis: To quantify solid residues left after leaching.

3.7 Environmental Impact Analysis

When old batteries are thrown away in the wrong way, they release Mn, Zn, and other heavy metals into the soil and water, which can harm the environment and people's health. Using strong acids and synthetic reductants in traditional ways makes the problem worse.

This study's approach helps the environment by:

Using glucose and ascorbic acid as green reductants because they are safer and better for the environment than chemical ones.

Allowing the recovery of Mn and Zn, which makes it less necessary to mine new minerals.

Helping Bangladesh's growing battery use have less of an impact on the environment and encouraging circular economy practices.

3.8 System Relevance to Bangladesh

Bangladesh doesn't have any official battery recycling plants. Most used batteries end up in landfills or informal scrapyards. The process that was created here is meant to be:

1.Low-cost because glucose is cheap and easy to find in the area.

2.Scalable because industrial reactors can handle the moderate temperature and mild acid needs.

3.Eco-friendly, which fits with Bangladesh's need for long-term solutions for dealing with waste.

This model can help build a national system for recycling dry-cell batteries.

Chapter 4: Methodology

This study followed a structured methodological framework to establish a sustainable hydrometallurgical route for the recovery of zinc (Zn) and manganese (Mn) from spent dry-cell batteries. The process was designed to align with environmental sustainability, material efficiency, and economic feasibility. The methodology is divided into four principal stages:

1. Collection and Pre-treatment of Spent Batteries
2. Reductive Acid Leaching
3. Selective Precipitation and Metal Recovery
4. Quantification, Efficiency Analysis, and Cost Evaluation

4.1 Collection and Pre-treatment of Spent Batteries

- **Sample Collection:**
  Spent zinc–carbon (Zn–C) batteries were collected from household and institutional sources. To ensure safe handling, all batteries were discharged prior to dismantling. Controlled discharge was performed using motors with varying torque levels, simulating actual power draw, followed by verification with a multimeter.
- **Dismantling and Separation:**
  After discharge, the battery casings were carefully cut open using insulated cutters. Internal components such as the steel casing, graphite rod, and paper separators were removed. Only the **black mass** (active cathodic material containing MnO_2, Zn, and conductive carbon) was retained.
- **Grinding and Drying:**
  The recovered black mass was homogenized by mechanical grinding. To remove moisture and volatile impurities, it was oven-dried at **110 °C for 12 hours**.
- **Washing and Impurity Removal:**
  To reduce the concentration of soluble salts (e.g., ammonium chloride, zinc chloride) that interfere with leaching, the powder was washed with deionized (DI) water at a **10:1 liquid-to-solid ratio**. The suspension was filtered using Whatman 42 filter paper. The residue was re-dried at **110 °C for 12 hours**, yielding purified black mass ready for leaching.

- **Chemical Composition Verification:**
  The composition of the washed black mass was verified using X-ray fluorescence (XRF) analysis, showing the presence of approximately **55% Mn and 20% Zn**, consistent with prior literature reports.

4.2 Reductive Acid Leaching

- **Preparation of Leachant Solution:**
  Leaching solutions were prepared using **1 M H_2SO_4** as the primary leachant. To improve dissolution of Mn and Zn, environmentally benign reductants—**glucose** and **ascorbic acid**—were introduced. The choice of reductants was based on their reducing properties, renewability, and non-toxic nature, making them suitable substitutes for conventional reductants like hydrogen peroxide.
- **Experimental Conditions:**
  Leaching experiments were carried out under controlled conditions:
    - **Temperature:** 80 °C
    - **Stirring speed:** 800 rpm
    - **Duration:** 3 hours
    - **Reaction vessel:** 250 mL glass beaker on a magnetic hotplate stirrer
    - **Filtration:** Whatman 42 filter paper

- **Experimental Design:**

A factorial experimental design was adopted to study the effect of reagent dosage and black mass loading. Four variations were considered for each reductant:

Experiment No.	H2SO4 (1M) (ml)	Reagent amount (g)	Black mass (g)	Reagent Used
1	50	2.25 (Low)	5 (Low)	Glucose
2	50	13.5 (High)	5 (Low)	Glucose
3	50	2.25 (Low)	10 (High)	Glucose
4	50	13.5 (High)	10 (High)	Glucose
5	50	2.25 (Low)	5 (Low)	Ascorbic Acid
6	50	13.5 (High)	5 (Low)	Ascorbic Acid
7	50	2.25 (Low)	10 (High)	Ascorbic Acid
8	50	13.5 (High)	10 (High)	Ascorbic Acid

Filtration and Leachate Collection:

At the end of the reaction, the slurry was filtered to separate the metal-rich leachate (containing dissolved Zn^{2+} and Mn^{2+}) from solid residues. The filtrate was preserved for subsequent metal recovery, while residues were discarded.

4.3 Selective Precipitation and Metal Recovery

- **Sequential Precipitation Strategy:**
  The filtered leachate was subjected to pH-controlled precipitation using NaOH solution:
  - **Zinc Recovery:** Zn^{2+} was precipitated as $Zn(OH)_2$ at pH 8.
  - **Manganese Recovery:** Mn^{2+} was precipitated as $Mn(OH)_2$ at pH 12.
- **Rationale for Sequential Recovery:**
  Since Zn and Mn have different solubility products, adjusting the pH sequentially enabled selective recovery of each metal, minimizing cross-contamination and improving purity.
- **Collection and Drying of Precipitates:**
  The precipitated hydroxides were filtered, washed thoroughly with DI water to remove traces of acid or salts, and dried under ambient conditions. The dried materials represented the recovered Zn and Mn fractions.

4.4 Metal Quantification, Efficiency Analysis, and Cost Evaluation

- **Quantification Using Atomic Absorption Spectroscopy (AAS):**
  Dried precipitates were analyzed using AAS at INARS, BCSIR, Dhaka. Concentrations obtained in ppm were converted to g/kg and subsequently expressed as recovery efficiency (%) using the formula:
  Recovery Efficiency (%)=Mass of Metal RecoveredMass of Metal in Original Black Mass (XRF)×100Recovery Efficiency (%)=Mass of Metal in Original Black Mass (XRF)Mass of Metal Recovered×100
- **Comparative Performance Analysis:**
  The efficiency of glucose and ascorbic acid was benchmarked against conventional reductants (citric acid, H_2O_2) reported in literature. Results showed optimum recoveries of

74.83% Mn and 77.43% Zn with glucose, and 54.98% Mn and 52.32% Zn with ascorbic acid.

- **Economic Assessment:**
  Cost estimation was performed for each optimum trial based on reagent usage and local market prices. Results indicated that glucose-based leaching is more economical, with a total processing cost of ~118 Tk per batch, compared to ascorbic acid (~149 Tk per batch).

Chapter 5: Results and Analysis

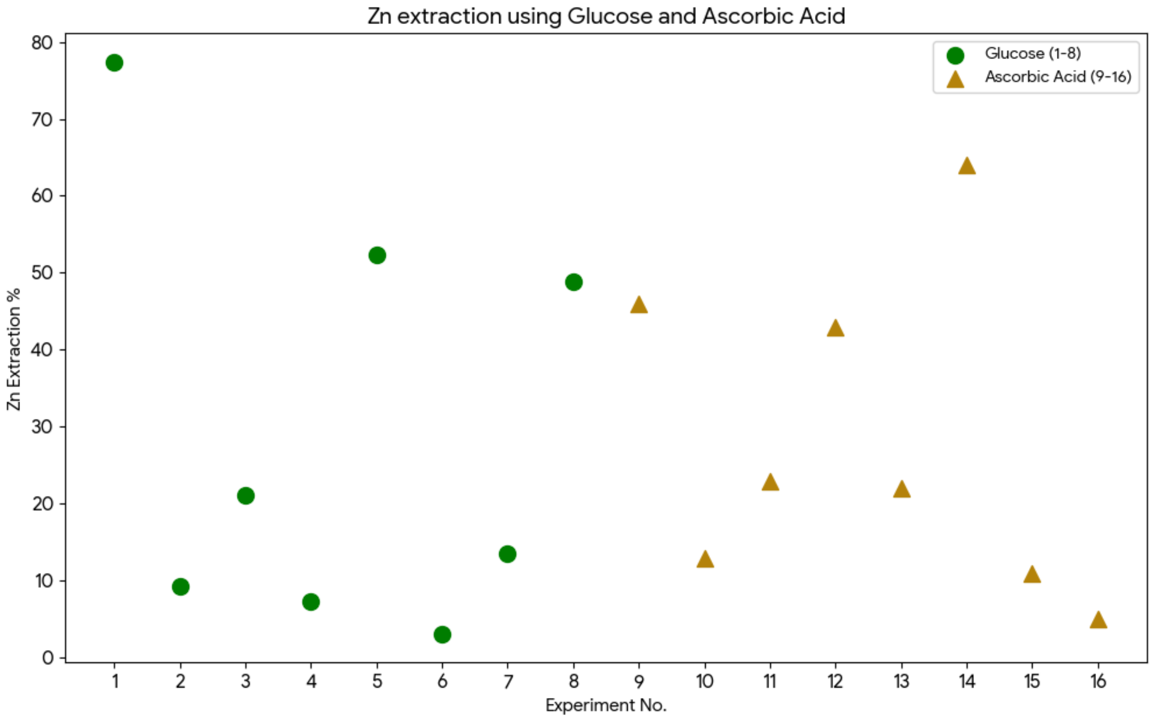
This chapter presents the outcomes of the experimental work, analyzing the efficiency of zinc (Zn) and manganese (Mn) recovery from spent Zn–C batteries using glucose and ascorbic acid as green reductants. The discussion integrates the experimental data, the effects of varying operating conditions, and the comparative economic and environmental implications of the results.

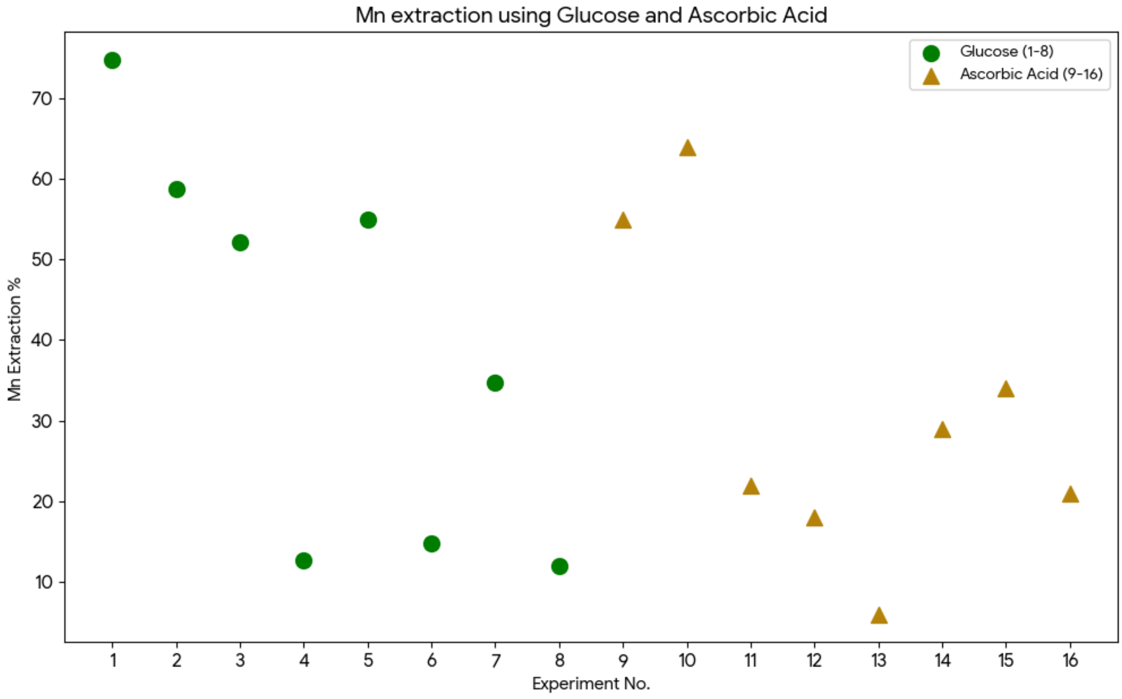
5.1 Extraction Performance under Different Conditions

The experimental trials revealed that the recovery efficiency of Zn and Mn was strongly dependent on reductant type, reductant dosage, and black mass loading. Among all trials, the optimum condition was obtained when **2.25 g glucose**was used with **5 g black mass**, achieving **74.83% Mn extraction** and **77.43% Zn extraction**. In contrast, the best result with ascorbic acid under similar conditions yielded **54.98% Mn** and **52.32% Zn**, clearly indicating the superior performance of glucose.

High reductant dosages (13.5 g) consistently lowered efficiency for both metals, suggesting that excess organic matter reduces the effective acid-to-solid ratio, increases slurry viscosity, and may lead to unwanted side reactions that hinder dissolution. Similarly, increasing the black mass loading to 10 g reduced recovery due to acid limitation and mass transfer resistance. Thus, the results confirm that an optimal balance between reductant amount and solid loading is essential for maximizing recovery efficiency.

Experiment No.	**Mn Extraction %**	**Zn Extraction %**
1 (optimum)	74.83	77.43
2	58.77	9.28
3	52.21	21.04
4	12.65	7.32
5 (optimum)	54.98	52.32
6	14.8	3.15
7	34.67	13.46
8	22.86	48.86


Zn extraction using Glucose and Ascorbic Acid
Zn Extraction %
Experiment No.
0
10
20
30
40
50
60
70
80
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
Glucose (1-8)
Ascorbic Acid (9-16)

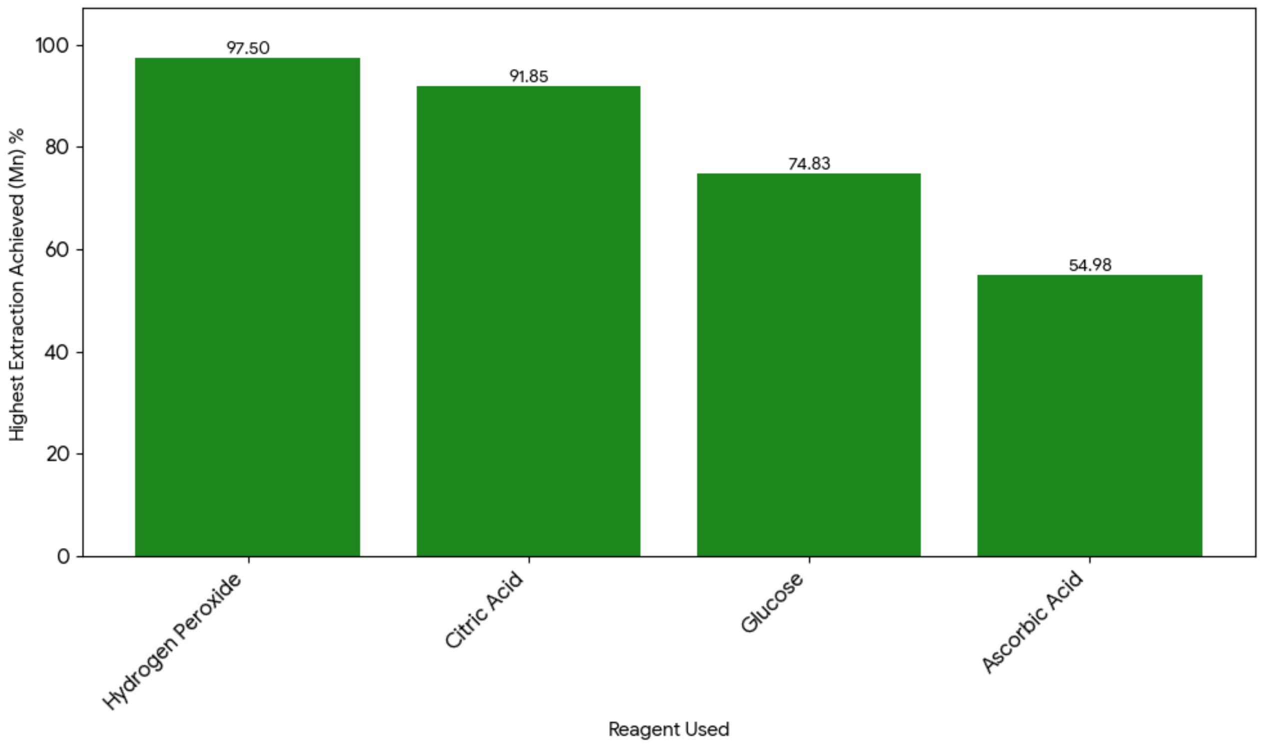

Mn extraction using Glucose and Ascorbic Acid
Mn Extraction %
Experiment No.
10
20
30
40
50
60
70
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
Glucose (1-8)
Ascorbic Acid (9-16)

5.2 Influence of Reductant Type: Glucose vs. Ascorbic Acid

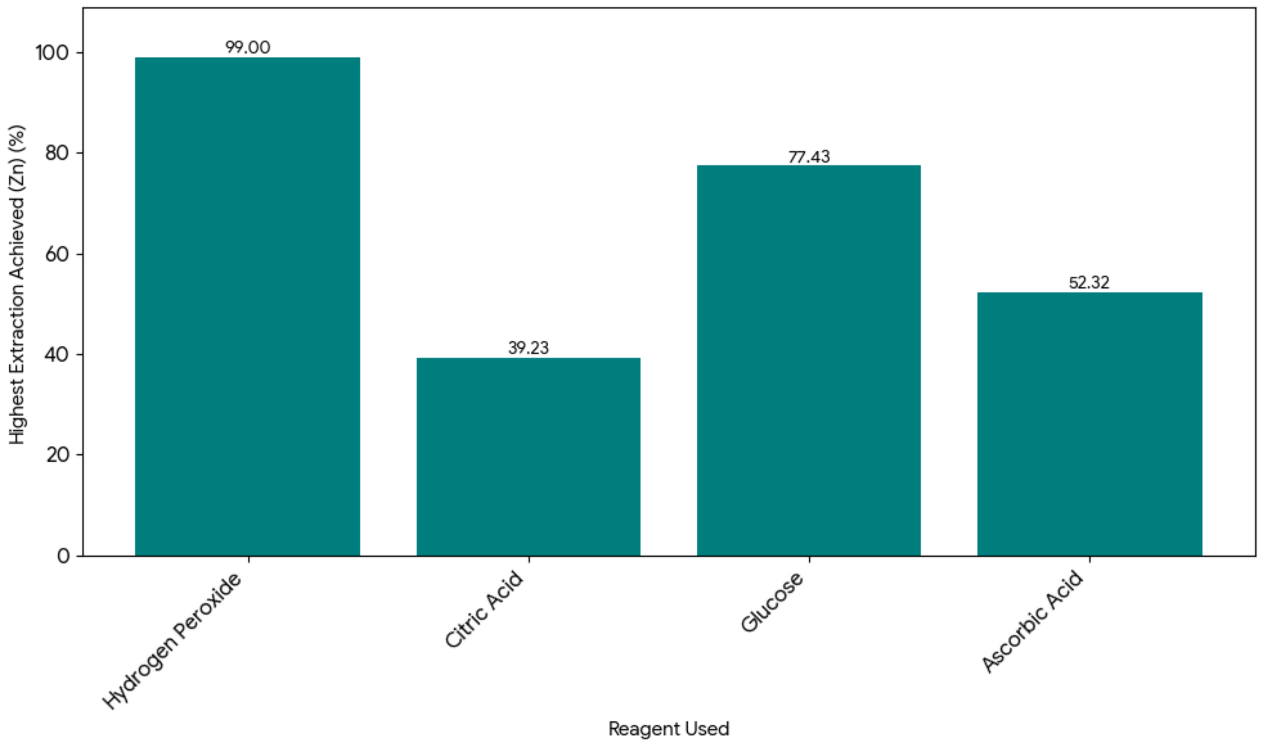
The comparison between the two reductants demonstrated that glucose was consistently more effective and economical than ascorbic acid. On average, glucose yielded higher Mn recoveries and produced the single best trial result for Zn. The stronger reducing capability of glucose under acidic conditions enhances the conversion of MnO_2 to soluble Mn^{2+}, improving dissolution and facilitating simultaneous Zn release. Ascorbic acid showed moderate performance but was less stable under the experimental conditions and required higher cost per unit of extraction. This indicates that glucose not only ensures higher technical recovery but also aligns better with the goal of sustainable and low-cost green chemistry.

5.3 Selective Recovery and Efficiency Analysis

Following leaching, sequential precipitation with NaOH enabled selective recovery of Zn at pH 8 and Mn at pH 12. The effectiveness of this approach was confirmed through Atomic Absorption Spectroscopy (AAS), which provided precise quantification of recovered metals. Correlation between Mn and Zn extraction efficiencies showed that conditions favorable for one metal generally benefited the other, although some selective shifts were observed. For example, certain high-dose experiments favored Mn while suppressing Zn recovery, whereas other cases showed relatively higher Zn selectivity. Overall, the optimum glucose condition achieved balanced co-recovery, yielding gram-scale recoveries of approximately **2.06 g Mn** and **0.76 g Zn** per 5 g of processed black mass. These results highlight the viability of pH-controlled precipitation as a simple, scalable method for separating and purifying target metals from complex leachates.



100
80
60
40
20
0
Highest Extraction Achieved (Mn) %
97.50
91.85
74.83
54.98
Hydrogen Peroxide
Citric Acid
Glucose
Ascorbic Acid
Reagent Used



100
80
60
40
20
0
Highest Extraction Achieved (Zn) (%)
99.00
39.23
77.43
52.32
Hydrogen Peroxide
Citric Acid
Glucose
Ascorbic Acid
Reagent Used

Analysis of Reagent Performance

The table compares the extraction efficiency of different reductants for manganese (Mn) and zinc (Zn) recovery from spent dry-cell batteries. Both literature data and experimental results are included.

Hydrogen Peroxide (Not Green)

- **Mn Recovery:** >97.5%
- **Zn Recovery:** >99%
- **Source:** Literature (Al Mahbub et al., 2015)
- **Analysis:** Hydrogen peroxide demonstrated the highest recovery rates for both Mn and Zn. However, it is **not considered green** due to safety hazards, instability, and potential environmental impact. While efficient, its large-scale application may lead to handling and sustainability concerns.

Citric Acid (Green)

- **Mn Recovery:** 91.85%
- **Zn Recovery:** 39.23%
- **Source:** Literature (Al Mahbub et al., 2015)
- **Analysis:** Citric acid provided excellent Mn recovery but significantly lower Zn extraction. As a biodegradable and non-toxic organic acid, it qualifies as a green reagent, but its limited Zn recovery makes it less favorable compared to other options.

Glucose (Green, Our Experiment)

- **Mn Recovery:** 74.83%
- **Zn Recovery:** 77.43%
- **Analysis:** Glucose achieved a balanced recovery of both Mn and Zn, though Mn recovery was lower than citric acid and hydrogen peroxide. However, glucose is cheap, biodegradable, and widely available in Bangladesh, making it highly promising for sustainable industrial-scale adoption. Its **cost-effectiveness** offsets the moderate recovery efficiency.

Ascorbic Acid (Green, Our Experiment)

- **Mn Recovery:** 54.98%
- **Zn Recovery:** 52.32%
- **Analysis:** Ascorbic acid showed moderate recovery for both metals, lower than glucose and citric acid. Despite its strong reducing power, the efficiency was less favorable under the conditions tested in this experiment. The reagent cost is also higher compared to glucose, which limits industrial feasibility.

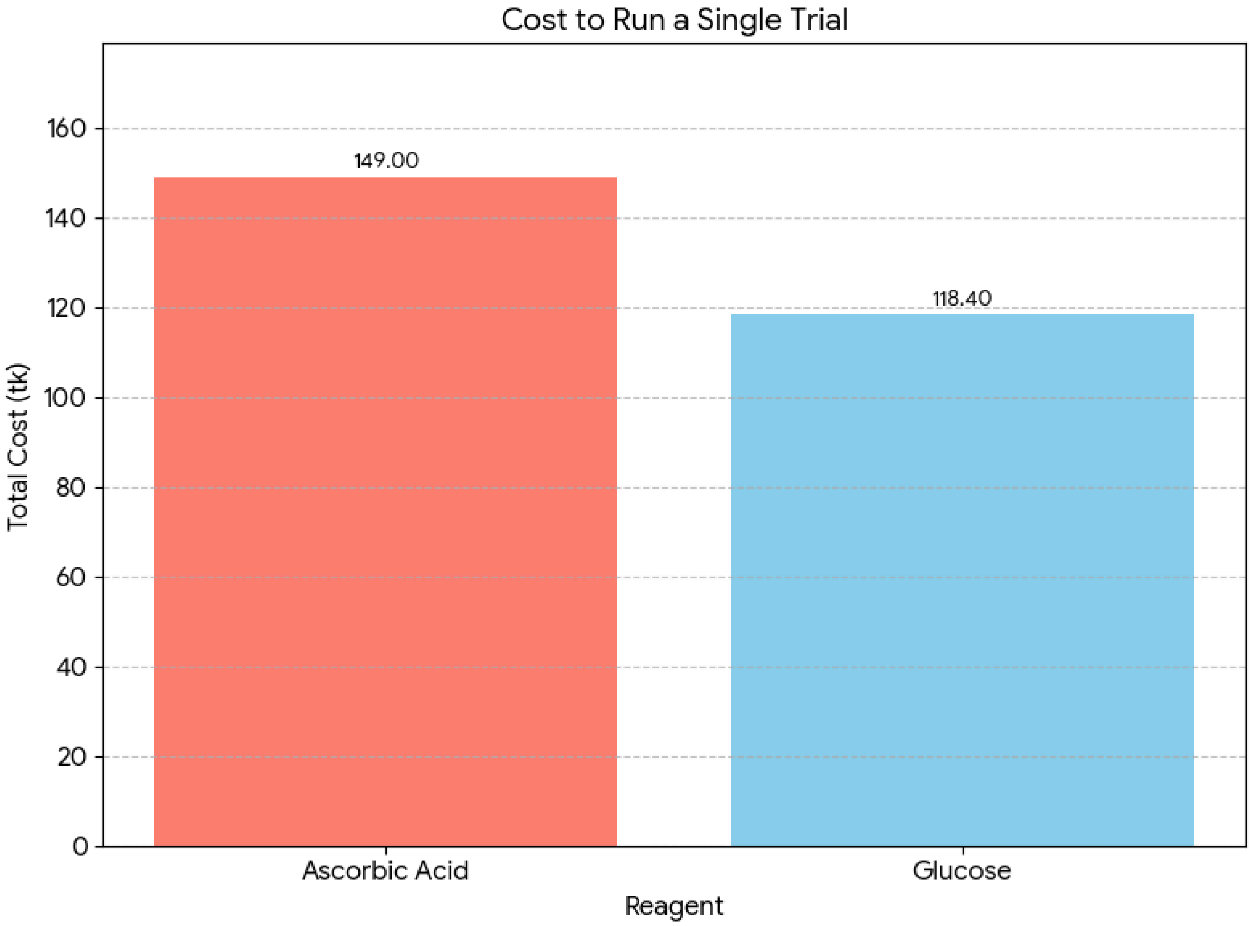
Key Findings from Comparison

1. **Hydrogen peroxide** is the most effective chemically, but not environmentally sustainable.
2. **Citric acid** achieves high Mn recovery but fails in Zn recovery, limiting its overall use.
3. **Glucose** balances Mn and Zn recovery with good overall performance, while being cost-effective and green, making it the **most practical solution** for Bangladesh.

4. **Ascorbic acid** is environmentally safe but less efficient than glucose under the tested conditions.

5.4 Economic and Environmental Implications

The cost analysis revealed that the glucose-based process was significantly more economical than the ascorbic acid route. For the optimum trial, glucose required approximately **118 Tk per batch**, compared to **149 Tk for ascorbic acid**, translating into a lower cost per percentage of recovery efficiency. From an environmental standpoint, both reductants are green alternatives to conventional agents such as hydrogen peroxide or strong mineral acids, but glucose has the added advantage of being renewable, inexpensive, and less hazardous. In comparison with literature benchmarks, while peroxide-assisted systems can achieve very high recoveries (>95%), they involve higher chemical hazards and costs. The glucose system, therefore, represents a balanced compromise between efficiency, safety, and sustainability. The findings suggest that this process can be scaled up for industrial application in Bangladesh, providing a circular-economy solution to the growing problem of battery waste.


Cost to Run a Single Trial
Total Cost (tk)
160
140
120
100
80
60
40
20
0
149.00
118.40
Ascorbic Acid
Glucose
Reagent

Chapter 6: Conclusion and Recommendations

6.1 Conclusion

This study investigated the recovery of manganese (Mn) and zinc (Zn) from spent dry-cell batteries using a hydrometallurgical approach based on sulfuric acid leaching with glucose and ascorbic acid as green reductants. The black mass, primarily composed of manganese dioxide and zinc oxide, was first washed, dried, and characterized using XRF and AAS. The results confirmed Mn and Zn as the major constituents, consistent with literature values.

Experimental leaching trials demonstrated that:

- **Sulfuric acid alone** provided significant dissolution of zinc, but manganese extraction remained limited due to the stability of MnO_2.

- **Ascorbic acid** acted as a strong reductant, successfully converting insoluble Mn^{4+} species into soluble Mn^{2+}, thereby enhancing manganese recovery rates.

- **Glucose**, while less effective than ascorbic acid, offered a cost-effective and environmentally safer alternative, making it attractive for large-scale applications in Bangladesh.

- **Process parameters** such as acid concentration, reductant dosage, temperature (80 °C), and reaction time had notable influence on extraction efficiency, with optimized conditions yielding higher overall recoveries.

The study also highlighted the **environmental benefits** of adopting green reductants. Unlike conventional methods that rely on hazardous chemicals, glucose and ascorbic acid are biodegradable, non-toxic, and reduce the environmental footprint of recycling processes. Additionally, this work establishes a potential framework for introducing sustainable battery recycling in Bangladesh, where no formal recycling infrastructure currently exists.

Overall, the findings confirm that green reductant-assisted hydrometallurgy is a promising route for zinc and manganese recovery, offering both economic and ecological advantages.

6.2 Recommendations for Future Works

Although the present study achieved promising results, further work is required to advance the process toward industrial adoption. Future research should focus on:

1. **Optimization Studies:** Conducting systematic parametric optimization using techniques such as Design of Experiments (DOE) or metaheuristic algorithms (e.g., Genetic Algorithm) to fine-tune reagent ratios, temperatures, and reaction times.

2. **Scale-Up Investigations:** Extending laboratory experiments to pilot- and industrial-scale reactors, examining reactor design, mixing efficiency, and heat management.

3. **Alternative Green Reductants:** Exploring other low-cost, biodegradable reducing agents (e.g., organic acids from agricultural waste, molasses-derived sugars) to further reduce reagent costs.

4. **Kinetic and Thermodynamic Modeling:** Developing detailed kinetic models to describe Mn and Zn leaching mechanisms and predict recovery performance under different conditions.

5. **Life Cycle and Economic Analysis:** Assessing the feasibility of industrial adoption through cost–benefit analysis, environmental life-cycle assessment (LCA), and comparison with conventional recycling and mining practices.

6. **Integration with Circular Economy:** Investigating how the recovered metals can be reused in local industries (e.g., fertilizers, alloys, or battery re-manufacturing) to close the material loop in Bangladesh.

7. **Policy and Infrastructure Development:** Collaborating with policymakers to design regulations and collection systems that ensure safe disposal and systematic recycling of spent batteries

6.3 Final Remark

The rapid growth of battery consumption in Bangladesh and worldwide calls for urgent development of sustainable recycling solutions. This study demonstrates that green reductant-assisted hydrometallurgy can serve as an effective pathway for recovering valuable metals while minimizing environmental damage. By bridging scientific innovation with eco-friendly practices, the work not only contributes to advancing waste management strategies but also supports broader goals of resource conservation and circular economy. With continued research, scale-up, and policy support, such approaches can transform hazardous waste into valuable resources and play a vital role in building a cleaner, greener future.

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