

Efficient recycling of zinc from alkaline spent batteries using environmental-friendly strategies: a contribution to the circular economy

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Abstract

In the context of the circular economy, the production of new batteries, based on recycled materials from spent batteries, is the most energy efficient strategy, maximizes the reuse of the recycled materials and contributes to "closing the loop" of the alkaline batteries lifecycle. Thus, the main aim of this work was to evaluate the possibility of using ultrasound and microwaves to assist the (acid or alkaline) leaching of Zn in high yield from spent alkaline batteries and to compare the results with those obtained using the conventional leaching procedure. Both (microwave- and ultrasound-assisted leaching) strategies increased (≥ 92 and $\geq 80\%$ for acid and alkaline leaching, respectively) the extraction of Zn compared with the best results of conventional leaching [1.5 mol/L H₂SO₄, 3 hours: 90% of Zn; 6 mol/L NaOH, 3 hours: 42% of Zn] at 80°C. Moreover, they also proved to be more environmentally-friendly approaches for the extraction of Zn from spent alkaline residues since a concentrated (acid: ≥ 18.7 g/L Zn; alkaline: about 16.5 g/L Zn) Zn solution with adequate purity for subsequent Zn recovery was obtained using significantly decreased leaching times (≤ 23 minutes) and concentrations (1 mol/L H₂SO₄ or 4 mol/L NaOH) of chemicals.

Keywords: spent alkaline batteries, microwave-assisted leaching, ultrasound-assisted leaching, zinc recovery

1. Introduction

Over the last decades, the consumption of spent batteries has significantly increased due to their extensive applications in various electronic devices, being a large amount of them discharged on the environment by disposal of batteries in landfill sites (Barrett *et al.*, 2011; Sayilgan *et al.*, 2009a). This disposal can pose a serious threat to the environment related to the harmful metal contained in batteries and potential risk of dispersion of metals into the groundwater (Granata *et al.*, 2012; Tarasova *et al.*, 2012). Moreover, incineration of batteries produces toxic fume and air pollution (Cruz-Díaz *et al.*, 2015; Provazi *et al.*, 2011). Presently, with the growing attention on the minimization of wastes and environmental protection, recycling and reutilization of valuable materials is of great

interest. Many technologies have been widely applied to recover valuable metals contained in the spent batteries, such as physical, pyrometallurgical and hydrometallurgical methods (Cheret and Santen, 2007; Huang *et al.*, 2009; Ku *et al.*, 2016). Recycling of spent batteries using hydrometallurgical method represents more selective, lower energy consumption, less expensive and effective process compared to the others (Freitas *et al.*, 2007; Provazi *et al.*, 2011; Sayilgan *et al.*, 2009b). All these characteristics contribute to "closing the loop" of the alkaline batteries lifecycle. Based on all these facts, the main aim of this work was to develop environmental-friendly strategies to recover Zn with high efficiency and selectivity from spent alkaline batteries.

2. Material and methods

2.1. Preparation and characterization of the spent alkaline batteries

Spent alkaline batteries from different sizes, brands and origins were collected and manually dismantled. Dismantling product, such as plastic, paper pieces and ferrous and non-ferrous scraps were discarded. The obtained paste was dried for 24 h at 105 °C, crushed in a domestic miller and finally sieved to obtain particle size smaller than 1 mm. Two-steps neutral leaching process with deionized water was performed in part of the powder using a shaking bath with temperature control at a solid/liquid (S/L) ratio (1:5) by stirring at 200 rotations per minute (RPM) at 80 °C for 1 h. Afterwards, the powder was dried for 24-48 h at 105 °C to standardize the weight. This process was intended to remove K from the residue which may increase the consumption of H₂SO₄ during subsequent acid leaching. Finally, both washed and original powders were digested with H₂SO₄ 2 mol/L and ascorbic acid 26 g/L. Metal concentrations were determined by atomic absorption spectroscopy with flame atomization (AAS-FA) using a PerkinElmer Analyst 400 spectrometer. The structure of the dried powder was characterized by X-ray diffraction (XRD) with a Philips X'Pert X-ray diffractometer using Cu K α radiation under operating conditions of 40 mA and 45 kV with a step size of 0.04° and a scan step time of 30 s.

2.2. Leaching of the powders

Acid and alkaline leaching tests were carried out using washed and non-washed powders, respectively. For both, conventional, microwave- and ultrasound-assisted leaching were evaluated using a S/L 1:10. For all experiments, at least three replicates were performed. For conventional leaching, a shaking bath with temperature control at 80 °C and agitation (200 RPM) was used. Variations in the H₂SO₄ concentration (between 0.5 and 2 mol/L) and NaOH concentration (between 2 and 6 mol/L) for time (1 and 3 h) were evaluated for acid and alkaline leaching, respectively. For microwave-assisted leaching, a polytetrafluoroethylene (PTFE) bomb was used in a domestic microwave oven (800W, 2.45 GHz). In acid leaching, variations in the H₂SO₄ concentration (between 0.5 and 2 mol/L) and time (30 and 60 s) for 1 cycle microwave heating were studied. For alkaline leaching, 4 mol/L NaOH was used for leaching time between 30 and 240 s and 1 or 3 cycles of heating. Between cycles and before filtration, samples were allowed to cool for 20 min. Ultrasound-assisted leaching was carried out using a Bandelin Sonoplus HD 2200 (power of 200 W and output frequency of 20 kHz ± 500 Hz) with a 3 mm titanium microtip. For acid leaching, ultrasonic parameters were varied, i.e. the pulse (0.1 and 0.5 s) and the wave amplitude (20 and 60%) for H₂SO₄ concentration (between 0.5 and 1.5 mol/L) and time (between 1 and 6 min). In the case of alkaline leaching, 4 mol/L NaOH was used to evaluate the influence of the leaching time (between 1 and 16 min) for fixed pulse (0.1p) and amplitude (20%). Falcon tubes with conical bottoms were used to minimize the dead zone in sonochemistry.

3. Results and discussion

3.1. Characterization of the spent alkaline batteries

Results of quantitative analyses of the residue after total digestion indicated that washed residue was composed by 20, 28 and 0.35 % of Zn, Mn and Fe, respectively, while non-washed residue was made of 20, 27 and 0.36% of Zn, Mn and Fe, respectively. Moreover, XRD analysis evidenced that the major phases of washed and non-washed residues were ZnO (41 and 42 %, respectively) and ZnMn₂O₄ (27 and 24%, respectively) together with graphitic carbon (25 and 28 %, respectively). A small amount of Mn₃O₄ (6%) was also found in both residues. The metal composition of the residue was in good agreement with previous works (De Souza and Tenório,

2004; Salgado *et al.*, 2003; Sayilgan *et al.*, 2009b; Veloso *et al.*, 2005).

3.2. Acid leaching

Acidic treatment of spent alkaline batteries residues solubilizes totally ZnO and MnO oxides but not other Mn compounds (De Michelis *et al.*, 2007; Knight *et al.*, 2015). Results obtained by XRD evidenced that the residue contains Mn mainly in higher oxidation states (Mn³⁺ and Mn⁴⁺), which cannot be completely dissolved under acidic conditions. As it was detailed in section 2.2, the influence of concentration of H₂SO₄ and time were studied using conventional-, microwave- and ultrasound-assisted leaching (Table 1). For conventional leaching, increasing the leaching time from 1 to 3h indicated that more time (3h) was required for equilibrium establishment. For this period of time, a higher extraction yield was observed with 1.5 mol/L H₂SO₄ (90 and 18 % for Zn and Mn, respectively) compared to 0.5 and 1 mol/L H₂SO₄ (Table 1). The Zn selectivity, expressed by the Zn/Mn ratio, decreased from 3.5 to 3.3 when the acid concentration increased from 1.5 to 2 mol/L H₂SO₄ due to the same leaching extraction for Zn (90%) and higher Mn extraction (20%). Microwave- and ultrasound-assisted leaching experiments were performed to evaluate if Zn extraction yield could be improved using less chemical reagents in a faster way. From the results obtained for the microwave assays (Table 1), it was possible to see that the recovery of Zn was almost quantitative using 1 mol/L H₂SO₄ and 30 s leaching time. For this reason, this condition was selected as the best on regarding the lower H₂SO₄ concentration and leaching time. The effect of ultrasound assisted leaching was studied at two different concentrations of H₂SO₄ (1 and 1.5 mol/L) since using 0.5 mol/L H₂SO₄ for conventional and microwave leaching resulted in lower extraction yield. The results obtained proved that Zn leaching extraction did not improve significantly for more than 2 min using 1 and 1.5 mol/L H₂SO₄ (data not shown). Therefore, ultrasound-assisted leaching assays lasting 2 min and using 1 mol/L H₂SO₄ were chosen as the best conditions regarding to high Zn extraction (92%), lower H₂SO₄ concentration and leaching time, as well as the greatest Zn selectivity (Zn/Mn ratio of 5.1).

3.3 Alkaline leaching

Regarding to the selective dissolution of metallic Zn and ZnO in an aqueous NaOH solution over Mn oxides, alkaline leaching process was pointed out to be a suitable leaching method (Buzatu *et al.*, 2013; Shin *et al.*, 2007).

Table 1. Influence of the time and concentration of H₂SO₄ on Zn and Mn leaching efficiency from the washed residue using different acid leaching methods.

Method	Time	Zn%				Mn%			
		H ₂ SO ₄ , M				H ₂ SO ₄ , M			
		0.5	1	1.5	2	0.5	1	1.5	2
Conventional	3h	61	86	90	90	12	15	18	20
Microwave	30s	77	94	94	96	13	19	19	19
Ultrasound	1min	-	86	92	-	-	9.8	10	-
	2min	-	92	95	-	-	13	14	-

First, the conventional method was used for comparative purposes. The leaching assays, performed in the non-washed residue using 4 and 6 mol/L NaOH, resulted in very low Zn extraction for 1 (30 and 34%) and 3 h (38 and 42%), respectively. The low Zn extraction yield, obtained in this work, can be explained by the presence of ZnMn₂O₄ in the residue, which was not soluble under alkaline conditions compared to the residue studied by Buzatu *et al.* (2013) and Shin *et al.* (2007), which was mainly composed by metallic Zn and ZnO. Considering the low Zn extraction yield (42%) obtained from conventional method using 6 mol/L NaOH for a long leaching time (3h) and the small increase (4%) in the extracted Zn when the NaOH concentration was varied from 4 to 6 mol/L, the potential of the microwave- and ultrasound- assisted leaching were evaluated using a NaOH concentration of 4 mol/L.

For ultrasound-assisted leaching, the influence of the leaching time (between 1 and 14 min), maintaining the pulse and amplitude at 0.1 p and 20%, respectively, on the Zn extraction was studied (Table 2). The results showed that ultrasound originated higher (48%) Zn extraction after 3min compared to the conventional method (3h) and reached the maximum Zn dissolution (81%) at 14min. These results clearly evidence that ultrasound- assisted leaching appears to be more promising than conventional method because double Zn leaching was obtained using the same concentration of NaOH in much less operation time. For all alkaline leaching conditions tested, the concentration of Mn in the leached solution was less than 0.01%.

4. Conclusion

Different (conventional, microwave- and ultrasound-

Table 2. Influence of the time and concentration of NaOH on the Zn leaching efficiency from the non-washed residue using different alkaline leaching methods.

NaOH, M	Conventional		Microwave (1 cycle)					Microwave (3cycles)				Ultrasound				
	Time (h)		Time (min)					Time (min)				Time (min)				
	1	3	0.5	1	2	3	4	0.5	1	2	3	3	6	10	12	14
4	30	38	34	68	75	82	84	46	76	87	87	48	65	73	76	81
6	34	42	-	-	-	-	-	-	-	-	-	-	-	-	-	-

For microwave assays, the effect of leaching time using 4 mol/L NaOH in 1 cycle was studied. After 30s, the yield Zn extraction (34%) was similar to the one obtained after 3h using conventional method. After 3 min, the maximum extraction was 82% and no significant increase was obtained for higher leaching times. Additionally, the application of microwave heating was performed in 3 cycles of different time followed by a cooling step of 20 min to determine if higher Zn extraction could be achieved. The results indicated a small increase in the Zn extraction (5%) using 3 cycles of 3 min. Considering that the required time for using 3cycles is much longer than 1 cycle, this increment seems to be negligible. Thus, 1 cycle during 3min of leaching time was selected considering the best compromise between the consumption of energy during leaching time and the Zn extraction yield.

assisted) leaching methods were applied for deionized water washed and non-washed residues obtained from spent batteries. In table 3, the extraction yield, the Zn and Mn concentrations of the leached solutions, selectivity of Zn over Mn, as well as the purity of Zn in the solutions using the optimized conventional, microwave- and ultrasound-assisted conditions for acid and alkaline leaching are presented.

For acid leaching, microwave- and ultrasound-assisted strategies promoted a very fast extraction of Zn using lower acid consumption than conventional process. Moreover, the Mn concentration present in the acid solution of both methods is appropriate for promoting further electrowinning of Zn (Freitas and De Pietre, 2004; Moscardini *et al.*, 2009).

Table 3. Summary of the results obtained for the best conditions using the three methods for acid and alkaline leaching.

	Acid leaching using H ₂ SO ₄			Alkaline leaching using NaOH		
	Conventional 3h,1.5M, 80°C	Microwave 30 s of 1 cycle, 1M	Ultrasound 2min, 1M	Conventional 3h,6M, 80°C	Microwave 3 min of 1 cycle, 4M	Ultrasound 14min, 4M
Zn, %	90	94	92	42	82	81
Mn, %	18	19	13	< 0.01	< 0.01	< 0.01
Zn (g/L)	18.2	19.2	18.7	8.4	16.5	16.7
Mn (g/L)	5.2	5.5	3.7	3 x 10 ⁻³	2 x 10 ⁻³	3 x 10 ⁻³
Zn/Mn	3.5	3.5	5.1	2800	8265	5553
Zn purity,%	77.7	77.7	83.3	99.9	99.9	99.5

From alkaline leaching results, microwave- and ultrasound-assisted leaching strategies were both better alternatives for the leaching of Zn than the conventional method. In addition, under these conditions, alkaline leaching was extremely selective for Zn (purity of 99.9 %), which allows subsequent recovering of Zn by precipitation with high purity (Machado *et al.*, 2010). As a conclusion, it is clear that for both acid and alkaline leaching, the achievements obtained using microwave- and ultrasound-assisted leaching are promising approaches for environmental friendly recovery of Zn from spent alkaline batteries regarding to the higher extraction yield, faster leaching operation time and lower consumption of chemicals used.

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