

Article

A Novel Procedure for Comprehensive Recovery of Zinc Fluoride, Manganese Fluorides, Manganese Dioxide, and Carbon Powder from the Electrode Powder of Spent Alkaline Batteries

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Citation: Wang, L.-P.; Hsu, W.-T.; Chen, Y.-J.; Chen, Y.-F.; Lin, I.-C.; Zhou, H.; Kou, M.; Sreearunothaia, P. A Novel Procedure for Comprehensive Recovery of Zinc Fluoride, Manganese Fluorides, Manganese Dioxide, and Carbon Powder from the Electrode Powder of Spent Alkaline Batteries. *Sustainability* **2023**, *15*, 13216. <https://doi.org/10.3390/su151713216>

Academic Editor: Giovanni Esposito

Received: 24 July 2023

Revised: 23 August 2023

Accepted: 31 August 2023

Published: 3 September 2023



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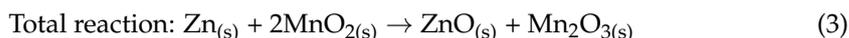
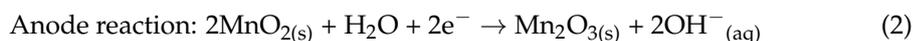
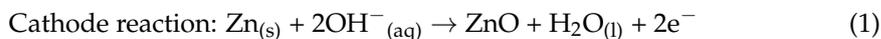
Abstract: In this paper, a novel procedure is proposed for comprehensively recovering zinc fluoride (ZnF_2), manganese fluorides [$MnF_{x(x=2,3)}$], manganese dioxide (MnO_2), and carbon powder from the electrode powder of spent alkaline batteries. Firstly, hydrofluoric acid (HF) leaching is conducted on the electrode powder of spent alkaline batteries. Secondly, potassium permanganate ($KMnO_4$) is introduced into the leachate to selectively precipitate manganese (Mn) ions to recover MnO_2 . Subsequently, the water content in the leachate is evaporated to recover ZnF_2 . Finally, the leaching residue is leached again by using HF, after which the water content in the leachate is evaporated to recover MnF_x . The results indicated that under optimal conditions of a HF concentration of 4 M, a leaching time of 15 min, and a liquid–solid ratio of 5 mL/g, the optimal leaching selectivity for Zn and Mn was achieved and the leaching efficiencies of Zn and Mn were 97.83% and 39.94%, respectively. When $KMnO_4$ with a dosage ($KMnO_4/Mn$ ion molar ratio) of 0.5:1 was added to the leachate, MnO_2 with a grade of 91.68% and a Mn recovery of 39.07% was obtained. In addition, ZnF_2 with a grade of 97.98% and a Zn recovery of 96.15% was also obtained after removing the water content from the leachate via evaporation. Under the optimal conditions of a HF concentration of 2 M, a leaching time of 15 min, and a liquid–solid ratio of 10 mL/g for the leaching residue, followed by removing the water content in the leachate via evaporation, MnF_x with a grade of 94.20% and a Mn recovery of 59.46%, was obtained. The residue of the re-leaching process was carbon powder. The effectiveness of the proposed recovery procedure was confirmed.

Keywords: alkaline battery; zinc fluoride; manganese fluorides; manganese dioxide; carbon powder; battery recycling

1. Introduction

An alkaline battery is a primary battery with an alkaline electrolyte. Currently, most alkaline batteries available in the market are zinc–manganese dioxide ($Zn-MnO_2$) batteries. These batteries contain a cathode made of Zn, an anode made of MnO_2 and carbon powder, and a potassium hydroxide electrolytic solution. The discharge reactions of the aforementioned batteries are expressed in Equations (1)–(3). When alkaline batteries discharge electricity, the cathode (i.e., Zn) is oxidized to $Zn(OH)_2$, which results in the release of electrons. The produced $Zn(OH)_2$ then becomes dehydrated and finally forms zinc oxide

(ZnO). Concurrently, the anode (i.e., MnO₂) absorbs electrons and is reduced to MnOOH. Carbon powder helps to improve the conductivity of the anode. As the voltage decreases, MnOOH is further reduced to Mn₂O₃. After alkaline batteries are fully discharged, they cannot be recharged and become spent batteries [1].



According to the statistics compiled by the Environmental Protection Administration, Executive Yuan, Taiwan, more than 4000 tons of spent batteries every year have been recycled in Taiwan over the past 10 years, and more than 80% of these batteries were alkaline batteries [2]. By removing the iron shells, copper needles, and plastic of spent alkaline batteries, spent electrode powder containing ZnO, manganese oxides, and carbon powder can be obtained. This powder can be separated and recycled to provide the secondary sources of such metals.

Several studies have been reported to recover Zn and Mn from the electrode powder of spent alkaline batteries. Sadeghi et al. [3] and Sayilgan et al. [4] have conducted reviews on this critical issue. Most of these studies adopted pyrometallurgical techniques such as volatilization [5] or roasting [6] at a high temperature, or hydrometallurgical techniques such as leaching with various reagents including sulfuric acid (H₂SO₄) [7] and the addition of oxalic acid (H₂C₂O₄) or citric acid (C₆H₈O₇) as the reducing agent [8,9], sodium hydroxide (NaOH) [7,10], ammonium carbonate (NH₄)₂CO₃ [7], and ammonium chloride (NH₄Cl) [11], followed by precipitation [8], solvent extraction [12], or electrolysis [13]. In addition, most of them recovered Zn or Mn from the electrode powder of spent alkaline batteries as their hydroxides or oxides.

Different from the aforementioned studies, in this study, we developed a novel procedure for comprehensively recovering zinc fluoride (ZnF₂), manganese fluorides [MnF_{x(x=2,3)}], manganese dioxide (MnO₂), and carbon powder from the electrode powder of spent alkaline batteries. ZnF₂ is mainly used as a raw material for producing special optical glass [14–17] or as a fluorination agent in chemical syntheses and thin-film production [18]. MnF_x can be used as a fluorination agent in thin-film production [18] or organic chemical syntheses [19], as well as in the fabrication of alloys [20], special glass, and lasers [21]. Moreover, MnO₂ is primarily used to produce electrolytic MnO₂ electrode powder for alkaline and zinc–carbon batteries, and to produce oxidants such as KMnO₄. Carbon powder can be used as a raw material for activated carbon production. To the best of our knowledge, ZnF₂ and MnF_x are currently manufactured via the chemical syntheses of Zn or Mn compounds with fluoride, using chemical reagents as the raw materials. No study has been reported to obtain ZnF₂ and MnF_x through waste recycling. In addition, the recovery of Zn and Mn from the electrode powder of spent alkaline batteries as their fluorides has never been reported. In this procedure, firstly, hydrofluoric acid (HF) leaching was conducted on the electrode powder of spent alkaline batteries. Secondly, potassium permanganate (KMnO₄) was introduced into the leachate to precipitate manganese (Mn) ions to recover MnO₂, after which the water content in the leachate was evaporated to recover ZnF₂. Finally, the leaching residue was re-leached using HF, after which the water content in the leachate was evaporated to recover MnF_x. The residue of the re-leaching process was carbon powder. We investigated the leaching selectivity of HF for the Zn and Mn extracted from the electrode powder; the precipitation efficiency of KMnO₄ for the Mn ions in the leachate; the leaching efficiency of HF for the Mn in the leaching residue; and the grade (i.e., purity or content) and recovery of ZnF₂, MnF_x, and MnO₂. In addition, the recovered products were characterized.

2. Materials and Methods

2.1. Materials

The spent alkaline batteries used in this study were manufactured by Energizer Holdings, Inc., St. Louis, MO, USA. The batteries were manually disassembled to obtain their iron shells, copper needles, plastic, and electrode powder. The electrode powder was washed with water to remove the water-soluble electrolyte potassium hydroxide from it. After solid–liquid separation, the solid phase was placed in an oven at 373 K for 12 h to remove residual water. The dehydrated electrode powder was then ground and pulverized until it could pass through a 100-mesh (0.149 mm) sieve. The particle size distribution (PSD) of the powder sample is shown in Figure 1; the powder had a medium particle size (D_{50}) of 13.52 μm and was distributed between 2.092 μm (D_{10}) and 47.32 μm (D_{90}). The PSD was analyzed by using a particle size analyzer (Microtrac X100 produced by Honeywell Co., Ltd., Charlotte, NC, USA). One specimen was sampled for subsequent sample analyses after being uniformly mixed. The X-ray diffraction (XRD) crystal-phase analysis result for the electrode powder of the spent alkaline batteries is displayed in Figure 2. The result was obtained using an XRD spectrometer (Bruker D2 Phaser, Blue Scientific, Cambridge, UK). The electrode powder mainly contained ZnO, MnO₂, Mn₂O₃, and carbon, which is in agreement with the result obtained by Belardi et al. [22].

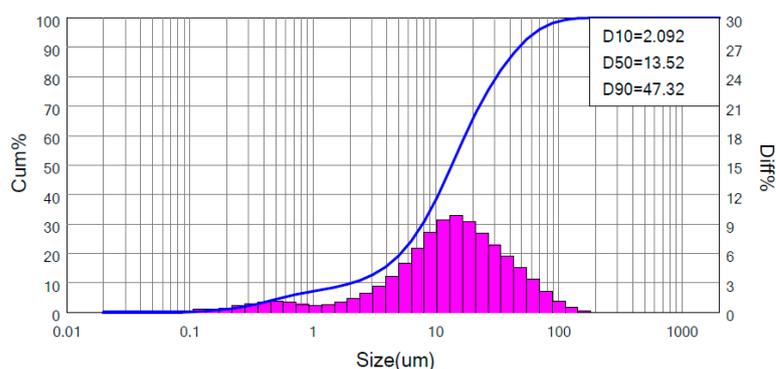


Figure 1. Particle size distribution of the electrode powder of spent alkaline batteries.

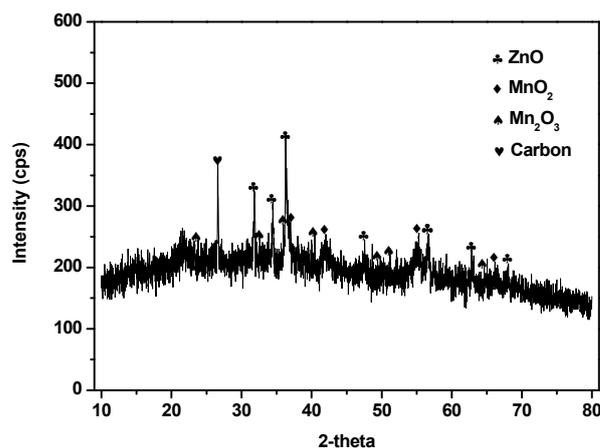


Figure 2. XRD analysis result for the electrode powder of spent alkaline batteries.

The result of the elemental composition analysis for the electrode powder is presented in Table 1. This powder contained 27.36 wt.% of Zn, 40.71 wt.% of Mn, 15.06 wt.% of carbon, and 16.87 wt.% of other elements (mainly potassium and oxygen). The Zn and Mn contents were determined by digesting the electrode powder via aqua regia digestion and performing analyses using an inductively coupled plasma optical emission spectrometer (ICP-OES, Optima 8300, Perkin Elmer, Waltham, MA, USA). The carbon content was

determined by calculating the weight of the residue obtained after aqua regia digestion as a percentage of the electrode powder. HF (concentration: 49%; UniRegion Bio-Tech Co., Hsinchu, Taiwan) was used in the leaching experiments, and KMnO_4 (purity: 99%; Emperor Chemical Co., Ltd., Taipei, Taiwan) was used as the oxidizing agent in the precipitation experiments. All the reagents used in this study were of reagent grade.

Table 1. Elemental composition of the electrode powder.

Element	Zn	Mn	C	Others
Content	27.36 wt.%	40.71 wt.%	15.06 wt.%	16.87 wt.%

2.2. Methods

Figure 3 depicts the flowchart of the proposed procedure for comprehensively recovering ZnF_2 , MnF_x , MnO_2 , and carbon powder from the electrode powder of spent alkaline batteries. Firstly, batchwise HF leaching experiments were conducted on the electrode powder of the spent alkaline batteries (~2 g) in a 100 mL Teflon beaker equipped with a stainless steel magnetic stirrer (PC-420D, Corning Inc., New York, NY, USA) under specific HF concentrations of 1–5 M, liquid–solid ratios of 2.5–20 mL/g, and leaching times of 5–60 min. Unless otherwise stated, all the experiments in this study were conducted at 298 K, and stirring was performed at 300 rpm. After the leaching experiments were completed, solid–liquid separation was performed using a centrifuge (Tabletop Centrifuge Model 4000, KUBOTA Corporation, Osaka, Japan) to obtain the leachate and leaching residue. A total of 5 mL of the leachate was sampled and filtered through a 0.2 μm membrane. The concentrations of Zn and Mn in the leachate specimen were analyzed using the ICP-OES to determine the leaching efficiencies of Zn and Mn, which were calculated on the basis of the initial Zn and Mn contents in the electrode powder. Unless otherwise stated, the calibration curves used in the ICP-OES measurements were created using standard solutions of Zn and Mn nitrates ranging from 0 mg/L to 100 mg/L, with a coefficient of determination (R^2) of 0.999.

Next, batchwise KMnO_4 precipitation experiments were conducted on the leachate in the 100 mL Teflon beaker for 60 min under specific KMnO_4 dosages of KMnO_4/Mn ion at a molar ratio of 0.1:1–0.85:1. After the precipitation experiments were completed, solid–liquid separation was performed by using the centrifuge to obtain the leachate and precipitate. A total of 5 mL of the leachate was sampled and filtered through a 0.2 μm membrane. The concentrations of Zn and Mn in the leachate specimen were analyzed using the ICP-OES to determine the precipitation efficiencies of Zn and Mn, which were calculated on the basis of the initial concentrations of Zn and Mn in the leachate. Moreover, the precipitate was dried at 373 K for 12 h in an oven (KOE-72, KO TSAO Specialty Instrument & Supplies Co., Ltd., Taipei, Taiwan), and the crystal phases of the precipitate were analyzed using the XRD spectrometer (Bruker D2 Phaser, Blue Scientific). The chemical configuration of the precipitate was analyzed using X-ray photoelectron spectroscopy (XPS) (PHI 5000 VersaProbe, ULVAC-PHI Inc., Kanagawa, Japan). Subsequently, the grade of Mn in the precipitate (i.e., the content or purity) was analyzed using the ICP-OES after conducting aqua regia digestion, and the recovery of Mn was calculated on the basis of the initial Mn amount in the electrode powder, i.e., the content of Mn in the precipitate multiplied by the weight of the precipitate (i.e., the amount of Mn in the product) and divided by the amount of Mn in the original sample of the electrode powder of spent alkaline batteries. Furthermore, the leachate was evaporated at 373 K for 12 h in the oven to remove its water content. The solid obtained from the leachate was characterized and this solid's Zn grade and recovery were analyzed using the same methods as those used for the precipitate.

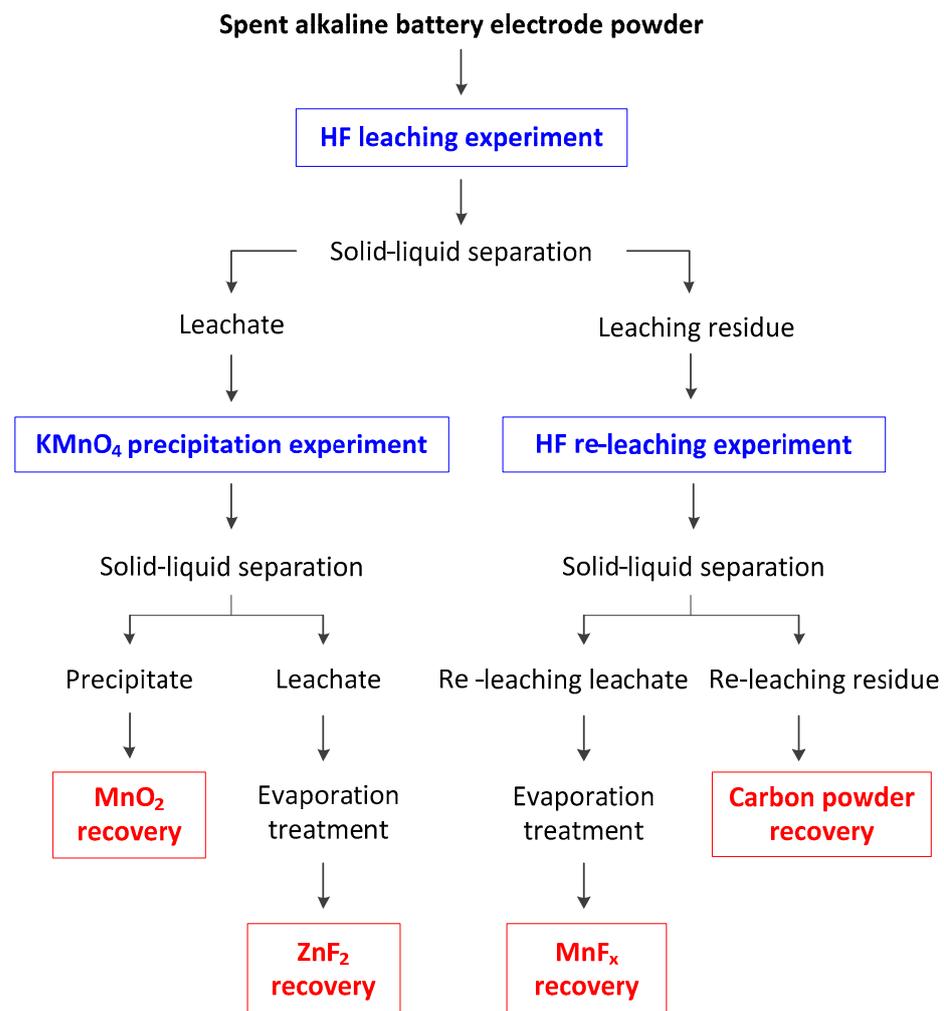


Figure 3. Flowchart of the proposed procedure for comprehensively recovering ZnF₂, MnF_x, MnO₂, and carbon powder from the electrode powder of spent alkaline batteries.

Finally, batchwise HF re-leaching experiments were performed on the HF leaching residue. These experiments were performed using the same method as that used in the HF leaching experiments conducted on the electrode powder. Leaching residue (~0.9 g) was used in each experiment under specific HF concentrations of 1–5 M, liquid–solid ratios of 5–20 mL/g, and leaching times of 5–60 min. The concentration of Mn in the leachate after the HF re-leaching experiments was analyzed using the ICP-OES to determine the leaching efficiency of Mn, which was calculated on the basis of the initial Mn content in the HF leaching residue. Subsequently, the leachate was evaporated at 373 K for 12 h in the oven to remove its water content. The solid deposited from the leachate was characterized and this solid's Mn grade and recovery of Mn were analyzed using the same methods as those used in the KMnO₄ precipitation experiments. Each type of experiment in this study was performed at least in duplicate, and the mean value and standard deviation of each parameter were calculated and plotted. In addition, a duplicate test was also beneficial for obtaining enough final products for quantitative and qualitative analysis.

3. Results and Discussion

3.1. HF Leaching Experiments on the Electrode Powder

3.1.1. Effects of the HF Concentration on the Leaching Efficiencies of Zn and Mn

The effects of the HF concentration on the leaching efficiencies of the Zn and Mn in the electrode powder are illustrated in Figure 4. The experimental settings were as follows: HF concentration = 1–5 M, liquid–solid ratio = 5 mL/g, leaching time = 60 min, leaching

temperature = 298 K, and stirring velocity = 300 rpm. When the HF concentration was 1 M, the leaching efficiencies of Zn and Mn were 3.3% and 3.1%, respectively. As the HF concentration increased, the leaching efficiencies of Zn and Mn also increased. When the HF concentration reached 4 M, the leaching efficiencies of Zn and Mn were 97.83% and 39.94%, respectively. When the HF concentration was 5 M, the leaching efficiency of Zn did not increase considerably, whereas that of Mn increased to 59.8%. At a HF concentration of 4 M, Zn was almost fully leached, the highest difference in leaching efficiency between Zn and Mn was observed, and the leaching selectivity for Zn and Mn was optimal. Thus, 4 M was the optimal HF concentration in the leaching experiments.

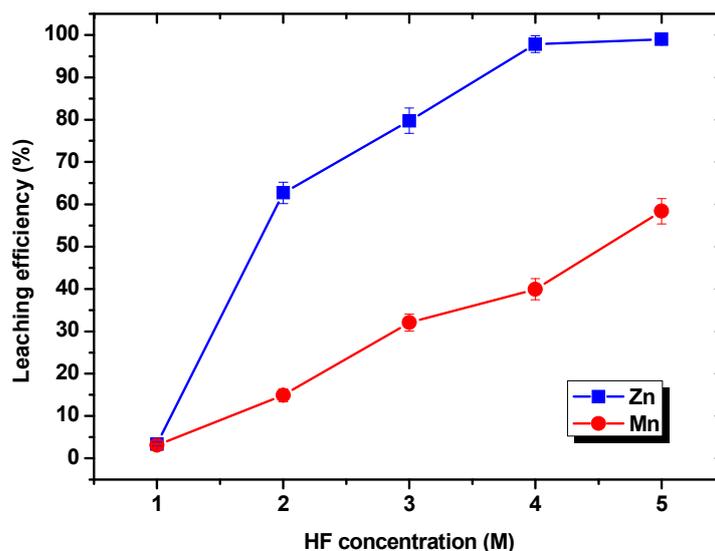


Figure 4. Effects of the HF concentration on the leaching efficiencies of Zn and Mn in the electrode powder (experimental conditions—electrode powder amount: ~2 g, liquid–solid ratio: 5 mL/g, leaching time: 60 min, leaching temperature: 298 K, and stirring velocity: 300 rpm).

3.1.2. Effects of the Liquid–Solid Ratio on the Leaching Efficiencies of Zn and Mn

The effects of the liquid–solid ratio on the leaching efficiencies of the Zn and Mn are illustrated in Figure 5. The experimental settings were as follows: liquid–solid ratio = 2.5–20 mL/g, HF concentration = 4 M, leaching time = 60 min, leaching temperature = 298 K, and stirring velocity = 300 rpm. When the liquid–solid ratio was 2.5 mL/g, the leaching efficiencies of Zn and Mn were 71.11% and 21.04%, respectively. As the liquid–solid ratio increased, the leaching efficiency of Mn increased. When the liquid–solid ratio was 5 mL/g, the leaching efficiencies of Zn and Mn were 97.83% and 39.94%, respectively. When the liquid–solid ratio was ≥ 10 mL/g, the leaching efficiencies of Zn and Mn were 99.73% and 99.70%, respectively. As the liquid–solid ratio increased, the quantity of fluoride ions in the leachate that could react with ZnO and MnO increased; thus, the leaching efficiencies of Zn and Mn also increased. An increase in the liquid–solid ratio beyond 10 mL/g failed to increase the leaching efficiencies of Zn and Mn. At a liquid–solid ratio of 5 mL/g, the leaching selectivity for Zn and Mn was optimal. In contrast, when the liquid–solid ratio reached 10 mL/g or higher, the leaching selectivity for Zn and Mn was nonexistent. Thus, the optimal liquid–solid ratio was 5 mL/g in this study.

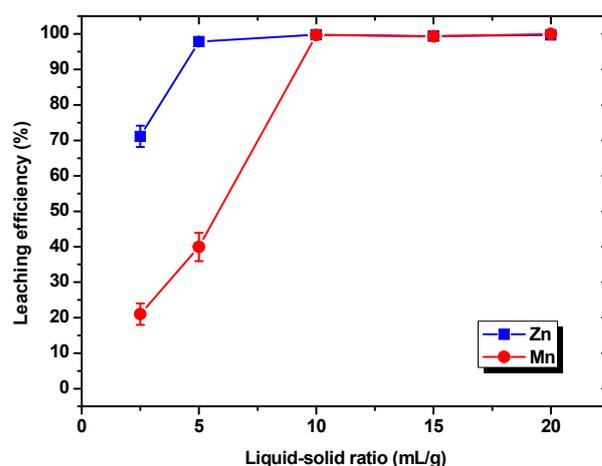


Figure 5. Effects of the liquid–solid ratio on the leaching efficiencies of the Zn and Mn in the electrode powder (experimental conditions—electrode powder amount: ~2 g, HF concentration: 4 M, leaching time: 60 min, leaching temperature: 298 K, and stirring velocity: 300 rpm).

3.1.3. Effects of the Leaching Time on the Leaching Efficiencies of Zn and Mn

The effects of the leaching time on the leaching efficiencies of Zn and Mn are illustrated in Figure 6. The experimental settings were as follows: leaching time = 5–60 min, HF concentration = 4 M, liquid–solid ratio = 5 mL/g, leaching temperature = 298 K, and stirring velocity = 300 rpm. When the leaching time was 5 min, the leaching efficiencies of Zn and Mn were 42.14% and 31.49%, respectively. As the leaching time increased, the leaching efficiencies of Zn and Mn also increased. When the leaching time was 15 min, the leaching efficiencies of Zn and Mn were 97.83% and 39.94%, respectively. For leaching times longer than 15 min, the leaching efficiencies of Zn and Mn remained approximately 97% and 39%, respectively. Therefore, the optimal leaching time was 15 min in this study.

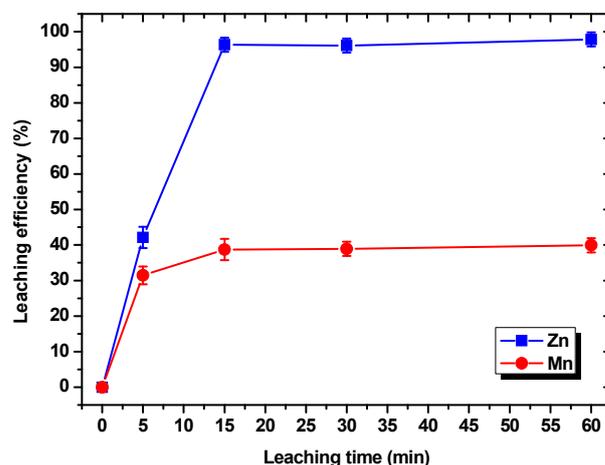


Figure 6. Effects of the leaching time on the leaching efficiencies of the Zn and Mn in the electrode powder (experimental conditions—electrode powder amount: ~2 g, HF concentration: 4 M, liquid–solid ratio: 5 mL/g, leaching temperature: 298 K, and stirring velocity: 300 rpm).

The forgoing HF leaching experiments indicated that the optimal leaching conditions were a HF concentration of 4 M, a liquid–solid ratio of 5 mL/g, and a leaching time of 15 min. These conditions produced Zn and Mn leaching efficiencies of 97.83% and 39.94%, respectively, and Zn and Mn concentrations (in the leachate) of 0.820 mol/L and 0.592 mol/L, respectively. The leachate obtained under the aforementioned conditions was used in the KMnO_4 precipitation experiments, whereas the leaching residue was used in the HF re-leaching experiments.

3.2. KMnO_4 Precipitation Experiments Conducted on the Leachate

3.2.1. Effect of the KMnO_4 Dosage

The Eh–pH diagrams of Zn and Mn are shown in Figure 7, which indicates the thermodynamic stability areas of the chemical species of Zn and Mn in an aqueous solution. These diagrams were obtained using the process calculation software of HSC chemistry version 6.0 (Outokumpu Technology, Helsinki, Finland) by choosing Zn or Mn as the main element and selecting the other element and fluoride (F) as the coexisting elements, with O and H at a temperature of 298 K and a pressure of 1 Pa. The molarities of Zn, Mn, and F were set as their concentrations in the leachate (i.e., 0.820 mol/L, 0.592 mol/L, and 4 mol/L, respectively). The upper and lower stability limits of water are indicated by the dotted lines in the Eh–pH diagrams. When the solution pH is between 2 and 6, increases in the redox potential cause (1) the Zn ions in the solution to exist as soluble $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ and remain ionic, but (2) the Mn ions to oxidize to insoluble MnO_2 and precipitate; this suggests that Zn and Mn ions can be separated via oxidation treatment. When the pH is higher than 6, however, increases in the redox potential cause the Zn and Mn ions in the solution to oxidize and form ZnMn_2O_4 . This phenomenon prevents the effective separation of Zn and Mn ions, and negatively affects the grade and recovery of the precipitation product MnO_2 .

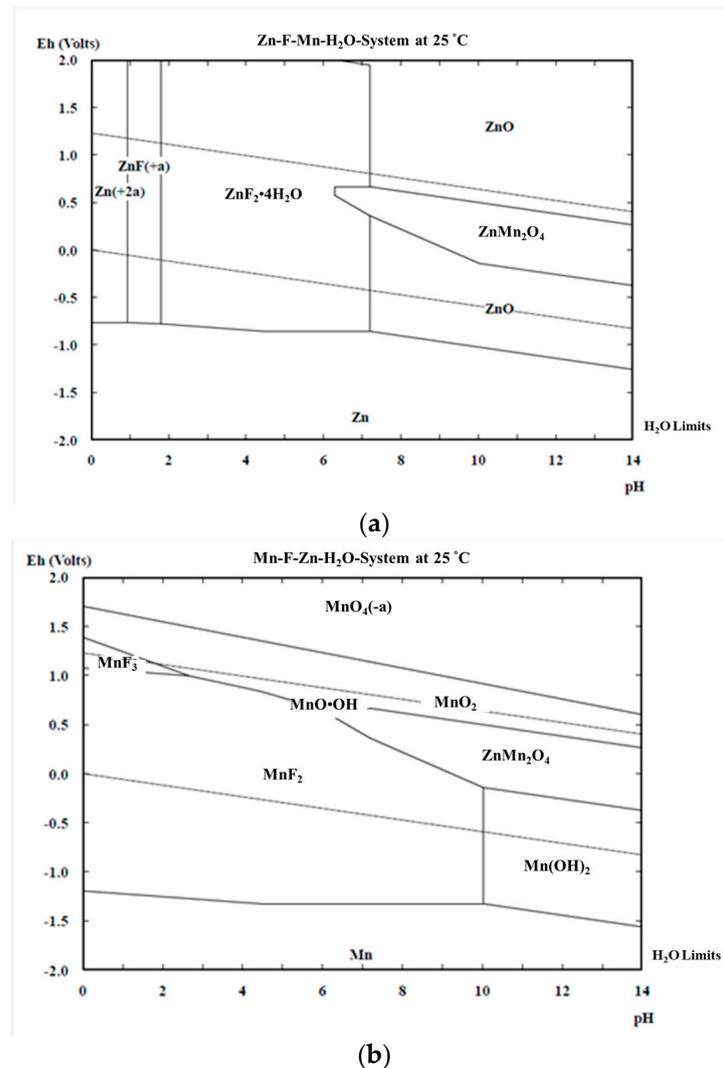


Figure 7. Eh–pH diagrams for the (a) Zn–F–Mn–H₂O and (b) Mn–F–Zn–H₂O systems (molarity of Zn: 0.820 mol/L, molarity of Mn: 0.592 mol/L, molarity of F: 4 mol/L, temperature: 298 K, and pressure: 1 Pa).

In this study, the electrode powder of spent alkaline batteries was leached using 4 M HF, and a leachate with a pH of approximately 3.0 was produced. Therefore, the oxidant KMnO_4 was added to the leachate directly without adjusting the pH, which caused the Mn ions in the leachate to react with KMnO_4 and form a MnO_2 precipitate. The relevant reaction equation is presented in Equation (4). This reaction prevents the formation of Zn–MnO, and thus facilitates the separation between Zn and Mn when the redox potential increases.



The effects of the KMnO_4 dosage on the precipitation efficiencies of Zn and Mn in the HF leachate are illustrated in Figure 8. The experimental settings were as follows: HF leachate volume = 50 mL, pH = 3.0, and KMnO_4/Mn ion molar ratio = 0.1:1–0.85:1. Sattar et al. used KMnO_4 to precipitate Mn in the leachate of spent lithium-ion batteries [23]. They conducted an experiment under the following optimal conditions: temperature = 298 K, reaction time = 60 min, and stirring velocity = 300 rpm. In this experiment, when the KMnO_4/Mn ion molar ratio was 0.1:1, the precipitation efficiencies of Zn and Mn were 0.38% and 14.49%, respectively. As the KMnO_4 dosage increased, the precipitation efficiency of Mn also increased. When the KMnO_4/Mn ion molar ratio was 0.5:1, the precipitation efficiencies of Zn and Mn were 2.37% and 97.43%, respectively. When the KMnO_4/Mn ion molar ratio increased beyond 0.5:1, the precipitation efficiency of Mn did not increase substantially. Thus, the optimal KMnO_4/Mn ion molar ratio was 0.5:1.

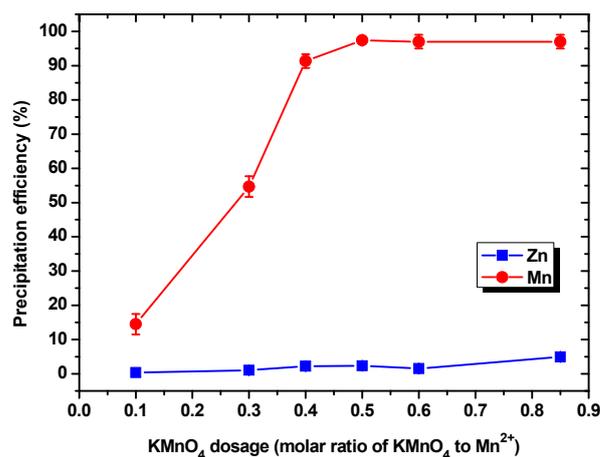


Figure 8. Effects of the KMnO_4 dosage on the precipitation efficiencies of the Zn and Mn in the leachate obtained via the HF leaching of the electrode powder (experimental conditions—leachate volume: 50 mL, pH: 3.0, precipitation temperature: 298 K, precipitation time: 60 min, and stirring velocity: 300 rpm).

3.2.2. Characterization of the Products Recovered after the Precipitation Experiments

Most of the Mn ions in the leachate were oxidized to MnO_2 and selectively precipitated after the addition of KMnO_4 . The XRD crystal-phase analysis result for the precipitate recovered after solid–liquid separation is illustrated in Figure 9. The recovered precipitate mostly contained MnO_2 in the form of $\alpha\text{-MnO}_2$. The XPS analysis result for the recovered precipitate is illustrated in Figure 10. Significant peaks at binding energies of 284.6 eV (C 1s), 528.2 eV (O 1s), 641.4 eV (Mn 2p_{2/3}), 653.2 eV (Mn 2p_{1/3}), 1018.6 eV (Zn 2p₃), and 1042.05 eV (Zn 2p₁) were detected. C 1s was attributable to the carbon tape used for the adhesion of the powder sample in the XPS analysis. The results indicated the existence of O, Mn, and Zn in the recovered precipitate. The grade of MnO_2 and the Mn recovery of the recovered precipitate were 91.68% and 39.07%, respectively. The main impurity in the recovered MnO_2 was Zn, with a content of 2.21%. The experimental result displayed in Figure 8 indicates that the addition of KMnO_4 to the leachate resulted in a slight decrease in the quantity of Zn ions as MnO_2 formed via oxidation. Yang et al. [24]

and Maneechakr et al. [25] have noted that MnO_2 forms via oxidative precipitation because KMnO_4 addition leads to high activity. Such MnO_2 can be used as an adsorbent to adsorb the divalent positive ions of solutions. In addition, Rashid et al. [26] indicated that MnO_2 can adsorb Zn ions from solutions. Thus, the Zn ions in the leachate were adsorbed by the precipitated $\alpha\text{-MnO}_2$, which caused the grade of MnO_2 to decrease.

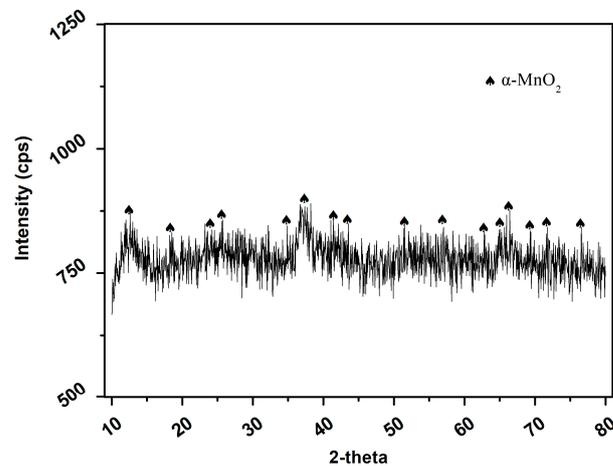


Figure 9. XRD analysis result for the recovered precipitate obtained via the addition of KMnO_4 to the leachate (experimental conditions— KMnO_4 dosage (molar ratio of KMnO_4 to Mn ions): 0.5:1, leachate volume: 50 mL, pH: 3.0, precipitation temperature: 298 K, precipitation time: 60 min, and stirring velocity: 300 rpm).

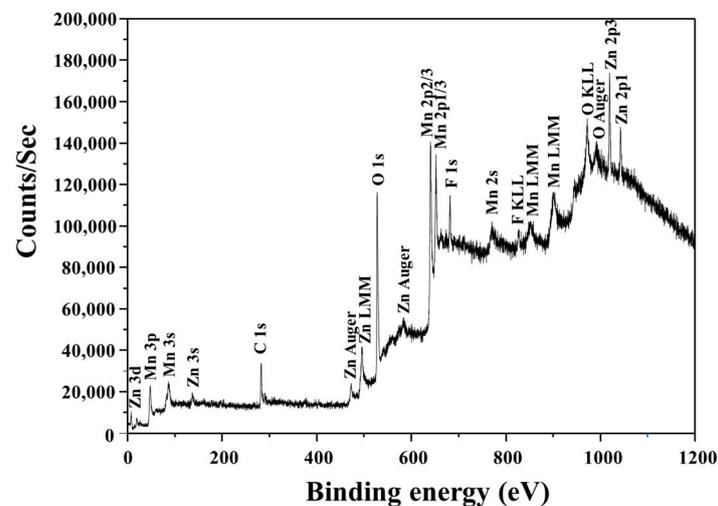


Figure 10. XPS analysis result for the recovered precipitate obtained via the addition of KMnO_4 to the leachate (experimental conditions— KMnO_4 dosage (molar ratio of KMnO_4 to Mn ions): 0.5:1, leachate volume: 50 mL, pH: 3.0, precipitation temperature: 298 K, precipitation time: 60 min, and stirring velocity: 300 rpm).

The remaining leachate mainly consisted of Zn, fluoride, and potassium ions. The remaining leachate was dehydrated using the evaporation method to remove water, and a solid precipitate was recovered. The XRD crystal-phase analysis result for the recovered solid precipitate is shown in Figure 11. This solid precipitate mostly contained two types of Zn compounds: ZnF_2 and KZnF_3 . In addition, two types of Mn compounds, $\text{K}_2\text{Mn}_4\text{O}_9$ and K_3MnO_4 , were also identified. The XPS analysis result for the recovered solid precipitate is illustrated in Figure 12. Significant peaks at binding energies of 284.6 eV (C 1s), 528.2 eV (O 1s), 682.2 eV (F 1s), 641.4 eV (Mn 2p_{2/3}), 653.2 eV (Mn 2p_{1/3}), 1018.6 eV (Zn 2p₃), and 1042.05 eV (Zn 2p₁) were detected. C 1s was attributable to the carbon tape

used for the adhesion of the powder sample in the XPS analysis. The results indicated the existence of O, F, Mn, and Zn in the recovered precipitate. The aforementioned results were in agreement with those obtained by Guo et al. [27] and Huang et al. [28] when synthesizing ZnF_2 compounds. The formation of ZnF_2 was based on deposition, during which the Zn and F ions were combined and settled out when the water was evaporated. $KZnF_3$ formed when $KMnO_4$ was used for oxidative precipitation because the potassium ions remaining in the liquid reacted with ZnF_2 . The grade of ZnF_2 was 97.98%, with a Zn recovery of 96.15%. The main impurity in the recovered ZnF_2 was Mn with a content of 1.26%, because Mn ions could not be completely removed from the leachate when they were precipitated using the oxidative precipitation method. Thus, when ZnF_2 was recovered using the evaporation method, a small number of Mn ions bonded with potassium ions to form $K_2Mn_4O_9$ and K_3MnO_4 , which reduced the overall grade of ZnF_2 .

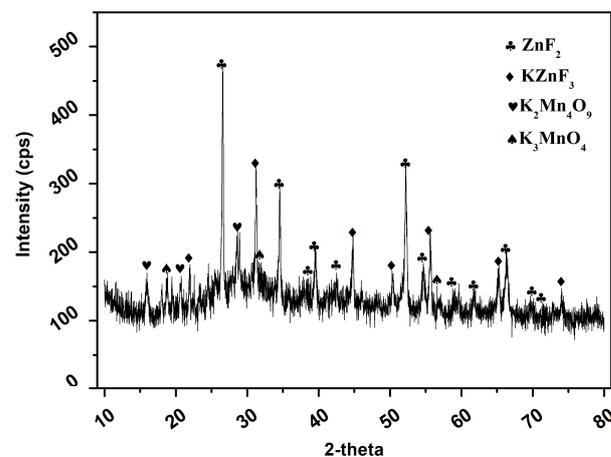


Figure 11. XRD analysis result for the solid precipitate recovered via evaporation from the remaining leachate obtained using $KMnO_4$ precipitation (experimental conditions— $KMnO_4$ dosage (molar ratio of $KMnO_4$ to Mn ions): 0.5:1, leachate volume: 50 mL, pH: 3.0, precipitation temperature: 298 K, precipitation time: 60 min, and stirring velocity: 300 rpm).

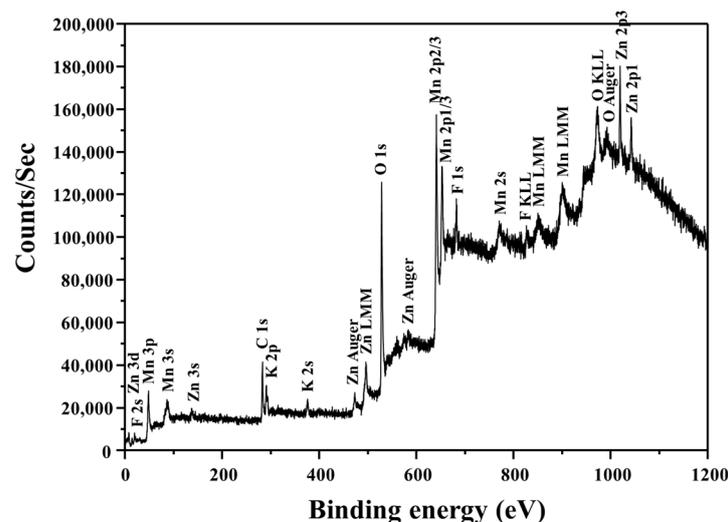


Figure 12. XPS analysis result for the solid precipitate recovered via evaporation from the remaining leachate obtained using $KMnO_4$ precipitation (experimental conditions— $KMnO_4$ dosage (molar ratio of $KMnO_4$ to Mn ions): 0.5:1, leachate volume: 50 mL, pH: 3.0, precipitation temperature: 298 K, precipitation time: 60 min, and stirring velocity: 300 rpm).

3.3. HF Releaching Experiments for the Leaching Residual

3.3.1. Effect of the HF Concentration on the Leaching Efficiency of Mn in the Leaching Residue

The leaching residue obtained after HF leaching primarily contained Mn and carbon, with Mn mainly existing in the forms of MnO_2 and Mn_2O_3 . The optimal Mn leaching efficiency (39.94%) obtained in the HF leaching experiments indicated that the amount of Mn in the leaching residue accounted for approximately 60% of that in the original electrode powder. Moreover, the results of the HF leaching experiments indicated that when the liquid–solid ratio was 10 mL/g, HF could leach and extract Mn from the electrode powder of spent alkaline batteries. Thus, we performed releaching experiments on the leaching residue by using HF to separate the Mn and carbon in this residue. The effect of the HF concentration on the leaching efficiency of Mn in the leaching residue of the electrode powder is displayed in Figure 13. The experimental conditions were as follows: leaching residue = 0.9 g, HF concentration = 1–5 M, liquid–solid ratio = 10 mL/g, leaching time = 60 min, leaching temperature = 298 K, and stirring velocity = 300 rpm. When the HF concentration was 1 M, the leaching efficiency of Mn was 65.9%. As the HF concentration increased, the leaching efficiency of Mn increased. When the HF concentration reached 2 M, the leaching efficiency of Mn was 99.08%, and the leaching efficiency did not increase substantially with a further increase in the HF concentration. Thus, the optimal HF leaching concentration was 2 M.

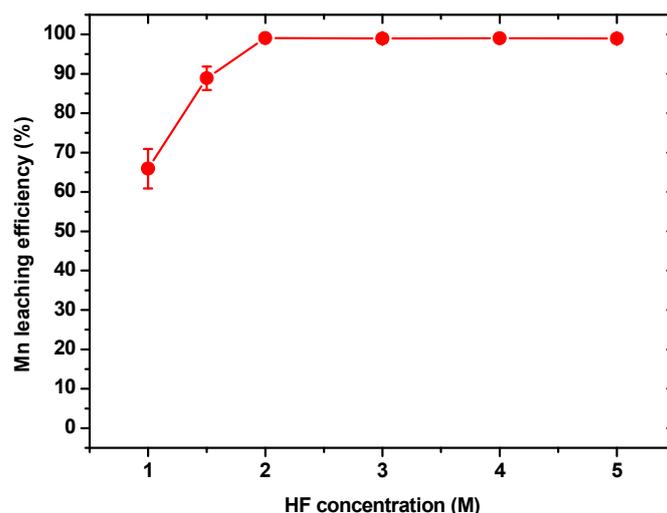


Figure 13. Effect of the HF concentration on the leaching efficiency of Mn in the HF leaching residue of the electrode powder (experimental conditions—leaching residue amount: ~0.9 g, liquid–solid ratio: 10 mL/g, leaching time: 60 min, leaching temperature: 298 K, and stirring velocity: 300 rpm).

3.3.2. Effect of the Liquid–Solid Ratio on the Leaching Efficiency of Mn in the Leaching Residue

The effect of the liquid–solid ratio on the leaching efficiency of Mn in the leaching residue of the electrode powder is illustrated in Figure 14. The experimental settings were as follows: leaching residue = 0.9 g, liquid–solid ratio = 5–20 mL/g, HF concentration = 2 M, leaching time = 60 min, leaching temperature = 298 K, and stirring velocity = 300 rpm. When the liquid–solid ratio was 5 mL/g, the leaching efficiency of Mn was 49.46%. As the liquid–solid ratio increased, the leaching efficiency of Mn also increased. When the liquid–solid ratio reached 10 mL/g, the leaching efficiency of Mn was 99.08%, and the leaching efficiency did not increase substantially with a further increase in the liquid–solid ratio. Therefore, the optimal liquid–solid ratio was 10 mL/g.

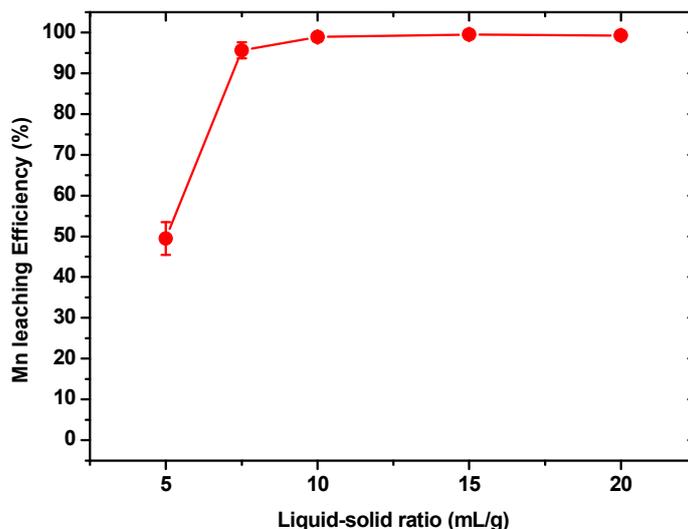


Figure 14. Effect of the liquid–solid ratio on the leaching efficiency of Mn in the leaching residue of the electrode powder (experimental conditions—leaching residue amount: ~0.9 g, HF concentration: 2 M, leaching time: 60 min, leaching temperature: 298 K, and stirring velocity: 300 rpm).

3.3.3. Effect of the Leaching Time on the Leaching Efficiency of Mn in the Leaching Residue

The effect of the leaching time on the leaching efficiency of Mn in the leaching residue of the electrode powder is illustrated in Figure 15. The experimental conditions were as follows: leaching residue = 0.9 g, leaching time = 5–60 min, HF concentration = 2 M, liquid–solid ratio = 10 mL/g, leaching temperature = 298 K, and stirring velocity = 300 rpm. When the leaching time was 5 min, the leaching efficiency of Mn was 77.26%. As the leaching time increased, the leaching efficiency of Mn also increased. When the leaching time reached 15 min, the leaching efficiency of Mn was 99.08%, and the leaching efficiency did not increase substantially with a further increase in the leaching time. Therefore, the optimal leaching time was 15 min.

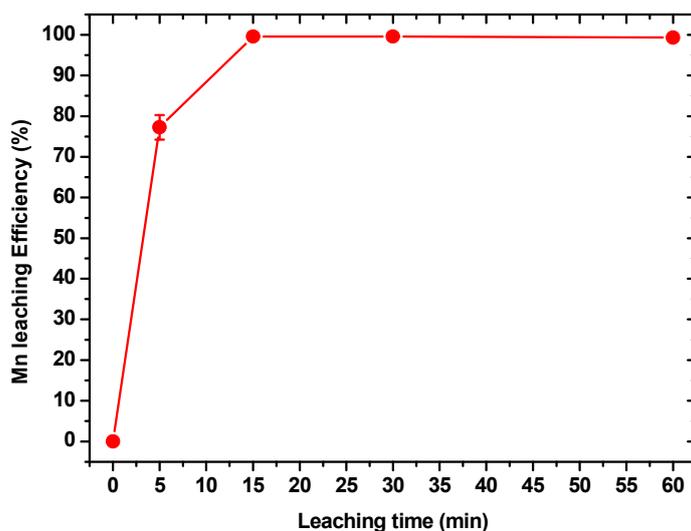


Figure 15. Effect of the leaching time on the leaching efficiency of Mn in the leaching residue of the electrode powder (experimental conditions—leaching residue amount: ~0.9 g, HF concentration: 2 M, liquid–solid ratio: 10 mL/g, leaching temperature: 298 K, and stirring velocity: 300 rpm).

The forgoing HF re-leaching experiments indicated that the optimal re-leaching conditions were a HF concentration of 2 M, a liquid–solid ratio of 10 mL/g, and a leaching time of 15 min. These conditions produced Mn leaching efficiencies of 99.08%.

3.3.4. Characterization of the Products Recovered after the Releaching Experiments

The leachate obtained after releaching and solid–liquid separation mostly contained Mn and fluoride ions. This leachate was dehydrated using the evaporation method to recover a solid precipitate from the leachate. The XRD crystal-phase analysis result for the aforementioned solid precipitate is depicted in Figure 16. The recovered solid precipitate mainly contained $\text{MnF}_2 \cdot 4\text{H}_2\text{O}$ and Mn_2F_5 . The XPS analysis result for the recovered precipitate is illustrated in Figure 17. Significant peaks at binding energies of 284.6 eV (C 1s), 528.2 eV (O 1s), 682.2 eV (F 1s), 641.4 eV (Mn 2p_{2/3}), 653.2 eV (Mn 2p_{1/3}), 1018.6 eV (Zn 2p₃), and 1042.05 eV (Zn 2p₁) were detected. C 1s was attributable to the carbon tape used for the adhesion of the powder sample in the XPS analysis. The results indicated the existence of O, F, Mn, and Zn in the recovered precipitate. Bandemehr et al. [29] indicated that when MnF_2 and MnF_3 are mixed, they react with each other to form Mn_2F_5 . Therefore, the recovery of MnF_2 via the evaporation method resulted in the formation of Mn_2F_5 , as indicated by the XRD analysis result for MnF_x in this study. The formation of MnF_2 and Mn_2F_5 was the same as that of ZnF_2 , during which the Mn and F ions were combined and settled out when the water was evaporated. The grade of MnF_x was 94.20% and the Mn recovery was 59.46%. The main impurity in the recovered MnF_x was Zn with a content of 1.97%, because ZnO was not completely leached at the optimal Zn and Mn leaching selectivity during the releaching experiments. Thus, the leaching residue contained a small quantity of ZnO that was leached out with Mn after HF releaching. When MnF_x was recovered via the evaporation method, a small number of Zn ions bonded with fluoride ions to form ZnF_2 , which reduced the overall grade of MnF_x . The XRD crystal-phase analysis result for the releaching residue, which mostly contained carbon powder, is depicted in Figure 18. The grade of the carbon powder was 98.68%, with a recovery of 100%. The main impurity in the recovered carbon powder was Mn, with a content of 1.32%, due to a small amount of Mn in the leaching residue that was not completely leached out in the releaching process.

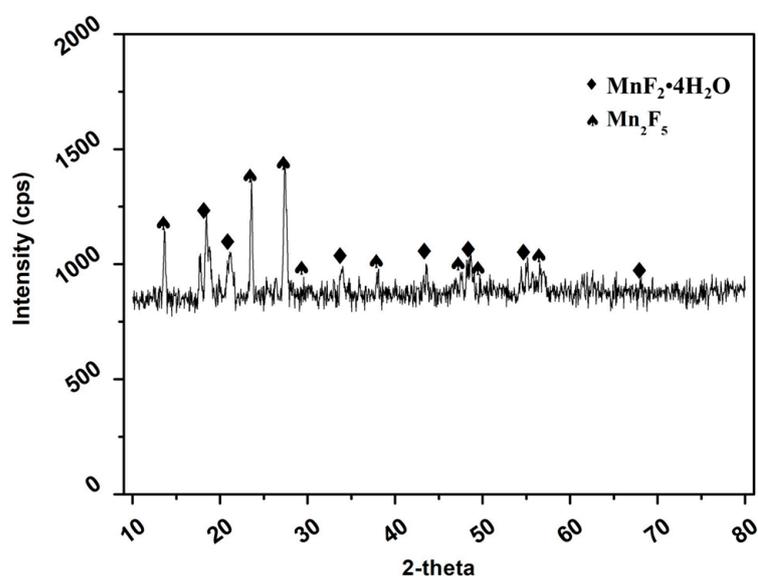


Figure 16. XRD analysis result for the solid precipitate recovered via evaporation from the leachate obtained in the HF releaching process (experimental conditions—leaching residue amount: ~0.9 g, HF concentration: 2 M, liquid–solid ratio: 10 mL/g, leaching time: 15 min, leaching temperature: 298 K, and stirring velocity: 300 rpm).

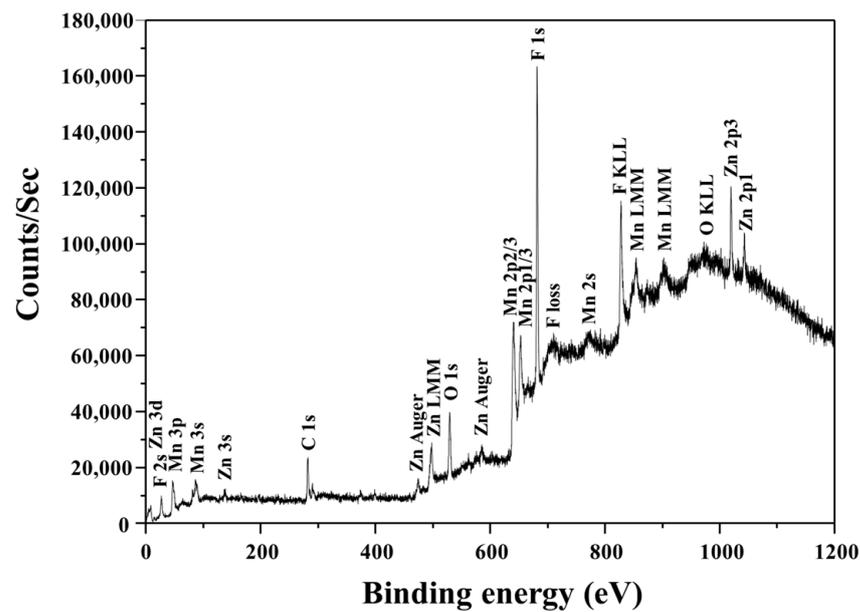


Figure 17. XPS analysis result for the solid precipitate recovered via evaporation from the leachate obtained in the HF leaching process (experimental conditions—leaching residue amount: ~0.9 g, HF concentration: 2 M, liquid–solid ratio: 10 mL/g, leaching time: 15 min, leaching temperature: 298 K, and stirring velocity: 300 rpm).

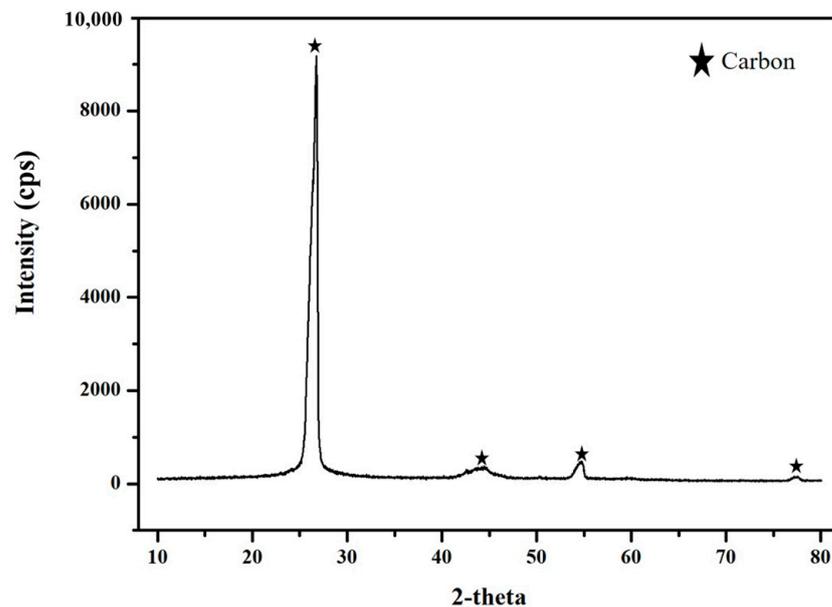


Figure 18. XRD analysis result for the leaching residue obtained in the HF leaching process (experimental conditions—leaching residue amount: ~0.9 g, HF concentration: 2 M, liquid–solid ratio: 10 mL/g, leaching time: 15 min, leaching temperature: 298 K, and stirring velocity: 300 rpm).

Based on the above experiments and results, the material balance of the proposed procedure for the treatment of 1 kg of electrode powder of spent alkaline batteries is presented in Figure 19.

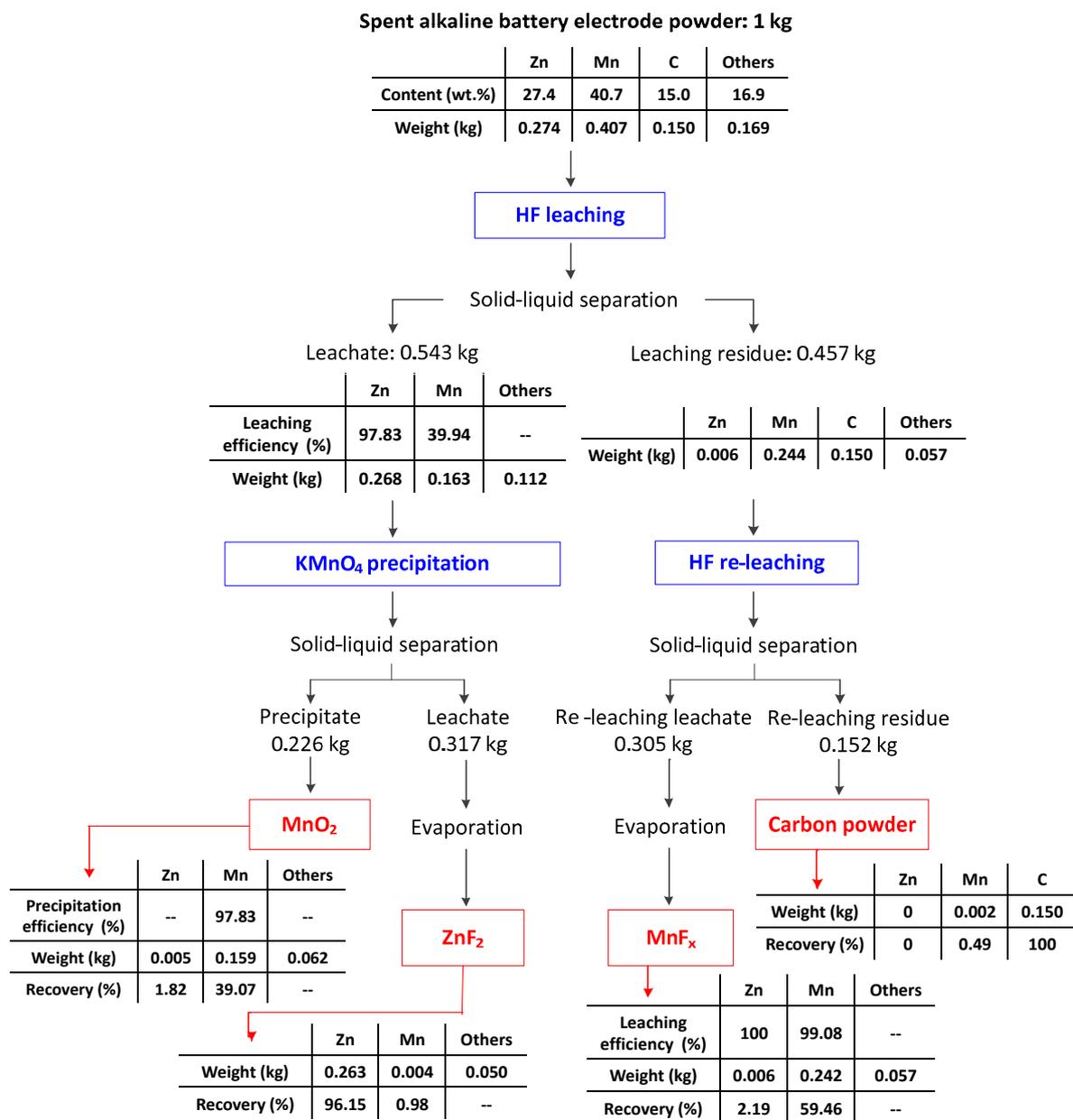
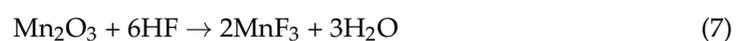
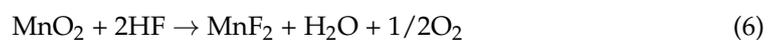


Figure 19. Material balance of the proposed procedure for the treatment of 1 kg of electrode powder of spent alkaline batteries.

3.4. Features and Future Perspective of the Proposed Procedure

In this study, the purpose of applying two-step HF leaching in the proposed procedure is to achieve the leaching selectivity for Zn and Mn in the electrode powder of spent alkaline batteries to recover their fluorides. The chemical reactions of Zn (mainly ZnO) and Mn (mainly MnO₂ and Mn₂O₃) in the electrode powder with HF can be expressed as follows:



The HF molarity for Mn leaching is higher than that for Zn leaching. In addition, the amount of Mn (40.71 wt.%) in the electrode powder is also more than that of Zn (27.36 wt.%). Therefore, less HF can fully leach out Zn, whereas more HF is needed to fully leach out Mn. Certainly, one-step leaching using more HF can be applied to fully leach out both Mn and Zn simultaneously, followed by evaporation or oxidation precipitation to recover them. However, when applying evaporation subsequently, fluorides of Mn and Zn coexist in the recovered solid so that they cannot be separated. In contrast, when applying oxidation precipitation subsequently, all of the Mn can be precipitated as MnO_2 , whereas Zn ions remain in the leachate and thus they can be separated. However, no Mn can be recovered as Mn fluorides. Consequently, two-step leaching was adopted in the proposed procedure. In the first step of leaching, less HF ($4 \text{ M} \times 5 \text{ mL/g} = 20 \text{ mmol/g}$) was applied to leach out all Zn and part of the Mn (ca. 40%). This is the reason why the leaching efficiency of Mn was low in the first step of leaching. The Mn was recovered as MnO_2 via the oxidation precipitation treatment; this was followed by recovering the Zn as ZnF_2 via evaporation. In the second step of leaching, less HF ($2 \text{ M} \times 10 \text{ mL/g} = 20 \text{ mmol/g}$) was able to leach out the rest of Mn (ca. 60%). The Mn was recovered as MnF_x via evaporation. Part of the Mn had been leached out in the first step of leaching and thus the leaching efficiency of Mn was high in the second step of leaching.

On the other hand, HF is used as the leaching agent in the proposed procedure. Although HF is a detrimental chemical, HF is an indispensable chemical reagent that is still used in many industrial processes, such as the etching of silicon wafers or glass components, and the cleaning of stainless steel. The reason why HF is utilized in the proposed procedure is that HF plays a key role in providing fluoride ions that recover the products of ZnF_2 and MnF_x . If other acids were used as the leaching agent, Zn and Mn in the electrode powder of spent alkaline batteries could not be recovered as their fluorides. Specifically, the concentration of HF used in the proposed procedure is 2–4 M, which is a diluted HF solution compared to a concentrated one (ca. 28.4 M of a 49% HF solution with a density of 1.15 g/cm^3). Nowadays, ZnF_2 and MnF_x are produced using chemical reagents as the raw materials and HF is still needed for their production. The procedure proposed in this work demonstrates the feasibility of recovering them from the electrode powder of spent alkaline batteries, which is beneficial to achieving a circular economy. In addition, it is thought that the concept demonstrated in this work might possess the potential to be applied to recover metal fluorides from other metal-containing wastes. On the other hand, the purpose of this work is to propose an approach able to recover Zn and Mn as their fluorides (ZnF_2 and MnF_x) from the electrode powder of spent alkaline batteries. The performances of the final products might be lower than those produced using chemical reagents due to their lower purity. For practical applications, which might require high purity, the further purification of the final products is needed.

4. Conclusions

In this study, a novel procedure was developed for comprehensively recovering ZnF_2 , $\text{MnF}_{x(x=2,3)}$, MnO_2 , and carbon powder from the electrode powder of spent alkaline batteries. Firstly, HF leaching was conducted on the electrode powder of spent alkaline batteries. Secondly, KMnO_4 was introduced into the leachate to precipitate Mn ions in order to recover MnO_2 . Subsequently, the water content in the leachate was evaporated to recover ZnF_2 . Finally, the leaching residue was re-leached using HF, and the water content of the obtained leachate was then evaporated to recover MnF_x and carbon powder. The following results were obtained:

- (1) The HF leaching experiments conducted on the electrode powder indicated that under the optimal conditions of a HF concentration of 4 M, a leaching time of 15 min, and a liquid–solid ratio of 5 mL/g, the leaching efficiencies of Zn and Mn were 97.83% and 39.94%, respectively, and the optimal leaching selectivity for Zn and Mn was achieved.
- (2) The KMnO_4 precipitation experiments performed in order to precipitate the Mn ions in the leachate indicated that, when KMnO_4 with a dosage ($\text{KMnO}_4/\text{Mn ion molar}$

ratio) of 0.5:1 was added to the leachate, the precipitation efficiency of the Mn ions reached 97.43%. The grade and Mn recovery of the recovered α -MnO₂ were 91.68% and 39.07%, respectively. After removing the water content from the leachate via evaporation, ZnF₂ and KZnF₃ with a grade and Zn recovery of 97.98% and 96.15%, respectively, were recovered.

- (3) The HF leaching experiments on the leaching residue obtained in the HF leaching experiments indicated that, under the optimal conditions of a HF concentration of 2 M, a leaching time of 15 min, and a liquid–solid ratio of 10 mL/g, the leaching efficiency of Mn was 99.08%. After removing the water content in the leachate via evaporation, MnF_x, including MnF₂·4H₂O and Mn₂F₅, with a grade and Mn recovery of 94.20% and 59.46%, respectively, was recovered. The residual of the re-leaching process was carbon powder.

The method proposed in this paper enables the effective recovery of Zn and Mn from the electrode powder of spent alkaline batteries in the forms of ZnF₂ and MnF_x.

Author Contributions: Conceptualization, L.-P.W.; methodology, L.-P.W.; investigation, W.-T.H., Y.-J.C., Y.-F.C. and I.-C.L.; writing—original draft preparation, L.-P.W.; writing—review and editing, P.S., H.Z. and M.K.; supervision, L.-P.W. and P.S.; project administration, L.-P.W. and P.S.; funding acquisition, L.-P.W., P.S., M.K. and H.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was financially supported by the NTUT-TU Joint Research Program under Grant No. NTUT-TU-111-02, and Matching Fund between Thammasat University and the National Taipei University of Technology under Grant No. MF 3/2565, and in part by USTB-NTUT Joint Research Program (grant number TW201909, NTUT-USTB-108-06) and the R.O.C. Ministry of Science and Technology under Grant No. MOST 110-2221-E-027-038.

Data Availability Statement: The data are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Takamura, T. Primary Batteries—Aqueous Systems. Alkaline Manganese–Zinc. *Encycl. Electrochem. Power Sources* **2009**, 28–42. [CrossRef]
2. Ministry of Environment Executive Yuan, R.O.C. Taiwan. Available online: <https://cdx.moenv.gov.tw/CDX/main.aspx> (accessed on 6 May 2021).
3. Sadeghi, S.M.; Helena, J.J.; Soares, M.V.M. A critical updated review of the hydrometallurgical routes for recycling zinc and manganese from spent zinc-based batteries. *Waste Manag.* **2020**, *113*, 342–350. [CrossRef]
4. Sayilgan, E.; Kukrer, T.; Civelekoglu, G.; Ferella, F.; Akcil, A.; Veglio, F.; Kitis, M. A review of technologies for the recovery of metals from spent alkaline and zinc–carbon batteries. *Hydrometallurgy* **2009**, *97*, 158–166. [CrossRef]
5. Belardi, G.; Lavecchia, R.; Medici, F.; Piga, L. Thermal treatment for recovery of manganese and zinc from zinc–carbon and alkaline spent batteries. *Waste Manag.* **2012**, *32*, 1945–1951. [CrossRef]
6. Hu, X.; Robles, A.; Vikström, T.; Väänänen, P.; Zackrisson, M.; Ye, G. A novel process on the recovery of zinc and manganese from spent alkaline and zinc-carbon batteries. *J. Hazard. Mater.* **2021**, *411*, 124928. [CrossRef]
7. Shin, S.-M.; Kang, J.-G.; Yang, D.-H.; Kim, T.-H.; Sohn, J.-S. Comparison of Acid and Alkaline Leaching for Recovery of Valuable Metals from Spent Zinc-carbon Battery. *Geosystem Eng.* **2008**, *10*, 21–26. [CrossRef]
8. Sayilgan, E.; Kukrer, T.; Yigit, N.; Civelekoglu, G.; Kitis, M. Acidic leaching and precipitation of zinc and manganese from spent battery powders using various reductants. *J. Hazard. Mater.* **2010**, *173*, 137–143. [CrossRef]
9. De Michelis, I.; Ferella, F.; Karakaya, E.; Beolchini, F.; Vegliò, F. Recovery of zinc and manganese from alkaline and zinc-carbon spent batteries. *J. Power Sources* **2007**, *172*, 975–983. [CrossRef]
10. Sadeghi, S.M.; Vanpeteghem, G.; Neto, I.F.F.; Soares, H.M.V.M. Selective leaching of Zn from spent alkaline batteries using environmentally friendly approaches. *Waste Manag.* **2017**, *60*, 696–705. [CrossRef]
11. Nogueira, C.; Margarido, F. Selective process of zinc extraction from spent Zn–MnO₂ batteries by ammonium chloride leaching. *Hydrometallurgy* **2015**, *157*, 13–21. [CrossRef]
12. Salgado, A.L.; Veloso, A.M.; Pereira, D.D.; Gontijo, G.S.; Salum, A.; Mansur, M.B. Recovery of zinc and manganese from spent alkaline batteries by liquid–liquid extraction with Cyanex 272. *J. Power Sources* **2003**, *115*, 367–373. [CrossRef]
13. Ubaldini, S.; Fornari, P.; Massidda, R.; Michelis, I.D.; Ferella, F.; Vegliò, F. Mn–Zn Recovery From Wastes By Hydrometallurgical Applications. In Proceedings of the 11th International Mineral Processing Symposia, Antalya, Turkey, 21–23 October 2008.

14. Zhou, L.; Huang, F.; Dou, B.; Li, Y.; Ye, R.; Wang, H.; Xu, S. Sensitization effect between Ln^{3+} ions in zinc fluoride glasses for MIR applications. *Ceram. Int.* **2019**, *45*, 10640–10645. [[CrossRef](#)]
15. Huang, F.; Guob, Y.; Tiana, Y.; Xu, S.; Zhanga, J. Intense 2.7 μm emission in Er^{3+} doped zinc fluoride glass. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2017**, *179*, 42–45. [[CrossRef](#)]
16. Sharma, Y.; Surana, S.; Dubedi, R.; Joshi, V. Spectroscopic and radiative properties of Sm^{3+} doped zinc fluoride borophosphate glasses. *Mater. Sci. Eng. B* **2005**, *119*, 131–135. [[CrossRef](#)]
17. Nazabal, V.; Poulain, M.; Olivier, M.; Pirasteh, P.; Camy, P.; Doualan, J.-L.; Guy, S.; Djouama, T.; Boutarfaia, A.; Adam, J. Fluoride and oxyfluoride glasses for optical applications. *J. Fluor. Chem.* **2012**, *134*, 18–23. [[CrossRef](#)]
18. Gastev, S.; Hoffman, K.; Kaveev, A.; Reeves, R.; Sokolov, N. Laser spectroscopy of epitaxial manganese and zinc fluoride films on silicon. *J. Cryst. Growth* **2004**, *268*, 536–542. [[CrossRef](#)]
19. Jones, L.F.; Raftery, J.; Teat, S.J.; Collison, D.; Brechin, E.K. Manganese (III) fluoride as a new synthon in Mn cluster chemistry. *Polyhedron* **2005**, *24*, 2443–2449. [[CrossRef](#)]
20. Hou, X.; Zhang, X.; Ma, Q.; Tang, X.; Hao, Q.; Cheng, Y.; Qiu, T. Alloy Engineering in Few-Layer Manganese Phosphorus Trichalcogenides for Surface-Enhanced Raman Scattering. *Adv. Funct. Mater.* **2020**, *30*, 1910171. [[CrossRef](#)]
21. Ayres, D.C.; Hellier, D.G. *Dictionary of Environmentally Important Chemicals*; CRC Press: Boca Raton, FL, USA, 1997; p. 195, ISBN 0-7514-0256-7.
22. Belardia, G.; Balliranob, P.; Ferrini, M.; Lavecchiac, R.; Medicic, F.; Pigac, L.; Scoppettuoloc, A. Characterization of spent zinc-carbon and alkaline batteries by SEM-EDS, TGA/DTA and XRPD analysis. *Thermochim. Acta* **2011**, *526*, 169–177. [[CrossRef](#)]
23. Sattar, R.; Ilyas, S.; Bhatti, H.N.; Ghaffar, A. Resource recovery of critically-rare metals by hydrometallurgical recycling of spent lithium ion batteries. *Sep. Purif. Technol.* **2019**, *209*, 725–733. [[CrossRef](#)]
24. Yang, H.; Tang, X.; Luo, X.; Li, G.; Liang, H.; Snyder, S. Oxidants-assisted sand filter to enhance the simultaneous removals of manganese, iron and ammonia from groundwater: Formation of active MnO_x and involved mechanisms. *J. Hazard. Mater.* **2021**, *415*, 125707. [[CrossRef](#)] [[PubMed](#)]
25. Maneechakr, P.; Mongkollertlop, S. Investigation on adsorption behaviors of heavy metal ions (Cd^{2+} , Cr^{3+} , Hg^{2+} and Pb^{2+}) through low-cost/active manganese dioxide-modified magnetic biochar derived from palm kernel cake residue. *J. Environ. Chem. Eng.* **2020**, *8*, 104467. [[CrossRef](#)]
26. Rashid, M.; Ejaz, M. Adsorption studies of ultra-trace concentrations of zinc on manganese dioxide from aqueous solutions. *Int. J. Radiat. Appl. Instrumentation. Part A. Appl. Radiat. Isot.* **1986**, *37*, 501–504. [[CrossRef](#)]
27. Guo, Y.; Wuttk, S.; Vimont, A.; Datur, M.; Lavalle, J.C.; Teinz, K.; Kemnitz, E. Novel sol-gel prepared zinc fluoride: Synthesis, characterisation and acid-base sites analysis. *J. Mater. Chem.* **2012**, *22*, 14587–14593. [[CrossRef](#)]
28. Huang, B.; Hong, J.-M.; Chen, X.-T.; Yu, Z.; You, X.-Z. Mild solvothermal synthesis of KZnF_3 and KCdF_3 nanocrystals. *Mater. Lett.* **2005**, *59*, 430–433. [[CrossRef](#)]
29. Bandemehr, J.; Zimmerhofer, F.; Ivlev, S.I.; Pietzonka, C.; Eklund, K.; Karttunen, A.J.; Huppertz, H.; Kraus, F. Syntheses and Characterization of the Mixed-Valent Manganese (II/III) Fluorides Mn_2F_5 and Mn_3F_8 . *Inorg. Chem.* **2021**, *60*, 12651–12663. [[CrossRef](#)]

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