


TECHNICAL COMMUNICATION

# Preparation and Characterization of Manganese and Zinc Oxides Recovered from Spent Alkaline and Zn/C Batteries Using Biogenerated Sulfuric Acid as Leaching Agent

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Manganese, zinc and mixed manganese-zinc oxides were synthesized after a biohydrometallurgical process to recycle alkaline and Zn/C batteries. A mixture of alkaline and Zn/C batteries was leached with biogenerated sulfuric acid. The effect of pulp density, time and use of additives, namely, H<sub>2</sub>O<sub>2</sub> and Na<sub>2</sub>SO<sub>3</sub>, was studied. Using an *S/L* = 0.04 g ml<sup>-1</sup>, 2 h, 5 vol.% H<sub>2</sub>O<sub>2</sub> or 1 wt.% Na<sub>2</sub>SO<sub>3</sub> at 30°C and in one step, 99% Zn and 90–98% Mn were extracted. After leaching, manganese (MnO<sub>x</sub>) and zinc oxides (ZnO) were obtained by sequential precipitation first with KMnO<sub>4</sub> and then with Na<sub>2</sub>CO<sub>3</sub>, recovering 90% Mn and 95% Zn. Additionally, a mixed manganese-zinc oxide was obtained by precipitation with NaOH until pH = 8 (ZM) recovering 28% Mn and 95% Zn. The Mn/Zn ratio was higher for the MnO<sub>x</sub> catalysts. Characterization by x-ray diffraction (XRD) and transmission electron microscopy (TEM) revealed the presence of α-MnO<sub>2</sub> in MnO<sub>x</sub> with globular shape, wurtzite in ZnO oxide with spherical shape and a mixture of ZnO wurtzite and ZnMn<sub>2</sub>O<sub>4</sub> in the ZM sample with platelet-type shapes.

## INTRODUCTION

In many countries of the world, spent batteries are usually disposed of in landfills with the domestic garbage, which increases the risk of releasing hazardous substances and constitutes a waste of resources.<sup>1</sup> Many of the components of the batteries could be recycled, avoiding the release of hazardous substances to the environment and, in addition, providing valuable materials to important products and production processes.<sup>2</sup> Alkaline and Zn/C batteries mainly contain manganese and zinc, which in high concentrations are toxic.<sup>3–5</sup> The Directive 2006/66/EC of the European Parliament and of the Council<sup>6</sup> demands that 50% of battery weight has to be recycled. In addition, according to InfoMine the zinc and manganese price in April 2018 was 3160 USD ton<sup>-1</sup> and 2040 USD ton<sup>-1</sup>, respectively.<sup>7</sup>

Zn consumption has exceeded production in the last years.<sup>8</sup> Although Mn production is sufficient, its consumption is rising because of the increase in

primary and secondary battery consumption.<sup>9</sup> Consequently, secondary sources of Zn and Mn, such as spent alkaline and Zn/C batteries, could be explored.

Pyrometallurgy and hydrometallurgical processes are the two common routes used for battery recycling,<sup>10</sup> the hydrometallurgical process being less expensive.<sup>11</sup> In hydrometallurgical processes, Mn and Zn are typically leached using acidic and reductive media and then Mn and Zn are selectively recycled by simultaneous electrowinning, electrolytic processes, selective precipitation or liquid-liquid extraction.<sup>12–16</sup> One of the most important industrial applications of manganese oxides is oxidation catalysis.<sup>17–19</sup> Likewise, ZnO is widely utilized in applications such as optical and electronic devices, solar cells and gas sensors.<sup>20,21</sup> Additionally, transition-metal oxides (e.g., Mn<sub>2</sub>O<sub>3</sub> and ZnMn<sub>2</sub>O<sub>4</sub>) with relatively higher theoretical capacities have been used to replace the graphite anode of lithium-ion batteries.<sup>22</sup>

One of the aims of this work is to improve the leaching process of a mixture of spent alkaline and Zn/C batteries using biogenerated sulfuric acid, reported in a previous paper,<sup>23</sup> by studying the effect of the solid/liquid ratio, temperature, time and use of additives. Furthermore, the selective recovery and characterization of manganese and zinc oxides, as well as a mixed manganese-zinc oxide, were studied to synthesize materials that could be reused in different technologic applications.

## EXPERIMENTAL

### Battery Pretreatment

Over a hundred spent alkaline and Zn/C batteries (AAA, AA and D size) of different trademarks were collected from the CICPBA Campus in the City of La Plata, Argentina. First, spent batteries were separated and manually dismantled into different parts, such as zinc rolled tins, ferrous scraps, copper caps, carbon rod, plastic films and paper pieces.

The powders from the anode and cathode, which were about 40–64% of the total weight of the dismantled batteries, were mixed, dried, ground by milling and sieved to obtain a mesh size < 200  $\mu\text{m}$ . Before leaching, the powder was first washed with deionized water, dried at 120°C for 24 h and finally calcined in air at 750°C for 4 h.

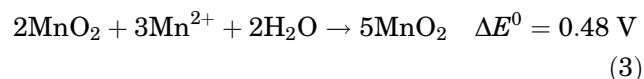
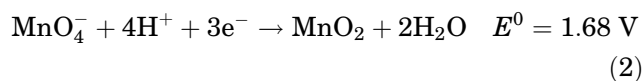
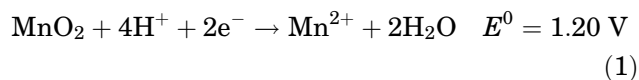
### Leaching Experiments

The leaching experiments were carried out in an Erlenmeyer flask stirred with magnetic agitation. In a typical procedure, a certain amount of battery powder was extracted with 50 ml of biologic sulfuric acid for a certain period of time. The effect of pulp density and time was studied. Additionally, leaching experiments were carried out using  $\text{Na}_2\text{SO}_3$  or  $\text{H}_2\text{O}_2$  as additive to study whether the addition of other reducing agents improves leaching efficiency.

The production of the biogenerated sulfuric acid was described by Falco et al.<sup>24</sup>

### Recovery of Mn and Zn Oxides

After leaching, a manganese oxide ( $\text{MnO}_x$ ) was prepared by the reaction with  $\text{MnO}_4^-$  and  $\text{Mn}^{2+}$  according to the following reactions:



The oxide was prepared as follows: 100 ml of  $\text{KMnO}_4$  0.100 M (anhydrous 99%) was added dropwise to 100 ml of the leaching liquor, and the suspension was stirred at 30°C for 1 h. The following reaction.

The product was filtered, washed with distilled water, dried at 120°C for 24 h, and finally calcined in air at 500°C for 2 h.

After the separation of manganese, 100 ml of 0.100 M  $\text{Na}_2\text{CO}_3$  solution was added dropwise to 100 ml of the remaining solution containing  $\text{Zn}^{2+}$ , and the suspension was stirred at 30°C for 1 h. The final product was filtered, washed with distilled water and dried at 120°C for 24 h. Finally, the solid was calcined in air at 500°C for 2 h to obtain ZnO.

Alternatively, a mixed zinc-manganese oxide (ZM) was synthesized as follows: a 0.100 M NaOH solution was added dropwise to 100 ml of the leaching liquor until reaching pH 8, and the suspension was stirred at 30°C for 1 h. The product was filtered, washed with distilled water and dried at 120°C for 24 h. Finally, the solid was calcined in air at 500°C for 2 h.

A flow sheet of the process is plotted in Fig. 1.

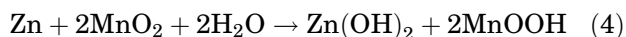
### Powder Characterizations

The composition of the samples was measured in a Varian AA 240 Atomic Absorption spectrophotometer after digestion by the  $\text{HNO}_3$ -HCl (1:3) method. The samples were characterized by x-ray diffraction (XRD) methods using a Philips diffractometer, using Cu  $K\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation at  $0.02^\circ \text{ min}^{-1}$  scanning speed and a counting time of 2 s per step. Transmission electron microscopy (TEM) measurements were performed with a JEOL 100 CXII microscope operated at 100 kV.

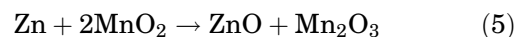
## RESULTS

### Characterization of Spent Batteries

The overall reaction of the alkaline cell during discharge is as follows:<sup>25</sup>



whereas in a Zn/C cell during discharge the following overall reaction occurs:



The results of the chemical analysis of the spent battery powder, without treatment and after being washed and calcined in air at 750°C, are listed in Table I. The main elements are manganese and zinc. Iron, chlorides and potassium were also detected. Potassium and chlorides are derived from the electrolyte. Potassium hydroxide is present in alkaline batteries, whereas ammonium chloride is present in Zn/C batteries.

Preparation and Characterization of Manganese and Zinc Oxides Recovered from Spent Alkaline and Zn/C Batteries Using Biogenerated Sulfuric Acid as Leaching Agent

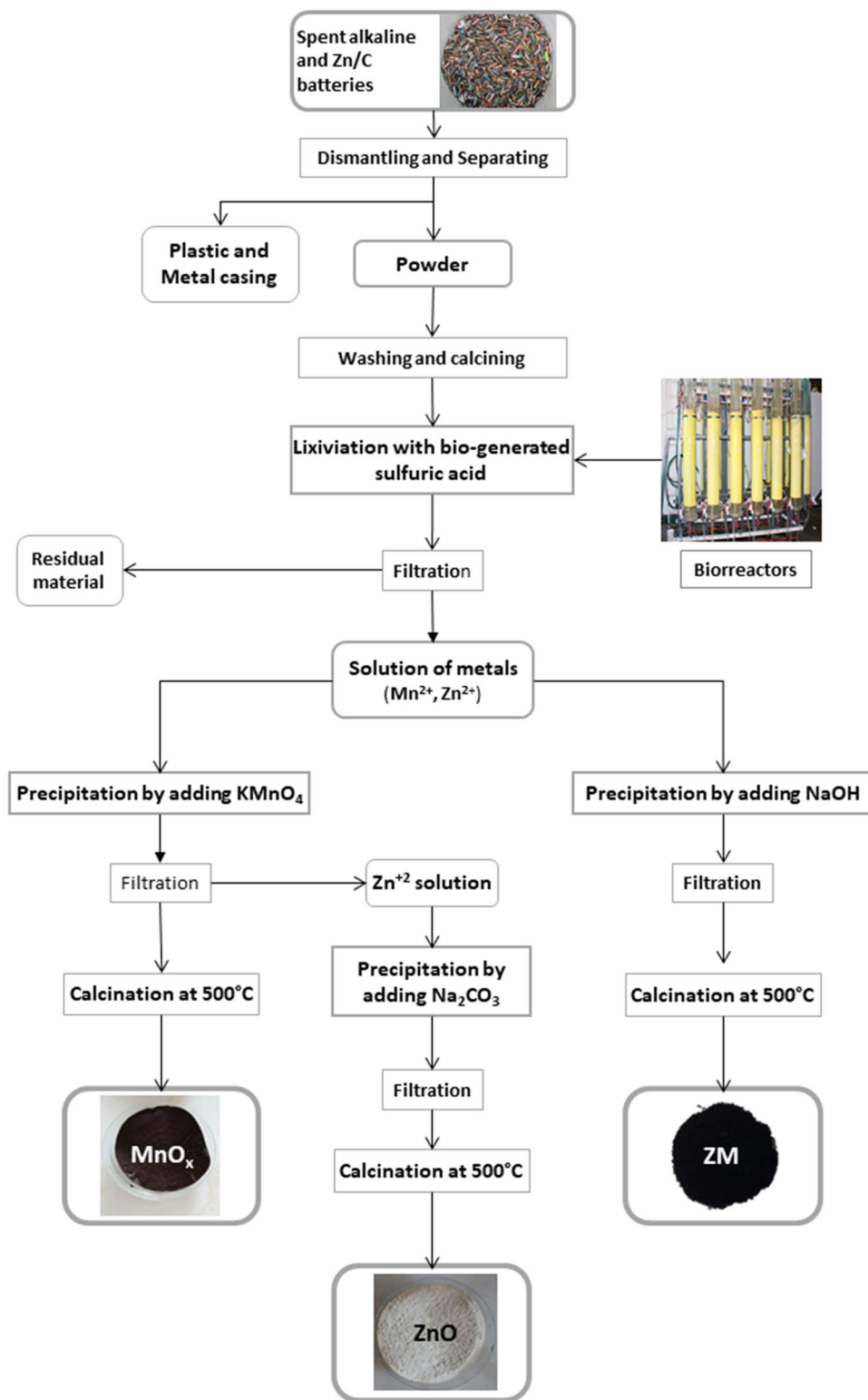


Fig. 1. Flow sheet of the process to recover manganese and zinc oxides from spent batteries.

**Table I. Composition of the mixture of spent alkaline and Zn/C battery powder before and after washing and calcined at 750°C**

Element	Original powder <sup>a</sup> (wt.%)	Washed and calcined <sup>a</sup> at 750°C (wt.%)
Mn	33.0	37.5
Zn	18.5	27.5
Fe	1.1	1.3
K	3.5	0.2
Cl	3.4	0.12

<sup>a</sup>Determination of metal and nonmetal by atomic absorption spectrometry.

For the powder without treatment, these values are in agreement with data reported in the literature for mixtures of batteries in the ranges 30–40 wt.% Mn and 20–25 wt.% Zn.<sup>26,27</sup>

The increase in the Zn and Mn grades in the washed and calcined powder was due to the removal of potassium and chloride during washing and the volatile matter that was driven off from the sample during calcination.

The x-ray diffraction pattern of the original powder (Fig. 2) presents diffraction lines corresponding to graphite C, ZnO wurtzite (JCPDS 36-1451), hetaerolite ZnMn<sub>2</sub>O<sub>4</sub> (JCPDS 71-2499) and hausmannite Mn<sub>3</sub>O<sub>4</sub> (JCPDS 89-4837).

After calcination, the diffraction lines corresponding to ZnO are higher, whereas the peak corresponding to graphite diminishes their intensity, in agreement with the results presented in Table I.

## Leaching Experiments

For all the leaching experiments, the powder of the mixture of the anode and cathode of the spent alkaline and Zn/C batteries used was dried, washed with water and calcined at 750°C.

Taking into account the phases detected by XRD (Fig. 2), the following reactions (including the  $\Delta G^\circ$  form Ref. 28) are inferred to have occurred during leaching:

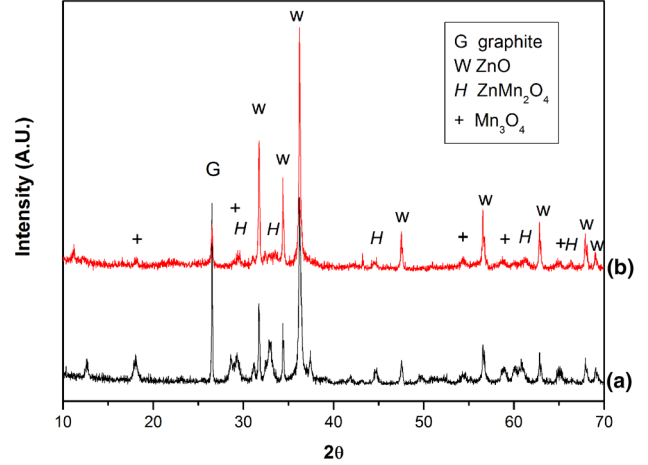
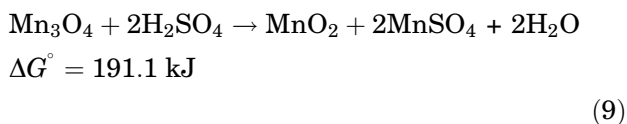
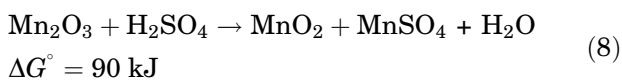
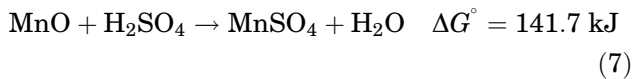
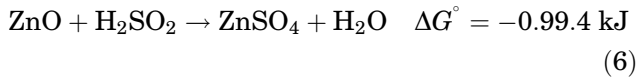
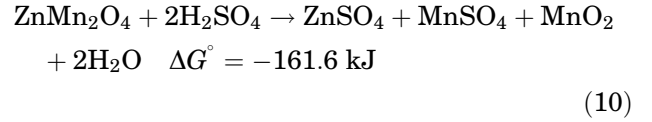


Fig. 2. X-ray diffraction patterns of battery powders: (a) dried at 120°C and (b) washed, dried, and calcined in air at 750°C. (G) graphite; (w) ZnO; (+) Mn<sub>3</sub>O<sub>4</sub>; (H) ZnMn<sub>2</sub>O<sub>4</sub>.



Therefore, a reducing agent is needed to reduce Mn<sup>4+</sup> to Mn<sup>2+</sup>, which is soluble in sulfuric acid.<sup>29</sup> Polythionates species present in the bio generated sulfuric acid could leach MnO<sub>2</sub> according to Eq. 11:

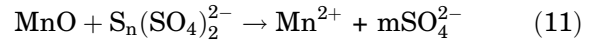


Figure 3a shows the influence of pulp density (solid/liquid ratio, *S/L*) on the leaching efficiency of zinc and manganese using biogenerated sulfuric acid as leaching agent. The extraction of both metals increases when smaller solid/liquid ratios are used. The most selective condition for zinc and manganese extraction was found using 0.04 g ml<sup>-1</sup> solid/liquid ratio.

Figure 3b shows that the zinc and manganese extraction efficiency increases significantly up to 120 min. Beyond 120 min, the extraction efficiency for manganese and zinc is no longer significant.

Even though the biogenerated sulfuric acid has reducing species, and they are the ones responsible for the dissolution MnO<sub>2</sub>, it is evident that their concentration is not enough for efficient leaching. The bio-generated sulfuric acid used in this work is equivalent to 0.10 M sulfuric acid solution plus 0.05 M polythionates.<sup>24</sup>

To increment Mn extraction efficiency, we investigated sulfuric acid leaching in the presence of sodium sulfite and hydrogen peroxide.

As shown in Fig. 3c, the addition of 1 wt.% Na<sub>2</sub>SO<sub>3</sub> to the biogenerated sulfuric acid increases the Zn and Mn extraction efficiency from 90% to 99% and from 37% to 90%, respectively.

Preparation and Characterization of Manganese and Zinc Oxides Recovered from Spent Alkaline and Zn/C Batteries Using Biogenerated Sulfuric Acid as Leaching Agent

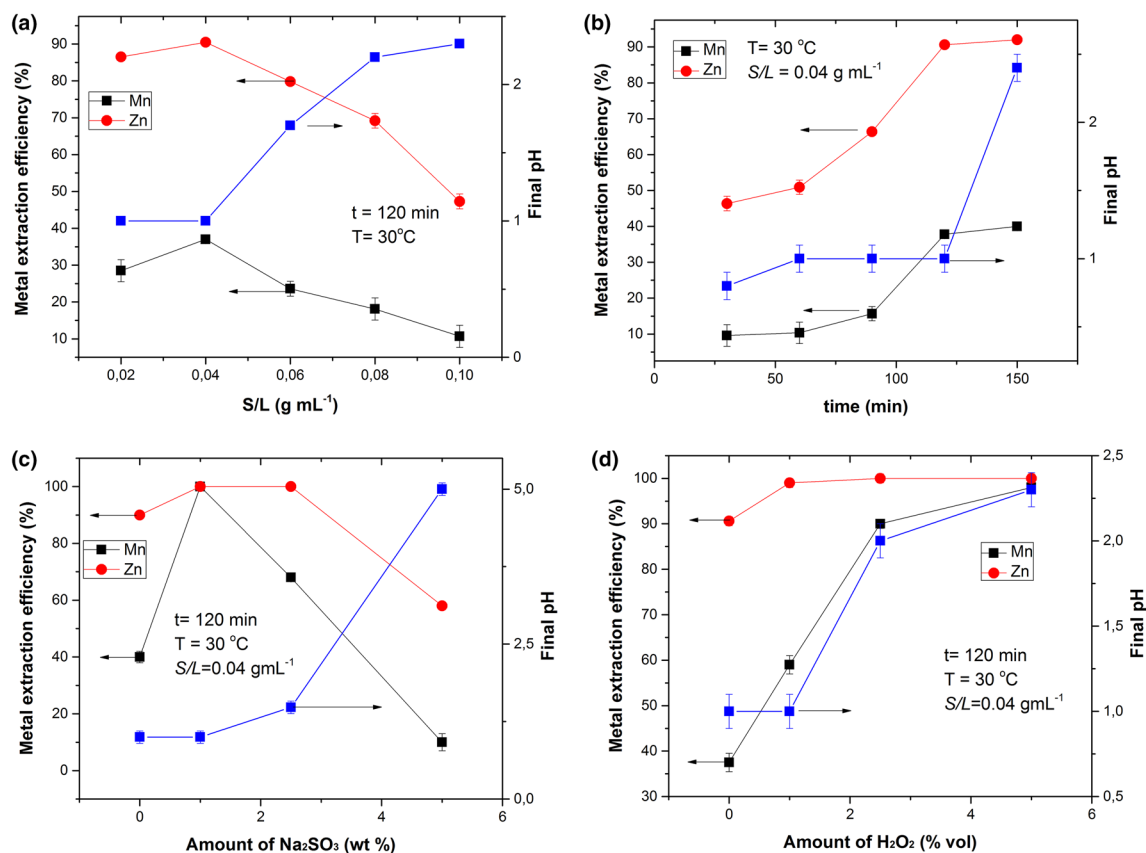
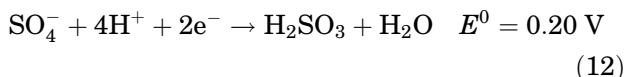
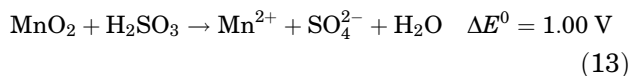


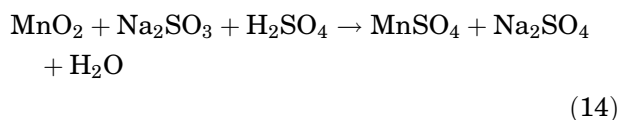
Fig. 3. Extraction efficiency for Zn and Mn versus: (a) the S/L ratio (120 min, 30°C); (b) time (S/L ratio = 0.04 g ml<sup>-1</sup>, 30°C); (c) the amount of added Na<sub>2</sub>SO<sub>3</sub> (S/L ratio = 0.04 g ml<sup>-1</sup>, 120 min, 30°C); and (d) the amount of added H<sub>2</sub>O<sub>2</sub> (S/L ratio = 0.04 g ml<sup>-1</sup>, 120 min, 30°C).



The difference of the standard electrode potentials ( $\Delta E^0$ ) for the dissolution of MnO<sub>2</sub> in acidic solutions in the presence of Na<sub>2</sub>SO<sub>3</sub> is obtained by combining Eqs. 1 and 12:



The addition of sulfite enhances MnO<sub>2</sub> dissolution in sulfuric media according to Eq. 14:

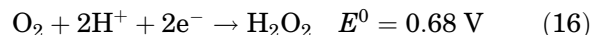
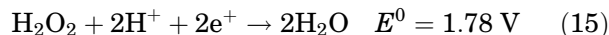


A greater amount of sulfite does not improve the extraction efficiency of Mn or Zn, possibly because of the increment of the pH associated with Na<sub>2</sub>SO<sub>3</sub> addition.

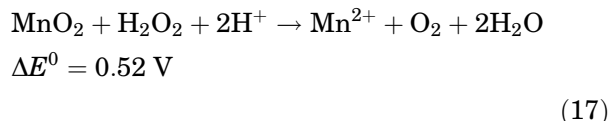
The effect of H<sub>2</sub>O<sub>2</sub> on the leaching of zinc and manganese from spent battery powder is shown in Fig. 3d. When 1 vol.% of H<sub>2</sub>O<sub>2</sub> was added, nearly 99% of Zn extraction was achieved and Mn

extraction increased from 40% to 60%. A further increment of H<sub>2</sub>O<sub>2</sub> led to a 100% increase in Zn extraction and continuously increased Mn extraction to almost 98% up to 5 vol.% H<sub>2</sub>O<sub>2</sub>.

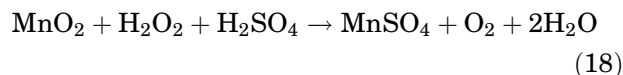
H<sub>2</sub>O<sub>2</sub> can act as an oxidative agent as well as a reducing agent in acid solutions, according to the following chemical reactions:



The difference of the standard electrode potentials ( $\Delta E^0$ ) for the dissolution of MnO<sub>2</sub> in acidic solutions in the presence of H<sub>2</sub>O<sub>2</sub> is obtained by combining Eqs. 1 and 16:



Thus, the reaction between sulfuric acid and MnO<sub>2</sub> in the presence of H<sub>2</sub>O<sub>2</sub> can be presented as follows:





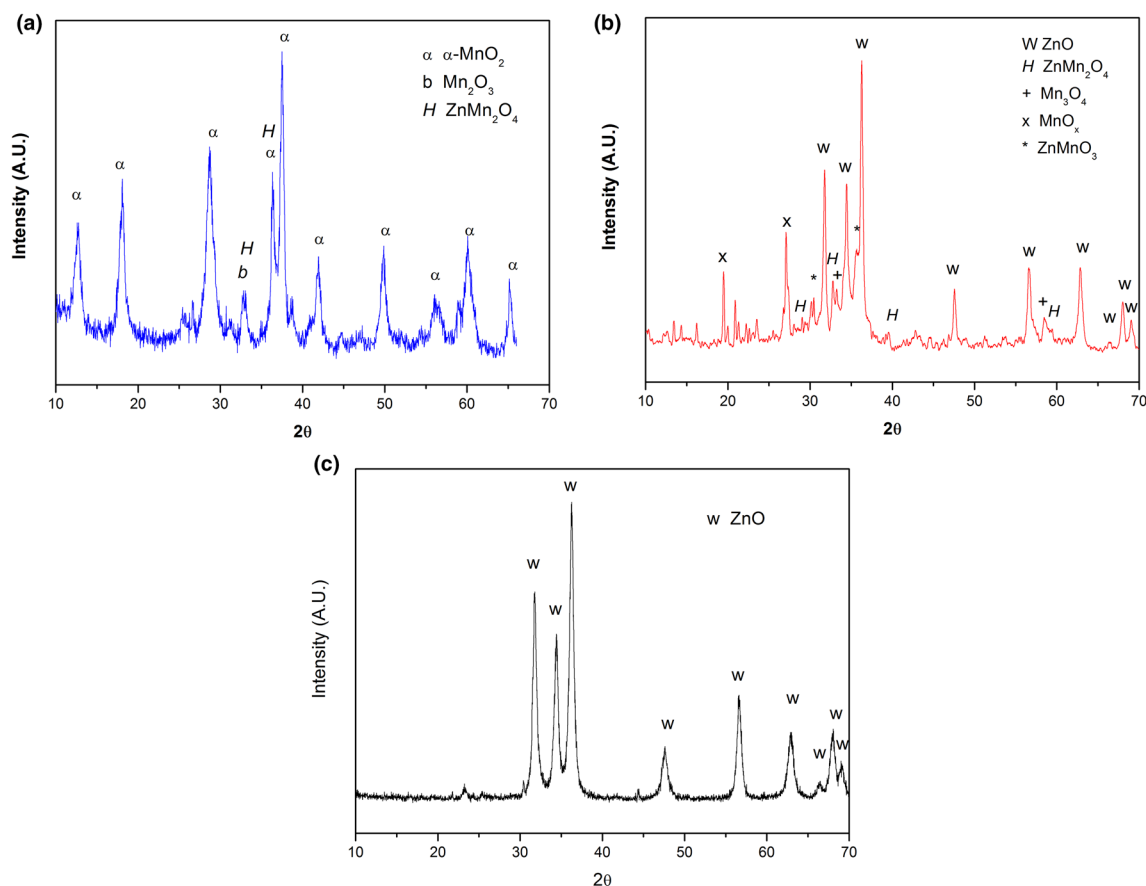


Fig. 4. X-ray diffraction patterns of the recovered samples: (a) MnO<sub>x</sub>, (b) ZM, and (c) ZnO. (w) ZnO; (α) αMnO<sub>2</sub>; (b) Mn<sub>2</sub>O<sub>3</sub>; (x) MnO<sub>x</sub>; (+) Mn<sub>3</sub>O<sub>4</sub>; (H) ZnMn<sub>2</sub>O<sub>4</sub>; (\*) ZnMnO<sub>3</sub>.

The addition of 1 wt.% Na<sub>2</sub>SO<sub>3</sub> and 5 vol.% H<sub>2</sub>O<sub>2</sub> enhanced the Zn and especially Mn extraction efficiency. As mentioned before, a reducing agent is required for the dissolution of MnO<sub>2</sub> in sulfuric acid media. It seems that the polythionate species S<sub>n</sub>(SO<sub>3</sub>)<sub>2</sub><sup>2-</sup>, generated in the metabolism of *AT* bacteria, are insufficient for the complete dissolution of MnO<sub>2</sub>, and certain amounts of other reducing agents are needed for an enhanced extraction of Mn using the biogenerated sulfuric acid.

For recovering Mn and Zn from batteries, the powder was leached using biogenerated sulfuric acid, with an *S/L* ratio of 0.04 g ml<sup>-1</sup>, for 120 min at 30°C and with 5 vol.% H<sub>2</sub>O<sub>2</sub>.

### Characterization of the Recovered Oxides

After leaching and precipitation with KMnO<sub>4</sub>, 90% Mn was recovered. A subsequent addition of Na<sub>2</sub>CO<sub>3</sub> precipitated 95% Zn. The coprecipitation of Mn and Zn with NaOH recovered 95% Zn and 28% Mn.

The samples MnO<sub>x</sub>, ZM and ZnO had an Mn/Zn ratio of 2.5, 0.4 and 0.01 wt.%, respectively. The sulfur content in the samples was 2.5, 1.0 and 2.0 wt.% for MnO<sub>x</sub>, ZM and ZnO, respectively. Additionally, some K was found in MnO<sub>x</sub> and Na in ZM.

The x-ray diffraction patterns of the samples are shown in Fig. 4. MnO<sub>x</sub> presents diffraction lines corresponding to the αMnO<sub>2</sub> phase (JCPDS 04-0779), and additionally some diffraction lines corresponding to Mn<sub>2</sub>O<sub>3</sub> (JCPDS 89-4836) or ZnMn<sub>2</sub>O<sub>4</sub> were detected. No peaks corresponding to ZnO were found.

The most intense diffraction lines in the ZM sample correspond to hexagonal ZnO wurtzite. Additionally, small peaks corresponding to mixed manganese-zinc phases, ZnMn<sub>2</sub>O<sub>4</sub> and ZnMnO<sub>3</sub> (JCPDS 19-1461), and pure manganese oxides were detected.

The diffraction peaks of the recovered zinc oxide can be identified as belonging to a ZnO phase with a hexagonal wurtzite crystal structure in which the strong diffraction peaks appear at (1 0 0) (0 0 2) and (1 0 1).<sup>30</sup>

Figure 5 shows the TEM images of the recovered oxides. MnO<sub>x</sub> presents small globular particles, characteristic of manganese oxides prepared with KMnO<sub>4</sub> precursor.<sup>31</sup> In the ZM sample, the particles display platelet-type shapes with no fibrous particles. According to the literature, this might be attributed to ZnO-rich particles even if the formation of a new spinel phase is also detected, which can display the same particle shape when the starting precursor is ZnSO<sub>4</sub>.<sup>32</sup>

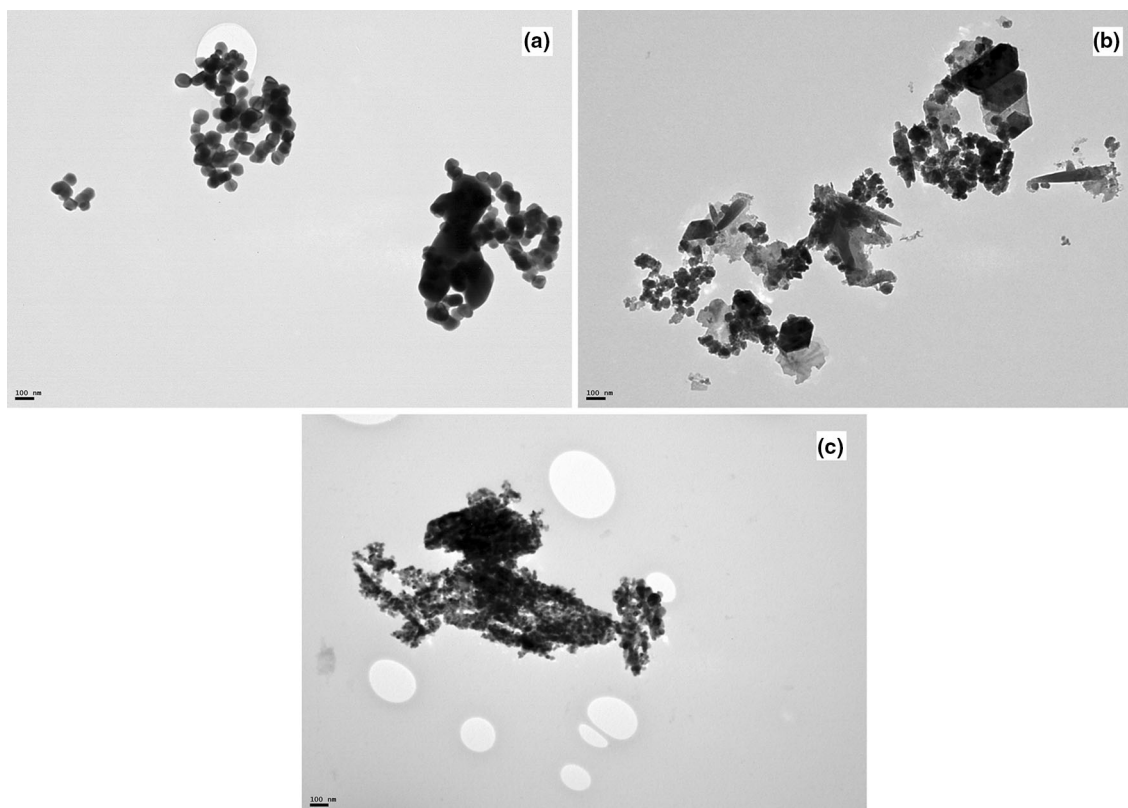


Fig. 5. TEM images of the different recovered oxides: (a)  $MnO_x$ , (b) ZM, and (c) ZnO.

The TEM image of the ZnO sample showed the formation of spherical-shaped particles with diameters of about 20 nm. Similar morphologies observed by TEM were reported by Ahmad et al.<sup>33</sup> over ZnO nanoparticles.

Spent batteries can be used as raw materials to synthesize different manganese and zinc oxides, which could be used for different applications.

## CONCLUSION

Spent alkaline and Zn/C batteries can be harmful to the environment and can be a source of materials. Battery recycling therefore promises significant environmental and economic benefits. A biohydrometallurgical route to separate zinc and manganese from spent alkaline and Zn/C batteries has been proposed in this work. Total zinc and manganese leaching can be achieved in one single step using biogenerated sulfuric acid with an  $S/L$  ratio of  $0.04 \text{ g ml}^{-1}$  for 120 min at  $30^\circ\text{C}$  and with 5 vol.%  $\text{H}_2\text{O}_2$  or 1 wt.%  $\text{Na}_2\text{SO}_3$ . After leaching, an acidic solution containing zinc and manganese remained. Manganese and zinc could be selectively recovered, and a Zn-Mn mixture oxide could also be synthesized.

The recovery of manganese and zinc after selective separation was 90% and 95%, respectively. Coprecipitation of Mn and Zn recovered 95% Zn and 28% Mn.

XRD and TEM analyses demonstrate the formation of  $\alpha\text{MnO}_2$  with the typical globular shape of manganese oxides, spherical ZnO particles with wurtzite structure in the obtained ZnO and a mixture of ZnO and Zn-Mn spinel in the ZM sample. Spent alkaline and Zn/C batteries can be used as raw materials to prepare different manganese and zinc oxides that have potential technologic applications.

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