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# Wastewater Treatment of the Automotive Sector with a Circular Economy, Water Reuse, and ZLD Approach

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## **Declaration**

I hereby declare that the work presented in this thesis, entitled “*Wastewater Treatment of the Automotive Sector with a Circular Economy, Water Reuse, and ZLD Approach*,” is my original research carried out in the *Department of Industrial & Information Engineering & Economics, University of L’Aquila*. This work has not been submitted in part or in full for the award of any other degree or diploma at this or any other university.

All the information derived from the published or unpublished work of others has been duly acknowledged and referenced in the text.

I take full responsibility for the contents of this thesis.

This thesis is submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of L’Aquila.

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## **Dedication**

I dedicate this thesis to my beloved family, whose endless love, patience, and encouragement have been my greatest strength throughout this journey.

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## Abstract

This research addresses the critical challenge of sustainable wastewater treatment and management within the automotive sector, championing the principles of the circular economy (CE), water reuse, and Zero Liquid Discharge (ZLD). Industrial activities consume approximately 22% of global water, with 80% of generated effluent being directly discharged into water bodies, posing significant environmental and health risks. The imperative for treating and reusing industrial wastewater is therefore profound, directly contributing to United Nations Sustainable Development Goal 6 (SDG 6), "Clean Water and Sanitation," by focusing on innovative strategies for water-intensive recycling processes. The research encompasses four distinct case studies, each tackling wastewater generated from the hydrometallurgical recycling of key automotive components. For wastewater from spent Lithium-ion Batteries (LIBs) recycling, which presented a high Chemical Oxygen Demand (COD) of 5390 mg/L and basic pH (10.17), the Fenton process was optimized, achieving a maximum COD removal of 98.79%. An economically favorable condition, at a cost of 23.23 €/m<sup>3</sup>, achieved 94.79% COD reduction, rendering the treated water (COD 56.90 mg/L) suitable for recycling into subsequent hydrometallurgical processes, supporting lithium recovery and ZLD. Wastewater from spent Alkaline Batteries (SABs) recycling, characterized by a highly basic pH (11.7) and significant levels of barium, lead, strontium, and a COD of 9715 mg/L, underwent a crucial acidic precipitation pre-treatment at pH 1. This step effectively reduced Ba, Pb, and Sr concentrations to negligible levels (0.1-0.3 mg/L) and substantially reduced COD by 72% to 2727 mg/L. Subsequent Fenton treatment achieved up to 84.11% COD removal, with optimization via central composite design identifying optimal conditions (7.91% H<sub>2</sub>O<sub>2</sub> and 1.5 g/L Fe<sup>2+</sup>) that yielded 81.37% COD removal with minimized cake generation and reagent consumption. The final treated water, primarily sodium sulfate (13.8 g/L), allows for its recovery via evaporation-crystallization, further enhancing circularity. In the case of In-Mold Structural Electronics (IMSEs) recycling, wastewater from silver extraction was acidic (pH 1.39) with high COD (14.48 g/L), iron (8.69 g/L), copper (117 mg/L), and thiourea. Direct Fenton treatment was applied without preliminary pH correction, achieving 93.6% COD removal and over 99% removal of both Fe and Cu without additional ferrous sulfate, leveraging the inherent iron content. UV-VIS analysis confirmed the effective decomposition of thiourea. This efficient treatment allows for a 90% reduction in water consumption, supporting a Minimal Liquid Discharge (MLD) approach, and offers a cost-effective alternative to wastewater disposal (81.60 €/m<sup>3</sup> vs. 150 €/m<sup>3</sup>). Finally, for spent Permanent Magnets (NdFeB) recycling,

wastewater from Rare Earth Element (REE) extraction was acidic (pH 3.04) and rich in iron (32366 mg/L), boron, and praseodymium. This study focused on iron recovery using oxalic acid. Optimal conditions were identified as 80% stoichiometric oxalic acid addition at 25 °C, achieving 85.3% iron recovery while simultaneously removing a significant portion of praseodymium (94%) and boron. A secondary lime precipitation step ensured the removal of residual iron and other elements. Thermal analysis confirmed the decomposition of precipitated iron oxalate into iron oxide at an optimal calcination temperature of 214.5 °C, contributing to resource recovery. Overall, this research consistently demonstrates that integrating advanced wastewater treatment technologies into hydrometallurgical recycling processes is not only technically feasible but also economically viable and environmentally essential for achieving sustainable industrial ecosystems within the circular economy model. By maximizing water reuse and recovering valuable resources, this thesis provides a pathway to minimize industrial water footprints, protect natural ecosystems, and ensure long-term water security for future generations.

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## **Chapter: 1. Introduction**

Water is a vital resource for all life on our planet [1]. It is necessary for food and energy security, contributing to human health and well-being, and eradicating hunger and poverty [2]. Additionally, some experts believe that water plays a pivotal role in facilitating effective climate adaptation measures [3,4]. On Earth, approximately 98% of water is found in seas, with only 2% being freshwater, which is essential for drinking and other uses. Unfortunately, this limited amount of freshwater is increasingly being polluted by human and industrial activities, leading to contamination [5,6]. This increase is particularly evident in the industrial sector, which consumes approximately 22% of global water [7–10]. The primary cause of water contamination comes from various sources, including industries, mining activities, sewage, chemical fertilizers, radioactive waste, and the rapid expansion of urbanization. These factors negatively impact the environment, deplete resources, and create challenges for different forms of life [5]. Regrettably, 80% of the generated effluent is discharged directly into water bodies, posing significant risks of environmental pollution and endangering aquatic ecosystems and human health [7–10]. According to a report from the World Health Organization (WHO), the use of unsafe wastewater for drinking, sanitation, and other purposes has resulted in the deaths of 10 million people [11]. Due to population growth and industrial development, the rapid increase in water demand may lead to issues such as scarcity, drought, and waste generation. These challenges can be mitigated through efficient wastewater treatment and management systems.[12].

### **1.1: Importance of Wastewater Treatment in a Circular Economy**

Within the transformative framework of the circular economy (CE), which aims to replace the traditional linear "take-make-use-dispose" model by striving to keep products, materials, and resources in the economy for as long as possible and minimizing waste generation, wastewater treatment is undergoing a significant evolution. Water is essential for life and sustainable development, but increasing global population and industrialization have led to rapidly increasing freshwater demand and widespread water stress [13,14]. With over a billion people already lacking adequate drinking water, there is an urgent need for sustainable water management [13]. Historically, wastewater, particularly industrial wastewater, has been viewed primarily as a waste product requiring treatment to remove pollutants and protect the environment and public health [12,15]. However, the CE perspective recognizes wastewater not as a disposal challenge, but as a valuable resource that can be integrated into recycling processes to close resource loops [16,17].

Industrial wastewater is especially significant in this context, characterized by diverse contaminants but also carrying a variety of potentially valuable resources. The CE approach promotes the recovery of these materials for industrial reuse, contributing to environmental sustainability and potential economic benefits [17]. A key focus within these recycling processes is the recovery of metals, including heavy metals and precious elements. Technologies such as electrochemical methods (e.g., electrosorption, ion exchange), membrane processes (e.g., MF-RO), and biological treatments are crucial for extracting these metals [18].

Furthermore, the recycling and reuse of treated industrial water is fundamental to achieving full circularity [14,17]. Reclaimed water from industrial processes can serve as a reliable alternative water supply for various industrial applications, significantly reducing the demand on finite freshwater resources [17,19]. While challenges remain, such as ensuring the treated water quality meets the specific needs of different applications and addressing potential risks from residual pollutants, the integration of advanced recycling technologies allows for effective pollutant removal and resource extraction. This transformation of industrial wastewater management through comprehensive recycling processes is thus integral to building a more resource-efficient, environmentally sustainable, and economically viable industrial ecosystem within the circular economy model. This paradigm shift helps minimize waste generation and keeps valuable materials and water in circulation, directly supporting the core objectives of the circular economy.

## **1.2: Sustainability and Alignment with UN Sustainable Development Goals (SDGs)**

Sustainable water management is essential for life, human health, ecological balance, and industrial processes like recycling. However, increasing global population, industrialization, and climate change are significantly raising water demand, putting immense pressure on freshwater resources. Given that only about 0.3% of the world's water is readily accessible for human use [13], the uneven global distribution of water and increasing pollution further complicate this, highlighting the necessity of treating and reusing wastewater, especially in water-intensive industries.

In response, the United Nations adopted Sustainable Development Goal 6 (SDG 6), “Clean Water and Sanitation,” as part of the 2030 Agenda for Sustainable Development, given in the *Figure 1*. SDG 6 aims to ensure water and sanitation are available and managed sustainably for all by 2030 [20]. The SDG 6 Global Acceleration Framework was launched in 2020 to speed up progress, focusing on pollution reduction, safe water reuse, and protecting water-related

ecosystems [1,21]. Importantly, SDG 6 is connected to broader sustainable development outcomes, influencing goals related to health (SDG 3), poverty alleviation (SDG 1), food security (SDG 2), decent work (SDG 8), responsible consumption (SDG 12), innovation (SDG 9), and climate action (SDG 13) [1,22,23].

This thesis contributes to these objectives by focusing on sustainable wastewater treatment strategies in hydrometallurgical recycling. These processes, used to recover valuable materials from spent automotive batteries, in-mold structural electronics, and permanent magnets, are inherently water-intensive. Without proper treatment and reuse systems, they could worsen water scarcity and environmental degradation. Therefore, integrating robust wastewater treatment technologies into these recycling activities is essential for both operational sustainability and advancing SDG 6, particularly Target 6.3, which focuses on improving water quality, increasing recycling, and reducing hazardous substance discharge. By enabling the purification and recirculation of process water, this research minimizes reliance on freshwater and significantly reduces polluted effluent discharge. This directly aligns with circular economy principles and supports responsible resource consumption and production (SDG 12). Furthermore, adopting these advanced treatment practices promotes green technology development and sustainable industrial innovation, contributing to SDG 9 and supporting economic opportunities within the circular economy (SDG 8). Overall, treating and reusing wastewater in industrial recycling is a critical strategy for sustainable development. By aligning water management with the SDGs, especially SDG 6, this research shows a path to reducing industrial water footprints, protecting natural ecosystems, and ensuring long-term water security for future generations.

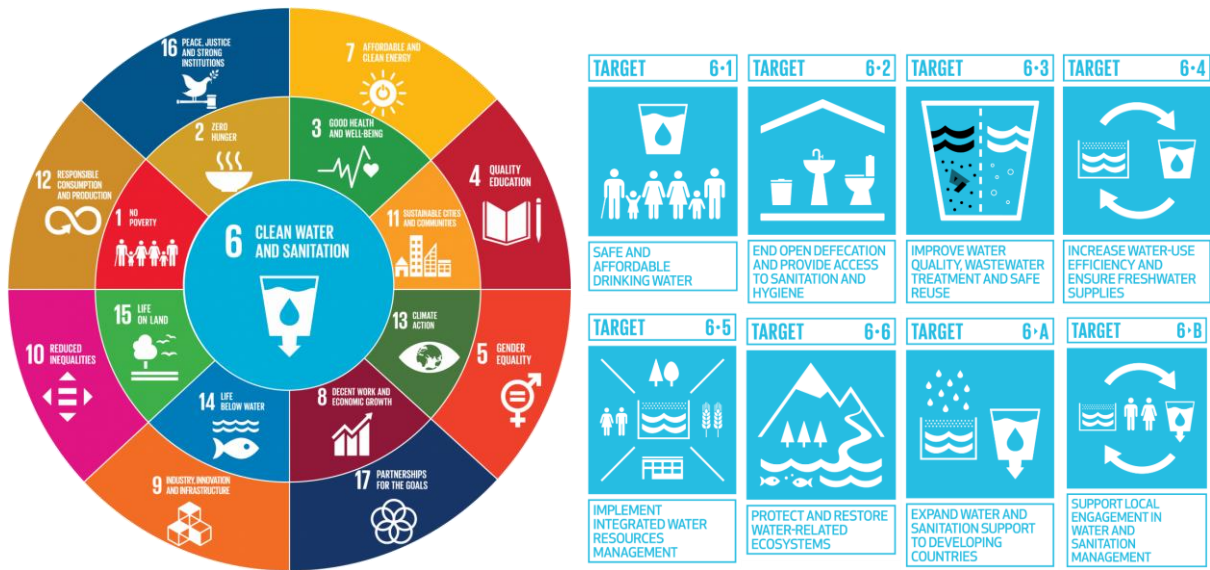


Figure 1: Sustainable Development Goal 6: Clean Water and Sanitation and Its Interlinkages with Other SDGs.

### 1.3: Research Objectives

The main objectives of this PhD research are:

- To develop innovative wastewater treatment technologies for the automotive sector, guided by circular economy principles and aimed at maximizing the reuse of treated water.
- To minimize the industry's reliance on freshwater resources by promoting Zero Liquid Discharge (ZLD) strategies.
- To implement advanced treatment methods that prevent adverse impacts of wastewater on water quality and ecosystems.
- To integrate sustainable wastewater management into automotive manufacturing practices, supporting the shift towards environmentally responsible operations.
- To contribute to Sustainable Development Goal 6 (Clean Water and Sanitation) by reducing water consumption and wastewater discharge in alignment with global environmental targets.

### 1.4: Structure of the Thesis

This thesis is structured into seven chapters, each designed to address critical aspects of research into sustainable wastewater treatment within the automotive sector, with a particular focus on resource recovery and its connection to global sustainability objectives.

- **Chapter 1: Introduction.** This chapter establishes the significance of water as an essential natural resource and outlines the global challenges related to water scarcity and pollution. It emphasizes the importance of clean water in the context of the United Nations Sustainable Development Goals (SDGs), specifically Goal 6: Clean Water and Sanitation. Furthermore, it introduces the concept of water reuse in industrial processes, highlighting its potential to support sustainable manufacturing within the automotive sector.
- **Chapter 2: Literature Review.** This chapter provides a comprehensive review of existing research and technological advancements relevant to the four experimental projects covered in this thesis. Each project addresses a specific source of industrial wastewater and its treatment within the broader context of automotive or battery-related processes
  - Treatment of wastewater generated during the recycling of spent lithium-ion batteries. This section reviews the chemical composition of this wastewater, focusing on treatment methods for the removal of heavy metals and other hazardous substances.
  - Treatment of wastewater produced during the recycling of spent alkaline batteries. This discusses the nature of leachate from alkaline batteries and assesses current technologies for contaminant removal and water purification.
  - Treatment of wastewater produced during the recovery of silver from in-mold structural electronics (IMSE) in the automotive sector. This section examines wastewater generated during silver recovery processes and explores treatment strategies that address metal removal and environmental compliance in electronic waste streams.
  - Recovery of iron and treatment of wastewater produced during rare earth element (REE) recovery from spent permanent magnets used in automotive applications. This review focuses on integrated approaches for recovering iron while treating acidic wastewater produced during REE leaching processes, highlighting both environmental and economic considerations.
- **Chapter 3: Spent Lithium-ion Batteries Recycling.** This chapter presents the experimental methodology, results, and analysis related to the treatment of wastewater generated from the recycling of spent lithium-ion batteries.

- **Chapter 4: Spent Alkaline Batteries Recycling.** This chapter outlines the procedures, experimental findings, and discussions for the treatment of wastewater from spent alkaline battery recycling.
- **Chapter 5: Recycling of In-Mold Structural Electronics.** This chapter details the experimental work and discussion concerning the treatment of wastewater produced during the recovery of silver from in-mold structural electronics.
- **Chapter 6: Recycling of Spent Permanent Magnets.** This chapter presents the methodology and findings related to iron recovery and wastewater treatment from the REE recovery process applied to spent automotive permanent magnets.
- **Chapter 7: Conclusion.** The final chapter summarizes the key findings of the research and discusses their implications for sustainable wastewater management in industrial settings.

## Chapter: 2. Literature Analysis

### 2.1: Lithium-ion Spent Batteries

#### 2.1.1: Sources and Composition of Wastewater from Spent Li-Ion Batteries

Wastewater from the recycling of used lithium-ion batteries (LIBs) is generated throughout various stages of the process, such as discharging, mechanical sorting, crushing, leaching, solvent-based extraction, and electrolyte recovery. Each of these steps introduces different kinds of specific contaminants and pollutants, leading to a complex wastewater mixture that contains acids, salts, heavy metals, flammable electrolytes like  $\text{LiBF}_4$ ,  $\text{LiPF}_6$ , and  $\text{LiClO}_4$ , and organic solvents [24]. Dangerous heavy metals, including lead, manganese, along with lithium, present significant ecological risks [25,26]. Additionally, new pollutants such as graphene materials [27,28], metal oxides [29], and ionic liquids [30,31], further increase environmental strain. Improper disposal of LIBs can contaminate soil and groundwater with fluorides, organic electrolytes, and heavy metals, resulting in serious environmental problems [32,33].

*Wenz et al.* [34] analyzed the wastewater produced during the Electrohydraulic Fragmentation (EHF) process used in recycling spent Li-ion batteries, as detailed in *Table 1*. This analysis suggests that biological treatment methods may not be effective for treating this type of wastewater due to the inhibitory effects of certain compounds on microorganisms. Instead, physical-chemical techniques appear to be more efficient for recovering organic solvents and lithium, as well as for recycling water to reduce overall water usage.

The mechanical treatment of LIBs separates key components like iron shells, anodes, cathodes, and copper and aluminum foils, as well as electrolytes for further processing. However, this process also generates a considerable amount of wastewater that contains fluorides and organic solvents, leading to potential contamination [35]. Fluoride compounds, which originate from the breakdown of battery electrolytes during leaching and mechanical separation, contribute to water pollution. Contaminants such as benzene, ester compounds, and lithium hexafluorophosphate ( $\text{LiPF}_6$ ) are particularly resistant and persistent to microbial breakdown [36]. Grinding, another step in the recycling process, typically requires wet conditions, which leads to the production of a substantial amount of wastewater. During the leaching stage, various acids like  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{HNO}_3$  are used to extract valuable metals such as cobalt, manganese, lithium, and nickel from the materials of used batteries, resulting in wastewater that contains high concentrations of acids and dissolved metals [37]. This critical step in metal recovery significantly adds to wastewater contamination, requiring proper treatment to prevent environmental harm. Metals such as cobalt and nickel often exceed safe levels, posing risks to

aquatic ecosystems if untreated wastewater is released. Following leaching, solvent extraction is commonly employed to recover metals from the leachate [38], but this process produces large quantities of oily wastewater [39]. The recovery of one ton of metal can generate approximately 20,000 liters of oily wastewater, which contains potentially toxic and carcinogenic compounds, including di(2-ethylhexyl) phosphoric acid (P204) and 2-Ethylhexyl phosphoric acid mono(2-ethylhexyl) ester (P507), as well as 260# solvent oil. Untreated discharge of this wastewater can severely impact the environment and pose considerable risks to human health [40].

The recycling of lithium-ion batteries produces a large volume of wastewater, primarily due to the electrolyte, which contains lithium salts such as lithium hydroxide and lithium carbonate, along with organic solvents like diethyl carbonate and ethylene carbonate [41]. These organic solvents further complicate the treatment process and pose significant risks to both the environment and human health. The acids used during resource recovery also lower the pH of the wastewater by increasing its acidity. The lithium-ion battery electrolyte, a mixture of organic solvents, lithium salts, and other chemicals and hazardous substances, can easily contaminate soil, water, and air, causing adverse environmental effects [41]. Organic solvents, which make up about 84% of the electrolyte, include compounds such as dimethyl carbonate, methyl ethyl carbonate, and ethylene carbonate [41–43]. Furthermore, toxic products like HF and PF<sub>5</sub> are released, further increasing the contamination of water and air [41].

The complex nature of wastewater produced during the recycling of LIBs requires advanced treatment practices to address its diverse pollutants. Common methods for treating this type of wastewater include chemical precipitation [44], electrodialysis [45], solvent extraction [46], activated carbon [47], ion exchange, and electrocoagulation [48]. However, the presence of various pollutants at different concentrations makes it challenging to develop a single treatment process that can effectively address all the contaminants. Therefore, a combination of physical and chemical [34] treatment methods are often used to reduce organic solvents, heavy metals, and other harmful substances to safe levels, ensuring the wastewater is safe for discharge or reuse.

Table 1: Characteristics of wastewater produced during the Electrohydraulic Fragmentation (EHF) process for recycling of spent LIBs [34].

| Elements | Concentration | Elements             | Concentration |
|----------|---------------|----------------------|---------------|
| pH-value | 7.7           | Conductivity (ms/cm) | 2.1           |

|                       |       |                          |      |
|-----------------------|-------|--------------------------|------|
| COD (mg/L)            | 3,176 | BOD <sub>5</sub>         | 563  |
| COD/BOD <sub>5</sub>  | 5.6   | Fluoride (mg/L)          | 84.5 |
| Total fluorine (mg/L) | 695   | Total Phosphorous (mg/L) | 215  |
| Lithium (mg/L)        | 168   | Cobalt (mg/L)            | 0.2  |
| Calcium (mg/L)        | 20.7  | Magnesium (mg/L)         | 1.3  |

## 2.1.2: Wastewater Treatment Technologies

### 2.1.2.1: Physical Treatment Methods

These methods primarily involve separating pollutants from wastewater through physical or mechanical means without any chemical change. Common methods mentioned include adsorption, sedimentation, and filtration.

*Prasakti et al.* [47] investigated granular activated carbon (GAC) and activated carbon block (CTO) for removing sodium (Na) and lithium (Li) from artificial wastewater mimicking that of lithium iron phosphate (LFP) battery recycling. GAC showed higher removal efficiencies of 11.71% for lithium and 19.51% for sodium within 20 minutes, while CTO achieved 10.33% for lithium and 14.65% for sodium. The adsorption capacity decreased after 20 minutes due to saturation. The study suggests the potential of activated carbon in treating LIBs recycling wastewater, although further optimization is needed. *Siti Nurkhopipah et al.* [49] explored the use of a fixed-bed column with activated carbon to remove lithium, phosphate, and sodium from LFP battery cathode recycling wastewater. They found that the best removal efficiencies of 95.22% for lithium, 96.42% for sodium, and 68.02% for phosphate were achieved at the lowest flow rate of 10 mL/min. This indicates that a slower flow rate allows for a longer contact time between the wastewater and the activated carbon, enabling more effective adsorption of the target ions. The breakthrough times (335 minutes for lithium, 441 minutes for sodium, and 126 minutes for phosphate) provide information about the longevity of the activated carbon bed before it becomes saturated, and its removal efficiency drops below an acceptable level. The maximum adsorption capacities calculated using kinetic models ( $8.75 \times 10^5$  mg/g for Li,  $8.85 \times 10^5$  mg/g for Na, and  $3.91 \times 10^5$  mg/g for  $\text{PO}_4^{3-}$ ) highlight the potential of activated carbon to adsorb substantial amounts of these ions under optimal conditions. This study demonstrates that activated carbon can be highly effective for treating LFP wastewater when used in a fixed-bed column with an optimized flow rate, providing valuable data for designing such treatment systems. *Zhang et al.* [50] investigated the use of forward osmosis (FO) for treating wastewater containing organophosphorus from the lithium-ion batteries recycling process, focusing on developing efficient draw solutes. They found that their synthesized pH-sensitive zinc complex, ZnATMP-3Na, exhibited superior performance compared to other

tested compounds and conventional draw solutes like  $\text{NH}_4\text{HCO}_3$  and  $\text{NaCl}$ .  $\text{ZnATMP-3Na}$  showed minimal solute loss, high osmotic pressure, and an impressive water recovery efficiency of 8.3 LMH (liters per square meter per hour). The high osmotic pressure is crucial for driving water across the semipermeable membrane from the wastewater to the draw solution. The minimal solute loss is important for preventing contamination of the treated water and maintaining the effectiveness of the draw solution. The significant water recovery efficiency indicates the potential of this draw solute to effectively desalinate the wastewater. Furthermore, at a 0.6M concentration,  $\text{ZnATMP-3Na}$  achieved a water flux of 12.7 LMH, which is 136% higher than that of  $\text{NaCl}$ , a commonly used draw solute. This superior water flux signifies a much faster rate of water purification. The pH-responsive nature of  $\text{ZnATMP-3Na}$ , allowing for easy regeneration and reuse, makes it a potentially cost-effective and sustainable option for FO in treating organophosphorus-containing wastewater. The researchers attributed its superior performance to its expanded cage-like structure, strong ionic properties, and high solubility, which contribute to a higher osmotic driving force. These results suggest that  $\text{ZnATMP-3Na}$  is a promising novel draw solute that could enhance the efficiency and sustainability of FO technology in the treatment of specific types of wastewater from LIB recycling.

#### **2.1.2.2: Chemical and Electrochemical Treatment Methods**

Chemical processes used in wastewater treatment involve introducing chemical compounds to convert dissolved or colloidal pollutants into harmless substances through chemical reactions [51]. These processes are capable of rapidly oxidizing and completely degrading organic contaminants [52]. Some studies have focused on chemically modifying absorbent materials or synthesizing novel materials for this purpose, while others have explored electrochemical methods alongside traditional chemical treatments for impurity removal.

One approach involves the use of chemically and physically activated mesoporous carbons for the sorption of metal ions. *Conte et al.* [53] investigated the effectiveness of these materials in removing  $\text{Co}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Ni}^{2+}$ , and  $\text{Mn}^{2+}$  from battery leachates. They found that chemical activation with  $\text{NaClO}_2/\text{H}_2\text{O}_2$  significantly improved metal sorption by increasing carboxylic acid functional groups. In single-metal solutions, chemically activated carbon removed over 80% of  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Mn}^{2+}$ , achieving sorption capacities exceeding 20 mg/g, while  $\text{Li}^+$  removal remained low at 20%. In multi-metallic solutions, rapid sorption kinetics were observed, reaching equilibrium within 15 minutes, with  $\text{Co}^{2+}$  sorption at 18 mg/g and negligible lithium uptake ( $q_{\text{Li}} = 0.33 \text{ mg/g}$ ). Desorption with  $\text{H}_2\text{SO}_4$  allowed for effective metal recovery,

doubling their initial concentrations. Furthermore, sequential activation (physical followed by chemical) resulted in even better sorption performance, reaching 24.2 mg/g for  $\text{Co}^{2+}$ , 21.0 mg/g for  $\text{Ni}^{2+}$ , and 22.3 mg/g for  $\text{Mn}^{2+}$ , with complete metal removal at a 20 g/L dosage within 60 minutes. This study highlights the potential of chemically activated mesoporous carbon for the selective removal of divalent cations from LIB recycling wastewater. Another chemical treatment method investigated was the use of a natural sphalerite (NS) photocatalyst ((Zn, Fe)S) for treating oily wastewater from solvent extraction in LIB recycling by *Meirong et al.* [40]. This oily wastewater is rich in extractants like 260# solvent oil, P2O<sub>4</sub>, and P5O<sub>7</sub>, and is challenging to treat due to high salt and organic contaminant concentrations. Fe doping in NS enhanced visible light absorption and carrier mobility. The introduction of H<sub>2</sub>O<sub>2</sub> further increased photocatalytic activity by inhibiting electron-hole pair recombination, leading to the production of active species ( $\text{H}_+$ ,  $\cdot\text{O}_2$ , and  $\cdot\text{OH}$ ) that effectively degrade organic contaminants. Under optimized conditions (2 g/L NS, 0.2 mol/L H<sub>2</sub>O<sub>2</sub>, 101.5 mW/cm<sup>2</sup> visible-light intensity, and pH 3.0), 86.20% total organic carbon (TOC) removal was achieved. This method presents a cheap and environmental photocatalyst for treating oily wastewater. However, it is inefficient for degrading organic compounds in high-salinity oily wastewater, and nano-photocatalysts can destabilize and aggregate in the presence of anions, reducing their effectiveness.

Electrochemical methods, such as redox-mediated bipolar membrane electrodialysis (redox-BMED), were explored by *Kim et al.* [54] for sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>) recovery in LIB recycling. Traditional bipolar membrane electrodialysis (BMED) for Na<sub>2</sub>SO<sub>4</sub> removal generates H<sub>2</sub>SO<sub>4</sub> and NaOH but suffers from high energy use, fouling, and low economic viability. Redox-BMED utilizes a ferri-/ferrocyanide ( $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ ) redox reaction instead of water-splitting, operating at 1.2 V for improved energy efficiency. An optimized CEM-AEM-BPM-CEM membrane setup achieved 95% current efficiency, 205 mmol/m<sup>2</sup>/h SRR, and 0.55 kWh/kg Na<sub>2</sub>SO<sub>4</sub> energy consumption, resulting in a 50% reduction in operational costs. The use of monovalent cation-selective membranes enhanced system stability. Redox-BMED offers considerably lower energy consumption and operational costs but has limited economic feasibility due to the high cost of ion-exchange membranes. *Cho et al.* [55] studied bipolar electrodialysis for desalinating sodium sulfate wastewater to recover sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and sodium hydroxide (NaOH). They found that increasing applied voltage reduced process time but increased energy consumption, with 25 V being optimal. A 1.3 M Na<sub>2</sub>SO<sub>4</sub> solution yielded the best ion flux and recovery efficiency. Under optimized conditions (25 V, 1.3 M Na<sub>2</sub>SO<sub>4</sub>, 0.1 M H<sub>2</sub>SO<sub>4</sub>, 0.1 M NaOH, F/A/B = 1.5:1.0:1.0), a 98%

desalination rate was achieved, recovering 97.1% NaOH and 96.5% H<sub>2</sub>SO<sub>4</sub> with an energy consumption of 2.50 kWh per kg of Na<sub>2</sub>SO<sub>4</sub>. Bipolar membrane electrodialysis can recover valuable compounds. This study highlights bipolar electrodialysis as an effective method for treating sodium sulfate wastewater from the recycling process of LIBs while enabling resource recovery and environmental impact.

Adsorption using magnetic lithium ion-imprinted polymers (Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@IIP) for selective lithium recovery was explored by *Luo et al.* [56]. This material exhibited high selectivity for Li(I) over Na(I), K(I), Cu(II), and Zn(II), with fast adsorption kinetics, reaching equilibrium within 10 minutes, and a maximum capacity of 0.586 mmol/g at pH 6. It maintained over 92% adsorption capacity after five cycles and achieved effective treatment volumes of 140 and 110-bed volumes in fixed-bed column experiments, with 89.8% lithium recovery using 0.5 mol/L HCl. In real wastewater, it recovered 4.3 kg of lithium chloride per ton. While showing rapid kinetics and excellent selectivity for Li.

*Guo et al.* [57] investigated a two-stage precipitation method using Na<sub>2</sub>CO<sub>3</sub> and Na<sub>3</sub>PO<sub>4</sub> to recover lithium as Li<sub>2</sub>CO<sub>3</sub> and Li<sub>3</sub>PO<sub>4</sub>, respectively. Under optimized conditions, lithium recovery rates were 74.72% in the first stage and 92.21% in the second. The recovered Li<sub>2</sub>CO<sub>3</sub>, containing Na<sub>2</sub>CO<sub>3</sub> impurities, was further utilized to make LiMn<sub>2</sub>O<sub>4</sub> as a lithium-ion sieve. This cost-effective approach efficiently recovered lithium while reducing purification steps, enabling its reuse in battery materials. An integrated process of electro-electrodialysis (EED) and CO<sub>2</sub> capture for sustainable LIB recycling was developed by *Kim et al.* [58]. Simulations indicated 99% selective metal extraction from LCO materials, full recovery of 1.09 M NaOH, 2.04 M H<sub>2</sub>SO<sub>4</sub>, and CO<sub>2</sub> capture of 0.33 kg per kg of cathode materials. At a 50,000-ton annual capacity, the system projected a 21.90% reduction in the levelized cost of recycling (LOC<sub>R</sub>), offering a viable solution for LIBs recycling with reduced chemical dependency and lower greenhouse gas emissions. *Im et al.* [59] demonstrated the synthesis of LiFePO<sub>4</sub> (LFP) using refined Li<sub>3</sub>PO<sub>4</sub> recovered from wastewater. A simple purification step using deionized water increased Li<sub>3</sub>PO<sub>4</sub> purity from 94.60% to 98.86%. The purified lithium phosphate was then used to produce LFP cathodes with improved electrochemical performance, showing capacity retention and cycling stability. This study demonstrated a cost-effective and eco-friendly approach for lithium recovery, promoting both resource conservation and a Sustainable LIBs recycling process.

A two-stage solvent extraction process for fluorine and lithium recovery from LiF wastewater was developed by *Han et al.* [46]. The first stage, using di-2-Ethylhexyl phosphoric acid (D2EHPA), achieved 99.72% lithium recovery, producing battery-grade lithium chloride. The second stage extracted fluorine with 99.45% efficiency using a neutral solvent system. The final residue contained lithium (~1 mg/L) and fluorine (<6 mg/L), while high-purity lithium fluoride (LiF >99.95%) was obtained after LiOH stripping. This method significantly decreases waste, increases resource recovery, and reduces environmental impact. *Mufakhir et al.* [48] explored electrocoagulation (EC) for heavy metal removal using Fe-Al electrodes. At 40 A/m<sup>2</sup> for 30 minutes, maximum removal efficiencies were achieved: 99.32% for Ni, 98.76% for Co, 97.93% for Zn, 97.78% for As, and 90.73% for Cd, while Hg removal was lower at 31.84%. The dissolved electrode material and energy consumption were 0.32 g and 0.109 kWh/m<sup>3</sup>, respectively. This study showed that AC electrocoagulation presents an effective solution for heavy metals removal from wastewater in LIBs recycling.

#### **2.1.2.3: Biological Treatment Methods**

Biological treatment method relies on the inherent capability of microorganisms to absorb or decompose harmful substances present in the wastewater, thereby transforming hazardous pollutants into safer forms. These biological treatment methods are categorized into aerobic and anaerobic processes. Aerobic methods necessitate the presence of oxygen for the microorganisms to function and include common techniques such as activated sludge treatment and the use of stabilization ponds. In contrast, anaerobic methods operate in the absence of oxygen and involve systems like anaerobic digestion and septic tanks. Recently, a promising area of research has emerged focusing on the application of specific enzymes for water purification, marking a shift from the use of mixed enzyme systems towards more targeted enzymatic solutions [51,60].

*Yoo et al.* [61] investigated the biological treatment of wastewater originating from the recycling of spent lithium primary batteries using the bacterium *Acidithiobacillus ferrooxidans*. Their findings indicated that the presence of chromium (Cr) at concentrations up to 8000 g/m<sup>3</sup> and nickel (Ni) at concentrations as high as 13,000 g/m<sup>3</sup> did not inhibit the bacterial activity of *Acidithiobacillus ferrooxidans*. However, lithium (Li) at a concentration of 5000 g/m<sup>3</sup> did suppress the crucial process of Fe<sup>2+</sup> oxidation carried out by the bacteria. When this biological treatment was applied to actual wastewater from the battery recycling process, it resulted in a notable decrease in the pH of the wastewater to 1.8 and a significant reduction in the concentration of iron (Fe) from an initial 44,220 g/m<sup>3</sup> to 21,633 g/m<sup>3</sup>. This reduction in iron

concentration could potentially facilitate the recirculation and reuse of the treated water within the battery recycling process. The authors emphasized the need for further research to develop effective methods for the recovery or removal of Cr, Li, and Ni from the biologically treated wastewater, as their concentrations are anticipated to increase with the repeated recirculation of water within a closed-loop system.

#### **2.1.2.4: Hybrid and Integrated Approaches**

Hybrid and integrated processes combine multiple treatment methods to enhance the overall efficiency and effectiveness of wastewater treatment. These integrated approaches combine physical, chemical, and biological techniques to address the limitations of standalone processes. For instance, integrating diffusion dialysis (DD) and electrodialysis (ED) [45], and chelation and electrocoagulation [62] improve the removal of persistent contaminants and increase resource recovery. These hybrid approaches align with sustainability and circular economy principles by maximizing material reuse and minimizing waste. Ongoing research focuses on refining these approaches to optimize operational parameters and develop advanced materials to further enhance treatment efficiency.

*Kumar et al.* [63] designed a membrane-integrated hybrid system to improve the recovery of valuable metals from spent  $\text{LiFePO}_4$  batteries, promoting a more sustainable lithium-ion battery recycling process. The system utilizes an alkaline pretreatment with  $\text{NH}_4\text{OH}$  and  $\text{NaOH}$  to increase the pH to 5.53, efficiently removing Fe and Al while lowering turbidity. Following this, ultrafiltration removes the remaining Fe and Al, achieving a turbidity level below 2 NTU. Subsequently, nanofiltration is used to selectively separate lithium-ion from bivalent ions, such as  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Mn}^{2+}$ . Operating under optimal pressure of 10 bar and a  $2.25 \text{ m}^3/\text{h}$  crossflow rate, the nanofiltration membrane achieves a high rejection rate of  $\text{Mn}^{2+}$  (95.8%),  $\text{Co}^{2+}$  (94.6%), and  $\text{Ni}^{2+}$  (92.5%), while allowing 89.6% of  $\text{Li}^+$  to pass through. The bivalent metal ions are concentrated for further recovery, with 90% of the feed solution retained. The lithium-rich permeate is then processed to crystallize lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) using 4 M  $\text{K}_2\text{CO}_3$  at  $70^\circ\text{C}$ , resulting in a high-purity (99.5 wt%)  $\text{Li}_2\text{CO}_3$  with an 88.2% recovery rate. This multi-stage membrane system combines UF and NF for selective separation and purification, followed by lithium crystallization. It offers an efficient and environmentally friendly method for recovering valuable metals from spent lithium-ion batteries and can also be used to treat wastewater generated during the recycling process.

*Shin et al.* [64] explored an innovative approach for recovering transition metal ions ( $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Cd}^{2+}$ ) from highly saline battery manufacturing wastewater containing  $\text{Na}^+$ ,

Li<sup>+</sup>, K<sup>+</sup>, and Mg<sup>2+</sup>. This study demonstrates the effectiveness of the reaction-enhanced membrane cascade (REMC) to selectively bind and release transition metal ions under controlled pH conditions, enabling efficient separation of metals from salt while addressing the osmotic pressure challenges in membrane processes. The optimized reaction-enhanced membrane cascade (REMC) approach integrates ultrafiltration-based diafiltration for metal-salt fractionation with nanofiltration for concentration, achieving a 99% metal recovery yield and a 215-fold transition metal concentration, with purity above 99.98%. experiments with 16 different ion pairs confirmed the wide applicability of this approach. Crystallization experiments validate that the recovered product met battery-grade NiSO<sub>4</sub> standards. Moreover, the nanofiltration concentration step decreased the energy consumption by up to 75% compared to conventional distillation, achieving a Ni<sup>2+</sup> level from below 200 ppm to 43000 ppm. This investigation highlights a highly sustainable and efficient approach to recovering metals from wastewater produced during the battery recycling process, reducing environmental impact and improving resource utilization.

*Wu et al.* [45] investigated an integrated approach by combining diffusion dialysis (DD) and electrodialysis (ED) to recover Ni<sup>2+</sup> and H<sub>2</sub>SO<sub>4</sub> from the wastewater of the battery recycling process. In the diffusion dialysis (DD) process, an acid recovery rate of 75.96% and a Ni<sup>2+</sup> rejection rate of 97.31% were achieved at a flow rate of 300 L/h and a W/A flow rate ratio of 1:12. The nickel-rich solution obtained after diffusion dialysis (DD) could be reused in battery production. Following diffusion dialysis (DD), the recovered acid was further concentrated in a two-stage electrodialysis (ED) process, increasing the H<sub>2</sub>SO<sub>4</sub> concentration from 43.1 g/L to 150.2 g/L, making it suitable for reuse in the battery recycling process. The diluate from electrodialysis (ED) was repurposed as the diffusate for diffusion dialysis (DD), ensuring efficient resource utilization. This hybrid approach, shown in *Figure 2 (a,b)*, minimizes waste as well as enables the recovery and reuse of valuable metals, showing its practical potential for industrial-scale applications. *Mufakhir et al.* [62] explored a hybrid approach by combining chelation and electrocoagulation to remove metals such as cobalt (Co), cadmium (Cd), nickel (Ni), manganese (Mn), mercury (Hg), and arsenic (As) from spent battery recycling wastewater by using aluminum electrodes in a monopole parallel circuit. Two chelating agents, citric acid and chitosan, were evaluated to determine their effectiveness in enhancing metal removal. The results demonstrated that applying chelation before electrocoagulation achieved superior removal efficiencies compared to the reverse sequence. Chitosan, at an optimal concentration of 6 g/L, outperformed citric acid, achieving nearly complete removal (above 99.5%) of all

targeted metals under conditions of 25 A/m<sup>2</sup> current density and 30 minutes of contact time. The process also exhibited low energy consumption (0.0429 kWh/m<sup>3</sup>) and minimal electrode dissolution (0.4074 g). This study highlights the potential of integrating chelation and electrocoagulation as an efficient and cost-effective treatment for heavy metal removal from battery recycling wastewater.

*Miyashita et al.* [44] investigated the use of Al<sup>3+</sup> at high temperatures to check the accelerated decomposition of PF<sub>6</sub><sup>-</sup> in wastewater of the lithium-ion batteries recycling process. PF<sub>6</sub><sup>-</sup> is challenging to treat due to its persistent nature in aqueous solutions, making it a considerable hurdle in the hydrometallurgical recycling of spent lithium-ion batteries. In the first method, a 10 mM LiPF<sub>6</sub> solution was heated with 100 mM Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> for 24 hours at 90 °C, resulting in over 90% decomposition of PF<sub>6</sub><sup>-</sup>. Ca(OH)<sub>2</sub> was subsequently added to precipitate PO<sub>4</sub><sup>3-</sup> and F<sup>-</sup> as ettringite, decreasing fluorine and phosphorus concentrations in the supernatant to 0.77 mM and 0.028 mM, respectively. while in the second method, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and Ca(OH)<sub>2</sub> were pre-mixed at different concentrations before heating the solution, which buffered the pH drop during PF<sub>6</sub><sup>-</sup> decomposition by forming Al(OH)<sub>3</sub>. However, this method resulted in lower removal efficiencies 38% for fluorine and 86% for phosphorus, compared to the first method. The study highlighted that using an adequate amount of Ca(OH)<sub>2</sub> after the decomposition of PF<sub>6</sub><sup>-</sup> is important for the high removal rate of fluorine and phosphorus. *Kim et al.* [65] studied the use of an electrochemical approach (shown in *Figure 2(c)*) to recover lithium and eliminate organic contaminants simultaneously from the wastewater generated during the recycling of spent batteries that contain 300 mg L<sup>-1</sup> of dissolved organic carbon (DOC) and 1900 mg L<sup>-1</sup> of lithium. They developed an integrated system consisting of a manganese oxide (LMO) electrode for lithium recovery and a boron-doped diamond (BDD) electrode for organic pollutant removal. Both electrodes were placed 0.5cm apart from each other in 20 mL of wastewater and operated at various constant currents (25-125 mA). Li extraction occurred until the cathode potential reached 0.2 V (vs Ag/AgCl), followed by the recovery of lithium in buffer solution until the LMO cathode reached 1.15 V (vs. Ag/AgCl). Furthermore, electrochemical analysis was conducted, including cyclic voltammetry under specific potential to assess the electrode performance. The system demonstrated high efficiency, producing a lithium-rich solution with a purity of 98.6 mol% and decreasing organic contaminants by 65% after repeated operations. The study highlighted the need to optimize current density for the effective recovery of lithium and the effectiveness of applying a higher charge to the boron-doped diamond (BDD) electrode for enhanced dissolved organic carbon (DOC) removal. This approach provides a

scalable solution to recover lithium, eliminating the need for separate steps for the removal of pollutants.

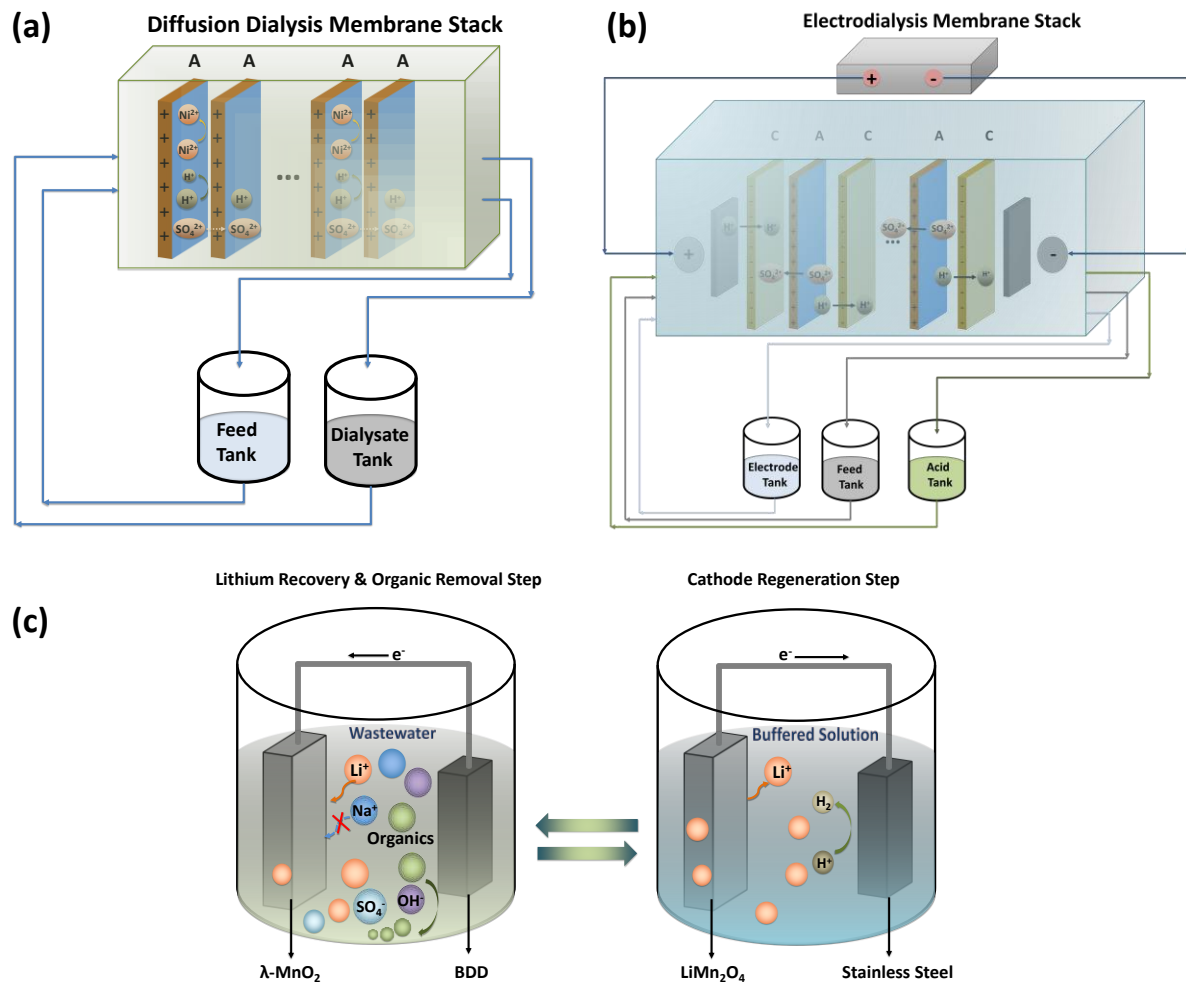


Figure 2: (a) the diffusion dialysis and membrane stack, (b) the electrodialysis and membrane stack, (c) the membrane-integrated hybrid system.

### 2.1.3: Impacts of Metals and Hazardous Compounds Present in LIBs Wastewater

Wastewater generated during the recycling of lithium-ion batteries contains a diverse range of pollutants that pose a serious threat to the environment and human health. These pollutants consist of heavy metals such as cobalt, cadmium, manganese, lead, lithium, and nickel [25,26], as well as inorganic salts including  $\text{LiPF}_6$ ,  $\text{LiClO}_4$ , and  $\text{LiBF}_4$  [24]. The impact of heavy metals on human health is shown in Figure 3 [66]. Furthermore, graphene [27,28], metal oxides [29], ionic liquids [30,31], fluorides, metal ions, and organic electrolytes such as ethylene carbonate (EC), methyl ethyl carbonate (EMC), dimethyl carbonate (DMC), ethylene carbonate and diethyl carbonate [32,33,41–43] contribute to wastewater complexity. Hazardous compounds like HF and  $\text{PF}_5$  [67], benzene and persistent ester compounds further worsen environmental

issues due to their resistance to microorganisms' degradation [36]. The release of these contaminants into the ecosystem can severely impact the environment, leading to ecological interruptions.

The U.S. classifies LIBs as containing some of the most toxic substances, categorizing them as hazardous due to their reactivity, flammability, corrosiveness, and leaching toxicity [67]. For example, the manganese oxide and aluminum foil in the cathode despite containing valuable metals can cause damage to the human lungs by inhalation [68], cobalt oxides damage the lungs and cause haemorrhage and congestion, and exposure to nickel oxide can lead to skin cancer [68]. Graphite also irritates the mucous membrane and eyes [69]. Additionally, the hazardous lithium salt  $\text{LiPF}_6$  found in the electrolyte is highly corrosive and easily can decompose to generate hydrofluoric acid (HF), a highly dangerous substance [67]. Organic solvents such as ethyl methyl carbonate and ethylene carbonate are resilient to natural degradation. Their self-hydrolysis can produce compounds such as methanol dimethoxyethane, formic acid, and other hazardous products that can have a severe impact on the water, soil, and atmosphere [67]. Heavy metals need close attention due to their toxicity, bioaccumulation, and their persistent nature [70]. The contaminants and their impact on living things and the environment are mentioned in the *Figure 3*.

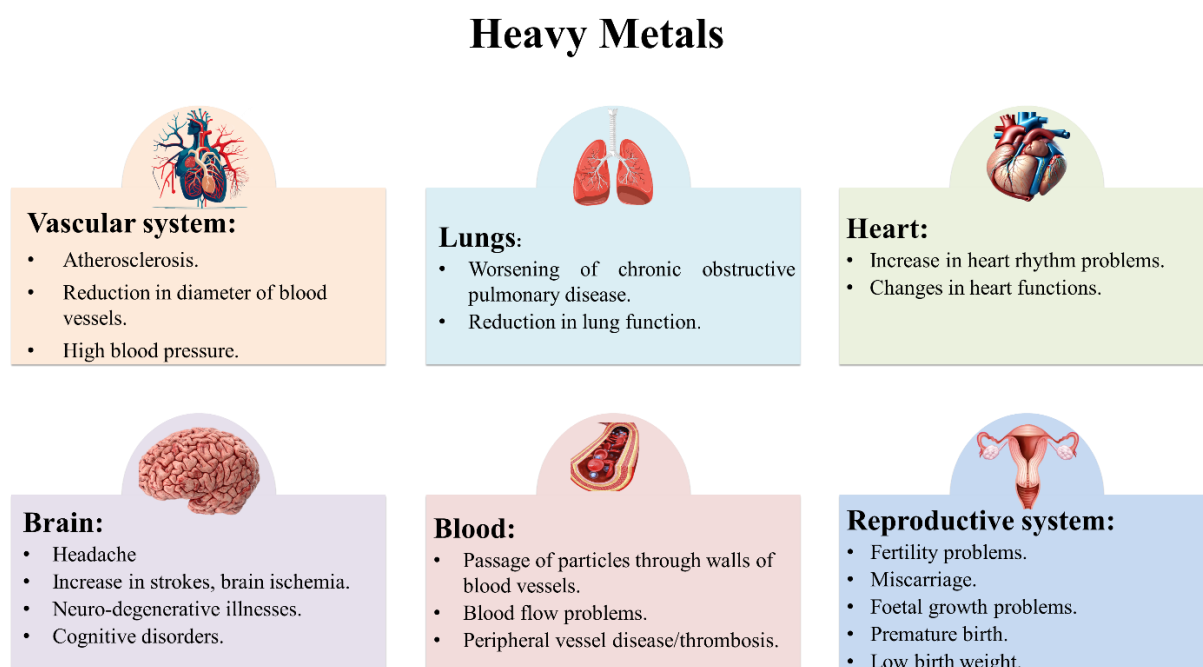


Figure 3: Effects of heavy metals on human health.

## **2.2: Spent Alkaline Batteries**

### **2.2.1: Overview of Spent Alkaline Batteries (SABS)**

Primary alkaline batteries are non-rechargeable portable energy sources that are widely used [71]. These are classified as a main type of primary battery, specifically alkaline Zn-Mn batteries [72]. The market for these batteries is substantial, with a global market evaluated between 5.8 and 7.6 billion USD in 2020 and expected to continue growing, particularly in the Asia Pacific region, from 6.2 thousand million USD in 2026 to 10.9 thousand million in 2028 [71]. In the United States, approximately 80% of portable batteries manufactured are alkaline dry cells, with global annual production exceeding 10 billion units [73]. The widespread consumption of electronic devices has made spent batteries, including alkaline types, an ongoing economic and ecological concern.

The composition of alkaline batteries includes several key materials, primarily manganese oxide ( $\text{MnO}_2$ ) and zinc (Zn), which serve as the cathode and anode materials, respectively [71,74]. Analysis of spent AA household alkaline batteries indicates major constituents such as Mn (19.5%), Fe (16.9%), and Zn (10.9%). Other components present include potassium (K) at 2.72%, copper (Cu) at 1.21%, and nickel (Ni) at 0.281%. The sources of these metals within the battery structure include Mn, Zn, Cu, and Ni, primarily distributed among the cathode, anode, anode collector, and cathode collector. Iron sources include the anode cap, metal separator, and cathode collector [74]. The high content of potassium (K) is contributed by the electrolyte, which is a potassium hydroxide (KOH) solution [71,74,75]. Decades ago, alkaline batteries contained mercury, but this is no longer the case since the 1980s [71]. According to the European list of Wastes (LoW), alkaline batteries are classified as absolute non-hazardous wastes (code 160604), with an exception for those containing mercury, which alkaline batteries no longer include [71,76].

Despite their non-hazardous classification in Europe, the disposal of the large volume of spent alkaline batteries presents significant challenges. These batteries are used all over the world, they create a large amount of waste. Most alkaline batteries in the US still go to landfills at end-of-life [73]. In the EU, out of an estimated 201,000 tonnes introduced in 2015, only 36% were collected, while 17% were lost to municipal waste streams (either incinerators or landfills) and 29 % were recycled [77]. Collecting portable batteries for recycling is difficult because there are so many of them, they are spread out in many places, and each one is very small [73]. There is a lack of regulations in many areas for the proper storage and management of battery waste streams, leading to their accumulation in open settings and landfill environments [78].

The environmental concern associated with improper disposal, particularly landfilling, is primarily related to the potential leaching of hazardous substances [78]. Although classified as non-hazardous in the EU, landfilling of waste zinc-carbon or alkaline batteries can contribute to various environmental problems [79]. Heavy metals contained within the batteries, such as Cd, Ni, Zn, or Pb, can leach and cause contamination to the soil or water [79,80]. Spent battery waste contains a variety of toxic substances that can contaminate the environment and threaten human health. Research confirms that toxic chemicals like heavy metals continuously contaminate the environment [81]. Studies on heavy metal leaching from spent household batteries disposed of in municipal solid waste (MSW) have shown that the type of battery affects the concentration of heavy metals in leached solutions. Lower pH levels typically result in more metals being leached. Increased disposal of batteries in landfills can contribute to the leaching of metals, especially Mn and Zn, into the environment. Leaching of the electrolyte (KOH) from alkaline batteries has also been shown to increase soil pH in contaminated areas. Heavy metals like cadmium, nickel, zinc, copper, lead, chromium, and mercury identified in MSW landfill leachates can be partially traced back to batteries in the waste. While some laboratory tests found cadmium and nickel levels in leaching solutions to be below accepted landfill limits, concentrations of zinc and manganese were found to be greater than the fixed limits [75]. The amount of metals leaching from a landfill is dependent on many factors, including the age of the landfill, the condition of liners, and the processes in place to control effluent [73]. Health risks are associated with water and metal pollution during battery disposal [82]. One source suggests that risks to the environment from landfilling and incineration are not likely to be significant [75], but multiple other sources highlight the risks of heavy metal leaching and contamination [78,79,81]. This indicates a significant environmental risk related to the current prevalence of landfilling for spent alkaline batteries.

### **2.2.2: Recycling Processes for Alkaline Batteries**

Given the substantial volume of spent alkaline batteries generated globally, effective end-of-life management is crucial. Current technologies employed to recover valuable materials from spent batteries, including alkaline types, broadly fall into three main categories: mechanical processing, pyrometallurgy, and hydrometallurgy [74, 81,83]. Mechanical processing typically involves physical steps such as milling, crushing, dismantling, grinding, and magnetic separation to separate different components like metals, paper, plastic, and the "black mass" which contains the active materials [74,84,85]. However, mechanical methods alone are often limited in achieving high recovery and purity, sometimes being more effective for specific

battery types like NiMH [74]. Pyrometallurgy utilizes high temperatures to recover metals, often involving mechanical pre-treatment followed by melting or thermal processing [74, 77,86]. While pyrometallurgical techniques can stabilize hazardous metals, offer high metal recovery for some materials, and allow for valuable by-products, they require high energy consumption, significant equipment costs, and necessitate systems for dust collection and gas cleaning [30, 21]. Historically, there has been interest in recycling alkaline batteries along with steel in electric arc furnaces in the U.S., but this remains a hypothetical scenario with technical and regulatory hurdles [73].

Hydrometallurgical processes offer an alternative, generally considered a lower-cost approach and often more effective for recovering metals from chemically complex waste streams like spent batteries. These processes are applicable to various battery types, including alkaline, zinc-carbon, NiMH, and Li-ion batteries [81,87,88]. Hydrometallurgical routes for battery recycling typically involve a sequence of steps: physical pre-treatment, followed by chemical treatment which can include neutral leaching, acid or alkaline leaching, separation and purification of metals, and finally metal recovery [71, 81,84]. Physical pre-treatment in hydrometallurgy involves preparing the spent batteries, which can range from manual dismantling to separate components [71,85] to mechanical processes like crushing, grinding, attrition, and magnetic separation to isolate the metallic powder or "black mass" [71, 83,84,89,90]. Removing alkaline-soluble salts during the physical process, such as through washing cycles, can help reduce acid consumption in subsequent steps [71,89].

A significant consideration in hydrometallurgical recycling is the generation of liquid waste streams, often referred to as leachates or effluents. The leachate obtained after acidic leaching, for instance, is typically characterized by a very low pH and contains substantial concentrations of metals like iron, manganese, and zinc, as well as sulfates from the leaching acid. These residual solutions require treatment before discharge to avoid environmental contamination. Biological methods, such as using sulfate-reducing bacteria, are being investigated to treat these leachates, enabling the removal of sulfates and heavy metals [83]. Chemical pre-treatment steps, like adjusting pH using reagents such as NaOH, can also be employed to precipitate and remove metals, particularly iron. The proper management and treatment of these waste leachates are essential aspects of minimizing the environmental footprint of hydrometallurgical battery recycling.

### **2.2.3: Characteristics of Wastewater Generated from SAB Recycling**

Recycling processes for spent alkaline batteries, particularly those employing hydrometallurgical methods, inevitably generate liquid waste streams that require careful management. These effluents, often referred to as leachates, represent a significant consideration in the overall environmental footprint and feasibility of battery recycling technologies. The composition of this process wastewater is primarily dictated by the battery chemistry and the specific leaching agents and conditions used.

Analysis of leachate obtained from the hydrometallurgical recycling of spent alkaline batteries, specifically after leaching with a 2 M sulfuric acid solution at 80 °C for 5 hours, reveals a characteristic profile of contaminants. This raw leachate was highly acidic, exhibiting a very low pH, around 0.45. It contains substantial concentrations of metals, including iron (Fe), zinc (Zn), and manganese (Mn) [83,91]. Approximate concentrations reported include Fe at around 200 mg/L, Mn between 15–18 g/L, and Zn between 33–36 g/L. In addition to these metals, the leachate also contains a significant concentration of sulfates ( $\text{SO}_4$ ), approximately 13 g/L, resulting from the use of sulfuric acid as the leaching agent [91]. The presence of other metals like cadmium (Cd), nickel (Ni), copper (Cu), lead (Pb), chromium (Cr), and mercury (Hg) in battery waste is acknowledged [75], and while less prominent than Zn and Mn in alkaline batteries specifically, their potential presence in mixed battery streams or process effluents could occur. Electrolyte components, such as potassium from the potassium hydroxide (KOH) electrolyte used in alkaline batteries, could also potentially carry over into the leachate if not effectively removed during initial physical pre-treatment steps, like washing [71].

Regarding the load, the dominant constituents in the generated wastewater are inorganic, primarily the dissolved heavy metals (Fe, Zn, Mn) and sulfates [83,91]. The presence of substantial amounts of metals and metalloids in hydrometallurgical leachates contributes to their potential toxicity and environmental impact [81,83]. These discharged solutions, if not properly treated, pose risks of contaminating the environment. Heavy metals, in general, are known for their toxicity and ecotoxicity, and studies confirm that toxic chemicals like heavy metals continuously contaminate the environment [81]. For instance, precipitated metal sediments, such as iron-based sediments produced during pH neutralization of the leachate, can be unstable and potentially release loosely bound metal ions like zinc and manganese, raising environmental safety concerns [91,92]. These released metals are considered toxic. Therefore, effectively treating the wastewater generated from alkaline battery recycling is a crucial step to mitigate the environmental burden associated with these processes.

#### 2.2.4: Wastewater Treatment Technologies for SAB Recycling

*Lapinkangas et al.* [93] investigated the treatment of potassium-rich washing water generated during the recycling of spent alkaline batteries. This wastewater, produced by washing crushed battery black mass, is also known to contain ammonium ions. The primary technology explored was the precipitation of potassium as hazenite ( $\text{KNaMg}_2(\text{PO}_4)_2 \cdot 14\text{H}_2\text{O}$ ), a mineral that can potentially be used as a fertilizer. Precipitation experiments were conducted to study the effects of various operating parameters, including pH (9.5–12), temperature (10–40 °C), and Mg:K:PO<sub>4</sub> molar ratios ((1.0–1.5):1:(1.0–1.5)), using added phosphate and magnesium salts. The results showed that hazenite precipitated effectively in a wide alkaline pH range and was not significantly affected by pH or temperature within the tested ranges. Typical potassium removal efficiency was 60–65%, although a simultaneous excess of magnesium and phosphate increased removal to 78%. The presence of ammonium in the washing water did not inhibit hazenite formation or potassium precipitation. The precipitation kinetics were observed to be fast. This method provides a way to recover potassium from the wastewater, preventing its release into watercourses. Optimal conditions for minimizing resource use were found to be room temperature and alkaline pH without requiring excess chemicals. *Yang et al.* [83] investigated a novel, low-cost biochemical treatment technology for acidic leachates generated during sulfuric acid-based recycling of spent alkaline batteries. The raw leachate had a very low pH (~0.5) and high metal and sulfate content. The process involved a preliminary pretreatment to increase the pH to 5.0, which was most effective using 40% NaOH to reach pH 3.5 followed by biogenic ammonia to reach pH 5.0. This step achieved near-complete iron removal. Subsequently, the pretreated leachate was treated with sulfate-reducing bacteria (SRB) at 37 °C. SRB activity increased the pH further (~7.3), resulting in almost complete sulfate removal (99%) and significant metal precipitation as sulfides, achieving up to ~99% Zn and >84 % Mn removal from the liquid phase. High metal and sulfate concentrations were toxic to SRB, necessitating leachate dilution for effective biological treatment. This combined biochemical approach offers an effective alternative for managing these challenging effluents. *Yang et al.* [91] investigated the treatment of acidic hydrometallurgical waste leachate generated during spent alkaline battery recycling. The highly acidic leachate (pH ~0.45) contained significant concentrations of iron, zinc, and manganese. Their primary focus for wastewater treatment was the removal of iron through chemical precipitation by increasing the pH. Using alkaline reagents like Na<sub>2</sub>CO<sub>3</sub> or NaOH. They adjusted the pH of the raw leachate to 3.5, causing iron to precipitate. This process created a primary Fe-sediment (PFS), which was found to contain unstable metal sulfates of Fe, Zn, and Mn, raising environmental

concerns. A subsequent rinsing process of the PFS produced a more stable secondary Fe-sediment (SFS), mainly composed of schwertmannite, significantly reducing the leachable Zn, Mn, and sulfates. This initial iron removal step is crucial for managing the toxic leachate and preparing the liquid for the recovery of other valuable metals

## **2.3: In-Mold Structural Electronics**

### **2.3.1: Overview of In-Mold Structural Electronics**

In-Mold Structural Electronics (IMSEs) (shown in *Figure 4*) represents a significant advancement in the integration of electronic functionality within three-dimensional molded plastic parts [94,95]. As an evolution of In-Mold Decoration (IMD) and building upon the principles of printed electronics (PE), IMSE involves the printing of conductive, semiconductor, and dielectric inks onto thin polymeric films, which are subsequently thermoformed and then incorporated into injection molded parts. This innovative process allows for the creation of functional electronic devices with complex 3D shapes, offering advantages such as reduced space requirements, enhanced durability, and lighter product designs compared to traditional methods involving discrete electronic components and printed circuit boards (PCBs). The integration of electronic functions directly into the structural elements of a product marks a departure from conventional practices of encasing separate electronic assemblies within polymeric housings. This convergence of structural and electronic elements not only streamlines manufacturing processes but also opens up possibilities for novel product designs and functionalities across various industries, including automotive, consumer electronics, and medical devices [94].

The fabrication of IMSE components relies on a range of materials, with conductive inks playing a crucial role in establishing the electrical circuitry [94,96]. Among the various conductive materials utilized in printed electronics, silver-based solutions are a prevalent choice due to their superior electrical conductivity and good performance on polymeric substrates [97]. These conductive inks typically consist of silver micro or nanoparticles dispersed in a medium, with formulations often including additives to enhance ink deposition and end-use properties [96]. Different printing techniques, such as inkjet printing and screen printing, require conductive inks with specific viscosity characteristics and particle sizes; for instance, inkjet printing necessitates low viscosity inks with nanosized silver particles, while screen printing can accommodate higher viscosity inks with larger micrometric particles [94]. Besides silver, other metals like gold, platinum, copper, and nickel are also employed in conductive inks, along with carbon-based nanomaterials, which offer benefits like large-area

printing capability and mechanical flexibility, albeit with lower electrical conductivity compared to metal-based inks. Dielectric and semiconductor inks are also integral to IMSE, enabling the creation of complex electronic structures and functionalities within the molded parts [94]. The polymeric films used as substrates must possess properties compatible with printing, thermoforming, and injection molding processes, with common materials including polycarbonate (PC), polyethylene terephthalate (PET), and polyimide (PI) [98,99].

While IMSE offers numerous advantages in terms of design and functionality, the end-of-life management and potential for waste generation are important considerations from a sustainability perspective. IMSE components often constitute composite materials with inseparable layers of polymers and conductive inks, which can pose challenges for conventional recycling methods. Traditional waste electrical and electronic equipment (WEEE) recycling processes often involve shredding, followed by ferrous and non-ferrous metal separation, leaving a mixed fraction of light particles that are frequently landfilled or incinerated due to the difficulty and energy intensity of further separation [98]. The low metal content and high combustibility of printed electronics within IMSE structures make incineration a common end-of-life route, with potential for metallic fraction recovery but loss of the polymer components[100–102]. To address these challenges, research efforts are exploring strategies to enhance the recyclability of IMSE. One promising approach involves the incorporation of separation layers, such as polyvinyl alcohol (PVA) interlayers, between the polymer substrate and the conductive tracks. These water-soluble layers can facilitate the separation of printed conductive tracks from the polymer matrix through dissolution in water, enabling the recovery of both the metal and polymer fractions. The integration of such design-for-recyclability principles into IMSE manufacturing is crucial for minimizing waste generation and promoting a circular economy for electronic devices [98]. Further research into efficient and low-energy recycling technologies tailored to the specific material compositions of IMSE components is necessary to fully realize the environmental benefits of this emerging technology.

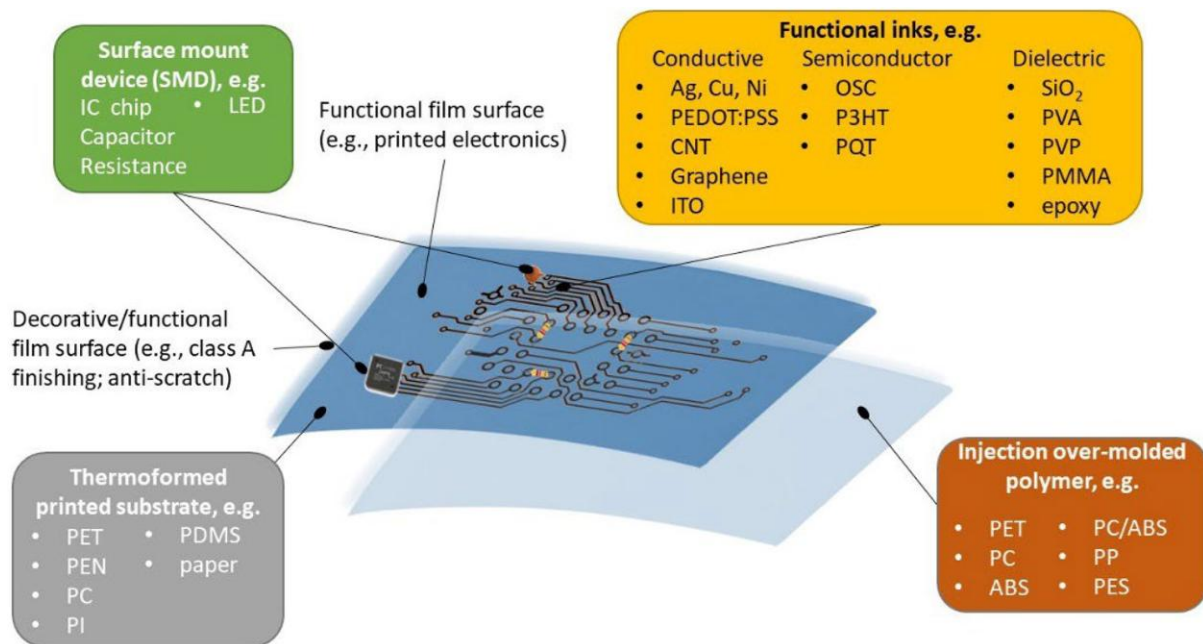


Figure 4: Common materials and respective fabrication processes used for IME.

### 2.3.2: Common Leaching Agents for Silver Extraction

Leaching serves as the essential initial step in the hydrometallurgical recovery of silver from secondary sources such as WEEE, including IMSEs and PCBs. This process involves dissolving the silver from the material into a solution. Several chemical agents are commonly investigated and employed for this leaching stage. Cyanide has a long history of commercial use in silver recovery processes, recognized for its high efficiency and relatively low cost [103,104]. However, its application is associated with significant environmental hazards and concerns. As alternatives, thiourea and thiosulphate leaching processes have been developed [105]. Thiourea leaching is seen as a promising option compared to cyanide, potentially offering better yields and being less poisonous [106]. It typically requires acidic conditions. Thiosulphate leaching is considered relatively cheap and less toxic than cyanide. Preprocessing of the WPCBs can significantly improve the efficiency of thiosulphate leaching [104]. These leaching methods prepare the silver-containing solution (leach liquor) for subsequent purification steps.

### 2.3.3: Wastewater Generation During Silver Recovery

Following the overview of In-Mold Structural Electronics (IMSE) and the materials employed, particularly silver in conductive inks, it becomes crucial to consider the processes involved in recovering this valuable metal from waste streams. The escalation of demand for silver in the electrical and electronics manufacturing sectors, coupled with insufficient conventional lean grade ores, necessitates broadening the scope to include secondary silver recovery and

recycling [104]. Among the various methods for recovering metals from electronic waste, hydrometallurgy is a widely applied technology [103,107–109]. This approach involves the use of aqueous solutions containing chemical reagents, such as inorganic or organic acids, to dissolve metals from the waste material, a process known as leaching [103,109]. Various leaching agents can be employed, including cyanide, thiourea, thiosulfate, and halides, depending on the source material and desired metals [104,110]. Hydrometallurgical processes are often favored due to advantages like lower capital cost, ease of control, reduced environmental effects compared to pyrometallurgy, and higher recovery of metals [104, 109,111] However, a significant consequence of hydrometallurgical silver extraction is the generation of substantial volumes of wastewater [112].

The wastewater streams originating from hydrometallurgical silver recovery processes are characterized by complex compositions and can contain hazardous substances. A common feature is their acidic pH, as acid leaching agents are frequently employed. For instance, a pilot-scale hydrometallurgical process for recovering silver and gold from WPCBs using HCl and HNO<sub>3</sub> resulted in acidic effluents [113]. These wastewaters also contain a variety of dissolved substances, prominently featuring heavy metal ions. Given that silver is the target metal for recovery, silver ions (Ag<sup>+</sup>) are frequently present in these industrial effluents and spent sources. Beyond silver, depending on the composition of the processed electronic waste (such as WPCBs, which contain copper, nickel, tin, and zinc), other heavy metals like copper, lead, zinc, cadmium, arsenic, chromium, and nickel may also be present in significant concentrations[103]. A specific pilot process targeting silver and gold recovery from WPCBs generated wastewater rich in nitrate (5 g/L) and chloride (50 g/L), tolerating metals at ppm level before treatment [113]. Furthermore, possible organic residues can contaminate these wastewater streams. For example, electroplating wastewater, another source of silver, is known to contain a considerable amount of organic compounds, including various surface-active agents, complexing agents like EDTA, citric acid, tartaric acid, ethanolamine, ethylene glycol, thiourea, and benzene sulfonic acid. Thiourea and thiosulfate are also mentioned as eluents used in ion exchange processes for silver recovery, which could contribute to the organic load in wastewater [104,114].

The environmental risks associated with discharging this untreated wastewater are substantial [115,116]. Heavy metals are considered toxic elements, and their presence in water, even at low levels, can cause damage to ecosystems and human life due to their high water solubility and non-biodegradability [112,117–121]. Silver ions, specifically, are known for their toxicity.

They can accumulate in organisms and transfer through the food chain, potentially leading to numerous diseases and disorders in humans. Exposure to  $\text{Ag}^+$  has been shown to inhibit ion uptake and cause ion regulatory failure in aquatic organisms [103]. The presence of silver in effluent can also result in its deposition in sediments [122]. Moreover, acidic wastewater itself poses an environmental problem, and the presence of various metal ions and potentially harmful organic compounds further underscores the necessity of effective wastewater treatment before discharge to protect environmental and human health.

#### **2.3.4: Wastewater Treatment Techniques in the Electronics Industry**

Wastewater generated from hydrometallurgical processes requires various treatment techniques to remove contaminants and recover valuable materials. Hydrometallurgy, which involves using aqueous solutions with chemical reagents for metal dissolution (leaching) followed by purification, often results in large quantities of wastewater. Historically, water quality wasn't always a primary consideration, with used water often simply discharged; however, in recent years, this water is being sent to treatment plants and circulated. The complex nature of these wastewaters, containing heavy metals, acids, and potentially other toxic substances like cyanide or organic complexing agents, necessitates tailored treatment approaches.

*Vlasopoulos et al.* [113] investigated the treatment of the wastewater generated by their integrated hydrometallurgical process for recovering silver and gold from waste PCBs. The effluents resulting from the sequential leaching stages were characterized as rich in nitrate (up to 5 g/L), chloride (up to 50 g/L), and containing residual metal ions (Fe, Ni, Cu, Zn, Pb) at levels up to the g/L range, depending on the stage. To treat this complex wastewater, a novel and effective biological denitrification system utilizing a packed-bed biofilm reactor was employed. Key operating parameters involved mixing the distinct effluent streams (WW1-WW4), neutralizing the mixture with NaOH, filtering to precipitate and remove a significant portion of soluble metals, and then diluting the resulting solution (mixW) with a nutrient broth, typically at a 1:6 ratio (1 part mixW to 5 parts broth). This dilution and nutrient addition aimed to adjust the high chloride content to a manageable salinity level (e.g., 5%) and provide essential organic and inorganic substances for the microbes. Further additions of NaCl, peptone (1.5 g/g  $\text{NO}_3^-$ ), and yeast (0.3 g/g  $\text{NO}_3^-$ ) were made to fine-tune the feed for the bioreactor. The bioreactor was a 2.7 L capacity upflow packed-bed reactor, inoculated with *Halomonas denitrificans*, which had been acclimated to tolerate a wide range of initial conditions, including nitrate concentrations up to 10,000 mg/L, pH from 3 to 8, salinity from 5% to 10%, and metal

concentrations up to 100 mg/L. Treatment was conducted in fed-batch mode over approximately 28 hours. The results from the biological treatment demonstrated high efficiency, achieving 99.8% nitrate removal. Nitrite, an intermediate product, was sequentially reduced completely, remaining below 0.1 mg/L after 28 hours. Residual metal concentrations in the treated water were successfully kept at very low levels, around 1 mg/L or less (e.g., <1 mg/L for Pb). *Ferella et al.* [123] examined the aerobic biological treatment of a spent tetramethylammonium hydroxide (TMAH) solution from a microelectronics industry to enable water reuse within a circular economy framework. The study utilized a pilot-scale plant composed of three continuous stirred tank reactors (CSTRs) in series. The wastewater was first neutralized to pH 7 and then fed to the reactors. Key operating parameters included initial operation in continuous mode for 14 days at a flow rate of 5 L/h, followed by 16 days in batch mode. The bioreactors had a volume of approximately 1.24 m<sup>3</sup> each and were maintained at a temperature of 20 ± 1 °C and a dissolved oxygen (DO) concentration of 2 ± 0.5 mg/L. The initial TMAH concentration in the feed was high, averaging 2161 mg/L. The results showed that during the initial continuous operation, microbial adaptation was slow, leading to biomass decrease and an increase in TMAH concentration. However, switching to batch mode resulted in rapid and efficient degradation of TMAH, achieving approximately 80% reduction in the first reactor and complete (100%) removal in the second and third reactors. The biological degradation pathway involved sequential conversion of TMAH to TMA, DMA, MMA, and ammonia. A significant finding was the high concentration of nitrates produced (150–250 mg/L in the later reactors during batch mode), resulting from nitrification of ammonia which became prevalent at lower TMAH concentrations. The discussion highlighted that while the aerobic biological process is effective for TMAH removal, particularly in batch operation after microbial adaptation, the resulting high nitrate levels necessitate a further denitrification step for the treated water to meet discharge limits and be suitable for reuse.

*Wahaab et al.* [124] investigated the chemical treatment of industrial wastewater from an electronics manufacturing industry. The treatment process involved sequential steps: initial pretreatments of wastewater from the nickel-chrome production line using alkaline chlorination for cyanide removal and chemical reduction for hexavalent chromium (Cr<sup>+6</sup>), followed by a final coagulation process applied to a mix of the pretreated water and end pipe effluent. Key operating parameters for pretreatment included maintaining a pH of 11 during alkaline chlorination over 2 hours with vigorous mixing at 200 rpm, adding chlorine water (100 mL/L). Chemical reduction involved adding sulfuric acid to achieve a pH of 3.0 or lower and adding

ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 6\text{H}_2\text{O}$ ), followed by lime addition to neutralize to a pH of 8.5. The final coagulation step was performed using the jar test procedure on a 1:1 mixture of pretreated and end pipe effluent, with stirring speeds ranging from 270 rpm initially down to 20–30 rpm for floc formation, maintaining a pH of 8.5. Various coagulants were tested, and the combination of  $\text{FeSO}_4$  at 60 mg/L and CaO at 80 mg/L (labelled C4) was found to be most effective. The results demonstrated that the sequential pretreatments achieved 100% removal of cyanide and almost 100% reduction of  $\text{Cr}^{+6}$ . The subsequent coagulation step with the C4 combination showed the highest treatment efficiency, reducing COD and BOD to 67 mg/L and 43 mg/L, respectively, and heavy metals to very low levels (e.g., total heavy metals at 0.54 mg/L), which were within the standard permissible limits for wastewater discharge according to environmental law 48/1982.

*Eksangsri et al.* [125] studied and examined the feasibility of reusing washed water in a flexible printed circuit board (FPCB) manufacturing factory, focusing on the final cleaning process. The process/technology involved treating the spent washed water, which had high conductivity and LPC, by splitting it into two streams: one fed before the existing Reverse Osmosis (RO) unit (Stream A) and the other before the ion-exchanger (Stream B). Key operating parameters included a target water consumption rate of 80 m<sup>3</sup>/d, requiring reuse water quality with conductivity less than 2  $\mu\text{S}/\text{cm}$  and Liquid Particle Counter (LPC) less than 500 particles/mL, and aiming for a 14-day operation cycle. The study evaluated the optimal ratio of Stream A to Stream B (A:B ratio). The results showed that direct reuse was impossible due to high conductivity. However, A:B ratios from 30:70 to 50:50 were found to technically satisfy the factory's operational criteria. The 30:70 ratio was identified as the most attractive alternative technically and economically, saving approximately 19,760 m<sup>3</sup> of raw water annually and offering a high return on investment (ROI) of 49.09%. The discussion emphasized that this integrated reuse approach effectively treats the spent water and extends the ion-exchanger's lifespan by reducing its load, providing a viable and sustainable solution for FPCB manufacturers facing increasing production demands and strict groundwater regulations.

*Sim et al.* [126] investigated the efficiency of an integrated membrane-adsorption system (shown in *Figure 5*) as a sustainable development approach for semiconductor-industry wastewater treatment. The process/technology combined two stages: immersed ceramic ultrafiltration membrane filtration (tested at 0.02  $\mu\text{m}$  and 0.1  $\mu\text{m}$  pore sizes), followed by adsorption using Graphene Shell Composite (GSC) in a fixed-bed column (tested at 2 cm, 4 cm, and 6 cm bed heights). Membrane filtration operated at 1 bar pressure and adsorption at a

flow rate of 9 mL/min. The results showed the 0.02  $\mu\text{m}$  membrane provided greater rejection for all parameters compared to the 0.1  $\mu\text{m}$  membrane, achieving near-complete removal of TSS, color, turbidity, and COD. The subsequent GSC adsorption, particularly at the 6 cm bed height, further polished the wastewater, achieving 100% TSS and COD removal along with high removal of other pollutants like ammonia-nitrogen and nitrate-nitrogen. The discussion highlighted that this integrated system offers a more sustainable and environmentally friendly alternative to conventional coagulation by avoiding chemical coagulants and sludge and significantly reducing pollutants to levels suitable for reuse and complying with strict water standards like Singapore's NEWater quality. Okazaki *et al.* [127] examined the water recycling system (WRS) utilizing a sequential membrane treatment for semiconductor industry wastewater. The process/technology involves pretreating three distinct wastewater streams (phosphor, acid, carbon) using dissolved air floatation (DAF), ion exchange (IEX), and biological treatment, which are then blended with filtered secondary sewage (industrial water). This blended feed is treated by Memcor continuous microfiltration (CMF), operating with polypropylene membranes of approximately 0.2 microns pore size, followed by reverse osmosis (RO) using cellulose acetate membranes, operating at a feed pressure of 20-28 kgf/cm<sup>2</sup> with 70% water recovery. The results showed the CMF consistently produced water with a silt density index (SDI) less than 3.5, and the RO units reduced total dissolved solids (TDS) to not greater than 100 mg/L, maintaining conductivity rejection above 90%. The discussion highlights the system's success since July 1998, producing 2100 m<sup>3</sup>/d of reclaimed water, which is blended with municipal supply to meet 40% of the factory's total water usage and serves as feed for demineralization and cooling, thereby addressing water scarcity and achieving operational savings.

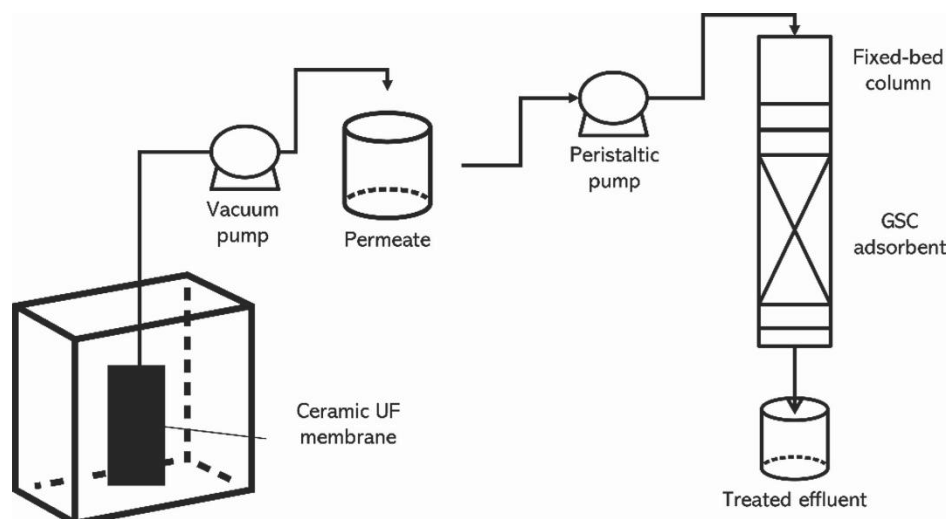


Figure 5: Laboratory-scale setup of an integrated membrane-adsorption system.

## 2.4: Spent Permanent Magnets

### 2.4.1: Composition of NdFeB Magnets and Associated Wastewater

NdFeB permanent magnets are primarily composed of neodymium (Nd), iron (Fe), and boron (B). Typically, they contain around 30 wt.% of rare earth elements (REEs), including neodymium, praseodymium (Pr), and dysprosium (Dy), and approximately 70 wt.% of iron [128]. Smaller amounts of other elements like cobalt (Co), nickel (Ni), aluminum (Al), and copper (Cu) may also be present to modify the magnetic properties [128–133]. Spent NdFeB magnets, sourced from end-of-life electronics, wind turbines, and industrial scraps, constitute a significant secondary resource for these valuable materials [134].

The hydrometallurgical treatment of these spent magnets through leaching with acidic solutions results in the generation of wastewater characterized by a complex mixture of dissolved metal ions. The primary constituents of this wastewater are the dissolved ions of the NdFeB magnet's components, notably neodymium, praseodymium, dysprosium, and a significant concentration of iron ions [134,135]. Iron, being the most abundant non-REE element, often constitutes a major contaminant in the leachate, with concentrations reaching as high as  $16990 \pm 500$  mg/L in some leachates [132]. The specific anions present in the wastewater are determined by the leaching agent employed; for example, sulfuric acid ( $\text{H}_2\text{SO}_4$ ) leaching introduces sulfate ions ( $\text{SO}_4^{2-}$ ) [134], while hydrochloric acid (HCl) leaching results in chloride ions ( $\text{Cl}^-$ ) [136]. Moreover, residual amounts of the leaching agent may also be present.

In addition to the primary and impurity metals from the NdFeB magnet itself, the wastewater can also contain dissolved ions of the minor alloying elements, such as nickel ( $\text{Ni}^{2+}$ ), cobalt ( $\text{Co}^{2+}$ ), copper ( $\text{Cu}^{2+}$ ), zinc ( $\text{Zn}^{2+}$ ), aluminum ( $\text{Al}^{3+}$ ), and gallium ( $\text{Ga}^{3+}$ ) [132, 135,137,138].

Understanding the detailed chemical composition of spent NdFeB magnets and the resulting wastewater characteristics, including the concentrations of both valuable REEs and contaminating elements, is fundamental for developing efficient and environmentally sound hydrometallurgical recycling processes. The variability in the composition of spent magnets underscores the importance of characterizing the specific waste stream being processed to optimize the leaching and subsequent separation stages.

#### **2.4.2: Common Leaching Agents for Spent Permanent Magnets**

Hydrometallurgy is widely recognized as a key method for recovering REEs from NdFeB magnet waste [135]. The core of this approach involves leaching, where chemical agents are used to dissolve the valuable metals. Common leaching agents include inorganic acids such as sulfuric acid ( $\text{H}_2\text{SO}_4$ ) [134], hydrochloric acid ( $\text{HCl}$ ) [133 from 4], and nitric acid ( $\text{HNO}_3$ ) [139]. For instance, complete leaching of REEs and iron from NdFeB magnets has been achieved using 2 M  $\text{H}_2\text{SO}_4$  at elevated temperatures like 75 °C [134]. Hydrochloric acid, at concentrations ranging from 1 to 8 mol/L and temperatures between 60 and 98 °C, is also effective in leaching NdFeB waste [140]. Organic acids, particularly oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) [128,141], citric acid ( $\text{C}_6\text{H}_8\text{O}_7$ ), and acetic acid ( $\text{CH}_3\text{COOH}$ ) [128], are also explored due to their potential for selective leaching and precipitation. Oxalic acid, for example, can be used to selectively leach REEs and subsequently precipitate them as oxalates. The efficiency of leaching is significantly influenced by process parameters such as acid concentration, temperature, leaching time, and liquid-to-solid ratio (L/S). Pre-treatment steps like demagnetization by heating (e.g., at 300 °C for 3 hours) and mechanical grinding to reduce particle size can enhance the surface area and improve leaching kinetics [134].

#### **2.4.3: Wastewater Characteristics and Iron Contaminant Behavior**

Wastewater generated during the hydrometallurgical treatment of NdFeB magnets is characterized by the presence of dissolved REE ions ( $\text{Nd}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Dy}^{3+}$ , etc.) and a significant concentration of dissolved iron ions ( $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ ), which constitute the major impurity. The leaching process also introduces anions corresponding to the acid used (e.g.,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ) into the solution. The high iron content in the leachate poses a substantial challenge for the subsequent separation and purification of REEs, often leading to co-precipitation and reduced purity of the recovered products [128,142]. To address this, various iron removal strategies are employed. One common method is precipitation of iron as hydroxides or oxides by adjusting the pH of the leachate using alkaline agents like sodium hydroxide ( $\text{NaOH}$ ) or ammonium hydroxide ( $\text{NH}_4\text{OH}$ ). For instance, raising the pH can precipitate ferric iron as  $\text{Fe}(\text{OH})_3$ .

Oxidation of ferrous iron ( $\text{Fe}^{2+}$ ) to ferric iron ( $\text{Fe}^{3+}$ ) using oxidizing agents such as  $\text{MnO}_2$  or by electrochemical means can facilitate its precipitation [132]. Furthermore, techniques like solvent extraction using reagents such as Cyanex 272 can be employed to selectively separate REEs from iron in the leach liquor [134,143]. Understanding the solubility and precipitation behavior of iron under different pH and chemical conditions is crucial for developing effective iron removal steps in the overall REE recovery process. Separated iron can potentially be recovered as a valuable by-product, such as iron oxide ( $\text{Fe}_2\text{O}_3$ ), which can be used as a pigment or in other applications, thus contributing to a more sustainable recycling process.

#### **2.4.4: Iron Recovery Techniques in Hydrometallurgy**

Hydrometallurgical processes often result in solutions containing significant iron concentrations, which can be either a valuable byproduct or an impurity requiring removal. Various techniques have been explored for the recovery of iron from these solutions, which can be broadly categorized into precipitation methods, solvent extraction and ion exchange methods, adsorption and membrane filtration technologies, and biological approaches.

##### **2.4.4.1: Precipitation Methods**

Precipitation is a widely employed technique for recovering iron from hydrometallurgical solutions due to its relative simplicity and cost-effectiveness. Different precipitating agents and controlling parameters like pH, temperature, and reagent concentration can influence the selectivity and efficiency of iron recovery. Adjusting the pH of a solution can induce the precipitation of metal hydroxides. For iron, ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) typically precipitates at a pH around 2 [128], while ferrous hydroxide ( $\text{Fe}(\text{OH})_2$ ) precipitates at a higher pH.

*Pietrantonio et al.* [139], investigated a room temperature hydrometallurgical process for the recovery of iron and rare earth elements from end-of-life wind turbine magnets, which involved a leaching step with nitric acid ( $\text{HNO}_3$ ). The leaching was performed at 25 °C with a solid-to-liquid (S/L) ratio of 1:3 for 24 hours, which achieved quantitative dissolution of the magnet without dissolving the polymeric film. Following leaching, iron precipitation was investigated using hydroxide anions from 40% w/w NaOH and 28% w/w  $\text{NH}_4\text{OH}$  at different pH values. The optimal conditions for iron removal, while leaving the greatest amount of REEs in solution, were obtained by precipitating iron as iron hydroxide(III) at pH 3.5. The experimental results showed no significant difference in the precipitation yield between NaOH and  $\text{NH}_4\text{OH}$ . The iron precipitate ( $\text{Fe}(\text{OH})_3$ ) was dried at 110 °C until constant weight, and ICP-OES analysis confirmed an iron hydroxide purity of 98%.

In another study, *Mehmet et al.* [132] investigated direct precipitation methods for iron removal from the leach liquor obtained after dissolving discarded Nd-Fe-B magnets in dilute sulfuric acid. Following the complete leaching process where more than 98% of dissolved iron was in the ferrous state, the authors conducted a chemical oxidation step using  $\text{MnO}_2$  at ambient temperature for 1 h, achieving more than 99% oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  with the addition of 1.5 times the stoichiometric requirement of  $\text{MnO}_2$ , which also increased the pH to  $0.75 \pm 0.1$ . Subsequently, ferric iron was precipitated as iron hydroxide by adjusting the pH above 3 using either  $\text{Ca}(\text{OH})_2$  or  $\text{MnO}$ . While  $\text{Ca}(\text{OH})_2$  addition at a slurry concentration of 100 g/L at 90 °C for 2 h resulted in >99% iron precipitation at pH 3.52 with 64 g  $\text{Ca}(\text{OH})_2$ /L of leachate, it also led to significant REM losses (up to ca. 23%), possibly due to co-precipitation with the formed gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). In contrast, using  $\text{MnO}$  addition (62 g  $\text{MnO}$  per L of leachate with 25 g/L slurry concentration at 60 °C for 2 h) achieved >99% iron precipitation as akageneite ( $\beta\text{-FeOOH}$ ) at a terminal pH of 3.79, with negligible losses of valuable metals ( $\leq 2\%$ ), thus proving to be a more successful method for selective iron removal without substantial REM co-precipitation.

**Oxalate Precipitation:** Oxalic acid ( $\text{H}_2\text{C}_2\text{O}_4$ ) is another effective precipitating agent for iron, forming iron oxalate. The solubility of ferrous oxalate ( $\text{FeC}_2\text{O}_4$ ) is very low, making it a suitable method for iron recovery [144,145].

*Yang et al.* [146] investigated the recovery of iron from red mud using a selective leaching process with oxalic acid, which included a pretreatment step with 3 mol/L  $\text{HCl}$  at a liquid-to-solid (L/S) ratio of 2:1 mL/g at room temperature for 1 h to reduce oxalic acid loss. Subsequently, the washed red mud was leached with oxalic acid in the presence of sulfuric acid at a mass ratio of washed red mud/ $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ / $\text{H}_2\text{SO}_4$  of 3:3:2 with an L/S ratio of 16:1 mL/g at 95 °C for 1.5 h, achieving an iron leach ratio of 94.15% while the aluminum leach ratio was 21.12%, and the iron content in the leached residue was 0.69%. The leached iron, primarily in the  $\text{Fe}(\text{III})$  state, was then reduced to  $\text{Fe}(\text{II})$  by adding iron scraps at 50 °C for 60 min, forming a precipitate of  $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ . Finally, the ferrous oxalate precipitate was decomposed in 9 mol/L  $\text{H}_2\text{SO}_4$  with an L/S ratio of 5:1 mL/g at 50 °C for 20 min to produce  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  and regenerate oxalic acid.

*Ghafar et al.* [147] investigated the purification of high-iron wet-process phosphoric acid using the oxalate precipitation method. The authors used oxalic acid to precipitate iron as ferrous oxalate dihydrate ( $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) from phosphoric acid produced by the dihydrate wet process

of Egyptian phosphate rock. Using a synthetic dilute phosphoric acid (28%  $P_2O_5$ ) with an iron content of 2.8% (w/w)  $Fe_2O_3$ , they determined the optimum conditions to be a clarification time of 2 h, reaction temperature of 60 °C, and an oxalic acid dose of 7.5 g per 100 g of 28%  $P_2O_5$  acid. Applying these conditions to the wet-process phosphoric acid (26%  $P_2O_5$ ) after a reduction step using iron scrap at 60 °C for 10 min to convert ferric ions to ferrous ions, the authors achieved an iron removal efficiency of 88% with  $P_2O_5$  losses of less than 1.0%. The low solubility of ferrous oxalate dihydrate in the dilute phosphoric acid medium was key to the high iron removal, and the method was considered promising compared to previous works due to its efficiency at higher  $P_2O_5$  concentrations and lower  $P_2O_5$  losses.

*Liu et al.* [140] investigated a novel process for the co-extraction of rare earth elements (REEs) and iron (Fe) from NdFeB sludge involving co-leaching with hydrochloric acid and stepwise precipitation. The NdFeB sludge was leached with 6 mol/L HCl at a liquid-solid ratio of 5:1 at 90 °C for 120 min, achieving leaching efficiencies of 99.84% for REEs and 99.21% for Fe. Subsequently, REEs were selectively precipitated using oxalic acid with a  $n(H_2C_2O_4):n(RE)$  ratio of 4.5:1 at a precipitation time of 30 min and a temperature of 60 °C, resulting in a REE precipitation efficiency of 98.43% with only 0.46% Fe coprecipitation, yielding  $RE_2(C_2O_4)_3 \cdot 10H_2O$  with a purity of 98.82%. Finally, Fe was recovered from the remaining solution by reduction precipitation with iron powder using a  $n(oxalic\ acid):n(Fe)$  ratio of 1.5:1 and a  $n(Fe):n(Fe^{3+})$  ratio of 1:1 at 30 °C for 30 min, achieving an Fe precipitation efficiency of 95.85% and producing  $FeC_2O_4 \cdot 2H_2O$  with a purity of 99.10%. The authors concluded that this process allows for high comprehensive utilization of resources and minimizes secondary solid waste and wastewater pollution, recovering 98.28% of REEs and 94.65% of Fe from NdFeB sludge.

*Taran et al.* [148] investigated the separation of iron impurities from kaolin using a leaching process with oxalic acid in a bench-scale stirred-tank reactor, optimizing the process with response surface methodology (RSM). The authors explored the effects of oxalic acid concentration (0.1–0.3 M), temperature (30–80 °C), and duration of the leaching test (2–4 days) on the dissolved iron concentration, maintaining a 10% solid content slurry in the reactor with agitation at 100 rpm and an initial pH adjusted to 2.5–3 using dilute  $NH_4OH$ . The results indicated that the optimum leaching conditions for maximum dissolved iron concentration (2290 ppm, ~80% removal) were 0.21 M oxalic acid, 77 °C, and a leaching duration of 4 days. However, it was observed that iron oxalate precipitate formed in experiments with a final pH above 4, leading to a higher-than-expected residual iron content in the kaolin after washing.

The minimum residual iron in kaolin (0.75%) was achieved at 0.3 M oxalic acid, 30 °C, 2 days, and a final pH of 3. The study concluded that oxalic acid leaching in a stirred tank reactor is a potentially efficient technology, with the optimized conditions and the control of pH being crucial factors for effective iron removal from kaolin

#### **2.4.4.2: Solvent Extraction**

Solvent extraction involves the transfer of a solute (metal ion) from an aqueous phase to an immiscible organic phase using a selective extractant.

*Choubey et al.* [134] investigated the recovery of rare earth metals (REMs) from discarded Nd-Fe-B magnets using a hydrometallurgical process that included a solvent extraction technique. Following the leaching of the magnets in 2 M H<sub>2</sub>SO<sub>4</sub> at 75 °C and a pulp density of 100 g/L, the authors explored the use of 35% Cyanex 272 as an extractant at an organic to aqueous (O/A) ratio of 1/1. The solvent extraction studies were carried out at room temperature, and the equilibrium pH was maintained in the range of 1 to 3.5 using ammonium hydroxide. The results indicated that at an equilibrium pH of 3.5, 99.1% Nd, 90% Pr, and total Fe were co-extracted into the organic phase in 10 minutes of mixing time. The authors noted that while high extraction efficiencies for REMs were achieved with Cyanex 272, the co-extraction of iron necessitated a multistage separation process, which was deemed economically less feasible, leading them to investigate direct precipitation methods as an alternative

*Wang et al.* [149] investigated a flash reduction and magnetic separation process for the separation and recovery of rare earth elements (REEs) and iron from NdFeB magnet scraps. The process involved initially subjecting the NdFeB calcine (containing 65.5% FeOx and 30.2% REOs) to a flash reduction in an H<sub>2</sub> atmosphere (30% H<sub>2</sub>, 70% N<sub>2</sub>) at an optimal temperature of 723 K with a particle size (D<sub>90</sub>) of 0.45 µm and an H<sub>2</sub> flow rate of 2 L/min for approximately 5 seconds. Under these conditions, the reduction rate of FeOx surpassed 95%, leading to the formation of metallic Fe and REOs. Subsequently, a two-step wet magnetic separation process using a magnetic tube with varying intensities was employed. The first step at a high intensity (≥100 mT) aimed for a high yield of metallic Fe, while the second step at a low intensity (<100 mT), specifically 40 mT, was used to enrich the Fe-rich phase further and recover REOs from it. This two-stage separation achieved a Fe-rich phase with a remarkable Fe distribution ratio of 90.2% and a yield of 67.4%, demonstrating an effective method for separating iron and enriching REOs from NdFeB magnet scraps.

## Chapter: 3. Wastewater Treatment of Spent Lithium-Ion Batteries

### 3.1: Introduction

Lithium-ion batteries (LIBs) have become indispensable in modern technology, serving as key components in electronic devices, electric vehicles, and energy storage systems, as illustrated in the *Figure 6*. Their widespread adoption is attributed to their high energy density [150], which allows for compact and efficient power storage, and low self-discharge rates [56], which helps maintain charge retention over extended periods [151–154]. By 2025, global demand for LIBs is expected to increase substantially, reaching approximately 400,000 tons [47]. Given that electric vehicle batteries typically reach the end of their lifespan within 5 to 8 years [41], the volume of spent LIBs entering the market is growing rapidly [36] because of the overpopulation and market demand [155]. In 2019 alone, the global market witnessed the introduction of approximately 218 GWh of LIBs, equating to over 1.2 million tonnes. Projections suggest that this figure could surpass 2,500 GWh (over 12.7 million tonnes) by 2030 [156,157]. *Figure 7(a)* illustrates the exponential rise in spent LIBs and the expanding market size of LIBs from 2008 to 2030 [158].

The urgent need for efficient recycling strategies for spent LIBs is a crucial aspect of achieving carbon neutrality in energy storage solutions [159,160]. Recycling these batteries not only conserves critical metal resources but also mitigates environmental and economic challenges. Spent LIBs contain hazardous materials such as heavy metal compounds, lithium hexafluorophosphate ( $\text{LiPF}_6$ ), benzene, and ester compounds, which are resistant to microbial degradation [36]. Improper disposal of these batteries can result in severe environmental contamination, as heavy metal ions, fluorides, and organic electrolytes leach into soil and groundwater, causing significant ecological damage [32,33]. Given the high solubility of heavy metal ions in aqueous environments, they can be readily absorbed by living organisms, entering the food chain and leading to serious health risks such as cancer, developmental disorders, and irreversible damage to the respiratory and nervous systems [161]. In extreme exposure cases, these contaminants can even be fatal [70]. Consequently, to comply with sustainability development goals and support environmental regulations. On a global scale, the UN's sustainable development goals [162] emphasize the importance of water management in sustainable development, calling for responsible management of wastewater across all industries. Similarly, in the European Union, the Water Framework Directives (WFD) [163] needs industries to strictly follow the regulations to protect water quality and control pollution. Likewise in the U.S., the Clean Water Act [164] seeks to protect water bodies from pollutants.

As the lithium-ion battery recycling industry grows, it is imperative to implement effective wastewater treatment strategies to reduce metal concentrations to permissible levels and follow the regulations imposed by the governing bodies [165].

Current commercial battery recycling technologies primarily fall into two categories: pyrometallurgy and hydrometallurgy. While pyrometallurgical processes operate on a large scale, they pose significant environmental and economic challenges, including hazardous emissions, greenhouse gas production, lithium losses, and high energy consumption due to required heat treatment, while hydrometallurgical processes—comprising leaching, neutralization, and precipitation [166,167] exhibit high recovery efficiency for key metal components (e.g., Li, Co, Mn, Ni) under milder operating conditions (40–80°C, 1 bar) with rapid reaction kinetics [168]. The hydrometallurgical techniques are anticipated to hold a significant share in the global market due to their simplified process, shown in *Figure 7(b)* [169]. Despite its advantages, hydrometallurgy also presents drawbacks, such as excessive chemical consumption, increased operating costs, and the generation of large volumes of wastewater [37,170–172], leading to secondary pollution from waste liquid disposal. This complex purification process involves leaching, wherein solvents dissolve valuable metals, followed by precipitation to recover target materials [47]. The use of inorganic acids for treating post-leaching fluorine-containing wastewater further exacerbates environmental and economic concerns, as it leads to secondary wastewater generation, freshwater consumption, equipment corrosion, and fluctuating pH levels [173–175].

The substantial wastewater produced during the recycling process necessitates efficient water management strategies. Ideally, this wastewater should be treated and reused within the hydrometallurgical process to optimize water usage and minimize environmental impact. However, ensuring the safety and quality of recycled water requires the effective removal of contaminants such as heavy metals and chemical oxygen demand (COD). Without proper treatment, wastewater discharge can infiltrate soil and groundwater, disrupting ecosystems and biodiversity [176–178].

As the demand for lithium-ion batteries continues to rise, so does the need for effective and sustainable wastewater treatment solutions. While extensive research has been done on the recycling processes of spent lithium-ion batteries, studies particularly addressing the wastewater treatment from lithium-ion batteries are limited. This work uniquely addresses the complex organic load and highly basic pH of LIB black mass washing water using optimized

Fenton oxidation, demonstrating a cost-effective pathway for high COD removal (up to 98.79%) and enabling continuous water reuse towards a Zero Liquid Discharge (ZLD) approach. The absence of effective treatment solutions presents considerable environmental and economic concerns, as wastewater contains pollutants such as organic contaminants, fluorinated compounds, and heavy metals that can adversely affect the soil and water bodies. To promote sustainable battery recycling, advanced wastewater treatment strategies must be developed to optimize water reuse and reduce environmental impact.

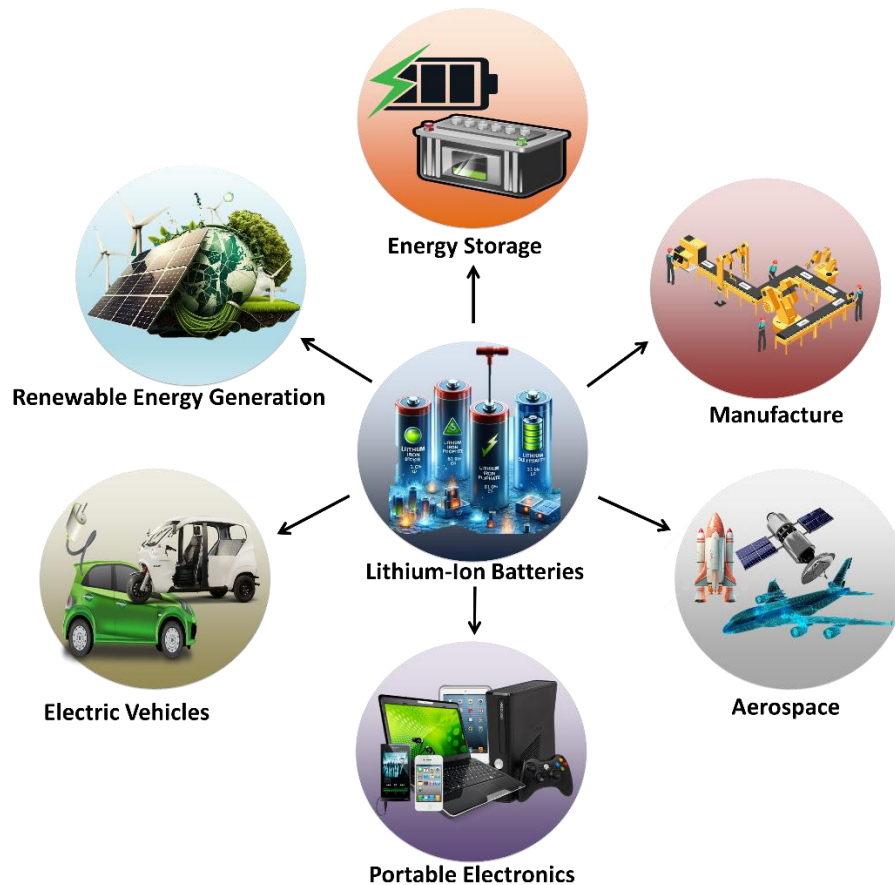


Figure 6: Incorporation of lithium-ion batteries in numerous applications [36].

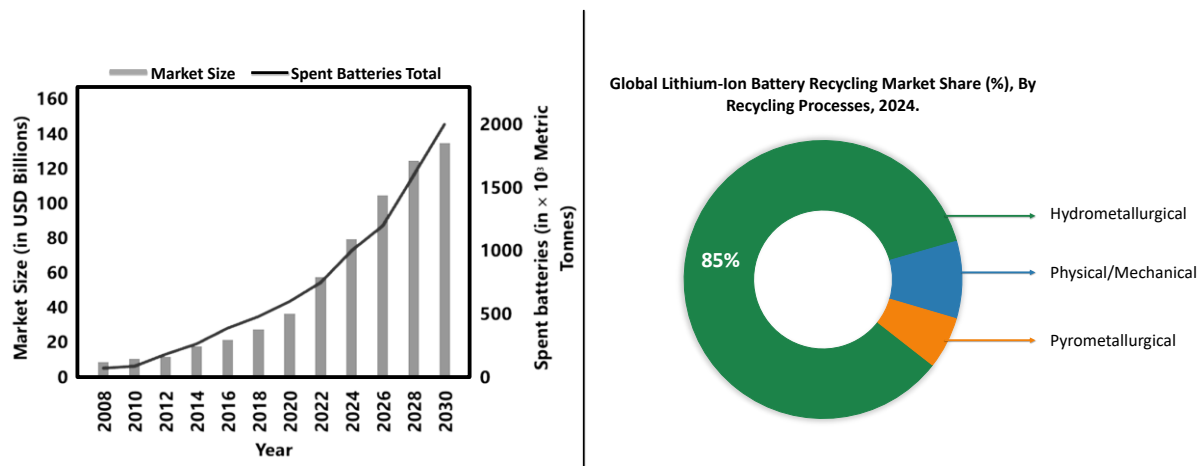


Figure 7: (a) Estimation of the Global Market Size and Total Spent of Li-ion Batteries from 2008-2030 [158] (b) Global Market Share of Lithium-Ion Battery Recycling by Process, 2024 [169].

### 3.2: Materials and Methods

The wastewater subjected to analysis originated from the washing process of the black mass derived from the spent lithium-ion batteries recycling process used in the automotive sector as part of the Vitality project. The wastewater exhibited basic characteristics with a pH of 10.17 and contained a high chemical oxygen demand (COD) of 5390 mg/L. Elemental analysis further identified the presence of Lithium (Li) at a concentration of 488.13 mg/L and Copper (Cu) at 14.2 mg/L. Iron (Fe) and Aluminum (Al) were also detected, but their concentrations were found to be less than 10 mg/L. For the experimental work, all chemicals utilized were of analytical grade. Key chemicals included hydrogen peroxide ( $\text{H}_2\text{O}_2$  30%) and ferrous sulfate (II) heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), which served as the source of  $\text{Fe}^{2+}$ . Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) was prepared as a 30% v/v solution and was employed to reduce the pH of the wastewater before the Fenton reaction. Post-Fenton process, calcium hydroxide solution prepared at a concentration of 10% w/v was added to the solution to increase the pH to precipitate iron and other metals as hydroxides, and to remove fluorides.

The experiments were conducted in a conical flask of 100 mL using 40 mL of sample for each test. Before the experiments, pH was adjusted to  $3.5 \pm 0.1$  using a 30 % (v/v) solution of  $\text{H}_2\text{SO}_4$ , which is the optimal pH for the Fenton process. Then the required amount of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  was added to the solution and shaken for 5 minutes to completely dissolve it. After that,  $\text{H}_2\text{O}_2$  was introduced in the required amount to initiate the reaction. The mixtures were subsequently agitated on a shaker (SKI 4, shaking incubator) at 200 rpm for 90 minutes under atmospheric pressure and room temperature. After reaction completion, the solution pH was increased to

8.5 ± 0.1 through the addition of lime (10 % w/v) to precipitate the iron, fluorides, and other metals present in the solution. the solutions were then kept for half an hour to settle down the precipitates. Finally, the treated solutions were filtered by using a nitrate cellulose filter with a pore size of 0.45 µm in a vacuum filtration system (STEROGLASS, Model ST510). The process diagram is given in *Figure 8*. To determine the characteristics of the water both before and after treatment, specific analytical techniques were applied. The COD concentration was measured using LCK 114 kits. The concentrations of elements, including Fe, Cu, Al, and Li, were analysed using inductively coupled plasma with optical emission spectroscopy (ICP-OES). A Hanna pH meter was used to measure the pH at the start and after the completion of the Fenton and lime treatment steps. Given the elevated COD level, a 2<sup>2</sup>-full factorial experimental design was chosen to investigate the process. The primary focus of this design was to assess the parameters influencing COD reduction. This design approach allows for the evaluation of the main effects of the factors (variables) and how they interact with each other. A 2<sup>2</sup>-full factorial design consists of all possible combinations of two factors, each tested at two levels, leading to four main experimental runs. The investigated factors and their corresponding levels are mentioned in *Table 2*. These factor ranges were selected to maintain a ratio of H<sub>2</sub>O<sub>2</sub> to Fe<sup>2+</sup> between 25:1 and 5:1 (w/w), a range known to be effective for Fenton oxidation [179]. This design facilitated the examination of both the individual impacts and the combined effects on the COD elimination efficacy. To check the consistency of the results and identify potential non-linear responses, three replicate experiments were also included at the centre point of the design.

The effectiveness of the Fenton process is influenced by various conditions, notably pH, Fe (II) concentration, H<sub>2</sub>O<sub>2</sub> dosage, and temperature [180–182]. Examining the individual and combined effects of all these factors would require extensive experimentation. So, optimum temperature and pH were selected for the experiments. The oxidizing ability of hydroxyl radicals (•OH) is directly impacted by the solution's pH. As pH decreases, the oxidation potential of •OH increases, enhancing its capacity [183]. In contrast, higher pH diminishes Fenton reagent activity because active Fe<sup>2+</sup> levels drop, and inactive iron precipitates form. Additionally, H<sub>2</sub>O<sub>2</sub> undergoes self-decomposition at elevated pH values [184]. Under highly acidic conditions, certain iron complex species decrease the interaction between Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> [181,182], lowering the Fenton process's effectiveness for breaking down organic compounds when the pH is at either extreme.

Table 2: Factors and Their Corresponding Levels Considered in the 2<sup>2</sup>-Factorial Design.

| Factors                               | Coded factors |    |
|---------------------------------------|---------------|----|
|                                       | -1            | +1 |
| H <sub>2</sub> O <sub>2</sub> (% v/v) | 5             | 15 |
| Fe <sup>2+</sup> (g/L)                | 2             | 5  |

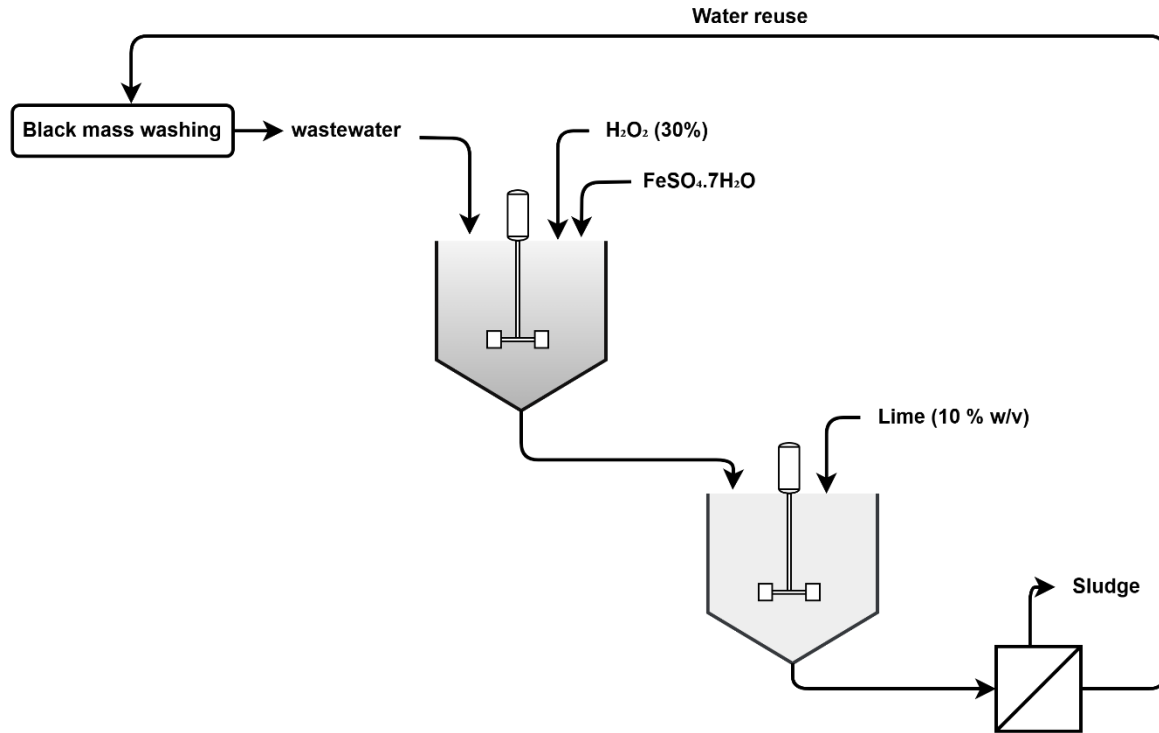


Figure 8: Process flow diagram for wastewater treatment produced during LIBs recycling.

### 3.3: Results and discussion

#### 3.3.1: Properties of wastewater

The constituents of the wastewater generated from washing the black mass of spent lithium-ion batteries were determined. An analysis revealed the presence of several elements. In addition to other components shown in the *Table 3*, Iron (Fe) and Aluminum (Al) were also detected in this wastewater, with their concentrations found to be less than 10 ppm.

Table 3: Analysis of Wastewater Generated during the recycling process.

|          |        |
|----------|--------|
| COD mg/L | 5390   |
| pH       | 10.17  |
| Li mg/L  | 488.13 |
| Cu mg/L  | 14.2   |

### 3.3.2: Experimental Design and Statistical Evaluation

To optimize the treatment process specifically aimed at reducing the chemical oxygen demand (COD), a  $2^2$ -full factorial experimental design was implemented. This design approach allowed for evaluating the effect of different variables and their combined effects on the target response, which was COD reduction. The design focused on two key factors:  $\text{H}_2\text{O}_2$  and the concentration of  $\text{Fe}^{2+}$ , supplied using ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ). The selected factors were evaluated at two levels:  $\text{H}_2\text{O}_2$  (5 and 15 % v/v) and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (2 and 5 g/L). These levels were selected to keep  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  ratio between 25:1 and 5:1 w/w [179]. This is the effective range for the organic matter degradation while minimizing the consumption of the reagents. The high value of COD (5390 mg/L) is primarily due to the organic electrolyte components such as dimethyl carbonate, ethylene carbonate, and other carbonate-based solvents present in the batteries. These persistent organic contaminants need to be degraded by using advanced oxidation processes such as Fenton. A  $2^2$ -factorial design was employed to investigate the main effect as well as the interaction between the factors on the efficiency of COD removal. Conditions and their corresponding COD abatement are presented in *Table 4*.

Table 4: Experimental Conditions and outcomes obtained from the  $2^2$ -factorial design.

| Tests | Treatments | A   | B   | A: $\text{H}_2\text{O}_2$ (30%)<br>(% v/v) | B: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$<br>(g/L) | Response (COD<br>removal%) |
|-------|------------|-----|-----|--------------------------------------------|-------------------------------------------------------|----------------------------|
| 1     | (1)        | -1  | -1  | 5.0                                        | 2.00                                                  | 60.35                      |
| 2     | a          | +1  | -1  | 15.0                                       | 2.00                                                  | 90.28                      |
| 3     | b          | -1  | +1  | 5.0                                        | 5.00                                                  | 94.79                      |
| 4     | ab         | +1  | +1  | 15.0                                       | 5.00                                                  | 98.79                      |
| 5     | 0          | 0.0 | 0.0 | 10.0                                       | 3.50                                                  | 92.03                      |
| 6     | 0          | 0.0 | 0.0 | 10.0                                       | 3.50                                                  | 92.33                      |
| 7     | 0          | 0.0 | 0.0 | 10.0                                       | 3.50                                                  | 92.08                      |

The experimental results showed a clear increase in terms of COD reduction with higher concentrations of either reagent ( $\text{H}_2\text{O}_2$  or  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ). The highest reduction in COD (98.79 %) was observed when both reagents were at their highest levels. The centre point experiments produced consistent results with an average COD reduction of approximately 92.15 %. This consistency suggests both good reproducibility of the process under these conditions and indicates minimal curvature within the investigated experimental space. To thoroughly analyze the results from the factorial design, statistical evaluations were performed using both Design Expert software and Yates' algorithm. Yates' algorithm was carried out manually within

Microsoft Excel to serve as a cross-validation method for the statistical findings. Both analysis approaches produced identical results regarding the significance and magnitude of the factors' effects. The calculated main effects (for H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup>), their interaction effect, and associated statistical metrics such as sum of squares (SS), F-values, P-values, and confidence levels are presented *Table 5*.

Table 5: Yates' algorithm analysis of the 2<sup>2</sup> factorial experiment at 95% confidence.

| Terms     | effect | SS     | F        | P        | 1-P   | Significance, (%) |
|-----------|--------|--------|----------|----------|-------|-------------------|
|           | 86.06  | --     | --       | --       | --    |                   |
| <b>A</b>  | 16.96  | 287.62 | 10962.63 | 0.00608  | 0.994 | 99.4              |
| <b>B</b>  | 21.48  | 461.24 | 17580.21 | 0.004801 | 0.995 | 99.5              |
| <b>AB</b> | -12.97 | 168.17 | 6409.646 | 0.007951 | 0.992 | 99.2              |

The analysis indicates that both main effects, specifically H<sub>2</sub>O<sub>2</sub> factor A and Fe<sup>2+</sup>, were found to be statistically significant. This means that changes in the concentration of either hydrogen peroxide or ferrous ions strongly contribute to the observed efficiency in removing COD from the wastewater. Furthermore, the interaction effect between H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> was also determined to be statistically significant. The value calculated for this interaction effect was -12.97, which is negative. This negative value suggests an antagonistic interaction. In practical terms, this means that while increasing either reagent individually improves COD removal, increasing both simultaneously results in a COD removal efficiency that is slightly less than what would be expected from simply adding the individual effects of each reagent. A possible explanation for this observed antagonistic interaction is the scavenging of hydroxyl radicals (<sup>•</sup>OH) by an excess amount of either Fe<sup>2+</sup> or H<sub>2</sub>O<sub>2</sub>. If there is too much of one or both reagents relative to the organic pollutants, these excess molecules can consume the highly reactive <sup>•</sup>OH radicals instead of the radicals reacting with the target contaminants. This process reduces the overall availability of <sup>•</sup>OH radicals for the decomposition of organic matter, thereby diminishing the effectiveness of the Fenton method at the highest combined concentrations compared to the sum of their individual effects.

Based on the statistical analysis and experimental data, a mathematical model was built using coded variables to describe the empirical relationship between the input factors and the resulting chemical oxygen demand (COD) removal efficiency. This model is expressed by the equation:

$$Y_{Calc} = 86.05 + 8.48x_1 + 10.74x_2 - 6.48x_1x_2$$

Where  $Y$  represents the predicted COD removal efficiency in percentage. The coded variable  $x_1$  corresponds to the concentration of  $\text{H}_2\text{O}_2$ , while  $x_2$  corresponds to the concentration of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . The coefficients associated with  $x_1$  (8.48) and  $x_2$  (10.74) are positive. These positive values confirm that increasing the concentration of either  $\text{H}_2\text{O}_2$  or  $\text{Fe}^{2+}$  individually leads to an improvement in COD removal efficiency.

The model also includes an interaction term ( $x_1x_2$ ) with a negative coefficient of -6.48. This negative value reflects the previously observed antagonistic effect. It indicates that when both reagents are increased simultaneously to their higher levels, the resulting COD removal efficiency is slightly less than the sum of their individual effects. As discussed earlier, this antagonistic interaction could be related to the scavenging of hydroxyl radicals ( $\cdot\text{OH}$ ) by excess  $\text{Fe}^{2+}$  or  $\text{H}_2\text{O}_2$  at high concentrations, which reduces the radicals available to degrade organic pollutants.

This interpretation of the model is visually supported by the 3D response surface shown in *Figure 9*, which illustrates a steady increase in COD abatement as the concentrations of both reagents increase. These visual representations confirm the statistical significance of the factors and the trend predicted by the model, including the nature of the interaction. It also enabled the construction of this predictive model, which can serve as a valuable tool to guide and optimize the Fenton treatment process in practical applications.

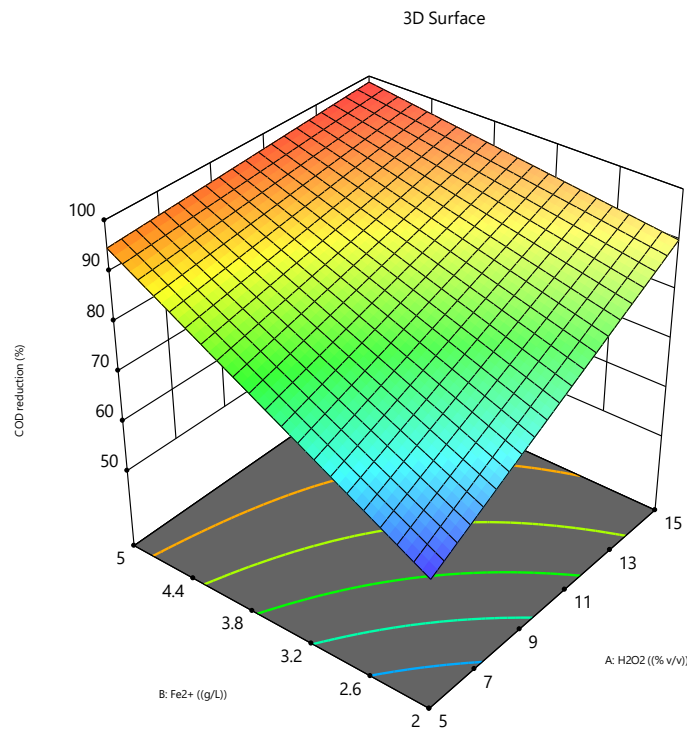


Figure 9: 3D Response Surface Modelling of COD Removal in Fenton Process.

### 3.3.3: Characteristics of Treated Wastewater

Following the Fenton treatment and subsequent lime precipitation, the constituents of the treated wastewater were analyzed and are presented in *Table 6*. While this treatment process successfully reduced many contaminants, the water still contains a high concentration of lithium, measured at 378.50 mg/L. For context, the initial wastewater from the black mass washing step of spent lithium-ion battery recycling had a high COD and basic pH and contained lithium. The Fenton process primarily targets COD removal. To manage the remaining high concentration of lithium in the treated water, the strategy is to recover the lithium over several cycles of the recycling process. As the treated water is recycled back into the hydrometallurgical process for subsequent cycles, the lithium concentration within the circulating water will gradually increase. Once this concentration reaches a sufficiently high level, the lithium will then be extracted. After the lithium extraction, the water will be treated again and recycled for further use in the process. This cyclical approach, involving treatment, reuse, and periodic lithium recovery, is designed to eventually lead to a zero-liquid discharge (ZLD) system. The ZLD objective is achieved by continuously reusing the treated water, thereby minimizing the need for freshwater consumption in the overall recycling process. The treated water, with its significantly reduced COD (56.90 mg/L) compared to the initial high COD (5390 mg/L in the raw wastewater), is considered suitable for recycling into these subsequent process cycles.

Table 6: Composition of treated water.

|          |        |
|----------|--------|
| COD mg/L | 56.90  |
| pH       | 8.50   |
| Li mg/L  | 378.50 |
| Cu mg/L  | 0.83   |

### 3.3.4: Mass Balance and Cost Estimation Overview

A mass balance was carried out to estimate the chemical consumption per cubic meter ( $\text{kg/m}^3$ ) of treated wastewater under each experimental condition tested. The chemicals included in this estimation were hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), and calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ). The Fenton process itself was conducted at a controlled pH of  $3.5 \pm 0.1$ . After the Fenton reaction, the pH was readjusted to  $8.5 \pm 0.1$  using a 10% (w/v) lime solution (calcium hydroxide). This pH adjustment using lime was done primarily to precipitate iron as hydroxides, although lime was also used to adjust the pH and remove fluorides. This step of raising the pH from approximately 3.5 to  $8.5 \pm 0.1$  determined the necessary quantity

of calcium hydroxide. The estimated quantities of these chemicals consumed per cubic meter of treated wastewater for each experiment are summarized in *Table 7*.

Table 7: Chemical consumption per m<sup>3</sup> of treated wastewater.

| Exp | H <sub>2</sub> O <sub>2</sub> (kg/m <sup>3</sup> ) | FeSO <sub>4</sub> ·7H <sub>2</sub> O (kg/m <sup>3</sup> ) | Ca(OH) <sub>2</sub> (kg/m <sup>3</sup> ) |
|-----|----------------------------------------------------|-----------------------------------------------------------|------------------------------------------|
| 1   | 55.5                                               | 9.96                                                      | 6.20                                     |
| 2   | 166.5                                              | 9.96                                                      | 7.25                                     |
| 3   | 55.5                                               | 24.89                                                     | 8.75                                     |
| 4   | 166.5                                              | 24.89                                                     | 8.35                                     |
| 5   | 111                                                | 17.42                                                     | 6.18                                     |
| 6   | 111                                                | 17.42                                                     | 6.10                                     |
| 7   | 111                                                | 17.42                                                     | 6.05                                     |

Following the mass balance, cost estimations were based on existing market prices of the reagents shown in *Table 8*. The expenditure per m<sup>3</sup> of treated wastewater was calculated for each experiment and compared against the achieved COD removal efficiency. This analysis highlighted a significant trade-off between treatment performance and operational expense. *Experiment 4*, which used the highest concentrations of both H<sub>2</sub>O<sub>2</sub> and FeSO<sub>4</sub>·7H<sub>2</sub>O, achieved the maximum COD removal of 98.79%. However, this condition also resulted in the highest treatment cost (62.02 €/m<sup>3</sup>). By contrast, *Experiment 3* achieved a comparable, high COD removal of 94.79%. This was accomplished at a significantly lower cost of 23.23 €/m<sup>3</sup>, making it more economically favorable. *Experiment 3* utilized the lower H<sub>2</sub>O<sub>2</sub> concentration but the higher Fe<sup>2+</sup> concentration. This suggests that optimizing the Fe<sup>2+</sup> dosage can improve treatment performance even with reduced H<sub>2</sub>O<sub>2</sub> input. The overall findings demonstrate that while higher reagent dosages maximize COD reduction, they may not be economically sustainable, suggesting that the condition in *Experiment 3* represents a promising compromise between efficiency and cost for potential industrial-scale applications. Furthermore, this economically optimized cost of €23.23/m<sup>3</sup> is substantially lower than typical disposal costs for complex hydrometallurgical wastewater, which often exceed €150/m<sup>3</sup>, strongly validating the financial benefits of integrating the Fenton process into the recycling stream as an alternative to external discharge.

Table 8: Cost analysis and COD removal efficiency.

| Exp | H <sub>2</sub> O <sub>2</sub> (€/m <sup>3</sup> ) | FeSO <sub>4</sub> ·7H <sub>2</sub> O (€/m <sup>3</sup> ) | Ca(OH) <sub>2</sub> (€/m <sup>3</sup> ) | Total Cost (€/m <sup>3</sup> ) | COD Removal (%) |
|-----|---------------------------------------------------|----------------------------------------------------------|-----------------------------------------|--------------------------------|-----------------|
| 1   | 19.43                                             | 1.00                                                     | 0.93                                    | 21.35                          | 60.35           |
| 2   | 58.28                                             | 1.00                                                     | 1.09                                    | 60.36                          | 90.28           |
| 3   | 19.43                                             | 2.49                                                     | 1.31                                    | 23.23                          | 94.79           |

|   |       |      |      |       |       |
|---|-------|------|------|-------|-------|
| 4 | 58.28 | 2.49 | 1.25 | 62.02 | 98.79 |
| 5 | 38.85 | 1.74 | 0.93 | 41.52 | 92.03 |
| 6 | 38.85 | 1.74 | 0.92 | 41.51 | 92.33 |
| 7 | 38.85 | 1.74 | 0.91 | 41.50 | 92.08 |

### 3.4: Conclusion

This research investigated the efficiency of the Fenton process for the treatment of wastewater produced during the washing step of black mass during the recycling of spent lithium-ion batteries. The produced wastewater had a basic pH of 10.17 with a COD value of 5390 mg/L. This effluent stream was treated to be reused in the process to reduce the consumption of freshwater and achieve a ZLD approach. A 2<sup>2</sup>-full factorial design was effectively employed to assess and optimize the dosages of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and ferrous sulfate (Fe<sup>2+</sup>) for maximizing COD reduction, with experiments conducted at a controlled pH of 3.5 ± 0.1. The Fenton process demonstrated significant efficacy, achieving a maximum COD removal efficiency of 98.79%. Statistical analysis confirmed that both H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> concentrations were statistically significant factors influencing COD removal. A significant, negative interaction effect between the two reagents was also identified, suggesting potential radical scavenging at higher combined concentrations. While the highest COD removal was achieved at the highest reagent dosages, a critical trade-off between treatment performance and operational cost was evident. Conditions represented by Experiment 3, utilizing a lower H<sub>2</sub>O<sub>2</sub> concentration (5% v/v) and higher Fe<sup>2+</sup> concentration (5 g/L), achieved a still high COD removal of 94.79% at a substantially lower cost compared to maximizing efficiency. This highlights the potential for optimizing reagent ratios for economic feasibility in industrial applications. The treated water, with its significantly reduced COD (56.90 mg/L), is suitable for recycling into subsequent process cycles, thereby supporting the ZLD objective and contributing to sustainable water management in the context of growing LIB recycling demands.

## **Chapter: 4. Wastewater Treatment of Alkaline Batteries**

### **4.1: Introduction**

Primary alkaline batteries, widely used as non-rechargeable portable energy sources, command a substantial global market, valued between 5.8 and 7.6 billion USD in 2020 and projected to grow from 6.2 billion USD in 2026 to 10.9 billion USD by 2028, particularly in the Asia Pacific [71]. In the United States, alkaline dry cells constitute about 80% of manufactured portable batteries, with global annual production exceeding 10 billion units [73]. The pervasive use of electronic devices has rendered spent batteries, including alkaline types, a continuous economic and ecological concern. Their global usage generates significant waste. For instance, in 2015, out of an estimated 201,000 tonnes introduced in the EU, only 36% were collected, 17% entered municipal waste streams (incinerators or landfills), and 29% were recycled [77]. Insufficient regulations in many regions for proper battery waste management lead to accumulation in open settings and landfills [78].

Hydrometallurgical processes provide a cost-effective and often more efficient alternative for recovering metals from complex waste streams such as spent batteries. Battery recycling via hydrometallurgical routes typically involves physical pre-treatment, followed by chemical treatment (e.g., neutral, acid, or alkaline leaching), metal separation, purification, and final recovery [71, 81,84]. A key aspect of hydrometallurgical recycling is the generation of liquid waste streams, termed leachates or effluents. For instance, leachates from acidic leaching are typically characterized by extreme pH and contain high concentrations of metals like iron, manganese, and zinc, plus sulfates from the leaching acid. Such residual solutions demand treatment before discharge to prevent environmental contamination.

Graphite and its derivatives are highly valued for their superior thermal stability, electrical conductivity, and chemical resistance [185,186], leading to widespread applications in electronics, metallurgy, aerospace, and chemical manufacturing. Increased graphite demand has driven higher production, consequently boosting graphite waste, particularly from spent batteries [187]. Purification processes remove impurities like  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{BaSO}_4$ , and  $\text{PbSO}_4$  to recover valuable materials from this waste. These methods often utilize strong acids and alkalis [188], producing wastewater with complex, hazardous compositions containing high concentrations of salts, heavy metals, and various anions [189]. Improperly treated, this presents significant environmental issues [187,190]. This underscores the challenge of

managing wastewater from modern technologies, necessitating effective, systematic treatment to comply with discharge standards and minimize ecological damage.

To counter these challenges, various wastewater treatment methods have been developed, including non-membrane techniques like adsorption [191], evaporation [192], ion exchange [193], and coagulation-flocculation [194,195], as well as membrane-based approaches such as electrodialysis [196], reverse osmosis [197], and nanofiltration [198]. However, many prove unsuitable for graphite industry wastewater due to its high ionic strength and complex chemical composition. Recent research emphasizes physicochemical strategies, with techniques like sorption, flotation, and ion exchange applied to hydrometallurgical wastewater to promote water reuse [199–201]. Given the imperative to meet the 2030 Sustainable Development Agenda water conservation goals, wastewater treatment must now prioritize resource recovery and environmental sustainability [202].

Coagulation-precipitation, while appealing for its simplicity and low cost [203] as a pre-treatment, it struggles with complete contaminant removal, persistent turbidity, and high cake generation, limiting its efficiency [204]. To overcome these, advanced oxidation processes, especially the Fenton process, have gained significant attention for degrading organic pollutants [205]. Recent studies demonstrate the Fenton method's high effectiveness in treating industrial wastewater with elevated chemical oxygen demand (COD) and metal concentrations [206]. *Ullah et al.* [207] reported a remarkable 93.6% COD reduction and 99.9% iron removal from hydrometallurgical effluents using this approach. Moreover, central composite design (CCD) optimization has improved pollutant removal while maintaining low treatment costs (€81.60/m<sup>3</sup>), positioning it as a viable substitute for traditional disposal techniques. These findings highlight the potential of integrating Fenton-based advanced oxidation into sustainable water management strategies [205,208]. An optimized Fenton process supports industrial water reuse, significantly reducing the freshwater footprint. However, its performance is largely pH-dependent, with peak catalytic activity occurring between pH 2.5 and 3.5 [209,210]. Reagent concentration and temperature are also critical [206,211]. Importantly, efficient treatment is achievable under ambient conditions, enhancing its industrial feasibility [212].

This research evaluates and designs effective pre-treatment strategies to reduce hazardous ion concentrations, enhance treatment efficiency, and enable the long-term reuse of graphite materials. The study focuses on wastewater generated during the hydrometallurgical recovery of graphite from alkaline spent batteries. A full factorial experimental design within the

Response Surface Methodology (RSM) framework, using a central composite design (CCD), was employed to statistically assess the influence of Fenton process parameters, with chemical oxygen demand (COD) reduction as the primary response. A novel integrated treatment approach is proposed, combining highly selective acidic precipitation to remove hazardous heavy metals (Ba, Pb, and Sr to negligible levels) with optimized Fenton oxidation, achieving up to 84.11% COD removal. This treatment enables the subsequent recovery of high-purity sodium sulfate (99.67%) through crystallization. The process offers a sustainable and cost-effective solution (€36.40/m<sup>3</sup>) for wastewater reuse and waste valorization, aligning with minimal liquid discharge (MLD) strategies and supporting the 2030 sustainable water management goals [202].

## 4.2: Materials and Methods

Wastewater for this study originated from a hydrometallurgical graphite recovery process using spent alkaline batteries. The effluent initially exhibited a highly basic pH of 11.7. Analytical-grade chemicals such as sulfuric acid (>95%), hydrogen peroxide (30% w/v), ferrous sulfate (FeSO<sub>4</sub>·7H<sub>2</sub>O), and sodium hydroxide (NaOH) were utilized for treatment. NaOH served dual purposes: pH adjustment and aiding iron precipitation after the Fenton process, ensuring the treated water's final pH was near neutral.

The detailed composition of the wastewater produced during the hydrometallurgical recovery of graphite from alkaline spent batteries is outlined in *Table 9*. As previously established, the as-received wastewater initially registered a pH of 11.7. A crucial pre-treatment step involved the significant reduction of this pH into an acidic range, achieved by introducing concentrated sulfuric acid. This action pursued two primary objectives: (1) to eliminate the majority of barium and lead, which were identified as the most concentrated and most hazardous elements within the sample, respectively, through their precipitation as barium sulfate salts, known for their near insolubility in acidic sulfate solutions; and (2) to establish the optimal pH level necessary for the subsequent initiation of the Fenton process. Following this initial pH adjustment, the wastewater underwent thorough mixing for 1 hour at 120 rpm at ambient temperature. This rigorous mixing stage effectively promoted the comprehensive precipitation of both barium and lead. Thereafter, the resulting solution was meticulously filtered and subsequently prepared for the ensuing Fenton treatment.

Initiating the Fenton process, the precise quantity of FeSO<sub>4</sub>·7H<sub>2</sub>O powder was added to the solution and stirred for 5 minutes. Subsequently, to commence the Fenton reaction, the

predetermined volume of 30% (w/v) H<sub>2</sub>O<sub>2</sub> was introduced. The entire mixture then underwent agitation on a shaker (SKI 4, Shaking Incubator) at 200 rpm for 90 minutes, maintained at ambient temperature and atmospheric pressure.

Table 9: Composition of the wastewater.

| Elements        | Mn | Zn  | Fe  | K    | Na     | Ca  | Ba    | Pb   | Sr  | COD  |
|-----------------|----|-----|-----|------|--------|-----|-------|------|-----|------|
| Conc.<br>(mg/L) | 29 | 4.3 | 3.4 | 26.1 | 3542.1 | 8.0 | 474.3 | 11.9 | 8.7 | 9715 |

Following the reaction, the pH was adjusted to  $8.5 \pm 0.1$  using a 20% (w/v) NaOH solution to precipitate iron and other metals as hydroxides. The solutions were settled for 30 minutes before filtration via a vacuum system (SteroGlass ST510) using 0.45  $\mu$ m nitrate cellulose filters. The solid residue, or filter cake, was dried overnight at 100 °C and then weighed.

COD reduction was quantified by measuring sample COD before and after the Fenton process using standard test kits and the following formula:

$$COD\ Reduction\ (\%) = \frac{COD_i - COD_f}{COD_i} \times 100$$

where COD<sub>i</sub> and COD<sub>f</sub> represent the solution's initial and final chemical oxygen demand, respectively, after the Fenton process. Solution metal content was analyzed via ICP-OES (Agilent Technologies, 5100). Due to the wastewater's high initial COD, a 2<sup>2</sup>-full factorial design within the RSM framework, incorporating three center and four-star points, initially evaluated hydrogen peroxide and ferrous sulfate effects and their interaction on COD removal. This design encompassed eleven experimental runs, enabling analysis of individual and interactive parameter effects at levels detailed in *Table 10*. Design-Expert 13 software facilitated the statistical analysis of collected data.

Table 10: Independent variables and their levels used in the experimental design.

| Variables                            | X<br>variable | Variable levels |    |   |    |            |
|--------------------------------------|---------------|-----------------|----|---|----|------------|
|                                      |               | - $\alpha$      | -1 | 0 | +1 | + $\alpha$ |
| H <sub>2</sub> O <sub>2</sub> (%V/V) | A             | 2.34            | 4  | 8 | 12 | 13.66      |

|                        |   |      |     |      |   |      |
|------------------------|---|------|-----|------|---|------|
| Fe <sup>2+</sup> (g/L) | B | 0.98 | 1.5 | 2.75 | 4 | 4.52 |
|------------------------|---|------|-----|------|---|------|

---

### 4.3: Results and Discussion

#### 4.3.1: Barium and lead removal

Before commencing the Fenton experiments, barium and lead were extracted from the wastewater. As presented in *Table 9*, the initial concentrations of Ba and Pb were 474 mg/L and 12 mg/L, respectively, at an initial pH of 11.7. These levels significantly surpassed acceptable discharge limits. To decrease barium and lead concentrations to approximately 0.1 mg/L, concentrated sulfuric acid was introduced to the wastewater to lower its pH, thereby inducing the precipitation of barium and lead as their corresponding insoluble sulfate salts. *Figure 10* illustrates the impact of pH adjustment on the removal efficiency of barium, lead, and strontium. It was observed that barium precipitation remained highly effective even at moderately neutral pH levels. Reducing the pH also facilitated the removal of lead (Pb), strontium (Sr), and trace amounts of other metallic impurities. However, the most efficient removal of Ba, Pb, and Sr was achieved at a pH of 1, as depicted in *Figure 10*. Consequently, the entire solution was adjusted to pH 1 before proceeding with the Fenton process.

The composition of the wastewater following the removal of barium, lead, and strontium is detailed in *Table 11*, affirming the high efficacy of this pre-treatment stage. Barium, lead, and strontium concentrations were reduced to negligible levels, with final concentrations as low as 0.1 mg/L for Ba and Pb, and approximately 0.3 mg/L for Sr. *Table 11* further indicates a substantial reduction in COD to 2712 mg/L after the precipitation process, representing about a 72% decrease. Once these elements were successfully removed, the pH was adjusted to  $3.5 \pm 0.1$  using a NaOH solution to optimize the oxidation efficiency of hydroxyl radicals ( $\cdot\text{OH}$ ), given that a lower pH enhances the stability and activity of  $\text{H}_2\text{O}_2$  [183]. Without this pH adjustment, the naturally high pH of the initial wastewater would have led to rapid decomposition of  $\text{H}_2\text{O}_2$ , compromising its oxidative performance [213,214].

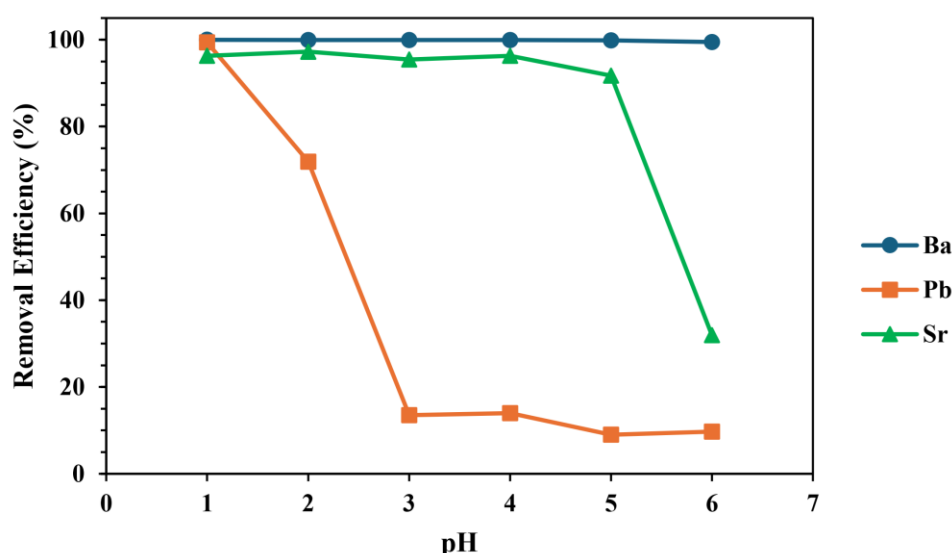


Figure 10: Barium, lead, and strontium removal efficiency as a function of pH.

Table 11: Composition of the wastewater after Ba removal at pH 1.

| Elements | Mn   | Zn  | Fe  | K    | Na     | Ca  | Ba  | Pb  | Sr  | COD  |
|----------|------|-----|-----|------|--------|-----|-----|-----|-----|------|
| Conc.    | 22.5 | 3.4 | 3.2 | 22.8 | 3499.5 | 4.1 | 0.1 | 0.1 | 0.3 | 2727 |
| (mg/L)   |      |     |     |      |        |     |     |     |     |      |

#### 4.3.2: COD reduction by the Fenton process

As noted previously, a full factorial design within the Response Surface Methodology (RSM) framework, encompassing eleven experimental runs, was implemented to assess how  $\text{H}_2\text{O}_2$  concentration and  $\text{Fe}^{2+}$  dosage influenced COD removal efficiency and the subsequent cake weight after filtration. The COD reduction efficiency was calculated relative to the initial COD of the solution following barium and lead precipitation, as specified in *Table 11*. The experimental design and the results, including COD reduction and solid cake formation after the Fenton process and treated wastewater filtration, are summarized in *Table 12*.

A preliminary review of the experimental data confirms that  $\text{H}_2\text{O}_2$  concentration significantly impacted COD reduction (*Table 12*). COD removal rates varied from 67.18% to 84.11%, with the highest efficiency attained at 12%  $\text{H}_2\text{O}_2$  and 4 g/L  $\text{Fe}^{2+}$  (Run 1). Nevertheless, a comparable COD reduction (83.62%) was also achieved in Run 7 with a lower iron dosage (1.5 g/L), suggesting that an excess of  $\text{Fe}^{2+}$  at the highest hydrogen peroxide level does not necessarily enhance treatment and might contribute to unnecessary cake formation. Similar findings were

reported by Vlyssides A. et al, [215] who obtained over 70% COD removal under various conditions, with optimized parameters yielding up to 88% COD reduction in wastewater from a wood processing industry. These outcomes underscore the wide applicability of the Fenton process for diverse wastewater streams, particularly those resistant to conventional biological treatments. *Table 12* highlights the strong reproducibility of the process, evidenced by consistent COD reduction results across three replicate center point runs: 79.27%, 80.94%, and 81.6% (Runs 2, 8, and 11). Concurrently, the corresponding filter cake production was 7.43, 7.10, and 6.90 kg per cubic meter of wastewater. The standard deviations for COD reduction efficiency and filter cake weight were 1.20 and 0.27, respectively.

Table 12: Experimental design, COD reduction, and the weight of the produced solid filter cake after the Fenton process.

| Parameters |                                      |                        | Responses         |                                    |
|------------|--------------------------------------|------------------------|-------------------|------------------------------------|
| Run        | H <sub>2</sub> O <sub>2</sub> (%V/V) | Fe <sup>2+</sup> (g/L) | COD Reduction (%) | Cake weight (kg/m <sup>3</sup> ww) |
| 1          | 12                                   | 4                      | 84.11             | 11.83                              |
| 2          | 8                                    | 2.75                   | 79.27             | 7.43                               |
| 3          | 4                                    | 1.5                    | 75.98             | 4.35                               |
| 4          | 4                                    | 4                      | 77.55             | 11.9                               |
| 5          | 13.66                                | 2.75                   | 83.98             | 6.85                               |
| 6          | 2.34                                 | 2.75                   | 67.18             | 8.35                               |
| 7          | 12                                   | 1.5                    | 83.62             | 4.03                               |
| 8          | 8                                    | 2.75                   | 80.94             | 7.1                                |
| 9          | 8                                    | 4.52                   | 82.56             | 11.6                               |
| 10         | 8                                    | 0.98                   | 80.63             | 2.53                               |
| 11         | 8                                    | 2.75                   | 81.6              | 6.9                                |

Regarding the generation of solid residues, *Table 12* demonstrates that the mass of the produced cake ranged from 2.53 to 11.9 kg/m<sup>3</sup>. Higher Fe<sup>2+</sup> concentrations unequivocally led to increased cake formation, as observed in Runs 1 and 4. Conversely, Run 10 achieved over 80% COD removal with the lowest cake generation (2.53 kg/m<sup>3</sup>), suggesting that even lower Fe<sup>2+</sup> dosages can still deliver efficient and sustainable results.

To statistically corroborate these trends, analysis of variance (ANOVA) was performed on the data. A p-value of less than 0.05 was designated as the criterion for identifying significant parameters. ANOVA indicated that H<sub>2</sub>O<sub>2</sub> concentration and its quadratic term significantly influenced COD reduction at a 95% confidence level, whereas Fe<sup>2+</sup> concentration was deemed insignificant. Based on the ANOVA, which reported a non-significant lack of fit, the following regression model was developed using the actual parameters:

$$\text{COD Reduction (\%)} = 65.276 + 3.539 H - 0.147 H^2$$

where H represents the H<sub>2</sub>O<sub>2</sub> concentration (% v/v) from a 30% w/v solution. The model incorporates both linear and quadratic terms for H<sub>2</sub>O<sub>2</sub> concentration, reflecting the non-linear behavior observed in the experimental data. This confirms that COD removal improves with increasing H<sub>2</sub>O<sub>2</sub> up to an optimal point, beyond which efficiency might decline due to curvature effects. The final model displayed an adjusted R<sup>2</sup> of 0.85, a predicted R<sup>2</sup> of 0.65, and an R<sup>2</sup> of 0.88, indicating strong agreement between predicted and experimental values (*Table 13*). The model exhibited high statistical reliability, with a low standard deviation of 1.88 and a non-significant lack of fit (p-value = 0.275), affirming its validity. The coefficient of variation (C.V.) was 2.36%, signifying high precision, while the adequate precision value surpassed the recommended threshold, reflecting a robust signal-to-noise ratio. Collectively, these findings confirm that the model for predicting COD reduction is both statistically robust and suitable for optimization.

Table 13: Analysis of variance for COD reduction results.

| Source                          | Sum of Squares | df | Mean Square          | F-value | p-value |                 |
|---------------------------------|----------------|----|----------------------|---------|---------|-----------------|
| <b>Model</b>                    | 214.32         | 2  | 107.16               | 30.24   | 0.0002  | significant     |
| A-H <sub>2</sub> O <sub>2</sub> | 180.11         | 1  | 180.11               | 50.83   | <0.0001 |                 |
| A <sup>2</sup>                  | 34.22          | 1  | 34.22                | 9.66    | 0.0145  |                 |
| <b>Residual</b>                 | 28.35          | 8  | 3.54                 |         |         |                 |
| Lack of Fit                     | 25.46          | 6  | 4.24                 | 2.94    | 0.2752  | not significant |
| Pure Error                      | 2.88           | 2  | 1.44                 |         |         |                 |
| <b>Cor Total</b>                | 242.67         | 10 |                      |         |         |                 |
| <b>Fit Statistics</b>           |                |    |                      |         |         |                 |
| <b>Std. Dev.</b>                | 1.88           |    | <b>R<sup>2</sup></b> |         | 0.8832  |                 |

|               |       |                                |         |
|---------------|-------|--------------------------------|---------|
| <b>Mean</b>   | 79.77 | <b>Adjusted R<sup>2</sup></b>  | 0.8540  |
| <b>C.V. %</b> | 2.36  | <b>Predicted R<sup>2</sup></b> | 0.6456  |
|               |       | <b>Adeq</b>                    | 14.0453 |
|               |       | <b>Precision</b>               |         |

To further assess the influence of process parameters on filter cake generation, ANOVA was also conducted for the cake weight response, with results presented in *Table 14*. The analysis revealed that Fe<sup>2+</sup> concentration was the sole statistically significant factor, possessing a p-value of < 0.0001, which affirmed its strong linear effect, as anticipated. Notably, H<sub>2</sub>O<sub>2</sub> concentration was not incorporated into the model as its effect on cake weight was less pronounced compared to Fe<sup>2+</sup> within the investigated range.

Drawing from the ANOVA, which indicated a non-significant lack of fit (*Table 14*), the subsequent regression model was formulated to predict filter cake generation in the process, based on the actual parameters:

$$\text{Cake weight (kg/m}^3 \text{ ww)} = -0.219 + 2.818F$$

Where F denotes the Fe<sup>2+</sup> concentration. The final model yielded an adjusted R<sup>2</sup> of 0.96, a predicted R<sup>2</sup> of 0.94, and an R<sup>2</sup> of 0.96, signifying excellent agreement between the predicted and observed values. The model exhibits a linear dependence on Fe<sup>2+</sup> concentration, supporting the earlier observation that cake formation increases proportionally with higher iron dosage. The standard deviation was low (0.67), and the lack of fit was not significant (p-value = 0.12), further corroborating the model's validity. The coefficient of variation was 8.84%, and the adequate precision was substantially above the recommended value of 4, implying a robust signal-to-noise ratio. These findings confirm that the model for cake weight prediction is statistically reliable and suitable for optimization.

Table 14: Analysis of variance for the weight of the produced solid filter cake after the Fenton process.

| <b>Source</b>      | <b>Sum of Squares</b> | <b>df</b> | <b>Mean Square</b> | <b>F-value</b> | <b>p-value</b> |                 |
|--------------------|-----------------------|-----------|--------------------|----------------|----------------|-----------------|
| <b>Model</b>       | 99.29                 | 1         | 99.29              | 223.87         | <0.0001        | significant     |
| B-Fe <sup>2+</sup> | 99.29                 | 1         | 99.29              | 223.87         | <0.0001        |                 |
| <b>Residual</b>    | 3.99                  | 9         | 0.4435             |                |                | not significant |
| Lack of Fit        | 3.85                  | 7         | 0.5502             | 7.84           | 0.1187         |                 |

|                       |        |                                |         |
|-----------------------|--------|--------------------------------|---------|
| Pure Error            | 0.1404 | 2                              | 0.0702  |
| <b>Cor Total</b>      | 103.28 | 10                             |         |
| <b>Fit Statistics</b> |        |                                |         |
| <b>Std. Dev.</b>      | 0.6660 | <b>R<sup>2</sup></b>           | 0.9614  |
| <b>Mean</b>           | 7.53   | <b>Adjusted R<sup>2</sup></b>  | 0.9571  |
| <b>C.V. %</b>         | 8.84   | <b>Predicted R<sup>2</sup></b> | 0.9387  |
|                       |        | <b>Adeq Precision</b>          | 35.0897 |

The statistical model developed from the experimental data was subsequently plotted across the investigated parameter range. *Figure 11(a)* displays the 3D response surface plot illustrating COD reduction as a function of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> concentrations. It vividly demonstrates that increasing H<sub>2</sub>O<sub>2</sub> enhances COD removal efficiency, particularly at moderate to high concentrations, whereas Fe<sup>2+</sup> exhibited a less pronounced effect. *Figure 11(b)* presents the normal probability plot of residuals. The points closely follow the straight line, signifying that the residuals are normally distributed and that the model satisfies the assumption of normality. The correlation between predicted and actual COD reduction values is shown in *Figure 11(c)*. Most points cluster near the diagonal line, confirming strong agreement between experimental and predicted responses, which further substantiates the accuracy of the developed regression model. *Figure 11(d)* plots the externally studentized residuals against the run number. All residuals, with one exception, fall within the acceptable range ( $\pm 4.11$ ), suggesting no significant deviations. The residuals appear randomly scattered, indicating a good model fit and the absence of systematic errors. These results collectively confirm that the model is statistically valid and suitable for predicting COD removal under varying concentrations of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> within the tested range.

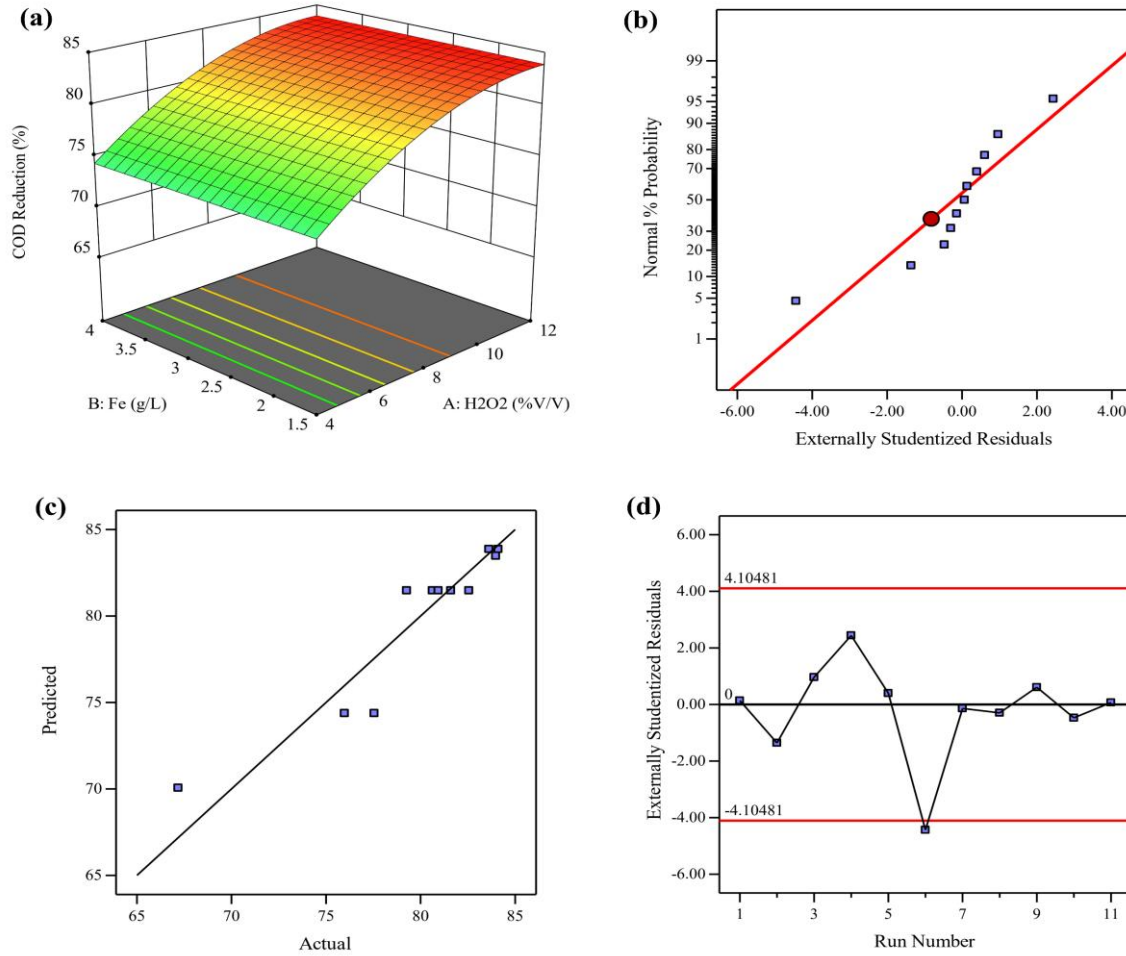


Figure 11: (a) 3D surface of the COD reduction versus H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> concentration, (b) Normal plot of residuals, (c) Predicted versus actual values, (d) Residual values versus Run.

The predictive model for cake weight also underwent evaluation. *Figure 12(a)* presents the 3D surface plot depicting the effect of H<sub>2</sub>O<sub>2</sub> and Fe<sup>2+</sup> concentrations on cake formation. *Figure 12(a)* clearly indicates a strong linear correlation between Fe<sup>2+</sup> concentration and cake weight. As Fe<sup>2+</sup> increases, the cake weight rises significantly, while H<sub>2</sub>O<sub>2</sub> demonstrates almost no effect within the tested range. The normal probability plot of residuals (*Figure 12(b)*) illustrates that the points align closely with the reference line, affirming that the residuals are normally distributed and that the model satisfies the assumption of normality. *Figure 12(c)* compares the predicted and actual values for cake weight. The close alignment of data points along the diagonal line confirms the model's accuracy and minimal deviation from experimental results. The distribution of residuals across experimental runs is depicted in *Figure 12(d)*. All values remain within the control limits ( $\pm 3.9$ ), and no discernible patterns are observed, indicating that the residuals are random and the model is free from systematic bias. Collectively, these

diagnostic plots support the reliability of the model in predicting cake generation based on  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  levels, with a high adjusted  $R^2$  value of 0.96 and a predicted  $R^2$  of 0.94. This suggests that the model can be confidently employed for process optimization.

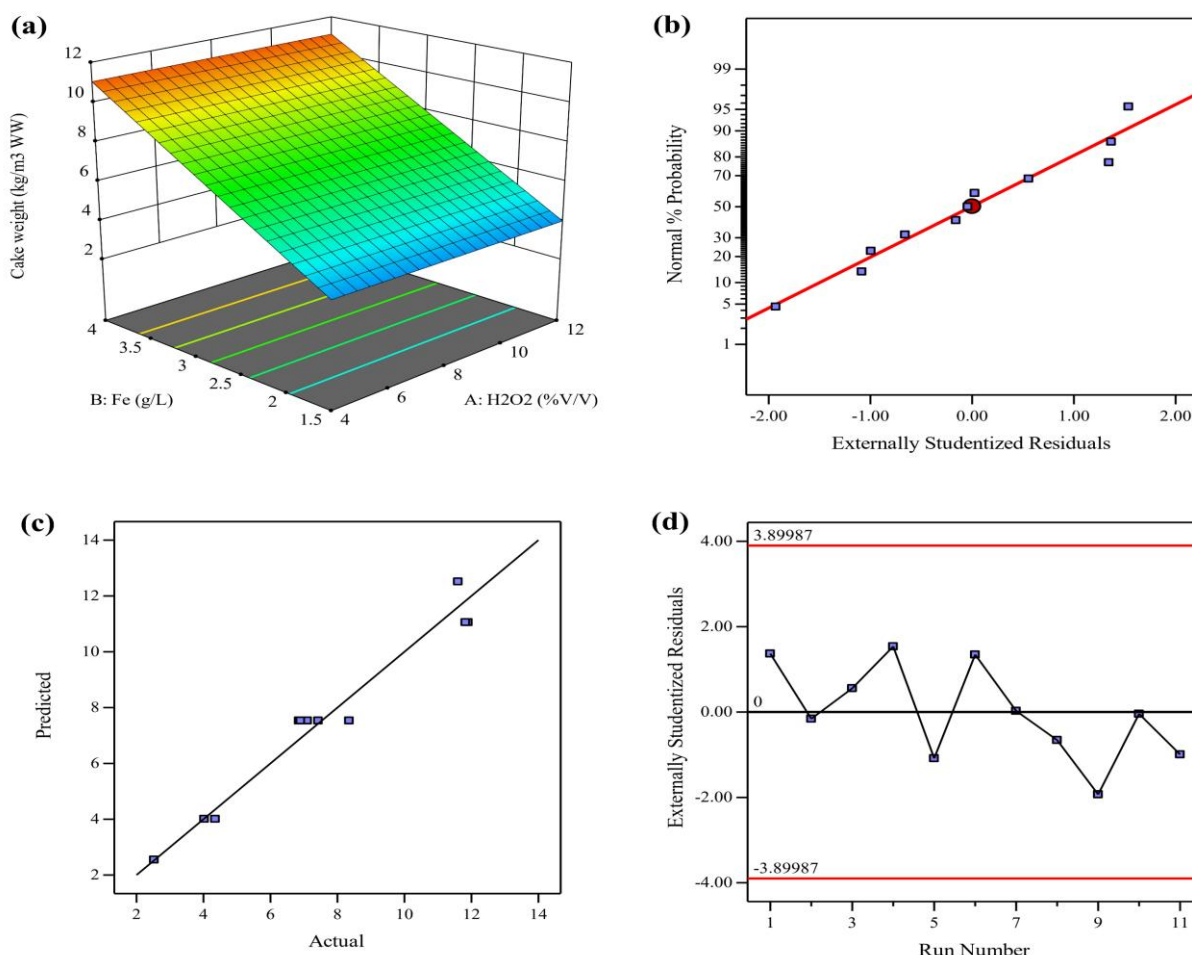


Figure 12: (a) 3D surface of the cake weight versus  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  concentration, (b) Normal plot of residuals, (c) Predicted versus actual values, (d) Residual values versus Run.

#### 4.3.3: Optimization of Treatment Parameters

To identify the most advantageous operating conditions, a multi-response optimization was executed, aiming for the simultaneous minimization of COD, cake weight, and  $\text{H}_2\text{O}_2$  consumption, leveraging the optimization tool within Design-Expert 13 software. The overall desirability function served as the optimization criterion. *Figure 13* presents the 3D surface plot illustrating composite desirability as a function of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$  concentrations. Desirability values range from 0 (least desirable) to 1 (most desirable). The plot reveals that higher desirability values (approximately 0.75) were achieved at moderate  $\text{H}_2\text{O}_2$  levels (around 7–8% v/v) in conjunction with low  $\text{Fe}^{2+}$  dosages (1.5 g/L). This region signifies a well-balanced

outcome where COD removal remains high, while both cake generation and reagent consumption are minimized. These results suggest that optimizing reagent input not only enhances treatment efficiency but also supports operational sustainability by reducing chemical load and solid waste generation.

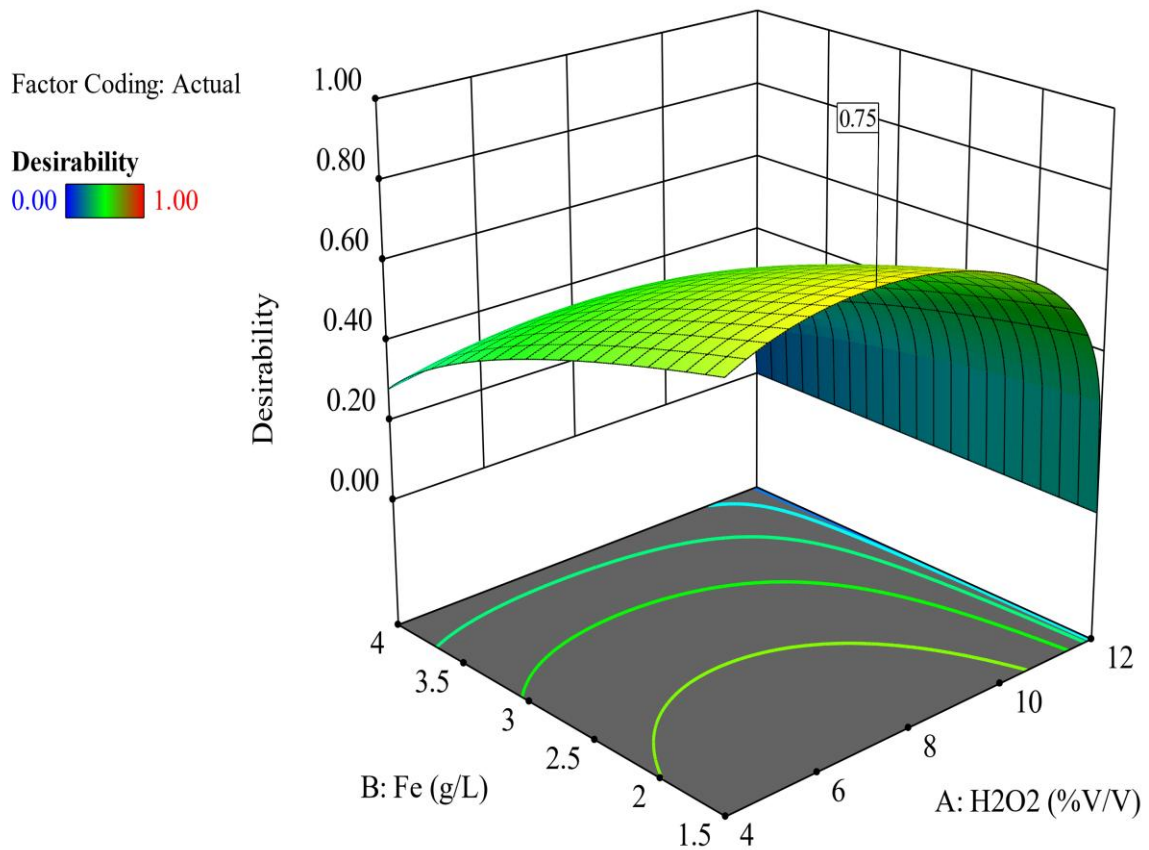


Figure 13: 3D surface of desirability for optimizing parameters to minimize final COD, cake weight, and H<sub>2</sub>O<sub>2</sub> consumption.

To further refine the multi-response optimization, eight plausible solutions were generated and evaluated based on their overall desirability scores. These solutions aim to concurrently minimize COD, cake weight, and H<sub>2</sub>O<sub>2</sub> consumption. *Table 15* summarizes the optimal parameter combinations. Among these, Solution 7, with 7.91% H<sub>2</sub>O<sub>2</sub> and 1.5 g/L Fe<sup>2+</sup>, yielded 81.37% COD removal and 4.01 kg/m<sup>3</sup> cake, achieving a desirability score of 0.749. While all solutions offered comparable cake outputs, Solution 7 provided the highest COD removal, establishing it as the most balanced and efficient option.

Table 15: The eight found solutions after optimization of the parameters to minimize final COD, cake weight, and H<sub>2</sub>O<sub>2</sub> consumption.

| Solution | H <sub>2</sub> O <sub>2</sub> (%V/V) | Fe <sup>2+</sup> (g/L) | COD<br>Reduction (%) | Cake weight<br>(kg/m <sup>3</sup> WW) | Desirability |
|----------|--------------------------------------|------------------------|----------------------|---------------------------------------|--------------|
| 1        | 6.90                                 | 1.5                    | 80.00                | 4.01                                  | 0.758        |
| 2        | 6.96                                 | 1.5                    | 80.078               | 4.01                                  | 0.758        |
| 3        | 6.84                                 | 1.5                    | 79.90                | 4.01                                  | 0.758        |
| 4        | 6.79                                 | 1.5                    | 79.82                | 4.01                                  | 0.758        |
| 5        | 7.02                                 | 1.5                    | 80.17                | 4.01                                  | 0.758        |
| 6        | 7.05                                 | 1.5                    | 80.22                | 4.01                                  | 0.758        |
| 7        | 7.91                                 | 1.5                    | 81.37                | 4.01                                  | 0.749        |
| 8        | 5.87                                 | 1.5                    | 78.28                | 4.01                                  | 0.748        |

This optimization was further visually represented in *Figure 14*, which illustrates the individual and overall desirability scores of the selected parameters in Solution 7. Both COD reduction (0.84) and cake weight (0.84) demonstrated high desirability, whereas H<sub>2</sub>O<sub>2</sub> usage (0.51) was moderately optimized. The combined desirability (0.75) validates the effectiveness of the chosen conditions for practical implementation. These findings underscore the feasibility of applying Fenton-based treatment to wastewater originating from graphite recovery processes

*Figure 15* depicts the complete wastewater treatment process, commencing with the untreated wastewater (dark orange, left), followed by the initial precipitation of Ba, Pb, and Sr, and concluding with the Fenton treatment. A notable color transformation occurs after the precipitation step (middle image), and the outcome is a clear, transparent solution obtained after Fenton treatment and subsequent filtration. ICP analysis confirmed the exceptional quality of the treated water, which primarily consisted of sodium sulfate (approximately 13.8 g/L sodium), with only trace levels of other impurities and a COD below 500 mg/L (*Figure 15*). These results highlight the process's effectiveness in removing all metallic contaminants and substantially reducing COD. The final solution is highly suitable for further treatment via evaporation–crystallization, facilitating water recovery and the production of nearly pure sodium sulfate as a by-product. The treated water underwent this process, resulting in the recovery of sodium sulfate dihydrate with high purity. The purity of the recovered salt was verified through ICP analysis and mass balance calculations. As presented in *Table 16*, the weight percentages of all impurities in the final product are minimal, with potassium being the predominant impurity at approximately 0.22%, culminating in a final purity of 99.67% for the recovered sodium sulfate dihydrate. Overall, the optimized process represents a promising

approach for sustainable water reuse and reduced environmental impact within graphite recycling operations at alkaline battery recycling facilities.

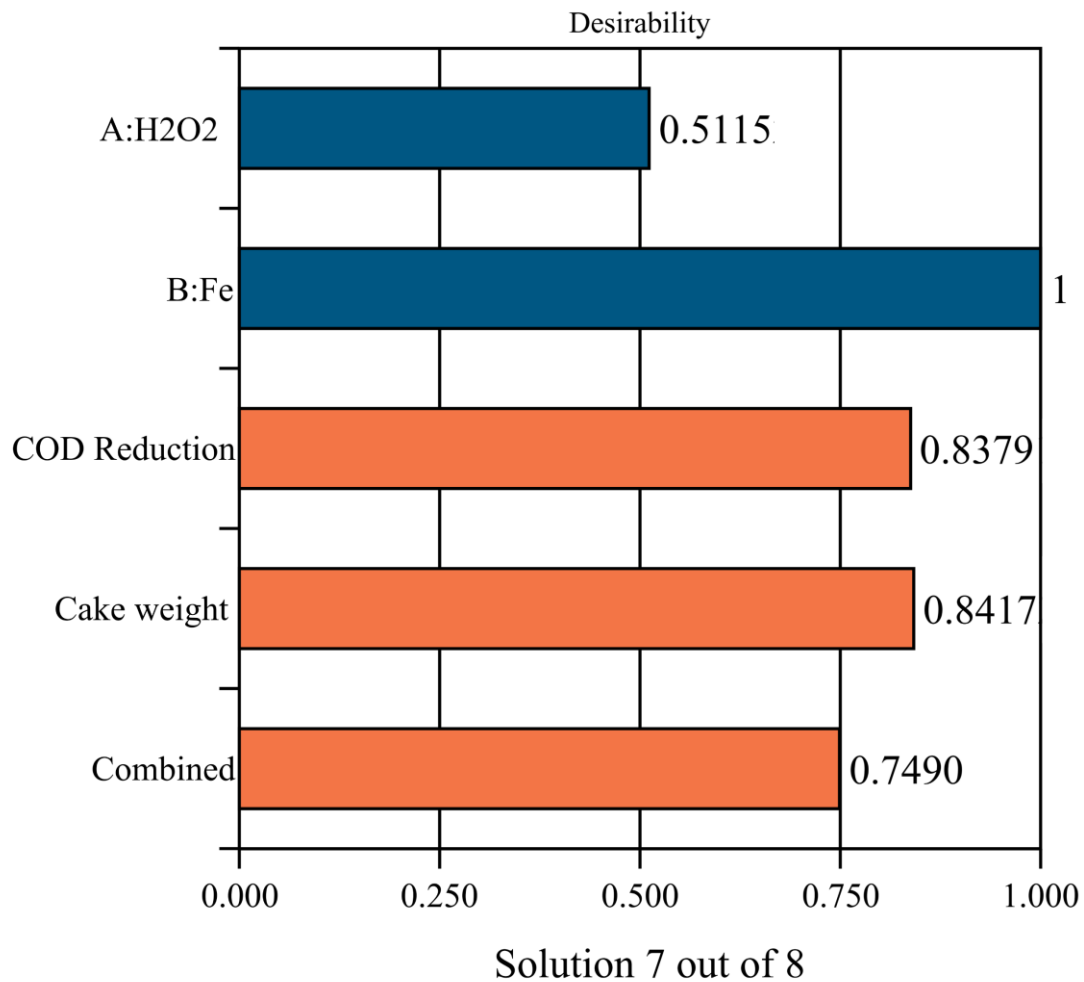


Figure 14: Bar graph of the optimized parameters to minimize final COD, cake weight, and H2O2 consumption, showing the desirability of each parameter in the selected conditions in Table 8 (Solution 7).

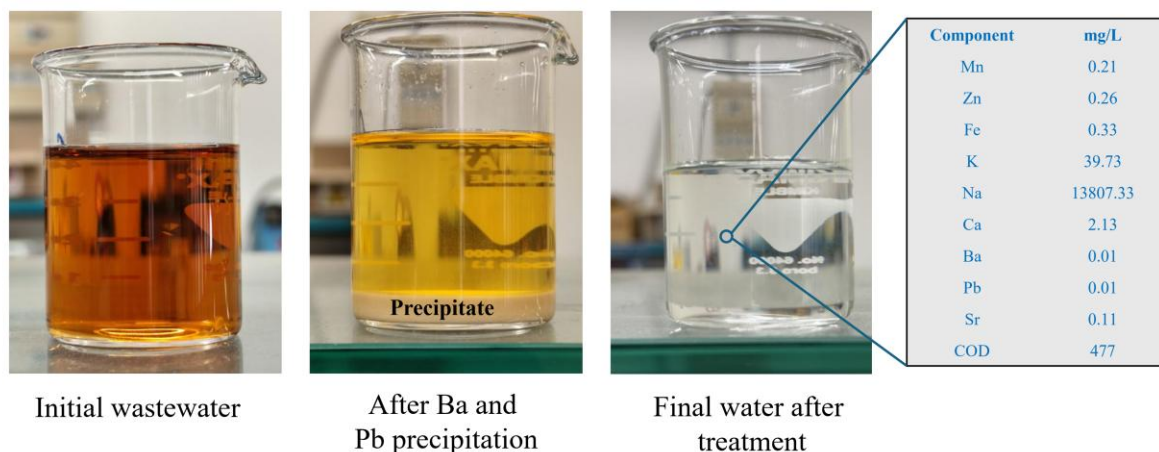


Figure 15: The changes in wastewater during the treatment.

Table 16: Weight percentage of the impurity elements and the purity of the recovered sodium sulfate.

| Elements | Mn     | Zn     | Fe     | K      | Ca     | Ba     | Pb     | Sr     | Na <sub>2</sub> SO <sub>4</sub> ·2H <sub>2</sub> O |
|----------|--------|--------|--------|--------|--------|--------|--------|--------|----------------------------------------------------|
| (wt.%)   | 0.0015 | 0.0019 | 0.0024 | 0.2220 | 0.0154 | 0.0002 | 0.0007 | 0.0008 | 99.6706                                            |

#### 4.3.4: Estimation of Mass Balance and Economic Evaluation of Treatment Process

Based on the optimized experimental conditions (Solution 7), mass balance calculations were performed. It was determined that treating 1 m<sup>3</sup> of wastewater necessitated 87.90 kg of H<sub>2</sub>O<sub>2</sub> (30% w/v), 7.50 kg of FeSO<sub>4</sub>·7H<sub>2</sub>O, and 2.50 kg of NaOH. This configuration achieved an average COD removal of 80.72%, leading to the generation of 4.72 kg of dry cake for every m<sup>3</sup> of treated wastewater. These values are consistent with the cake formation trends observed in previous sections and demonstrate the process's efficiency under controlled reagent inputs.

A preliminary cost evaluation was also undertaken (for Solution 7) based on reagent consumption. The costs of H<sub>2</sub>O<sub>2</sub>, FeSO<sub>4</sub>·7H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>, and NaOH were calculated per m<sup>3</sup> of treated wastewater, using approximate values derived from current market prices. The total treatment cost for one cubic meter of wastewater generated during the recovery of graphite from spent alkaline battery recycling was calculated to be €36.40. This condition maintained both high removal efficiency and reasonable chemical input. For comparative purposes, traditional disposal methods for similar hydrometallurgical wastewater can incur costs up to 150 €/m<sup>3</sup>, positioning the Fenton-based treatment as a significantly more economical and environmentally responsible alternative. Furthermore, the potential for recovering or reusing

the generated filter cake, predominantly composed of iron hydroxide, presents promising opportunities for circularity. Previous studies have indicated the potential for reintroducing iron-rich cake into oxidation reactions or recovering valuable metals through thermal treatment, potentially offsetting disposal costs and enhancing the overall system's sustainability [216,217].

#### 4.3.5: Process scheme

A process flow diagram, depicted in *Figure 16*, outlines the efficient treatment of 1 m<sup>3</sup> of wastewater produced during the hydrometallurgical recovery of graphite from spent alkaline batteries. The treatment process commences with the precipitation of Ba, Pb, and Sr by adjusting the pH to 1. The filtered wastewater from this initial step is then transferred to a second reactor for treatment via the Fenton process. This process is initiated by the addition of FeSO<sub>4</sub>·7H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>, which instigates the Fenton reaction to oxidize and degrade organic pollutants. Following the oxidation stage, NaOH is introduced to neutralize the acidic medium and facilitate the precipitation of Fe and other metal ions as hydroxide sludge. The mixture is then routed to a filtration unit for solid-liquid separation. The clarified effluent is directed to an evaporator-crystallizer, where water is recovered for reuse and sodium sulfate is crystallized as a by-product. Finally, the sludge generated during the filtration stage, before evaporation, necessitates appropriate handling and disposal.

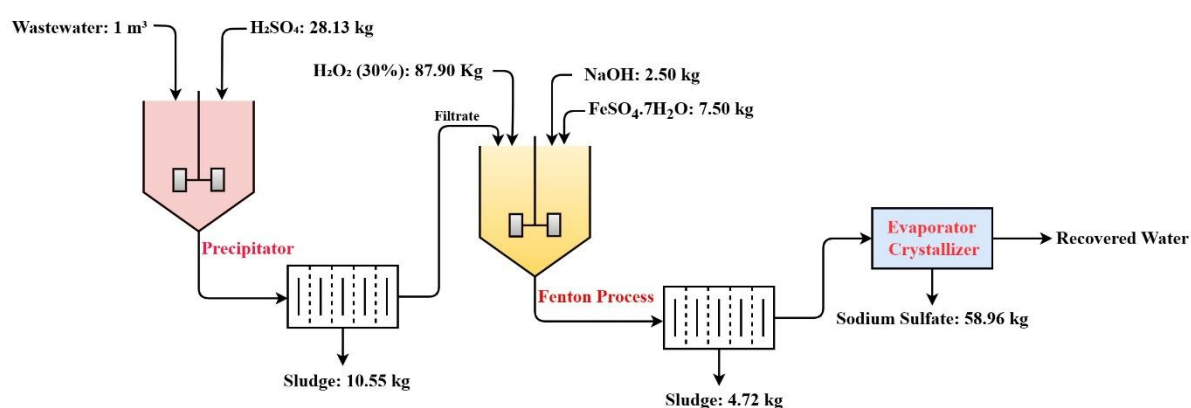


Figure 16: Flow diagram for efficient wastewater treatment investigated in this study.

#### 4.4: Conclusion

This study successfully demonstrated an effective methodology for treating wastewater generated during the hydrometallurgical recovery of graphite from alkaline spent batteries

using the Fenton process. Initial acidic precipitation effectively removed barium (Ba), lead (Pb), and strontium (Sr), ensuring compliance with discharge regulations. Subsequent Fenton treatment significantly reduced chemical oxygen demand (COD), achieving up to 84.11% removal. Analysis confirmed that  $\text{H}_2\text{O}_2$  concentration was the main factor influencing COD reduction, while  $\text{Fe}^{2+}$  had a minimal effect. Statistical models for COD reduction and cake weight demonstrated strong predictive performance, with adjusted  $R^2$  values of 0.85 and 0.96, respectively. Desirability analysis optimized conditions to 7.91% v/v  $\text{H}_2\text{O}_2$  and 1.5 g/L  $\text{Fe}^{2+}$ , achieving high COD removal, low cake generation, and moderate reagent consumption. These findings highlight the Fenton process's potential for integration into graphite recovery systems, fostering water reuse, reduced chemical usage, and minimized waste, thereby contributing to sustainable and environmentally responsible battery recycling.

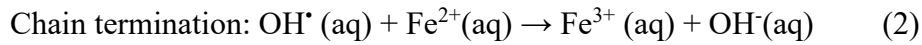
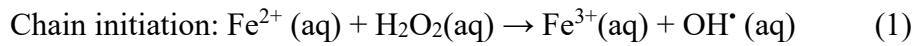
## Chapter: 5. Wastewater Treatment of In-Mould Structured Electronics from the Automotive Sector

### 5.1: Introduction

Water stands as a crucial natural resource that is indispensable for industrial production and is significantly within the realm of hydrometallurgical processes. These hydrometallurgical operations exhibit a substantial reliance on water, with their demand consistently increasing annually [200]. However, the extensive utilization of leaching solutions in specific hydrometallurgical activities leads to the generation of considerable volumes of wastewater [218], which is characterized by hazardous constituents such as heavy metals [200,219] and acidic pH levels [220]. These components present significant environmental risks, necessitating rigorous treatment protocols before their safe discharge. This situation is further intensified by rapid industrial growth and heightened productivity across various sectors, contributing substantially to the pollution of groundwater sources and aggravating the global issue of freshwater scarcity. Addressing these pressing concerns demands a unified approach and concerted effort towards sustainable wastewater management, recognizing its potential as a renewable resource that can be recovered and reused to alleviate water stress [199]. Consequently, extensive research endeavors have been directed towards exploring and developing diverse physicochemical methods, encompassing sorption, ion exchange, coagulation, and flotation, for the treatment of hydrometallurgical wastewater and the subsequent reuse of the treated water within the same process [199–201]. Given the escalating concerns regarding water scarcity and the global water goals established for 2030 [202], ensuring the sustainability of wastewater treatment methods becomes necessary. *Allayorov et al.* [200] have previously attempted to purify hydrometallurgical effluents through coagulation and precipitation, with a focus on reducing total hardness, optimizing reagents such as sodium carbonate, and utilizing aluminium and iron sulphate sorption materials as effective coagulants for wastewater impurities. Furthermore, *Sudibyo et al.* [220] explored electrocoagulation for treating laterite hydrometallurgy wastewater, specifically targeting nickel and metal reduction, achieving a reduction in turbidity and removing metal ions by deposition on the cathode using a tubular aluminium electrode.

Within this context, the advanced oxidation Fenton process is emerging as a promising technique for wastewater treatment. By leveraging the catalytic properties of iron salts in the presence of hydrogen peroxide, the Fenton process facilitates the efficient degradation of organic pollutants, thereby mitigating the environmental footprint of wastewater generated by

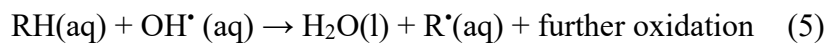
hydrometallurgical processes. The Fenton reaction enables the decomposition of hydrogen peroxide and the formation of highly reactive hydroxyl radicals ( $\text{OH}^\bullet$ ), which degrade organic pollutants into harmless compounds like  $\text{CO}_2$ , water, and inorganic salts. The mechanism of the Fenton process is shown in *Figure 17* [205]. The key reagents in Fenton's reaction are hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ferrous ions ( $\text{Fe}^{2+}$ ) [208], which initiates a chain reaction that proceeds as follows:



As illustrated in these equations, ferrous iron ( $\text{Fe}^{2+}$ ) initiates the reaction and catalyses the decomposition of  $\text{H}_2\text{O}_2$  into hydroxyl radicals [212,221–225]. However, the newly formed ferric ions ( $\text{Fe}^{3+}$ ) can also decompose hydrogen peroxide into water and oxygen, concurrently regenerating ferrous ions and radicals through Fenton-like reactions:



The organics (RH) undergo oxidation by hydroxyl radicals through proton abstraction, resulting in the production of organic radicals ( $\text{R}^\bullet$ ). These final products are highly reactive and can undergo further oxidation:



The primary operating conditions affecting the performance of the Fenton processes are pH, oxidant and catalyst concentrations, and temperature [206,211]. In terms of pH, Fenton processes exhibit maximum catalytic activity at a pH of approximately 2.5–3.5 [209,210], and ambient conditions can safely be used with good efficiency [212].

This research aims to explore the treatment of wastewater produced from a hydrometallurgical process for the recovery of silver from IMSEs to significantly reduce water consumption, since the treated water can be reused in the next cycles of the process. There are few works in the literature related to the development of hydrometallurgical processes for the recovery of metals that also address the treatment of generated wastewater; this is an area lacking significant research, thus presenting a novel avenue for investigation. Specifically, this study is among the first to successfully apply and optimize the Fenton process directly to highly acidic IMSE silver recovery effluent (pH 1.39), leveraging the inherent high iron content (8.69 g/L) as the catalyst

and achieving simultaneous high organic (93.6%) and metal contaminant (over 99% Fe/Cu) removal for minimized cost and near-total water recirculation. Many studies do not even characterize the wastewater generated by hydrometallurgical processes, often overlooking the associated environmental impacts and disposal costs. This oversight becomes even more significant when scaling the process to an industrial level. Proper wastewater treatment and reuse of the treated water are crucial for reducing freshwater consumption and ensuring both the sustainability and economic viability of the process. This work addresses this gap, offering a pathway to more sustainable industrial practices. Advanced oxidation processes are affected by many variables in terms of pollutant removal. Response surface methodology, particularly the central composite design, can be used to evaluate the influence of these variables and optimize the process. This study initially employed a full factorial design to determine the optimal dosage of Fenton reagents for COD abatement and then incorporated star points based on Fisher's test to create a central composite design for better model interpretation. The qualitative characteristics of the treated water confirmed its potential for reuse, significantly reducing the water footprint according to a minimal liquid discharge (MLD) approach. This study provides insights into wastewater treatment efficacy and its role in achieving sustainable water management goals for 2030 [202].

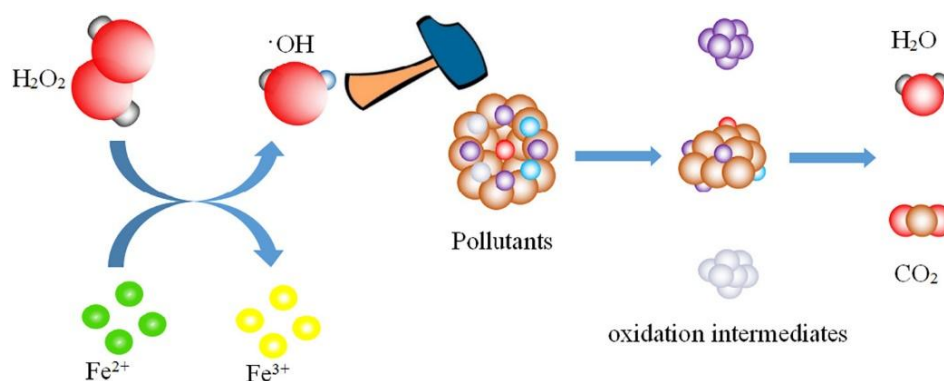


Figure 17: Reaction mechanism for the Fenton process

## 5.2: Materials and methods

The study focused on treating wastewater generated from a hydrometallurgical process designed for silver extraction from in-mold structural electronics (IMSEs) used in the automotive sector, which was conducted at a pilot scale as part of the EU Treasure project (Horizon 2020). The experiments utilized this specific wastewater, which was characterized as acidic with a pH of 1.39 and contained significant levels of pollutants: a Chemical Oxygen Demand (COD) of 14.48 g/L, a high concentration of iron (Fe) at 8.69 g/L, and copper (Cu) at

117 mg/L. All the chemical reagents used throughout the experimental work were of analytical grade. These included hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) with a concentration of 30 % (w/v), which served as the primary oxidant in the Fenton process. Ferrous sulfate (II) ( $\text{FeSO}_4 \times 7\text{H}_2\text{O}$ ) in powdered form was used as the catalyst to initiate the Fenton reaction. Additionally, calcium hydroxide was employed, prepared as a 10 % (w/v) lime solution. This lime solution played a crucial role in several stages: adjusting the initial pH of the wastewater for the Fenton reaction, precipitating iron and copper after the Fenton process as hydroxides, and ensuring the treated water reached a pH level within the neutral range suitable for potential reuse or discharge. Several analytical methods were employed to characterize the wastewater and monitor the effectiveness of the treatment process. The initial and final concentrations of COD in the wastewater were determined using the LCK 014 Hach cuvette test, which has a measurement range for COD between 1 and 10 g/L  $\text{O}_2$ . For the analysis of iron (Fe) and copper (Cu) concentrations, both before and after the Fenton treatment in each experiment, inductively coupled plasma with optical emission spectroscopy (ICP-OES) (Agilent technologies, 5100) was utilized. The initial pH of the wastewater was measured using a pH meter (Hanna). The Fenton experiments were conducted in conical flasks with a capacity of 100 mL, and for each experiment, a volume of 40 mL of wastewater was used. Initially, the pH of the wastewater was adjusted to approximately  $3.5 \pm 0.1$  using the prepared 10 % (w/v) lime solution. Following pH adjustment, the required quantity of powdered  $\text{FeSO}_4 \times 7\text{H}_2\text{O}$  was introduced into the reaction mixture and agitated for 5 minutes to ensure proper dissolution and distribution of the ferrous ions. The Fenton reaction was then initiated by adding the necessary amount of hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30 % w/v). The resulting reaction solutions were placed on a shaker (SKI 4, shaking incubator) at a speed of 120 rpm for a duration of 90 minutes at room temperature and atmospheric pressure to facilitate mixing and the reaction process. After the completion of the Fenton reaction, a post-reaction treatment step was implemented. The pH of the solutions was readjusted to  $8.5 \pm 0.1$  by adding the 10 % (w/v) lime solution. This alkaline pH aimed to precipitate the dissolved iron and copper ions in the form of hydroxides, facilitating their removal from the treated water. Following this pH adjustment and precipitation step, the solutions were allowed to stand for half an hour to allow sufficient time for the metal hydroxides to settle. Finally, the treated wastewater was filtered using a vacuum filtration system (STEROGLASS, Model ST510) equipped with a nitrate cellulose filter with a pore size of  $0.45 \mu\text{m}$  to remove the precipitated metal hydroxides and any other particulate matter. To gain qualitative insights into the changes in the organic composition of the wastewater due to the Fenton treatment, UV-VIS spectral analyses were conducted. These

analyses were performed using a UV-VIS spectrometer (Agilent Technologies, Cary 60) to compare the spectra of the wastewater before and after the Fenton treatment, particularly to assess the degradation of organic pollutants like thiourea. Given the high content of organic substances in the wastewater, the study adopted a factorial design approach to systematically investigate the Fenton process, with COD reduction selected as the primary target output. The experimental tests were initially designed according to a  $2^2$ -full factorial plan with three centre points. This initial plan was intended to identify the main effects of the two key variables (factors) under investigation and their potential interactions on the COD removal efficiency. A  $2^2$ -full factorial design inherently includes all possible combinations of the two factors, each tested at two different levels, resulting in four distinct experimental runs. To assess whether a more complex model could better represent the experimental data, a comparison was made between the critical Fisher (F) value and the experimentally obtained F-value. If the experimental F-value was found to be greater than the critical F-value, it indicated that incorporating quadratic terms into the model might significantly improve its fit. Consequently, star points were added to the experimental design to enhance its efficiency and robustness. The inclusion of these additional experimental runs at axial distances from the center points transformed the initial full factorial plan into a Central Composite Design (CCD). The CCD is specifically chosen as it allows for the estimation of quadratic effects of the factors, providing a more comprehensive understanding of their influence on the response variable. The investigated range for the factors (concentrations of hydrogen peroxide and ferrous sulfate) given in *Table 17* was carefully selected to maintain the  $\text{H}_2\text{O}_2/\text{Fe}^{2+}$  ratio within a specific range of 25:1 to 5:1 (w/w), based on prior research indicating this range to be effective for Fenton processes [24].

Table 17: Factors and levels investigated with the CCD.

| Factors                                   | Coded factors |    |       |        |
|-------------------------------------------|---------------|----|-------|--------|
|                                           | -1.414        | -1 | +1    | +1.414 |
| <b>H<sub>2</sub>O<sub>2</sub> (% v/v)</b> | 2.93          | 5  | 15.00 | 17.07  |
| <b>Fe<sup>2+</sup> (g/L)</b>              | 1.14          | 3  | 12.00 | 13.86  |

### 5.2.1: Theory

The efficiency of the Fenton process is significantly dependent on several operational parameters, including pH, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) dosage, ferrous iron ( $\text{Fe(II)}$ )

concentration, and temperature [180,181], with the simultaneous consideration of these factors requiring extensive experimentation. Specifically, the oxidation potential of hydroxyl radicals ( $\cdot\text{OH}$ ), the primary oxidizing species, is inversely related to pH, leading to enhanced oxidation at lower pH values [183]. However, the Fenton reagent's activity diminishes with increasing pH due to the reduction of active  $\text{Fe}^{2+}$  and the formation of inactive iron compounds, while hydrogen peroxide undergoes auto-decomposition at high pH [184]. Furthermore, at very low pH levels, the formation of specific iron complexes can impede the reaction between  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  [181,182], thereby decreasing the overall efficiency across extreme pH values. The literature suggests that the optimal pH range for maximizing catalytic activity in Fenton processes lies between 2.5 and 3.5, and that ambient temperature conditions can be effectively utilized.

### 5.3: Results and Discussion

#### 5.3.1: Composition of Wastewater

The composition of the wastewater generated from the hydrometallurgical process for recycling silver from IMSEs is presented in *Table 18*. This wastewater is acidic, with a pH of 1.39. It contains a Chemical Oxygen Demand (COD) of 14.48 g/L, an iron (Fe) concentration of 8.69 g/L, and a copper (Cu) concentration of 117.4 mg/L.

Table 18: Composition of wastewater generated by the hydrometallurgical process.

|                  |       |
|------------------|-------|
| <b>pH</b>        | 1.39  |
| <b>COD (g/L)</b> | 14.48 |
| <b>Fe (g/L)</b>  | 8.69  |
| <b>Cu (mg/L)</b> | 117.4 |

The high levels of COD and Fe in the wastewater are attributed to the chemicals employed in the hydrometallurgical process, specifically thiourea and ferric sulfate in an acidic medium.

#### 5.3.2: Factorial experimentation and statistical analysis

Preliminary experiments on the Fenton process, considering initial pH correction, indicated that adjusting the pH before the process might be unnecessary because the initial pH of the wastewater (1.39) was already suitable for initiating Fenton reactions. A lower pH enhances the oxidation potential of hydroxyl radicals ( $\cdot\text{OH}$ ), improving oxidation reactions. Conversely, at higher pH levels, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) decomposes more rapidly, affecting its stability and effectiveness in oxidation. Consequently, the Fenton process was investigated at a constant pH of 1.39 and room temperature, focusing only on the effects of two main factors: Fe(II) and

H<sub>2</sub>O<sub>2</sub>, using a 2<sup>2</sup>-full factorial plan with three center points. The experimental conditions and the results of the full factorial plan are detailed in *Table 19*.

Table 19: Experimental conditions and results of the 2<sup>2</sup>-full factorial plan.

|            | <b>A:</b> |          | <b>B:</b>                                   | <b>COD</b>                              | <b>Fe</b>      | <b>Cu</b>      |
|------------|-----------|----------|---------------------------------------------|-----------------------------------------|----------------|----------------|
| <b>Run</b> | <b>A</b>  | <b>B</b> | <b>H<sub>2</sub>O<sub>2</sub> (30%) (%)</b> | <b>FeSO<sub>4</sub>×7H<sub>2</sub>O</b> | <b>removal</b> | <b>removal</b> |
|            |           |          | <b>v/v)</b>                                 | <b>(g/L)</b>                            | <b>(%)</b>     | <b>(%)</b>     |
| <b>1</b>   | -1        | -1       | 5.0                                         | 3.0                                     | 66.7           | 98.6           |
| <b>2</b>   | 1         | -1       | 15.0                                        | 3.0                                     | 92.4           | 99.9           |
| <b>3</b>   | -1        | 1        | 5.0                                         | 12.0                                    | 63.8           | 97.0           |
| <b>4</b>   | 1         | 1        | 15.0                                        | 12.0                                    | 89.9           | 98.9           |
| <b>I</b>   | 0         | 0        | 10.0                                        | 7.5                                     | 84.4           | 98.8           |
| <b>II</b>  | 0         | 0        | 10.0                                        | 7.5                                     | 86.2           | 96.5           |
| <b>III</b> | 0         | 0        | 10.0                                        | 7.5                                     | 83.7           | 96.5           |

Analysis of variance (ANOVA) using Yates' algorithm revealed that factor A (hydrogen peroxide) was the only significant factor above the 95 % confidence level. It was also noted that the wastewater already contained a high concentration of iron (8.69 g/L), which might explain why factor B (Fe<sup>2+</sup> addition) was not significant for COD removal. Other studies have also found that Fe<sup>2+</sup> concentration is not always a significant factor [208,215].

The model equation was determined, incorporating the statistically significant factor (hydrogen peroxide). The ANOVA results and the derived equation are presented in *Table 20*. The same dataset was also analyzed using Design Expert-13 software, which confirmed the obtained results and the consistency of the derived equation

Table 20: Yate's algorithm for the 2<sup>2</sup>-factorial plan, confidence level at 95%.

| <b>Terms</b> | <b>Effect</b> | <b>SS</b> | <b>F-value</b> | <b>P-value</b> | <b>1-p</b> | <b>Significance, (%)</b> |
|--------------|---------------|-----------|----------------|----------------|------------|--------------------------|
| intercept    | 78.20         | -         | -              | -              | -          | -                        |
| a            | 25.90         | 670.88    | 413.02         | 0.03           | 0.97       | <b>96.87</b>             |
| b            | -2.77         | 7.67      | 4.72           | 0.27           | 0.73       | 72.54                    |
| ab           | 0.19          | 0.04      | 0.02           | 0.90           | 0.10       | 9.64                     |

Based on the results of the factorial plan, the following relation was obtained (Equation 6):

$$COD_{removal}(\%) = 78.20 + 12.95 \times X_1 \quad (6)$$

where  $X_1$  is the coded factor for hydrogen peroxide (% v/v). For optimization purposes, based on the comparison of experimental and critical Fisher values ( $F_{\text{experimental}} > F_{\text{critical}}$ ), star points were added to improve the goodness of the determined model for the experimental data. The results obtained after including the star points are shown in *Table 21*.

Table 21: Star points and their results in terms of COD, Fe, and Cu removal.

| Run | A      | B      | A:<br>H <sub>2</sub> O <sub>2</sub> (30%) (%)<br>v/v) | B: FeSO <sub>4</sub> ×7H <sub>2</sub> O<br>(g/L) | COD<br>removal<br>(%) | Fe<br>removal<br>(%) | Cu<br>removal<br>(%) |
|-----|--------|--------|-------------------------------------------------------|--------------------------------------------------|-----------------------|----------------------|----------------------|
| 1   | -1.414 | 0      | 2.93                                                  | 7.50                                             | 59.9                  | 100.0                | 99.8                 |
| 2   | 1.414  | 0      | 17.07                                                 | 7.50                                             | 92.3                  | 100.0                | 97.9                 |
| 3   | 0      | -1.414 | 10.00                                                 | 1.14                                             | 94.3                  | 100.0                | 91.4                 |
| 4   | 0      | 1.414  | 10.00                                                 | 13.86                                            | 87.0                  | 99.9                 | 99.8                 |

Analyzing the experimental results for COD removal, run 3 in *Table 21*, with a lower hydrogen peroxide concentration, exhibited higher efficiency than run 2. This suggests that an excess of iron and hydrogen peroxide can inhibit mineralization, leading to incomplete oxidation and reduced mineralization efficiency, as indicated in the literature [226].

ANOVA was conducted using Yates' algorithm to assess the impact of the two investigated factors and their interaction on COD removal at a 95 % confidence level using the F-test. This determined the significance of the effects relative to the experimental error, as shown in *Table 22*.

Table 22: Yate's algorithm for the CCD, confidence level at 95%.

| Terms                         | Coefficients | Std. Error | t-value | P-value  | 1-p    | Significance, % |
|-------------------------------|--------------|------------|---------|----------|--------|-----------------|
| Intercept                     | 84.74        | -          | -       | -        | -      | -               |
| x <sub>1</sub>                | 12.21        | 1.26       | 9.66    | 2.01E-04 | 0.9997 | <b>99.97</b>    |
| x <sub>2</sub>                | -2.00        | 1.26       | -1.58   | 1.75E-01 | 0.8253 | 82.53           |
| x <sub>1</sub> x <sub>2</sub> | 0.10         | 1.79       | 0.05    | 9.59E-01 | 0.0413 | 4.13            |
| x <sub>1</sub> <sup>2</sup>   | -5.63        | 1.50       | -3.74   | 1.34E-02 | 0.9866 | <b>98.66</b>    |
| x <sub>2</sub> <sup>2</sup>   | 1.66         | 1.50       | 1.10    | 3.20E-01 | 0.6800 | 68.00           |

The general quadratic model is given by Equation 7:

$$Y = a_0 + a_1x_1 + a_2x_2 + a_{12}x_1x_2 + a_{11}x_1^2 + a_{22}x_2^2 \quad (7)$$

where Y represents % COD removal, and  $x_1$  and  $x_2$  are the coded factors for  $H_2O_2$  and  $FeSO_4 \times 7H_2O$ , respectively. The ANOVA indicated that  $H_2O_2$  has a significant positive effect, while its squared term has a significant negative effect. The negative coefficient for the squared term of  $H_2O_2$  concentration suggests that while increasing  $H_2O_2$  initially improves COD reduction, there is a point beyond which further addition leads to a decrease in COD abatement. Based on the most significant factors ( $x_1$  and  $x_1^2$ ), a quadratic model for COD removal from wastewater was identified (Equation 8):

$$COD_{removal}(\%) = 84.74 + 12.21 x_1 - 5.63 x_1^2 \quad (8)$$

The goodness of this model is supported by the scatter diagram of predicted versus actual values, showing a strong correlation between experimental and theoretical data ( $R^2 = 0.96$ ). Based on the determined quadratic model, the optimal  $H_2O_2$  concentration for maximizing COD removal (91.38 %) was calculated to be 15.45 % v/v (1.05 as a coded value).

To test the model, a validation experiment was performed using this optimized  $H_2O_2$  concentration, resulting in a measured COD removal efficiency of 93.6 %. The difference in COD removal was within the experimental error, confirming the accuracy and reliability of the quadratic model in predicting the effectiveness of  $H_2O_2$  concentration for COD removal.

Figure 18 displays the response surface plot illustrating the variation of COD removal with different concentrations of hydrogen peroxide ( $H_2O_2$ ) and Fe(II) at pH 3.5. The plot clearly shows that  $H_2O_2$  concentration has a noticeable influence on COD removal efficiency, whereas the effect of Fe(II) is negligible.

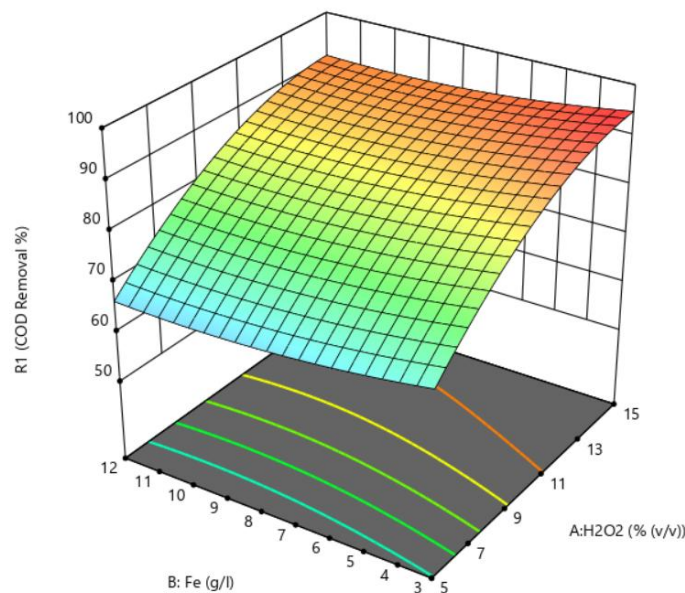


Figure 18: Response surface-plot for COD removal as a function of  $\text{H}_2\text{O}_2$  and  $\text{Fe(II)}$  at pH 3.5.

Figure 19 presents a graph demonstrating the strong alignment between predicted and actual responses, highlighting the precision of the model in forecasting COD removal under varying concentrations of  $\text{H}_2\text{O}_2$  and  $\text{Fe(II)}$  for IMSE wastewater treatment.

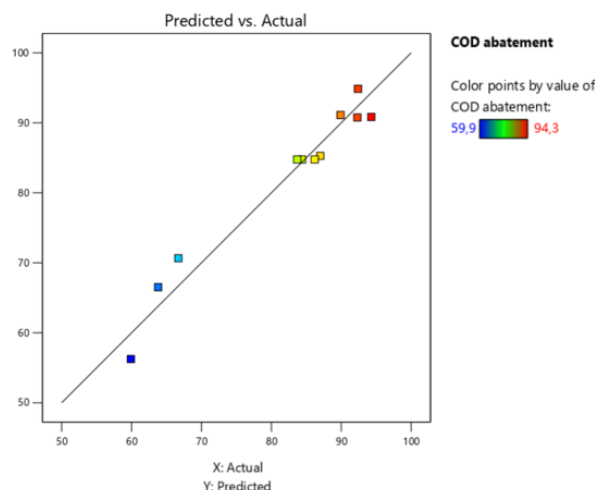


Figure 19: Predicted response vs Actual response for COD abatement (%) based on the determined model.

### 5.3.3: Water quality characteristics after treatment

Thiourea, used as a reagent to complex silver during the hydrometallurgical process, is the main contributor to the wastewater COD. UV-VIS analyses were conducted to evaluate the change in the thiourea peak after Fenton treatment. Figure 4 shows the spectra of the samples before and after the Fenton treatment. The blue curve, representing the wastewater sample before treatment, exhibits maximum absorption in the range of 230–250 nm, indicative of the presence of thiourea, consistent with other research [227,228]. The red curve, corresponding to the sample after Fenton treatment, shows a disappearance of the thiourea peak, indicating its decomposition into simpler organic substances by the radicals. Further analysis of the sample after Fenton treatment with a lower dilution factor revealed an absorption peak at approximately 300 nm (red curve in the upper right of Figure 20), confirming the degradation of thiourea into other organic substances by the Fenton process.

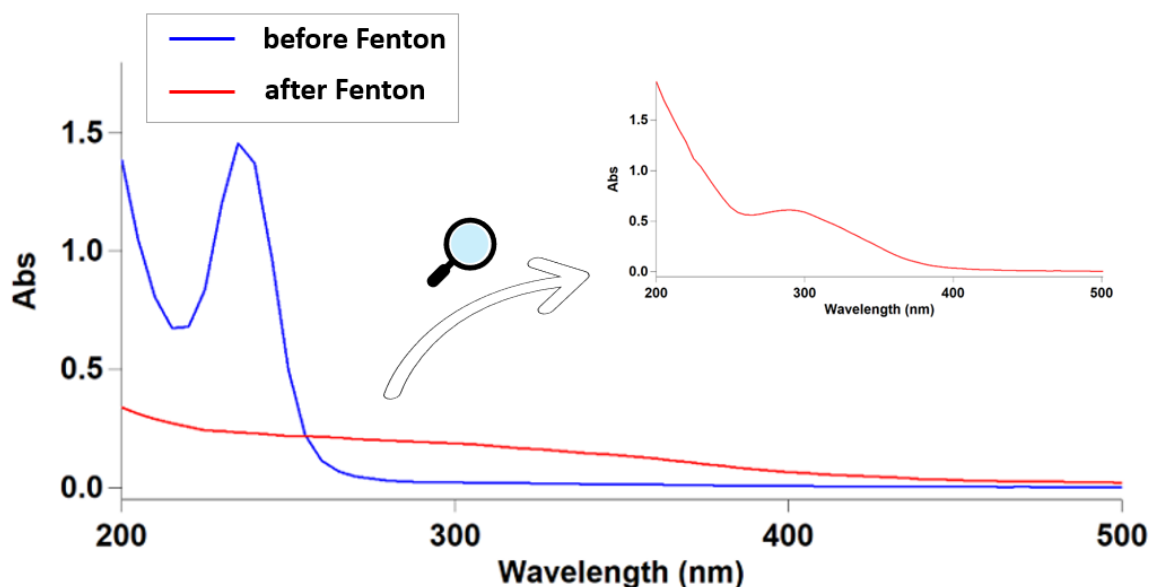


Figure 20: UV spectra of wastewater before Fenton treatment (blue curve) and after Fenton treatment at different dilution factors (red curves)

Table 23 presents the water composition after Fenton treatment and lime precipitation. The quality of the treated water meets the standards for direct discharge into the sewer. More importantly, it demonstrates its suitability for direct reuse in hydrometallurgical processes, enhancing operational efficiency and sustainability. This approach allows for a nearly 90 % reduction in water consumption, resulting in a water footprint of 42.7 L per 1 kg of silver using a Minimal Liquid Discharge (MLD) approach. This achievement of a low water footprint (42.7 L/kg Ag) significantly contrasts with conventional hydrometallurgical processes for WEEE, which typically generate substantial volumes of wastewater and traditionally rely on simple discharge practices.

Table 23: Composition of wastewater after treatment.

|                  |        |
|------------------|--------|
| <b>COD (g/L)</b> | 0.46   |
| <b>Fe (mg/L)</b> | < 0.10 |
| <b>Cu (mg/L)</b> | < 0.10 |

Proper treatment and reuse of wastewater from hydrometallurgical processes are crucial for preparing the leaching solution for subsequent cycles. Hydrometallurgical processes are primarily used for treating industrial waste and recovering secondary materials. It is essential to develop processes that avoid generating additional hazardous waste during metal reclamation and minimize freshwater usage to conserve this resource. While many studies

focus on metal recovery from industrial waste using hydrometallurgical methods, wastewater treatment in these processes is often overlooked. Therefore, adopting a sustainable approach known as ‘circular hydrometallurgy’ is vital.

#### 5.3.4: Mass balance and preliminary cost analysis

Figure 21 illustrates the flowsheet of the proposed treatment process, and a mass balance for treating one cubic meter of hydrometallurgical wastewater is reported based on the obtained results. The hydrometallurgical wastewater is directed to a reactor where hydrogen peroxide is added to initiate the Fenton reaction, aimed at degrading complex organic substances. Subsequently, in the same reactor, lime is introduced to neutralize the wastewater and precipitate iron and other contaminants. The treated water is then separated from the sludge using a filter press. The treated water can be reused, while the sludge requires proper disposal. This process necessitates specific reagent quantities: 171.5 kg of hydrogen peroxide (30 % w/v) and 42.5 kg of calcium hydroxide (10 % w/v) per cubic meter of wastewater. Calcium hydroxide serves a dual purpose: pH adjustment after Fenton treatment to near neutrality and precipitation of iron and other pollutants, facilitating their removal. The treatment process generates 190 kg of wet sludge per cubic meter of treated wastewater. Research suggests the potential reuse of iron-containing sludge as an iron source in the oxidation stage of the Fenton treatment [217] or the recovery of hazardous metals via thermal treatments [216] to minimize hazardous ferric waste and reduce overall treatment costs.

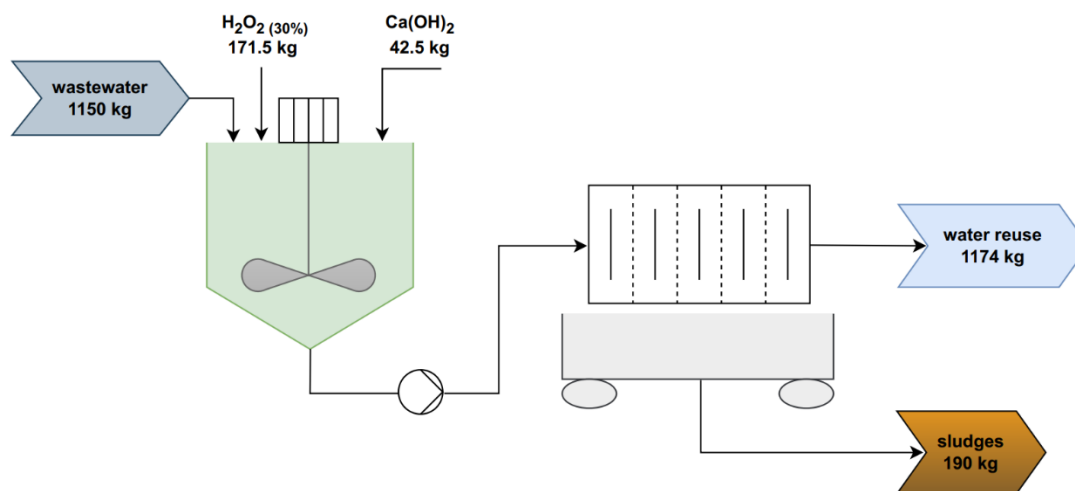


Figure 21: Flowsheet and mass balance for IMSEs wastewater treatment.

Based on the model optimization, the Fenton process was conducted at the initial wastewater pH of 1.39, without further adjustment, using a hydrogen peroxide (30 % w/v) concentration

of 15.45 % (v/v) and without any addition of ferrous sulfate. The results demonstrated significant removal percentages: 93.6 % for COD and 99.9 % for Fe and Cu. The high inherent iron concentration of 8.69 g/L acted as an effective internal catalyst, eliminating the need for external ferrous sulfate addition and aligning this research with methods advocating the reuse of iron sources, thereby minimizing operational costs associated with chemical reagents.

A preliminary cost analysis indicates a total expenditure of 81.60 €/m<sup>3</sup>, which is significantly lower than the typical disposal cost of hydrometallurgical wastewater estimated at 150 €/m<sup>3</sup>. This cost includes 60.02 € for hydrogen peroxide, 15.20 € for sludge disposal, and 6.38 € for calcium hydroxide. These financial findings highlight the cost-effectiveness of COD removal for ensuring sustainable water use.

The wastewater treatment section should not be viewed as an additional cost for hydrometallurgical plants but rather as a potentially cost-effective alternative to disposal. Furthermore, reusing treated water can substantially reduce the overall freshwater consumption in the hydrometallurgical process, aligning with the MLD approach. It is crucial to recognize that scaling up the process to an industrial level would be extremely challenging without proper wastewater management. Moreover, wastewater treatment minimizes health risks for workers by preventing exposure to toxic substances and reducing environmental impacts.

#### **5.4: Conclusion**

A study was conducted on the removal of iron (Fe), copper (Cu), and organic compounds, specifically with a Chemical Oxygen Demand (COD) of 14.48 g/L, in hydrometallurgical wastewater. This wastewater was generated by a process aimed at recovering silver from In-Mold Structural Electronics (IMSEs) within the automotive sector. The primary objective of this study was to treat this wastewater so that it could be reused in the same hydrometallurgical process, thereby achieving a reduction in wastewater production and the overall water footprint. To achieve higher removal percentages of the targeted contaminants, the Advanced Oxidation Process (Fenton) was employed. This process was implemented under optimized operative conditions. These conditions were identified through a combination of 2<sup>2</sup>-full factorial and Central Composite Design (CCD) experiments. The study successfully achieved a maximum COD removal of 93.62 % using a hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) concentration of 171.5 kg/m<sup>3</sup> and a calcium hydroxide concentration of 42.5 kg/m<sup>3</sup>. Furthermore, the removal percentages for both Fe and Cu exceeded 99 %. UV-VIS analyses provided evidence that the Fenton treatment effectively decomposed thiourea, which was used as a reagent to complex

silver during the hydrometallurgical process, into other organic compounds. Importantly, all experiments were conducted without any preliminary pH correction because the wastewater initially had a pH of 1.39, which was found to be suitable for the initiation of Fenton reactions. The study determined that the optimized Fenton condition, which resulted in a 93.62 % COD removal, had an associated cost of 81.60 € per m<sup>3</sup> of wastewater treated. This analysis suggests that while wastewater treatment might be perceived as an added expense for hydrometallurgical plants, it can be cost-effective when compared to the typical disposal costs. Additionally, the reuse of treated water can significantly reduce the overall freshwater consumption within the hydrometallurgical process, aligning with a Minimal Liquid Discharge (MLD) approach. The study underscores the critical point that scaling up the hydrometallurgical process to an industrial level would be extremely challenging without proper wastewater management. Moreover, effective wastewater treatment is essential for minimizing health risks for workers by preventing exposure to toxic substances and for mitigating potential environmental impacts.

## **Chapter: 6. Wastewater Treatment of Spent Permanent Magnets from the Automotive Sector**

### **6.1: Introduction**

The neodymium-iron-boron (NdFeB) magnetic material stands out as a crucial "permanent magnet" in modern technology, recognized for its strong coercive force, significant remanence, and notable magnetic energy product capabilities [229,230]. Consequently, NdFeB permanent magnets are extensively utilized across various contemporary industries and electronic technologies [231–234]. Driven by the expanding range of applications for these magnets, the global production of NdFeB has increased considerably since 2010. By the year 2016, the annual output of NdFeB magnetic materials had risen by 35% compared to 2010, reaching 132,800 tonnes, and further growth at an annual rate of 10% is anticipated [235,236]. Simultaneously, it is expected that over 10,000 tonnes of NdFeB scrap will be recovered annually from discarded electrical appliances [237]. The recycling of these spent magnets is particularly appealing due to their composition, which typically contains a substantial amount of rare earth elements (REEs), ranging from 30–40% [132,238]. Hydrometallurgy has emerged as a promising and effective approach for recovering metals, demonstrating significant success in the extraction of precious metals [239]. This method offers several advantages, including improved control over the process, enhanced environmental compatibility [240], lower capital investment, and the potential to recover a greater quantity of metal compared to traditional techniques [107,241]. However, these hydrometallurgical processes are heavily reliant on water, with demand continuously increasing each year [200]. A significant challenge arises from the extensive use of leaching solutions in certain hydrometallurgical operations, which generates substantial volumes of wastewater [218]. This wastewater often contains hazardous substances such as heavy metals [200,219] and exhibits acidic pH levels [220], posing considerable risks to the environment.

In line with the principles of sustainable hydrometallurgy outlined by Binnemans et al.[242], it is crucial to adopt strategies that improve the sustainability of these processes. Their insights emphasize the importance of minimizing waste generation and maximizing the recovery of resources to meet the growing demand for environmentally responsible metal extraction practices. Addressing these factors is essential for tackling the issues associated with wastewater production and mitigating the environmental hazards posed by heavy metals and acidic leaching solutions. Recognizing wastewater as a potentially renewable resource that can be reclaimed and recycled offers a promising avenue to alleviate water scarcity [199].

Consequently, significant research efforts have been directed towards investigating and advancing various physicochemical techniques, including sorption, ion exchange, coagulation, and flotation. The primary goal of these methods is to effectively treat hydrometallurgical wastewater and facilitate the reuse of the treated water within the same industrial processes. With increasing global concerns regarding water scarcity and the United Nations' Sustainable Development Goals for 2030 [202], ensuring the sustainability of wastewater treatment approaches has become an imperative.

Previous studies have explored different methods for treating hydrometallurgical wastewater. For instance, *Allayorov et al.* [200] focused on purifying hydrometallurgical effluents through coagulation and precipitation, specifically aiming to reduce total hardness by optimizing the use of reagents like sodium carbonate and employing aluminum and iron sulfate sorbents as effective coagulants for removing impurities. *Ullah et al.* [207] investigated wastewater generated during the hydrometallurgical extraction of silver from in-mold structural electronics, utilizing the Fenton process to achieve a COD reduction efficiency of 93.6%. *Sudibyo et al.* [220] employed electrocoagulation to treat wastewater from laterite hydrometallurgy, specifically targeting the reduction of nickel and other metals using a tubular aluminum electrode, achieving a 67% reduction in turbidity and reducing the nickel content in sludge to 0.62% by weight through deposition on the cathode.

Alongside rare earth elements (REEs), iron constitutes the other major metallic component found in spent magnets, making up 60–70% of their total mass [243–245]. Therefore, recovering iron from the NdFeB slurry is both necessary and highly significant. In this context, oxalic acid was employed to extract iron from the solution. This study specifically focuses on utilizing a hydrometallurgical technique to recover iron and manage the wastewater produced during the recovery of Rare Earth Elements (REE) from used permanent magnets. Oxalic acid was used for the extraction of iron, while lime was utilized to precipitate the residual iron and other elements present in the wastewater. Subsequently, the obtained iron oxalate was analyzed using X-ray Fluorescence (XRF), X-ray Diffraction (XRD), and Differential Scanning Calorimetry (DSC). This research aims to provide insights into the recovery of iron, the effectiveness of wastewater treatment, its environmental implications, and its potential contribution to achieving sustainable water management objectives by the year 2030 [202]. Specifically, this work establishes a novel, integrated hydrometallurgical route focused on recovering major valuable components by optimizing ambient-temperature oxalate precipitation for highly concentrated iron effluent (32.3 g/L), simultaneously achieving high

co-recovery of praseodymium (up to 94%) and validating the energy-efficient thermal pathway (214.5 °C) for iron valorization as an iron oxide byproduct.

## 6.2: Materials and Methods

The study investigated the recovery of iron from wastewater generated during the hydrometallurgical extraction of rare earth elements (REEs) from spent permanent magnets. This wastewater was produced at a pilot plant that processed spent permanent magnets sourced from the automotive sector as part of the NewRE project. The magnets were initially leached with citric acid ( $C_6H_8O_7$ ), followed by a liquid-liquid extraction to recover REEs, leaving behind an acidic inorganic phase (pH 3.04) that constituted the wastewater used in the experiments. The initial composition of this wastewater was analyzed, revealing significant concentrations of iron (Fe) at 32366 mg/L, boron (B) at 518.7 mg/L, and praseodymium (Pr) at 341.6 mg/L. All the chemicals used in the experiments were of analytical grade, including oxalic acid ( $C_2H_2O_4$ ) for iron recovery and calcium hydroxide ( $Ca(OH)_2$ ) for subsequent precipitation, which was prepared as a 10% weight/volume (w/v) solution.

The experimental investigation was designed to evaluate the effectiveness of oxalic acid in recovering iron from this specific wastewater. To achieve this, varying percentages of the stoichiometric amount of oxalic acid were added to the wastewater samples: 50%, 80%, and 100%. Furthermore, the influence of temperature was studied by conducting experiments at 25 °C, 40 °C, 50 °C, and 60 °C. This allowed for a comprehensive assessment of how different reaction conditions affected iron recovery efficiency. After the addition of oxalic acid, each sample was agitated in a shaker (SKI 4, shaking incubator) at 200 rpm for a duration of 1 hour to ensure optimal reaction kinetics. Following agitation, the resulting solutions were subjected to vacuum filtration (STEROGLASS, Model ST510) using 0.45-micrometer filter paper (nitrate cellulose) to separate the precipitated iron oxalate from the remaining solution.

The thermal behavior of the precipitated iron oxalate was examined using Differential Scanning Calorimetry (DSC 8500). The DSC analysis was performed under a nitrogen purge gas at a flow rate of 20 ml/min, with a temperature program that involved heating at a rate of 20 °C/min from 0 °C to 360 °C, followed by cooling back to 0 °C under the same conditions. This was done to determine the optimal temperature for thermal treatment of the iron oxalate. The solution remaining after the filtration of iron oxalate was then treated with a 10% (w/v) lime solution to precipitate any residual iron and boron present in the wastewater.

Finally, the concentrations of iron, boron, and praseodymium in the samples after the experiments were completed were analyzed using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) with an Agilent Technologies 5100 instrument. The study emphasizes that the experiments were reproduced under identical conditions to ensure the reliability and consistency of the results. A schematic diagram of the entire process is presented in *Figure 22* of the source. The initial composition of the wastewater before treatment is provided in *Table 24*.

Table 24: Composition of wastewater before treatment.

| Element           | Initial Concentration (mg/L) |
|-------------------|------------------------------|
| Iron (Fe)         | 32366                        |
| Boron (B)         | 518.7                        |
| Praseodymium (Pr) | 341.6                        |

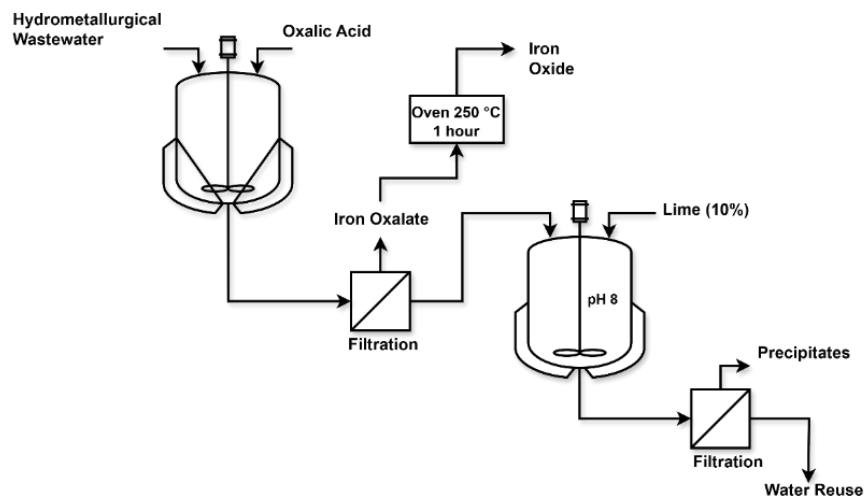
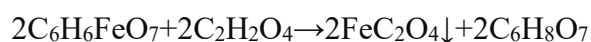


Figure 22: Schematic diagram of the process

## 6.3: Results and discussion

### 6.3.1: Effect of Oxalic Acid Concentration

The research explored the impact of varying the concentration of oxalic acid on the recovery of iron from wastewater generated during the hydrometallurgical processing of spent permanent magnets. Three distinct experiments were conducted, where the amount of oxalic acid added to the wastewater samples was set at 50%, 80%, and 100% of the stoichiometric requirement. The balanced chemical equation provided illustrates the reaction between ferrous citrate (assumed to be the form of iron in the wastewater) and oxalic acid to produce solid ferrous oxalate and citric acid.



The central aim of this part of the study was to identify the optimal oxalic acid concentration that would maximize iron recovery while minimizing the consumption of the reagent. The principle behind the iron precipitation relies on the significant difference in solubility between ferrous oxalate ( $\text{FeC}_2\text{O}_4$ ) and potential ferric oxalate complexes. The source [144,145]. highlights that ferrous oxalate is highly insoluble in water, indicated by its very low solubility product constants ( $K_{sp}$ ) of  $3.2 \times 10^{-7}$ . This low solubility facilitates the efficient precipitation of iron in the ferrous state [145,146]. Conversely, ferric iron ( $\text{Fe(III)}$ ) tends to form stable and soluble oxalate complexes [144], like  $\text{Fe(C}_2\text{O}_4)_3^{3-}$  and  $\text{Fe(C}_2\text{O}_4)_2^{2-}$  [145]. This characteristic makes  $\text{Fe(III)}$  less prone to precipitation as a simple oxalate salt compared to  $\text{Fe(II)}$ .

The experimental results revealed that the highest iron recovery (86.8%) was achieved when a 100% stoichiometric amount of oxalic acid was used. A slightly lower recovery of 85.3% was obtained with an 80% stoichiometric amount of oxalic acid. However, a substantial decrease in iron recovery to 65.2% was observed when the oxalic acid concentration was reduced to 50% of the stoichiometric value, suggesting that an insufficient amount of the precipitating agent limits the extent of iron precipitation and complexation.

The efficiencies sometimes exceeding the stoichiometric predictions, particularly at lower ratios, could be attributed to the preferential dissolution of more reactive metal phases. In such scenarios, even a limited amount of reagent might effectively attack the most readily extractable metal species, leading to significant dissolution. Furthermore, side reactions, complexation effects, or even partial catalytic behavior of the reagent could contribute to higher-than-expected metal solubilization.

The study emphasizes the negligible difference in iron recovery between the 80% and 100% stoichiometric conditions, suggesting that using 80% stoichiometric oxalic acid could be more efficient from a cost-effectiveness and reagent consumption perspective while achieving nearly the same level of iron recovery.

Table 25: Elements Recovery in oxalate form.

| Test | Oxalic Acid<br>(% Stoich) | Recovery in the oxalate (%) |      |      | Wt. of wet iron oxalate<br>(kg/m <sup>3</sup> ) |
|------|---------------------------|-----------------------------|------|------|-------------------------------------------------|
|      |                           | Fe                          | B    | Pr   |                                                 |
| 1    | 50                        | 65.2                        | 24.4 | 29.4 | 84.0                                            |
| 2    | 80                        | 85.3                        | 15.1 | 94.0 | 127.2                                           |

|   |     |      |      |      |       |
|---|-----|------|------|------|-------|
| 3 | 100 | 86.8 | 20.0 | 99.4 | 124.4 |
|---|-----|------|------|------|-------|

Table 26: Elements Recovery in Calcium Citrate.

| Test | Oxalic Acid<br>(% Stoich) | Removal in calcium citrate<br>(%) |      |      | Wt. of wet<br>calcium citrate<br>sludge (kg/m3) |
|------|---------------------------|-----------------------------------|------|------|-------------------------------------------------|
|      |                           | Fe                                | B    | Pr   |                                                 |
| 1    | 50                        | 17.5                              | 0.00 | 0.00 | 9.3                                             |
| 2    | 80                        | 10.5                              | 4.6  | 21.0 | 30.1                                            |
| 3    | 100                       | 40.9                              | 19.2 | 7.8  | 235.9                                           |

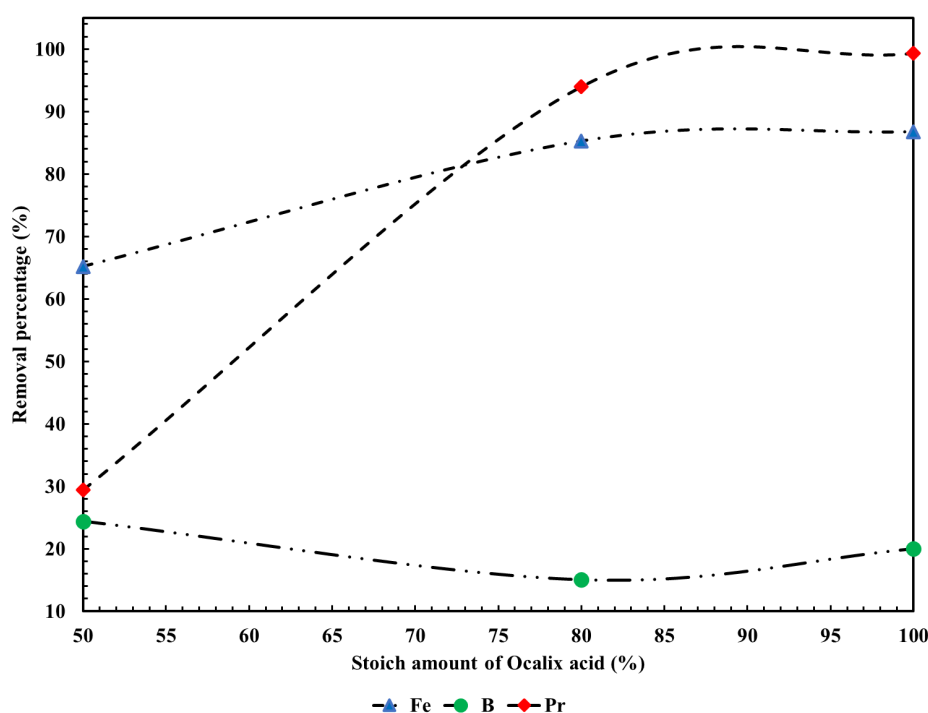


Figure 23: Effect of oxalic acid concentration on Iron recovery.

Figure 23 visually illustrates the effect of oxalic acid concentration on the recovery of these elements, confirming that iron precipitation generally increased with increasing oxalic acid concentration, with the recoveries at 80% and 100% being very similar. The recovery of praseodymium and boron was also influenced by the oxalic acid concentration. Praseodymium recovery showed a significant increase at 80% stoichiometric oxalic acid (94%) compared to 50% (29.4%), indicating that higher oxalic acid concentrations enhance the recovery of this REE in the oxalate precipitate, as shown in Table 25.

To ensure a more complete removal of iron and other elements, a secondary precipitation step using a 10% (w/v) lime solution at pH 8.5 was implemented. The precipitated iron and other

impurities were then separated by filtration. This two-stage approach aims to maximize overall recovery by initially precipitating iron as oxalate and subsequently removing any remaining dissolved iron and other elements through calcium citrate precipitation.

An intriguing observation was the significant increase in iron precipitation in the citrate sludge (40.9%) at a 100% stoichiometric amount of oxalic acid compared to the 80% condition (10.5%). The excess oxalic acid might have caused partial dissolution of the initially precipitated iron oxalate, which was then subsequently removed during the lime treatment. The increased weight of the calcium citrate sludge (235.9 kg/m<sup>3</sup>) at 100% stoichiometry, as shown in *Table 26*, might be attributed to the presence of unreacted oxalic acid or the formation of additional precipitates resulting from secondary reactions. The obtained iron oxalate was then subjected to thermal treatment at 250 °C for one hour, resulting in a 66.3% weight loss due to its decomposition into iron oxide and carbon dioxide. The reproducibility of these results was confirmed through repeated experiments under identical conditions.

### **6.3.2: Effect of Temperature**

The study also delved into the influence of temperature on the efficiency of iron recovery from the wastewater derived from spent permanent magnet recycling, employing oxalic acid as the precipitating agent. To ascertain the optimal temperature for this recovery process, a series of four experiments were conducted at distinct temperature points: 25 °C, 40 °C, 50 °C, and 60 °C. In each of these experiments, an 80% stoichiometric amount of oxalic acid was introduced to the wastewater samples. The resulting mixtures were then agitated for one hour at a consistent speed of 200 rpm to ensure thorough mixing and reaction. Following the agitation period, the solutions underwent filtration, and the concentrations of iron, boron, and praseodymium in the filtrates were meticulously determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The experimental findings, detailed in *Table 27*, revealed a clear inverse relationship between temperature and iron recovery. Specifically, the maximum iron recovery of 85.3% was observed at the lowest tested temperature of 25 °C. As the temperature increased, a significant decline in iron recovery was noted, with recovery rates dropping to approximately 50% at 40 °C, 50 °C, and 60 °C. This observation suggests that elevated temperatures may enhance the solubility of iron oxalate complexes, thereby hindering the precipitation process and leading to reduced recovery efficiency. This trend aligns with findings from other research, such as the work by Ling He et al. [234] which also identified 25 °C as the optimal temperature for iron recovery, noting a gradual decrease in efficiency with increasing temperature. Crucially, achieving the highest recovery (85.3%) at ambient

temperature (25 °C) provides a significant industrial advantage by eliminating the high energy consumption and specialized heating equipment associated with thermal precipitation processes, directly contributing to the economic and environmental sustainability of the overall recovery route. This phenomenon is likely attributable to the increased dissolution of iron oxalate at higher temperatures, potentially causing partial redissolution of the precipitate and a subsequent reduction in overall precipitation efficiency [246]. As depicted in *Figure 24*, the recovery of iron exhibits a sharp decrease at temperatures exceeding 25 °C. In contrast to iron, the recovery of praseodymium remained consistently high, ranging between approximately 93% and 94% across all tested temperatures, indicating that its precipitation is less sensitive to temperature variations compared to iron. Notably, the recovery of boron showed a slight increase with rising temperature, reaching a maximum of 17.8% at 60 °C, which the source suggests could be due to the formation of more stable boron-containing precipitates at higher temperatures.

Table 27: Recovery of Iron at different temperatures.

| Test No. | Temp (°C) | Percent recovery (%) |      |      |
|----------|-----------|----------------------|------|------|
|          |           | Fe                   | B    | Pr   |
| 1        | 25        | 85.3                 | 15.1 | 94.0 |
| 2        | 40        | 50.6                 | 5.3  | 93.6 |
| 3        | 50        | 49.8                 | 12.9 | 94.3 |
| 4        | 60        | 50.6                 | 17.8 | 92.6 |

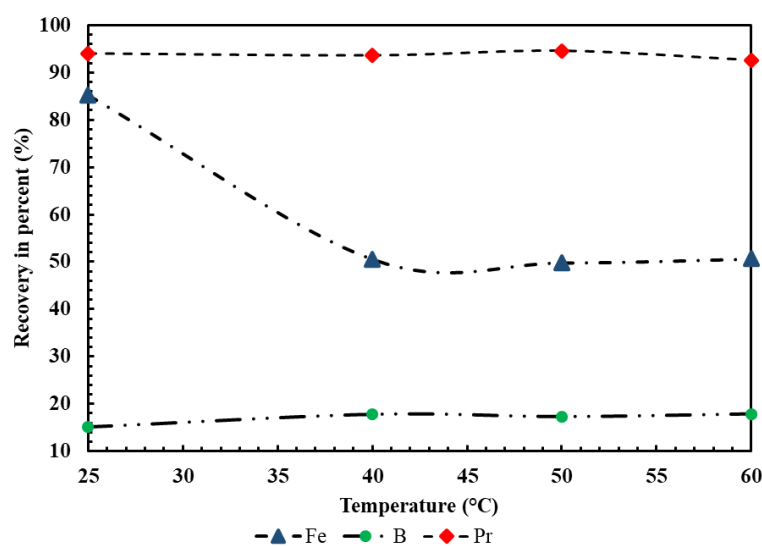


Figure 24: Effect of temperature on Iron recovery.

### 6.3.3: Thermal Behavior Analysis (DSC)

To gain a deeper understanding of the thermal stability and decomposition characteristics of the precipitated iron oxalate, Differential Scanning Calorimetry (DSC) was conducted. The resulting DSC thermogram, presented in *Figure 25*, exhibited a distinct and prominent endothermic peak occurring within a temperature range of 168.8 °C to 245.0 °C, with the apex of this peak, representing the most rapid rate of heat absorption, specifically recorded at 214.5 °C. This significant endothermic transition unequivocally corresponds to the thermal decomposition of the iron oxalate compound into iron oxide (likely  $\text{Fe}_3\text{O}_4$  as later confirmed by XRD) and gaseous carbon dioxide ( $\text{CO}_2$ ). Furthermore, the study quantified the amount of energy associated with this thermal decomposition process; the area integrated beneath the identified endothermic peak was measured to be 2739.7 mJ, which translates to a specific heat flow of 378.4 J/g. This quantitative data emphatically confirms that the decomposition of iron oxalate is an energy-intensive process, requiring a considerable input of thermal energy to proceed. These detailed findings derived from the DSC analysis provide crucial and fundamental insights into the temperature-dependent phase transformation and decomposition behavior of the recovered iron oxalate material. The identification of the optimal calcination temperature is critical for achieving the desired phase transformation of the iron compound while minimizing energy consumption and preventing unwanted side reactions.

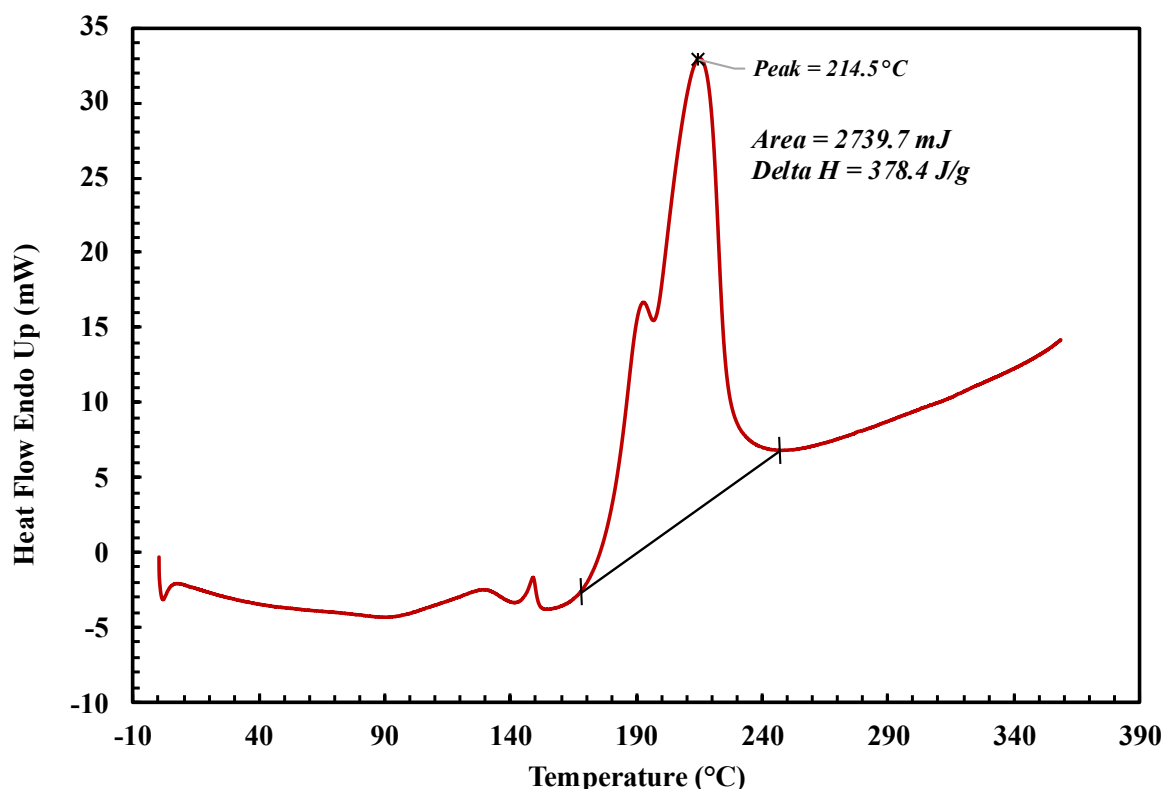


Figure 25: Thermal behaviour of the sample analyzed by DSC.

#### 6.3.4: Elemental Composition Analysis (XRF & XRD)

The analysis of the elemental composition, specifically using X-ray Fluorescence (XRF) and X-ray Diffraction (XRD) techniques, was conducted to understand the changes in the iron oxalate sample resulting from the calcination process. XRF analysis was performed on the iron oxalate samples both before and after they underwent thermal treatment at a temperature of 250 °C. The findings of this analysis, presented in *Table 28*, indicated the presence of iron (60.33%), neodymium (11.01%), and praseodymium (1.48%) in the sample that had not been calcined. The XRF analysis also revealed that other elements were present only in insignificant traces (less than 1%) in the untreated sample. After the calcination process at 250 °C, the percentages of these elements remained largely consistent, with iron at 59.7%, neodymium at 11.3%, and praseodymium at 1.5%. The percentage of undetected components, which include oxygen, volatiles, and light elements, was 26.3% before calcination and 26.2% after calcination.

Table 28: XRF Analysis of the Sample Before and After Calcination at 250 °C.

| Condition | Fe (%) | Nd (%) | Pr (%) | Undetected (%) (Oxygen, Volatiles, Light Elements) |
|-----------|--------|--------|--------|----------------------------------------------------|
|-----------|--------|--------|--------|----------------------------------------------------|

|                                    |      |      |     |      |
|------------------------------------|------|------|-----|------|
| <b>Before Calcination</b>          | 60.3 | 11.0 | 1.5 | 26.3 |
| <b>After Calcination at 250 °C</b> | 59.7 | 11.3 | 1.5 | 26.2 |

To further investigate the structural transformations occurring in the iron oxalate, XRD analysis was carried out on the samples both before and after the calcination process. The X-ray diffraction patterns, illustrated in *Figure 26*, clearly showed crystalline peaks corresponding to iron oxalate in the sample before calcination. However, after the sample was calcined at 250 °C, the XRD analysis revealed the emergence of new peaks. These new peaks were identified as corresponding to magnetite ( $\text{Fe}_3\text{O}_4$ ) and a carbon residue, indicating that the thermal treatment caused the transformation of iron oxalate into iron oxides.

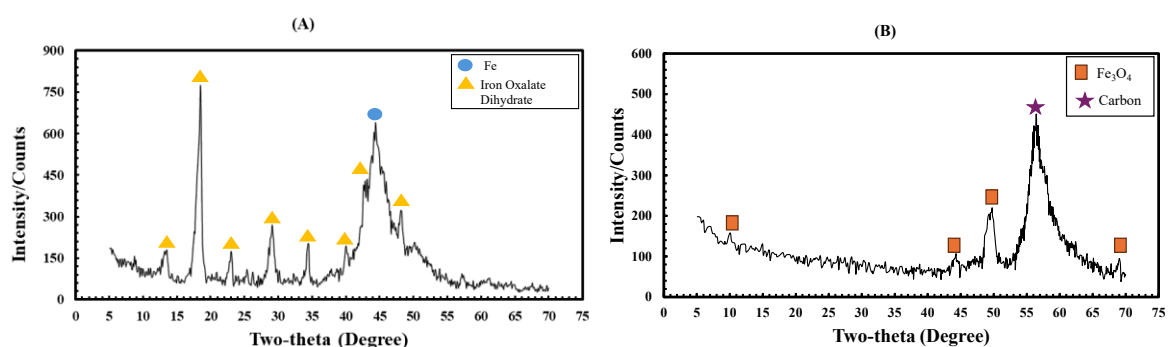


Figure 26: XRD analysis (A: Before calcination, B: After calcination at 250 °C)

Furthermore, a complementary method involving chemical attack was employed to determine the elemental composition of the samples before and after calcination. In this procedure, the samples were completely dissolved in aqua regia and heated to 150 °C for two hours to ensure maximum dissolution of all constituent elements. The concentrations of iron, praseodymium, and neodymium in these dissolved samples were then quantified using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP), and the results are presented in *Table 29*. The analysis showed that after calcination at 250 °C, the iron content increased from 25.9% to 55.9%, the praseodymium content increased to 1.07% from 0.6%, and the neodymium content increased to 7.8% from 4.6%. This observed increase in the percentage concentration of these elements is attributed to a concentration effect resulting from the removal of volatile components during the calcination process.

Table 29: Elemental composition of the samples before and after calcination.

| Elements Concentration (%) |
|----------------------------|
|----------------------------|

| Elements                    | Fe   | Pr  | Nd  |
|-----------------------------|------|-----|-----|
| Before Calcination          | 25.9 | 0.6 | 4.6 |
| After Calcination at 250 °C | 55.9 | 1.1 | 7.8 |

#### 6.4: Conclusion

In summary, this research emphasizes the critical importance of recycling Neodymium-Iron-Boron (NdFeB) magnetic materials, which are extensively utilized across a wide range of industrial and electronic applications due to their exceptional magnetic characteristics. The extraction of both Rare Earth Elements (REEs) and iron from spent magnets represents a significant opportunity for valuable resource recovery. This study specifically focused on the hydrometallurgical recovery of iron from wastewater that is produced during the process of extracting REEs, employing oxalic acid as the key reagent. The experimental investigations into the effects of both temperature and the concentration of oxalic acid provided crucial insights for the optimization of iron recovery. Furthermore, the observed partial removal of boron and praseodymium during the iron recovery process indicates the potential for the simultaneous extraction of multiple valuable elements. The subsequent precipitation of any residual iron from the wastewater using a lime solution demonstrated an effective strategy for wastewater treatment. The most favorable conditions for iron recovery were identified as a temperature of 25 °C, with practically the same high levels of recovery being achieved using both 80% and 100% stoichiometric amounts of oxalic acid. Importantly, the optimal calcination temperature for the precipitated iron oxalate was determined to be 214.5 °C through comprehensive Differential Scanning Calorimetry (DSC) analysis, a finding that was subsequently validated by X-ray Diffraction (XRD) analysis of the calcined product. Ultimately, this research provides valuable knowledge and contributes to the advancement of sustainable practices in the recycling and effective utilization of critical materials, as well as promoting the reuse of water within hydrometallurgical processes. These outcomes are in alignment with broader objectives related to environmental protection and the responsible management of resources.

## Chapter: 7. Conclusions

This thesis has comprehensively investigated and demonstrated innovative and sustainable wastewater treatment strategies specifically tailored for various hydrometallurgical recycling processes within the automotive sector. Recognizing water as a vital resource under immense pressure from industrial activities and increasing global demand, the main goal of this research was to shift from a traditional linear "take-make-use-dispose" model to a circular economy (CE) approach, prioritizing water reuse and aspiring towards Zero Liquid Discharge (ZLD). The findings presented herein are crucial for addressing widespread water stress, mitigating environmental pollution, and aligning industrial practices with the United Nations Sustainable Development Goals (SDGs), particularly SDG 6: Clean Water and Sanitation.

The core objectives of this PhD research were multifaceted: to develop innovative wastewater treatment technologies maximizing reuse, minimizing reliance on finite freshwater resources, preventing adverse environmental impacts from industrial effluents, integrating sustainable wastewater management into automotive manufacturing, and directly contributing to SDG 6. Each experimental chapter explored distinct and challenging wastewater streams generated from the recycling of critical automotive components, lithium-ion batteries, alkaline batteries, in-mold structural electronics, and spent permanent magnets, thereby offering tailored solutions that enhance operational sustainability and resource recovery.

In Chapter 3, the research focused on wastewater generated from the washing of black mass during spent lithium-ion battery (LIB) recycling. This effluent presented significant challenges, characterized by a highly basic pH of 10.17 and a substantial Chemical Oxygen Demand (COD) of 5390 mg/L, alongside notable concentrations of lithium (488.13 mg/L) and copper (14.2 mg/L). The Fenton advanced oxidation process proved highly effective in addressing this complex mixture, achieving a remarkable maximum COD removal efficiency of 98.79%. Statistical analysis rigorously confirmed the significance of both hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and ferrous iron ( $\text{Fe}^{2+}$ ) concentrations in driving COD reduction. Interestingly, a statistically significant negative interaction effect between the two reagents was identified, suggesting potential radical scavenging at higher combined concentrations. Economic optimization further revealed that a balanced approach, specifically Experiment 3, utilizing a lower  $\text{H}_2\text{O}_2$  concentration (5% v/v) and a higher  $\text{Fe}^{2+}$  concentration (5 g/L), achieved a still-impressive 94.79% COD removal at a substantially lower cost of €23.23 per cubic meter (€/m<sup>3</sup>) of treated wastewater, compared to the maximum efficiency scenario costing €62.02/m<sup>3</sup>. The treated water, with its COD reduced to 56.90 mg/L, was deemed suitable for recycling into subsequent

hydrometallurgical processes. This cyclical reuse strategy is pivotal for gradually concentrating lithium for eventual recovery and minimizing freshwater consumption, directly supporting the ZLD objective.

Chapter 4 addressed wastewater originating from the hydrometallurgical recovery of graphite from spent alkaline batteries. This wastewater was initially highly basic (pH 11.7) and contained a very high COD (9715 mg/L), along with hazardous concentrations of barium (474.3 mg/L), lead (11.9 mg/L), and strontium (8.7 mg/L). A critical pre-treatment step involving pH adjustment to 1 using sulfuric acid effectively precipitated and removed barium, lead, and strontium to negligible levels (approximately 0.1 mg/L for Ba and Pb), while also achieving a significant 72% reduction in COD. Following this, the Fenton process, applied after adjusting the pH to 3.5, further reduced COD by up to 84.11%. The  $\text{H}_2\text{O}_2$  concentration was identified as the main factor influencing COD reduction, whereas  $\text{Fe}^{2+}$  concentration, while critical for overall process chemistry, had a less pronounced direct effect on COD removal but significantly impacted solid cake formation. Multi-response optimization identified a practical set of conditions (7.91% v/v  $\text{H}_2\text{O}_2$  and 1.5 g/L  $\text{Fe}^{2+}$ ) that achieved 81.37% COD removal with minimal cake generation (4.01 kg/m<sup>3</sup>). The treated water, with COD below 500 mg/L, was then amenable to evaporation-crystallization, enabling water recovery for reuse and the production of high-purity sodium sulfate dihydrate (99.67%) as a valuable byproduct. Economically, the optimized treatment cost was calculated at €36.40/m<sup>3</sup>, which represents a substantial reduction compared to the typical €150/m<sup>3</sup> for conventional hydrometallurgical wastewater disposal, underscoring the economic viability of this sustainable approach.

The research in Chapter 5 focused on the treatment of wastewater generated during the recovery of silver from In-Mold Structural Electronics (IMSEs) in the automotive sector. This wastewater presented an acidic pH of 1.39 and an exceptionally high COD of 14.48 g/L, coupled with significant concentrations of iron (8.69 g/L) and copper (117.4 mg/L). Notably, the initial acidic pH was found to be directly suitable for initiating the Fenton reaction, eliminating the need for an additional preliminary pH adjustment step, which simplified the process. The Fenton process demonstrated remarkable efficacy, achieving 93.6% COD removal and over 99% removal of both iron and copper.  $\text{H}_2\text{O}_2$  concentration emerged as the most significant factor for COD reduction, while the addition of ferrous sulfate was rendered insignificant due to the inherent high iron content already present in the wastewater, which acted as a catalyst. UV-VIS spectral analyses confirmed the effective decomposition of thiourea, a primary organic contaminant, into simpler organic substances by the Fenton

treatment. The quality of the treated water, with COD reduced to 0.46 g/L and Fe/Cu concentrations below 0.1 mg/L, meets the standards for direct reuse in hydrometallurgical processes. This enables a nearly 90% reduction in water consumption, translating to a water footprint of 42.7 L per kilogram of silver recovered under a Minimal Liquid Discharge (MLD) approach. The cost analysis indicated that the optimized Fenton treatment costs €81.60/m<sup>3</sup>, which is considerably more economical than the estimated €150/m<sup>3</sup> for typical hydrometallurgical wastewater disposal, reinforcing its financial as well as environmental benefits.

Finally, Chapter 6 investigated the recovery of iron and the subsequent wastewater treatment from Rare Earth Element (REE) recovery processes for spent permanent magnets from the automotive sector. The wastewater, stemming from citric acid leaching, was acidic (pH 3.04) and contained high concentrations of iron (32366 mg/L), boron (518.7 mg/L), and praseodymium (341.6 mg/L). The study successfully demonstrated efficient iron recovery via oxalic acid precipitation. Using an 80% stoichiometric amount of oxalic acid achieved an 85.3% iron recovery, closely comparable to the 86.8% achieved with 100% stoichiometry, suggesting the former as a more cost-effective option for industrial implementation. This process also facilitated the partial co-recovery of praseodymium (up to 94%) and boron (up to 15.1%) in the oxalate precipitate. Temperature was identified as a critical parameter, with optimal iron recovery achieved at 25 °C; higher temperatures significantly reduced recovery efficiencies due to increased solubility of iron oxalate complexes, while praseodymium recovery remained largely unaffected. Differential Scanning Calorimetry (DSC) analysis pinpointed the optimal calcination temperature for the precipitated iron oxalate at 214.5 °C, where it decomposed into iron oxide (specifically magnetite, Fe<sub>3</sub>O<sub>4</sub>) and carbon dioxide, a finding corroborated by X-ray Diffraction (XRD) analysis. A subsequent lime precipitation step was implemented to remove any residual iron and other elements, ensuring comprehensive wastewater treatment. This integrated approach not only provides a method for recovering valuable iron as a byproduct but also ensures that the remaining wastewater is treated effectively for potential reuse in the broader REE recovery circuit.

In summation, this thesis makes significant contributions to the field of sustainable wastewater management within the automotive recycling sector. It has successfully developed and optimized diverse treatment technologies, primarily Fenton oxidation and targeted precipitation, to address the complex and hazardous wastewater streams arising from the recycling of LIBs, alkaline batteries, IMSEs, and permanent magnets. By demonstrating high

contaminant removal efficiencies, elucidating optimal operating conditions, and performing crucial economic viability assessments, this research validates the technical and financial feasibility of integrating advanced wastewater treatment into hydrometallurgical recycling processes. The consistent focus on water reuse, resource recovery (including valuable metals like lithium, iron, copper, and byproducts like sodium sulfate), and the minimization of waste aligns directly with circular economy principles and global sustainability objectives. This work explicitly bridges a critical research gap by providing integrated solutions for wastewater management, often overlooked in metal recovery studies.

The implications of these findings are profound. Implementing the strategies proposed in this thesis can substantially reduce the automotive industry's freshwater footprint, mitigate environmental pollution, and foster a more resource-efficient industrial ecosystem. The economic benefits, stemming from reduced disposal costs and the valorization of recovered materials, further strengthen the case for industrial adoption. This work promotes circular hydrometallurgy, where even wastewater is treated as a potential resource rather than waste. For future endeavors, further research could explore advanced valorization techniques for the generated sludges, refine the recovery of trace valuable elements, and conduct comprehensive life cycle assessments to quantify the holistic environmental benefits of these integrated systems at an industrial scale. Ultimately, this thesis provides a critical pathway towards building a more sustainable and resilient automotive sector, safeguarding our planet's vital water resources for generations to come.

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