

Article

Advances in the Sustainable Production of Fertilizers from Spent Zinc-Based Batteries

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Abstract: Wastes from spent batteries are a secondary source of raw materials. To ensure this, it is mandatory to design sustainable and low-cost processes. In the case of alkaline and zinc–carbon-based batteries, the high content of Zn and Mn makes them of interest in the development of fertilizers. The main objective of this research is to study the fertilizers production from spent zinc-based batteries, using sulfuric acid, citric acid (CIT) and glycine (GLY) solutions as leaching agents. Leaching with glycine at alkaline pHs shows a high selectivity of Zn over Mn, whereas the use of citric and sulfuric solutions leads to recoveries of Zn and Mn. Solutions with the highest Zn recoveries were tested in sand columns. Commercial ZnSO₄ heptahydrate was used as a control. For sulfuric acid, two solutions (H₂SO₄ 2M and 0.25M) were used. The elution of leached Zn and Mn in sand columns depended on the solution added. The Zn-Mn-CIT treatment showed a slight but steady increase in the leachates, reaching 70% and 75% of the total leached Zn and Mn, respectively, in the medium term. The Zn-Mn-H₂SO₄ 2M and ZnSO₄ treatments showed a similar behavior in Zn release. Both Zn-Mn-GLY and Zn-Mn-H₂SO₄ 0.25M treatments showed similar amounts of leached Mn in the medium term (77% of total leached Mn), differing in the leached Zn. Solutions from the leaching of spent black mass batteries, especially Zn-Mn-CIT or Zn-Mn-GLY, showed promising behavior as fertilizer from the point of view of Zn and Mn availability as nutrients.

Keywords: fertilizer; waste; black mass; zinc; manganese; citric; glycine



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1. Introduction

The supply of raw materials is essential for the economy of the European Union and its ecological transition, as well as for maintaining and improving the quality of life of its citizens. World metal's demand and price are increasing due to the global trend toward urbanization and industrialization with important negative impacts on the economy and the future of the ecological transition of the European Union. To reduce their foreign demand and the primary raw minerals exploitation, it is necessary to prolong the use of products, specifically through reuse, design for durability, reorientation, disassembly, upgrades, repair and sharing. Nevertheless, at the end of final use, it is necessary to develop eco-friendly, advanced and low-cost technologies to recover materials with high purity.

A battery is a source of electrical energy generated from an electrochemical reaction. Batteries are called primary batteries when the chemical reaction that produces electricity is irreversible. In this case, when all chemical energy is converted into electricity, it is discarded and must be managed as waste. On the other hand, secondary batteries are those

in which the chemical reaction that gives rise to electricity is reversible. Secondary batteries can be recharged and used repeatedly. According to statistics from the European Portable Battery Association (EPBA), a total of 5.8 billion units of portable batteries were placed on the European market by EPBA members in 2020 [1].

In the future, the new European Battery Regulation will ensure that batteries have a low carbon footprint, use the lowest possible content of harmful substances and use fewer raw materials for their fabrication from countries outside of the EU [2]. Furthermore, the new regulation aims for these end-of-life batteries to be collected, reused and recycled to a large extent within Europe [2]. In fact, the European Union Regulation 2023/1542 aims to prevent and reduce the negative impacts of batteries on the environment, as well as ensure that the value chain is safe and sustainable for all batteries, considering, for example, the carbon footprint of battery manufacturing, the ethical sourcing of raw materials and the security of supply, as well as reuse and recycling [2]. Starting 31 December 2025, recycling must achieve at least the following efficiency objectives: (a) recycling of 75% of the average weight of lead–acid batteries; (b) recycling of 65% of the average weight of lithium batteries; (c) recycling of 80% of the average weight of nickel–cadmium batteries; and (d) recycling of 50% of the average weight of other end-of-use batteries [2]. To achieve this, it is necessary to promote research and development of new recycling and treatment technologies that are profitable and environmentally friendly [3,4].

Alkaline and zinc–carbon batteries are portable primary batteries commonly used in household electronic gadgets, still accounting for 70% of the portable batteries. Due to their short useful life, a large number of end-of-life portable primary batteries are generated every year. Spent alkaline and zinc–carbon batteries contain valuable materials such as Zn and Mn compounds, Cu, graphite or steel that need to be recovered [5]. In another instance, old batteries can also contain toxic substances [6], whose discharge into the environment could cause soil or groundwater contamination. Today, commercial alkaline and zinc–carbon batteries placed on the market do not contain toxic elements such as Cd, Hg and Pb. However, the trace amount of these elements in the black mass originates mainly from old batteries that were present in the current waste stream. Therefore, from both economic and environmental points of view, the spent alkaline and zinc–carbon batteries need to be collected and managed appropriately. Recycling of spent alkaline and zinc–carbon portable batteries starts with their collection, followed by mechanical pre-treatment (sieving, shredding or magnetic separation), to produce several material fractions, namely, a brass fraction, a steel scrap fraction and a black mass fraction join to plastic films and paper pieces. The metal scrap fraction can be recovered in metal foundries, while the black mass composed mainly of Zn and Mn oxides with small quantities of graphite [7] can be treated with different processes to recover both metals. In general, the recovery of Zn and Mn from black mass can be achieved by hydrometallurgical or pyrometallurgical methods [8]. In a typical hydrometallurgical process, the black mass is subjected to acid leaching (mainly sulfuric acid), by which Zn and Mn are converted into soluble compounds such as ZnSO_4 and MnSO_4 [9]; afterward, Mn and Zn can be recovered separately as compounds by selective precipitation or as metals by purification, followed by electrowinning [10]. On the other hand, in a typical pyrometallurgical process, ZnO in the black mass is subjected to carbothermic reduction. At high temperatures, Zn is volatilized and condensed as ZnO in the flue dust and, meanwhile, Mn is concentrated in the solid residue [11]. The collected ZnO can be used as the feeding material at a Zn smelter to produce metallic Zn, whereas MnO can be used as feeding material for ferromanganese production or used as construction aggregates [5,6,11]. Instead of the benefits of current technologies for the recovery of Zn and Mn, there are important points that need to be improved [12]. Pyrometallurgical processes require high temperatures and are extremely energy-intensive. In addition, these processes may emit dust and release harmful gases that require cleaning and a dust collection system to prevent air pollution [13], and graphite, a critical raw material, is lost by combustion. Even though hydrometallurgical processes are characterized by lower environmental impact and energy consumption relative to

pyrometallurgical processes, the Zn and Mn end products achieved by hydrometallurgical treatment cannot be used directly in the production of new batteries, which constitutes an important drawback. More efficient separation processes are needed to recover Zn and Mn with high purity in order to return the metals directly back into the production of new batteries or other advanced uses. In addition, a fraction of Zn in the form of mixed refractory oxides is not recovered [8]. For all these reasons, it is interesting to develop technologies to obtain, perhaps not the pure metal Zn or Mn, but intermediate compounds that could be used in applications such as, for example, the production of fertilizers [14]. Globally, Zn deficiency is the most common micronutrient deficiency and affects a wide range of soil types in many different agricultural areas. Zn is essential in plant nutrition and is a key component of several enzyme systems, where it contributes to energy production, protein synthesis and growth regulation. Soils with very low concentrations of available Zn cause severe yield reduction and serious crop deficiencies that are not adequate to meet human nutritional requirements. In fact, low levels of Zn in food crops are believed to be responsible for Zn deficiency in humans, which is a common nutritional problem [15]. Biofortification through fertilization (application to soils, seeds and/or leaves) aims to increase the natural content of bioavailable nutrients in crop plants without changing their genetic composition and providing essential micronutrients to humans while increasing the quality of food products and agricultural yields. In addition to traditional Zn sources (such as Zn sulfate, Zn chloride, Zn oxide, Zn nitrate or Zn oxy-sulfate), the fertilizer market now offers complexes and natural or synthetic chelates whose use has increased considerably in recent years. Currently, for Zn, chelating and complexing agents such as EDTA (ethylenediaminetetraacetate), DTPA (diethylenetriaminepentaacetate), HEDTA (hydroxyethyl-ethylenediaminetriacetate), aminolignosulfonate, polyhydroxyphenylcarboxylate, EDDS (ethylenediamine disuccinate), lignosulfonate, humates, citrate, gluconates and heptagluconates are used [16].

In recent years, new methods have emerged to recover metals from minerals or waste that use low temperatures and eco-friendly technologies [17–19]. Recently, glycine, one of the simplest amino acids, has emerged as an efficient and environmentally friendly leaching agent of metals from oxide minerals and wastes [17,20–22]. Compared to other amino acids, glycine is relatively inexpensive. In alkaline conditions (above pH = 10), most of the glycine exists as an anion $\text{H}_2\text{NCH}_2\text{COO}^-$ and forms a strong complex with Cu (I), Cu (II), Co (II) or Zn (II). Additionally, amino acids have been introduced as natural chelating agents that increase the solubility and availability of micronutrients [23]. The effectiveness of these molecules as fertilizers depends on factors inherent in the molecule itself (stability constant) and on the properties of the soil in which they are applied, mainly its pH. The main characteristics that are sought in these molecules for them to be effective are that chelate is water soluble and stable against hydrolysis, that it binds easily to soil particles and that it is in a form suitable for the plant to absorb [24]. When the chelating agent gives up the micronutrient, it can resolubilize more of the native soil micronutrient, which is an advantage of these sources over traditional sources. Metal-complexing agents play an important role in the transport of metals from the solid phases of soils to the surface of plant roots. The relative efficiency of applying fertilizers containing complexing agents to crops per unit of micronutrient may be greater than that of applying inorganic sources [25]. However, the costs per unit of micronutrient of applying complexes may be higher [26]. For this reason, direct production of metal–glycine fertilizers by leaching of selected wastes can contribute to a cost reduction that has a wide application. As a first step for the production of fertilizers from spent zinc–carbon and alkaline batteries, the main objective of this research is to compare the behavior in sand columns of the mobility of different Zn and Mn solutions obtained by direct leaching of black mass with sulfuric acid-, citric acid- and glycine-based leaching agents. To achieve this objective, a black mass sample from zinc–carbon and alkaline batteries has been selected and physicochemically characterized. Then, the sample was treated with different leaching agents to extract Zn and/or Mn. Finally, the selected Zn/Mn solutions were used for dissolution kinetics experiments

conducted on sand columns. Column experiments can provide a better understanding of the long-term kinetic behavior of added sources and differentiate the behavior between species or chemical forms.

This objective is directly related to the ecological transition of Europe and to the environmental objectives set out in Regulation (EU) 2020/852 of the European Parliament and of the Council of 18 June 2020 [27]. Additionally, the results of this research will contribute to advancing the circular economy related to the recovery of high-purity metals for use in the same or new advanced technologies, reducing the exploitation of primary raw materials. It is established that the production of metals from secondary sources allows for reducing energy consumption and CO₂ emissions, saving resources (soil and water), reducing the exploitation of deposits, minimizing environmental impact, reducing waste generation and creating an economic benefit. Additionally, it will contribute to the prevention and control of pollution as a result of the development of eco-friendly technologies.

2. Materials and Methods

2.1. Feedstock

The black mass sample (BM) was provided by Envirobat España S.L (Guadalajara, Spain). These were characterized using X-ray diffraction (XRD) and X-ray fluorescence (XRF) at the SCAI (Universidad de Málaga). XRD was performed using a Bruker D8 ADVANCE diffractometer and XRF with an ARL ADVVANT XP + sequential model from THERMO. Electrical conductivity (EC), pH and redox potential (mV) were measured using a sample/distilled water solution (4 g L⁻¹) after stirring for 1 h, using Crison 222, micro pH 2000 (Crison, Barcelona, Spain) and pH 60 DHS equipment (XS Instruments, Carpy, Italy), respectively. The value of the redox potential was measured with the Ag/AgCl electrode. The content of graphite was calculated by thermogravimetric analysis using Labsys Setaram thermogravimetric analyzer. An amount of 20 mg of each sample was heated to 800 °C (heat rate: 15 °C min⁻¹) in air atmosphere (flow rate: 30 mL min⁻¹). The graphite content is calculated as the weight loss percentage between 350 and 800 °C.

2.2. Leaching Experiments

Leaching tests in an acidic medium were performed with 0.25, 0.5, 1.0 and 2 M sulfuric or citric acid solutions. An amount of 25 mL of each solution, together with 2.5 g of BM (mass/volume ratio of 1 g/20 mL), was poured into 250 mL Erlenmeyer flasks, which were then subjected to 250 rpm. The leaching experiments were carried out at room temperature and 60 °C for 2 h. After 2 h, the final leachates were filtered and the solid samples were washed with 25 mL of distilled water to recover any adsorbed metals. Finally, the total Zn and Mn extractions were determined by absorption atomic spectrometry (AAS) using an AAnalyst 400 by Perkin Elmer + software Winlab32 AA 20 flame (Shelton, CT, USA).

Leaching tests in the alkaline medium were performed using glycine at different selected molar ratios (6/1, 8/1 and 10/1), based on the black mass Zn content. An amount of 100 mL of each leaching solution with 1% vol of H₂O₂ and at a pH ranging from 7 to 12, together with 5 g of BM (mass/volume of 1 g/20 mL), were placed in 250 mL Erlenmeyer flasks. The pH of the solutions was adjusted by adding NaOH. Then, the flasks were stirred at 250 rpm at room temperature for 24 h. Once 24 h was approached, the final leachate was filtered and the solid sample was washed twice with 50 mL of acid water (pH ≈ 2.0) and distilled water to recover any metals that may have been adsorbed. Finally, the total Zn and Mn extractions were calculated on the basis of data obtained by absorption atomic spectrometry (AAS) using an AAnalyst 400 by Perkin Elmer + software Winlab32 AA flame.

2.3. Selection of Fertilizer Solutions

For the selection of Zn fertilizer solutions, the Zn content was determined. Three solutions with the highest Zn content using sulfuric, citric and glycine were selected for column experiments. Additionally, for the sulfuric solution, two concentrations were selected to compare the pH effect.

2.4. Column Experiments

Dissolution kinetic experiments were conducted using sand columns. Column experiments can provide a better understanding of the long-term kinetic behavior of added sources and differentiate the behavior between species or chemical forms [28]. The column test carried out was the one described by Milani [28], with some modifications. An amount of 15 cm high columns and 1.5 cm diameter were filled with 25 g of washed sand. The treatment was added and covered with a further 5 g of sand. A 10 mL/h flow of 0.01 M CaCl_2 solution was added from the top of the columns. The leachates were collected in 20 mL portions until a total of 400 mL. The amount of treatment was calculated to provide 5 mg of Zn to each column. The treatments used in this study were as follows: extract obtained from BM and H_2SO_4 2M [Zn-Mn- H_2SO_4 2M]; extract obtained from BM and H_2SO_4 0.25M [Zn-Mn- H_2SO_4 0.25M]; extract obtained from BM and citrate [Zn-Mn-CIT]; extract obtained from BM and glycine [Zn-Mn-GLY] and Zn sulfate heptahydrate (Merck) [ZnSO_4]. For the treatments studied, 3 replicates with a total of 15 columns have been set up. Three replicates per treatment were used, with a total of 15 leach columns. Statistical differences at $p < 0.05$, $p < 0.001$ and $p < 0.0001$ (*, ** and ***, respectively) (LSD test) were presented by different letters. Capital letters indicate the differences between treatments for the same volume of leachate (p -value for each leachate volume is indicated in the Zn-Mn-CIT treatment) and Roman letters indicate the differences between the accumulated Mn for each volume of leachate for the same treatment (p -value for each treatment is indicated at the lowest leachate volume). The evolution of the accumulated leached Mn for each of the treatments was fitted to a logistic model, and the parameters a , b and c of the model have been determined for each of the treatments. The ZnSO_4 treatment did not contribute Mn to the columns.

The concentrations of Zn and Mn in the leachates were quantified using atomic absorption spectrometry (AAAnalyst 900, Perkin Elmer). pH and electrical conductivity (EC) were measured using a Hamilton pH (LP238285, KCl 3M plus glycol electrolyte) and electrical conductivity (COND50, XS Instruments, Carpy, Italy) electrodes, respectively.

The evolution of accumulated leached Zn and Mn for each of the treatments was fitted to the logistic model of the type:

$$\text{leached Zn or Mn concentration} = a / (1 + b e^{(-c x)}) \quad (1)$$

where a is the maximum leached Zn or Mn concentration that the curve reaches when the volume tends to infinity; b and c are parameters indicating the curve gradient, the lower the b -value, the earlier the maximum concentration value is reached and the higher the c -value, the cumulative Zn or Mn concentration reaches high values at lower leached volumes.

3. Results and Discussion

3.1. Black Mass Characterization

The chemical composition of the black mass (BM) is shown in Table 1. The main elements of BM are Mn (37.89%) and Zn (25.45%), followed by K (4.77%), Na (1.91%), Mg (0.472%), Cl (0.569%), Fe (0.379%), S (0.238%), Ni (0.157%) and Ba (0.142%). Additionally, traces of other elements such as Si, Ti, Ca, Al and Cu, among others, were identified. The studied black mass (BM) has a composition similar to other black masses rich in Mn and Zn but with the highest content of both metals [29]. It is important to note that there are no traces of Hg or Cd. This may be because it is a more recent sample and the use of Cd and Hg in these batteries has been prohibited for years.

Table 1. Element content obtained by semiquantitative XRF analysis.

Sample	Element Content (wt%)														
	Mn	Zn	K	Na	Cl	Mg	Fe	S	Ni	Ba	Si	Ti	Ca	Cu	Al
BM	37.89	25.45	4.77	1.91	0.569	0.472	0.379	0.328	0.157	0.142	0.092	0.072	0.048	0.025	0.017

The XRD analysis of BM shows that the most notable crystalline phases are ZnO and pyrolusite (MnO_2), followed by graphite, periclase (MgO), K_2CO_3 and $\text{Al}(\text{OH})_3$. Table 2 shows the pH, Eh, electrical conductivity and graphite content of selected BM. The BM sample shows basic pH (10.83) and low EC ($356 \mu\text{S}/\text{cm}$). The graphite content of BM (6.61%) is slightly higher than those of other black masses [29,30]. This value is lower than that of the black mass of lithium [30,31], but since it is a critical material for the European Union, it would be interesting to study its recovery before or after the leaching of the main elements.

Table 2. Chemical properties and graphite content of black mass (BM).

Sample	Chemical Properties and Graphite Content of BM			
	pH	EC ($\mu\text{S}/\text{cm}$)	$E_{\text{HAg/AgCl}}$ (mV)	Graphite (%)
BM	10.83	356	385	6.61

3.2. Leaching Experiments

Figure 1 shows the percentage of Zn (Figure 1a,b) and Mn (Figure 1c,d) extracted with H_2SO_4 and citric acid solutions at 25 and 60 °C. The recovery of Zn increases with the concentration of sulfuric acid. With 0.25 and 0.5 M, the recovery of Zn increases with increasing temperature. However, the leaching efficiency using 1 M and 2 M sulfuric solutions was not significantly affected when the temperature was increased from 25 °C to 60 °C. The highest Zn recovery (Figure 1) obtained with 2 M sulfuric acid solution at 60 °C (35.68%) is lower than that obtained by other authors [8,32]. The recovery of Zn and Mn in both acidic and basic mediums should be improved, probably through thermal treatment of the black mass, a reduction in particle size, the use of microwave or ultrasound to assist the process and an increase in liquid/solid ratios, temperature and times [8,32].

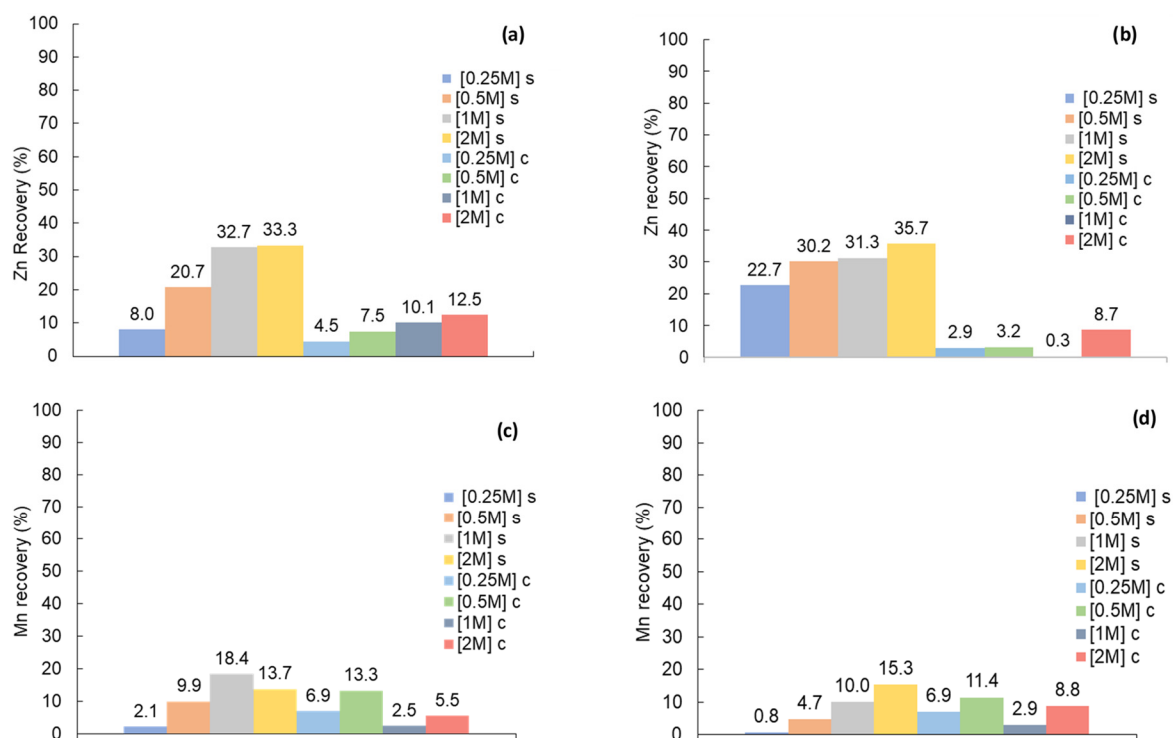


Figure 1. Percentage of Zn (a,b) and Mn (c,d) extracted with H_2SO_4 (named as s) and citric acid (named as c) at 25 °C (a,c) and 60 °C (b,d).

Figure 2 shows the percentage of Zn (Figure 2a) and Mn (Figure 2b) using glycine leaching solutions at different pHs (7–12) and glycine/metal ratios (6:1, 8:1 and 10:1).

Selective leaching of Zn over Mn using glycine leaching agents is observed. Although the final Zn recoveries were not high, it can be observed that there is a clear preference for glycine to form complexes with Zn compared to Mn, which is insoluble at alkaline pHs and was almost imperceptible in the final leachates (Figure 2). Glycine has been previously used for the recovery of metals from different minerals and wastes [17,20,21]. Studies show the great potential of glycine as a selective leaching agent. However, process optimization studies are still necessary to achieve higher recoveries.

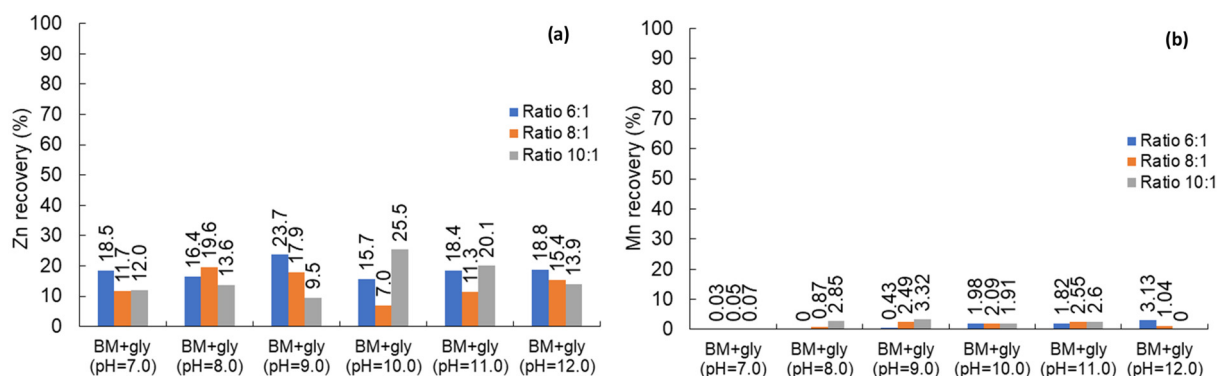


Figure 2. Percentage of Zn (a) and Mn (b) using glycine leaching solutions at different pHs and glycine/metal ratios.

It can be concluded that glycine leaching performed at alkaline pH and room temperature is selective for the recovery of Zn over Mn from spent black mass batteries. The highest Zn and Mn recoveries from spent black mass batteries have been obtained using sulfuric acid solutions.

3.3. Column Experiments

3.3.1. Leached Zn in Sand Columns

Figure 3 shows the evolution of the accumulated leached Zn in percentages with respect to the added Zn in the sand columns. The obtained values revealed distinct trends for the added treatments. The results indicated that the 0.25 M Zn-Mn-H₂SO₄ treatment achieved the highest percentages of total leached Zn at 400 mL, accounting for more than 98% of the leached Zn with respect to the total Zn added to the columns. This percentage was statistically higher ($p < 0.05$) than the rest of the treatments, among which there were no significant differences in the total leached Zn, which reached percentages of between 72.68 and 77.12% (Zn-Mn-CIT and ZnSO₄, respectively).

The trend shown with the Zn-Mn-H₂SO₄ 0.25 M treatment indicated that although the percentage of accumulated leached Zn was similar to other treatments (ZnSO₄, Zn-Mn-H₂SO₄ 2M and Zn-Mn-GLY) up to 60 mL leached, the accumulated leached Zn increased significantly ($p < 0.05$ or $p < 0.001$) from this leached volume onwards. The percentage of Zn leached accumulated at 80 mL reached 80% of the total Zn, stabilizing at leachate volumes above 160 mL (Figure 3), indicating a large increase in leached Zn in these collected volumes and a much slower and steady Zn leaching afterward. From a leached volume of 80 mL, the release of Zn in the leachate followed a linear correlation with a slope of 0.037 (cumulative leached Zn = $64.03 + 0.037 \times \text{leached volume}$; $p\text{-value} = 0.0000$, $R^2 = 93.02\%$).

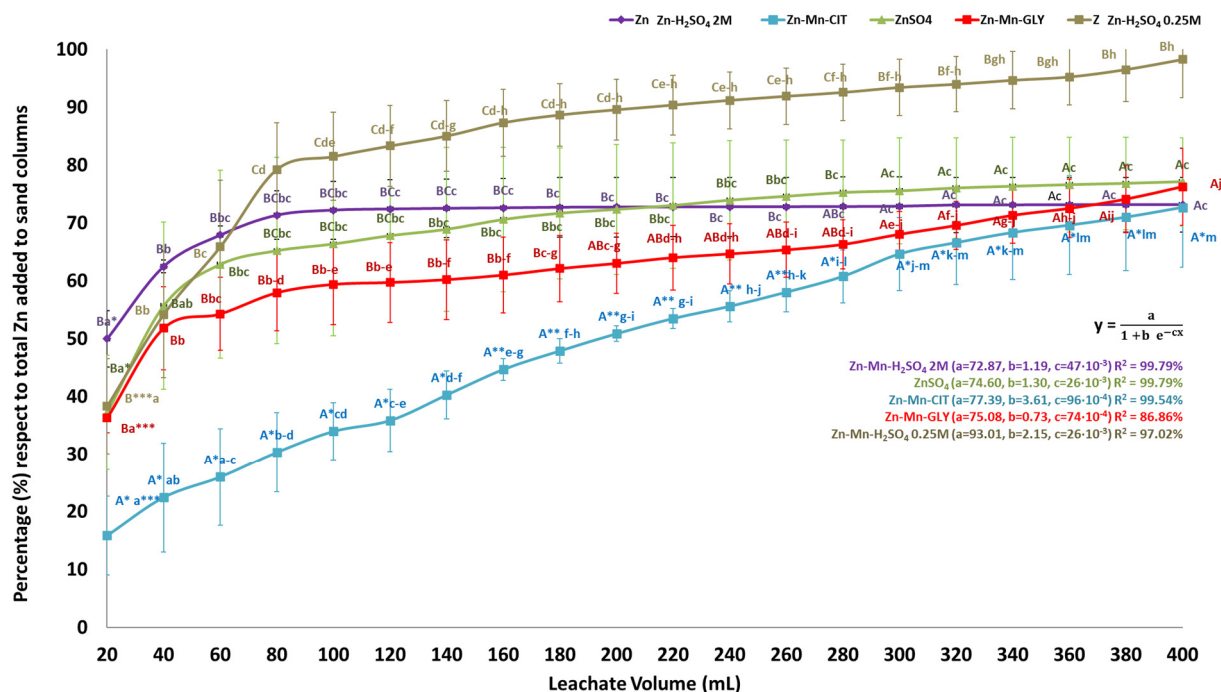


Figure 3. Accumulated leached Zn in percentages, with respect to the Zn added to the columns, for each volume of leachate collected. Extract obtained with H₂SO₄ 2M [Zn-Mn-H₂SO₄ 2M, purple]; extract obtained with H₂SO₄ 0.25M [Zn-Mn-H₂SO₄ 0.25M, brown]; extract obtained with citrate [Zn-Mn-CIT, blue]; extract obtained with glycine [Zn-Mn-GLY, red] and Zn sulfate heptahydrate (Merck) [ZnSO₄, green]. The vertical line at each of the data points represents the standard deviation from the mean. Statistical differences at $p \leq 5\%$ (LSD test) between sources for the same leached volume are indicated by capital letters and differences between the percentages of Zn leached at different volumes, for the same source, are indicated by lower case letters. ***, **, and * significant at 0.01%, 0.1%, and 5% levels.

The percentage of accumulated leached Zn did not show significant differences between the treatments of ZnSO₄ and Zn-Mn-H₂SO₄ 2M in any of the accumulated volumes. However, the values of the logistic model parameters showed slightly different behavior, with the Zn leaching of the ZnSO₄ treatment being much more progressive than that of the Zn-Mn-H₂SO₄ 2M treatment. The statistical analysis also showed a progressive increase in leached Zn with ZnSO₄ treatment up to 60 mL leachate accumulated and a further slight significant increase at 280 mL. However, the Zn concentrations accumulated with Zn-Mn-H₂SO₄ 2M remained without significant differences from 120 mL onwards.

The Zn-Mn-GLY treatment also released a substantial amount of Zn (51.82%) in the first 40 mL of leachate from the sand columns. From this volume onwards, the release of Zn concentration was more constant, reaching a linear correlation with a slope of 0.055 (accumulated Zn leached = $52.21 + 0.055 \times \text{leached volume}$; $p\text{-value} = 0.0000$, $R^2 = 97.29\%$).

The behavior of the Zn-Mn-CIT treatment is remarkable, as it clearly differs from the rest of the treatments from the first leachate collected. Although the concentration of Zn collected in the first leachate is statistically lower than the concentration of the rest of the treatments, the total amount of Zn collected in the final volume of 400 mL does not differ from most of the treatments (except for Zn-Mn-H₂SO₄ 0.25M). The percentage of Zn leached from this treatment shows a slight but constant increase in each of the leachates collected. The percentage of leached Zn fits a linear correlation with a slope of 0.15 (accumulated leached Zn = $18.61 + 0.15 \times \text{leached volume}$, $p\text{-value} = 0.0000$, $R^2 = 98.00\%$).

3.3.2. Leached Mn in Sand Columns

The Zn-Mn-H₂SO₄ 0.25 M, Zn-Mn-GLY and Zn-Mn-H₂SO₄ 2M treatments achieved the highest percentages of total leached Mn at 400 mL (Figure 4), representing 91.43, 88.15 and 78.16% of the leached Mn with respect to the total Mn added to the columns, respectively. These percentages were statistically higher ($p < 0.05$) than those leached by the Zn-Mn-CIT source, which recovered 53.68% of the added Mn. The evolution of the accumulated leached Mn as a percentage of the total added in the columns is shown in Figure 3. Again, the evolution of the cumulative leached Mn (Figure 3) for each of the treatments was fitted to the logistic model indicated above (Equation (1), Section 2). The results obtained show different trends with respect to the behavior of the added treatments. On the one hand, the treatments Zn-Mn-GLY and Zn-Mn-H₂SO₄ 0.25M show a similar trend with respect to the Mn accumulated throughout the leachates. Initially, a very high release rate occurs, with a total leached percentage of 52.26 and 46.52% (Zn-Mn-GLY and Zn-Mn-H₂SO₄ 0.25M, respectively) in 60 mL of collected volume. A slower and continuous leaching rate is observed in the subsequent volumes. On the other hand, the Zn-Mn-H₂SO₄ 2M treatment shows a very high release rate of Mn in the first leachates, with a percentage practically unchanged thereafter. The parameter values of the logistic model showed a different behavior of this treatment in the first volumes collected, as the lower value of parameter b and the higher value of parameter c indicate a higher Mn leaching. This trend is similar to that shown for Zn release in the leachates; however, in the case of leached Mn, there was no significant difference in the accumulated leached Mn in any case over the leached volume. Finally, the Zn-Mn-CIT treatment shows constant behavior throughout the leachates with respect to Mn release. The percentage of leached Mn fits a linear correlation with a slope of 0.10 (accumulated leached Mn = $16.82 + 0.10 \times$ leached volume, p -value = 0.0000, $R^2 = 96.53\%$).

The use of columns filled with a porous and inert medium, such as washed sand, has recently been used to evaluate the environmental behavior, dissolution kinetics and leaching capacity of different products [28,33–35]. The products tested in the columns formed by the most soluble species (ZnSO₄ and Zn-Mn-H₂SO₄ at both concentrations) released a substantial and rapid amount of Zn and Mn. This behavior is explained by the high solubility of these compounds (solubility of ZnSO₄ at 20 °C: 965 g/L, solubility of MnSO₄ at 20 °C: 700 g/L), with Zn and Mn in the form of Zn²⁺ and Mn²⁺ being carried away by the leachate flow. A basic problem with traditional sources of Zn and/or Mn is the high initial release rate of the nutrient, which can lead to a loss of nutrients and high environmental contamination [36]. In our study with the soluble sources, the amounts of Zn and Mn leached in the medium term (200 mL leached) were very high. The percentages between 91 and 99% of the total recovered Zn (Zn-Mn-H₂SO₄ 0.25M and ZnSO₄ treatments, respectively) and between 76.5% and 99.4% of the total recovered Mn (Zn-Mn-H₂SO₄ 0.25M and Zn-Mn-H₂SO₄ 2M, respectively) were reached in the medium term. This behavior corroborates the high release and leaching loss of Zn and Mn in the medium term with these treatments.

However, the release rates of Zn and Mn obtained with Zn-Mn-CIT were continuous and constant, having leached 70% of Zn and 74.6% of Mn in the medium term. This behavior could be related to the stability constant of the formed complex [36], which allows slow and constant leaching of Zn. According to Norvel [37], the mole fraction of the Zn and Mn complex in solution increases with decreasing pH in the range of 7 to 6.5 in the case of chelated Mn maximum at pH 6. This agrees with the pH values obtained in these leachates, which show a decrease in pH value from the first leachate (7.01) to the last leachate (6.41).

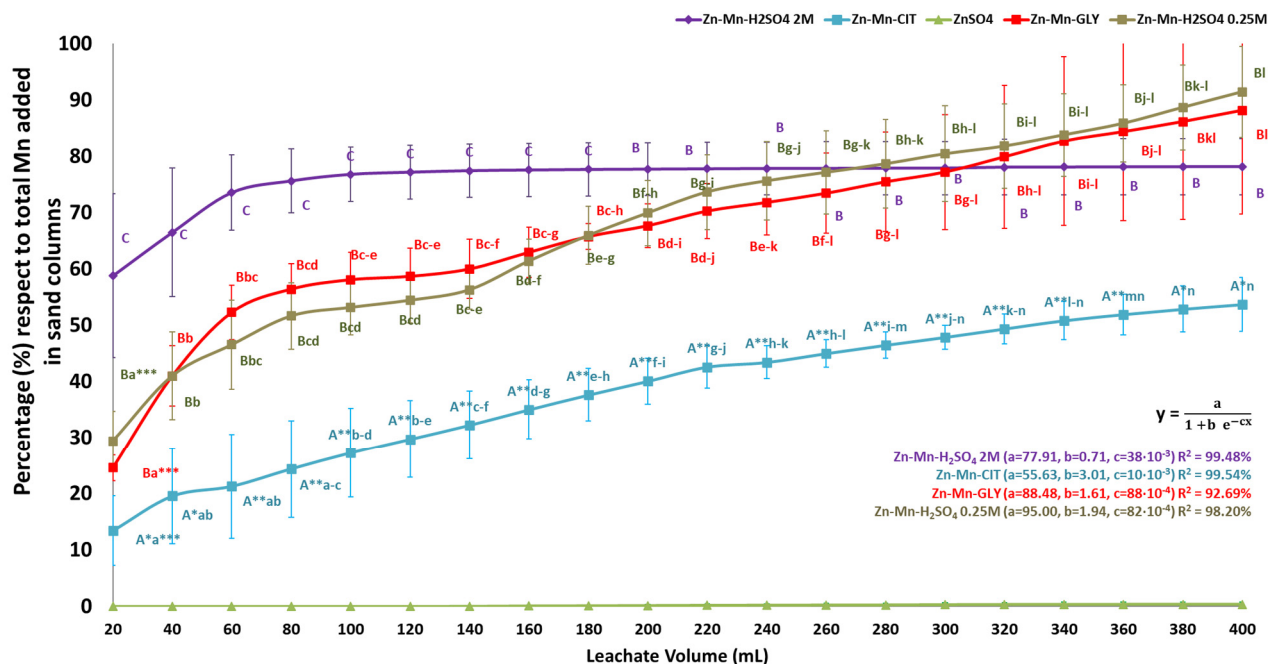


Figure 4. Accumulated leached Mn in percentages, with respect to the Mn added to the columns, for each volume of leachate collected. Extract obtained with H₂SO₄ 2M [Zn-Mn-H₂SO₄ 2M]; extract obtained with H₂SO₄ 0.25M [Zn-Mn-H₂SO₄ 0.25M]; extract obtained with citrate [Zn-Mn-CIT]; extract obtained with glycine [Zn-Mn-GLY] and Zn sulfate heptahydrate (Merck) [ZnSO₄]. The vertical line at each of the data points represents the standard deviation from the mean. Statistical differences at $p < 0.05$, $p < 0.001$ and $p < 0.0001$ (*, ** and ***, respectively) (LSD test) are presented by different letters. Capital letters indicate the differences between treatments for the same volume of leachate (p -value for each leachate volume is indicated at the Zn-Mn-CIT treatment) and roman letters indicate the differences between accumulated Mn for each volume of leachate for the same treatment (p -value for each treatment is indicated at the lowest leachate volume). The evolution of the accumulated leached Mn for each of the treatments was fitted to a logistic model, the parameters a , b and c of the model have been determined for each of the treatments. The ZnSO₄ treatment did not contribute Mn to the columns.

The Zn-Mn-GLY treatment showed intermediate behavior between the more soluble sources and the Zn-Mn-CIT treatment, especially in the Zn leaching study. A Zn release rate was observed in the first leached volumes similar to that of the more soluble sources (reaching, in the short term, 83% of the total leached). In the case of Mn, the release rate observed with this treatment was similar to that of Zn-Mn-H₂SO₄ 0.25M. This behavior could be due to the pH values in the solution, as the values obtained in the leachates ranged from 8.16 in the first leachate to 6.82 in the final collection. According to Norvell [37], Zn²⁺ and Mn²⁺ are more effectively chelated at lower pH in soils and nutrient solutions. However, the long-term behavior of this source shows a similarity to that of the Zn-Mn-CIT source. This behavior may be due to the high stability of the chelate complex [37], which allows a continuous release of nutrients. This slow release of nutrients release improves fertilizer efficiency and reduces losses and potential contamination [38].

3.3.3. pH and Electrical Conductivity of Leachates

The pH and EC values measured in the different leachates collected show an evolution over time (Figure 5A,B). The treatments with extreme initial pH values Zn-Mn-H₂SO₄ 2M and Zn-Mn-GLY with pH values at 20 mL of 1.98 and 8.16, respectively, reach similar values to the rest of the treatments from a collected volume of 220 mL. The pH values of the leachates collected from that volume reached 6.03 and 7.16 (Zn-Mn-H₂SO₄ 0.25M at 380 mL and Zn-Mn-H₂SO₄ 2M at 320 mL, respectively). The EC of the leachates showed

homogeneous values for all treatments and leachate volumes (from 1.90 mS cm^{-1} -Zn-Mn- H_2SO_4 0.25M at 40 mL- to 3.07 mS cm^{-1} -Zn-Mn- H_2SO_4 0.25M at 300 mL-), except for the Zn-Mn-GLY treatment at low collected volumes (up to 80 mL). These values were higher than for the rest of the treatments, reaching 5.9 mS cm^{-1} at 20 mL.

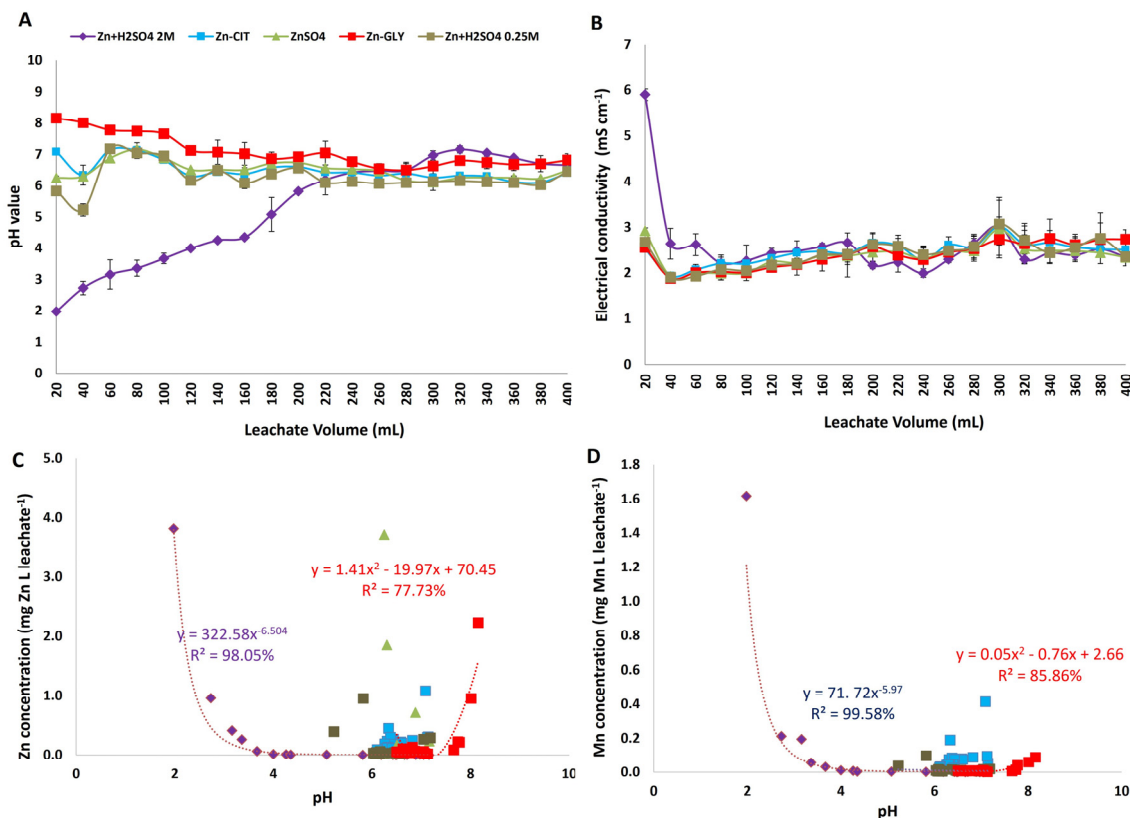


Figure 5. pH (A) and electrical conductivity values (B) measured in the different leachates collected and correlations between pH values and Zn (C) and Mn (D) concentrations in leachates. Extract obtained with H_2SO_4 2M [Zn-Mn- H_2SO_4 2M]; extract obtained with H_2SO_4 0.25M [Zn-Mn- H_2SO_4 0.25M]; extract obtained with citrate [Zn-Mn-CIT]; extract obtained with glycine [Zn-Mn-GLY] and Zn sulfate heptahydrate (Merck) [ZnSO₄]. The vertical line in each of the data points represents the standard deviation from the mean or stand error.

The correlation between the Zn and Mn concentration of each leachate and the pH or EC values only showed remarkable results in the case of the treatments Zn-Mn- H_2SO_4 2M and Zn-Mn-GLY with the pH measured in the extracts. As shown in Figure 5C,D, with the Zn- H_2SO_4 2M treatment, a negative exponential correlation was observed between the concentrations of Zn and Mn of the leachate and the pH value. With this treatment, the concentrations of Zn and Mn in the leachate decreased over the course of the collections, and an increase in the pH value was observed until stable pH values between 6.0 and 7.0 were reached. For the Zn-Mn-GLY treatment, a positive polynomial correlation was observed between the measured Zn and Mn concentrations and the pH value of the leachate. When applying this treatment, the Zn and Mn concentrations in the leachate decreased over the course of the collections, and a decrease in pH value was observed until it reached stable pH values between 6.0 and 7.0.

4. Conclusions

From the findings presented above, the following main conclusions can be drawn:

Glycine leaching performed at alkaline pH and room temperature is selective for the recovery of Zn over Mn from spent black mass batteries. The highest Zn and Mn recoveries from spent black mass batteries have been obtained using sulfuric acid solutions.

Solutions obtained by leaching of black mass from spent Zn-based batteries with sulfuric-, citric- and glycine-based solutions used as fertilizers showed a promising behavior, from the point of view of Zn and Mn nutrient availability, especially when applied as Zn-Mn-CIT or Zn-Mn-GLY complexes.

5. Future Research

The Zn recoveries obtained with experimental conditions used in this research are low compared to those from other studies, which indicates the influence of the starting residue and the need for future treatments to achieve higher recovery values.

To advance in the production of sustainable glycine- and citrate-based fertilizers from spent Zn-based batteries, further studies of their behavior in agricultural soils with different characteristics and their potential environmental risks are necessary.

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