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Leaching and separation of zinc from the black paste of spent MnO$_2$-Zn dry cell batteries

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Abstract

Spent batteries represent a source of hazardous materials when discarded without appropriate treatment. Investigations on the recovery of zinc from the black paste of spent MnO$_2$-Zn cell batteries were carried out. Leaching of zinc and manganese from the black paste of spent batteries using sulfuric or hydrochloric acid solutions was studied. It was found that leaching with sulfuric acid solution is more efficient than with HCl solution. Different parameters affecting the leaching of Zn(II) and Mn(II) with sulfuric acid were further studied. Extraction of Zn(II) and Mn(II) from the leaching sulfate medium by bis(2,4,4-trimethylpentyl) dithiophosphinic acid (CYANEX 301) diluted with kerosene was investigated. The factors affecting the extraction process, separately studied, include the effect of contact time, sulfuric acid concentration, CYANEX 301 concentration, phase ratio as well as temperature. The results indicated that, from sulfate medium, Zn(II) is more extracted than Mn(II). Selective stripping of Zn(II) was obtained using 5 M HCl. Application of the method on the leaching sulfate solution of the spent MnO$_2$-Zn dry cell black paste show the efficiency of the process, where the extraction and stripping of Zn(II) are 98% and 99%, respectively.
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Keywords: MnO$_2$-Zn dry cells; Zinc; CYANEX 301; Liquid–liquid extraction

1. Introduction

Spent batteries represent a serious pollutant in terms of heavy metals content when discarded in an inappropriate way. Among these, MnO$_2$-Zn cell batteries represent a major amount of the spent batteries waste. During the last decade, the producers of batteries were engaged trying to find substitutes for toxic substances still used in batteries, to match environmental requirements, although, the basic systems of the batteries and its composition remains more or less the same (steel, plastic, zinc, manganese dioxide, etc.). Most of these materials recovered by means of mechanical and chemical treatments show some advantages as they can be used as raw materials for batteries production.

Several methods to recover metal values from spent batteries are given in the literature but industrial routes are generally based on pyrometallurgical [1–4] and/or hydrometallurgical [5–7] operations. Hydrometallurgical routes commonly found are more economical and efficient than pyrometallurgical ones. Metal separation routes based on hydrometallurgical operations are characterised by lower energy consumption, higher metal selectivity and low air pollution, as there are no particles produced. Veloso et al. [8] proposed a method for selective separation of zinc and manganese from spent alkaline batteries. Their recycling route comprises the dismantling of the batteries to separate the spent batteries dust from other components and grinding the batteries dust to produce a black homogeneous powder. The powder was then leached in two sequential steps, "neutral leaching with water" to separate potassium and produce a KOH solution, followed by an "acidic leaching with sulfuric acid" to remove zinc and manganese from the powder. This was followed by selective precipitation of zinc and manganese using the KOH solution (pH around 11) produced in the neutral leaching step. In a modified ZINCEX process, as an example of hydrometallurgical route, zinc extraction from the leached liquor (pH 2) was performed with di-(2-ethylhexyl) phosphoric acid (D2EHPA) as extractant, leaving manganese in the raffinate while other metals such as copper, cadmium, nickel and mercury were cemented [6].

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A hydrometallurgical route based on the liquid–liquid extraction technique using bis-(2,4,4-trimethylpentyl)phosphinic acid [$(C_8H_{17})_2P(O)OH$], CYANEX 272, as extractant was investigated [7] for the selective separation of zinc and manganese from the solution resulting from leaching of spent alkaline batteries. Bench scale experiments have shown that zinc and manganese are easily separated using 20% (v/v) CYANEX 272 dissolved in Escaid 110 at 50 °C. Devi et al. [9] have obtained extractions of 99% for zinc and 5% for manganese using a sodium salt of CYANEX 272. The extraction and separation of Mn(II) and Co(II) from sulfate solutions have been carried out using sodium salts of di-(2-ethylhexyl) phosphoric acid (NaD2EHPA), 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC 88A) or CYANEX 272 in kerosene [10]. The percentage extraction of the metal ions was found to increase with increasing equilibrium pH with all extractants. Rickelton and Boyle [11] studied the extraction of Zn(II) from sulfate medium using CYANEX 272 and its sulfur analogues CYANEX 302, $(C_8H_{17})_2P(S)OH$, and CYANEX 301, $(C_8H_{17})_2P(S)SH$. The extraction of zinc with CYANEX 272 and CYANEX 302 was achieved at pH 3, while it was obtained at pH ≤ 2 when using CYANEX 301. For both extractants, sulfuric acid was used to strip the metal from loaded organic phases. A mixture of CYANEX 301 and CYANEX 302 has also been used to extract Zn(II) from chloride medium [12]. A simultaneous extraction and separation of Co(II) and Ni(II) from manganese and magnesium sulfate solutions have been carried out using CYANEX 301 diluted in Exxsol D-80 [13]. Statistical design and analysis of experiments were used in order to determine the main effects and interactions of the solvent extraction factors. A statistically designed experiment was also carried out in order to study the stripping of the cobalt and nickel from loaded CYANEX 301 organic phase by hydrochloric acid solution [13]. Gupta et al. [14] described a process for the recovery of pure Co(II), Ni(II) and Cu(II) from a hydrochloric acid solution of polymetallic sea nodules. An overnight contact of the nodule powder with 4 M HCl almost quantitatively leached these metal ions. From the leachate, Co(II) and Cu(II) were recovered by their extraction with CYANEX 923 and Ni(II) by extraction with CYANEX 301. A solution of 0.001 M H_2SO_4 was used for the stripping of Co(II) and Cu(II) and 5% NH_4Cl in 75% NH_3 for Ni(II).

In Egypt, dry cell batteries are produced from local and imported materials. The average production capacity is nearly 200 million pieces every year equivalent to 12 tonnes of batteries [15]. Because this quantity of cells is waste, the recovery of valuable materials from these recurring secondary resources would be beneficial to the national economy and environment.

In this respect, the work in this paper is directed to study the separation of zinc and manganese from the solution resulting from the acid leaching of the black paste of the spent MnO_2-Zn cells by extraction with CYANEX 301 in kerosene and study the factors affecting this separation. Batch experiments on the individual extraction and stripping of Zn(II) and Mn(II) from sulfuric acid medium were first carried out and best separation conditions were deduced. The efficiency of the proposed process for recovery of Zn(II) from the leached solution of the black paste batteries was also tested.

2. Experimental

2.1. Chemicals and reagents

Most chemicals and reagents used were of analytical reagent (AR) grade and used as received. Sulfate salts of zinc and manganese were Merck products, while sulfuric acid, hydrochloric acid, and xylenol orange supplied by BDH. CYANEX 301, bis(2,4,4-trimethylpentyl) dithiophosphinic acid, was kindly supplied by Cytec Inc., USA and used as received. Kerosene (non-aromatic) obtained from Misr Petroleum Ltd. Company, Egypt.

2.2. Recovery of black paste from spent MnO_2-Zn dry cell batteries

Spent MnO_2-Zn dry cell batteries, collected from waste yard, are mainly of the local trademark Kaha, Egypt, of different sizes, D and AA. The whole mass of these batteries was washed with tap water, rinsed and dried at ambient conditions. These dried cells were manually cut into halves along with their longitudinal axes using a machine fitted with tooth high-speed steel cutter. The active paste inside the cell has been removed and its weight represented 65.5% of the total weight of the spent batteries. This material was dried at 100 °C and ground in order to produce a dry black homogeneous powder. A water content of 11.6% was determined and the dry black powder represented 54.47% of the total weight of the spent batteries. Analysis of the major components of this dry powder, as determined by energy dispersive X-ray fluorescence, EDXRF, are 37.4% manganese, 12.2% zinc, 21.0% oxygen, 25.3% carbon, 3.1% chlorine and 0.5% potassium. This black powder paste represents the material under investigation.

2.3. Leaching tests

The dry black powder was first washed with distilled water prior to the acid leaching tests. Leaching tests of Zn(II) and Mn(II) from the black paste were carried out in a jacketed glass beaker. Each leaching test was performed under magnetic stirring and at constant temperature using a water bath with circulating system. Samples of 100 g of the dried black paste were added to a certain volume of the leach solutions. After stirring for 2 h, equilibrium leaching time, the leach solution was separated from the carbon paste by filtration and Zn(II) and Mn(II) were determined to obtain the percent leached in the different solutions.

2.4. Extraction–stripping procedures

Zinc and manganese solutions prepared by direct dissolution of a certain weight of zinc and manganese sulfate salts in a sulfuric acid medium gave solutions of concentrations 0.15 and 0.1 M, respectively. These concentrations are comparable to that obtained from leaching the black paste.

Batch extraction experiments were performed by shaking equal volumes (10 ml each) of aqueous phase containing a

known concentration of Zn(II) or Mn(II) and organic phase containing CYANEX 301 in kerosene in stoppered glass tubes using a thermostated shaking water bath adjusted at $25 \pm 1\,^\circ$C (except when studying the effect of temperature).

After equilibration, known aliquot volumes taken from the aqueous phase before and after extraction were used for determination of the metal ion concentration.

The distribution ratio, D, was calculated from the relation:

$$D = \frac{C_0 - C}{C} \tag{1}$$

where C_0 is the initial metal ion concentration in the aqueous phase before extraction and C is the metal ion concentration in the aqueous phase after extraction.

To assess the use of CYANEX 301 to separate Zn and Mn from sulfuric acid synthetic liquor, different parameters affecting the extraction of Zn(II) and Mn(II) from sulfuric acid solution were investigated using organic/aqueous (O/A) volume ratio of 1, unless otherwise stated. Predetermined time intervals were taken to study the effect of time on the extraction of 0.15 M Zn(II) and 0.1 M Mn(II) dissolved in 2 M sulfuric acid medium by 0.75 M CYANEX 301 in kerosene. It was found that 30 min are sufficient for extraction equilibrium of both metals.

Stripping experiments were carried out by vigorous shaking of 10 ml of the loaded organic phase (containing a known amount of the metal ion, C_{org}) with an equal volume of the aqueous acid solution under study for 30 min. The concentration of the metal ion in the aqueous phase, C_s, was determined and the percent strip calculated from the following relation:

$$\% \, \text{Strip} = \frac{C_s}{C_{org}} \times 100 \tag{2}$$

2.5. Analysis

Zinc and manganese concentrations were spectrophotometrically determined by the xylenol orange method [16] and formaldoxime method [17], respectively, using a Shimadzu UV–visible spectrophotometer model 160A. Energy-dispersed X-ray, EDX, at the Central Analytical Laboratory, Egyptian Atomic Energy Authority, analyzed the black paste material.

3. Results and discussion

3.1. Black paste leaching

The dry black powder was first washed with water several times to remove soluble salts. Analysis of this water fraction showed that it contains mainly zinc with concentration equivalent to 2.4% of the black paste powder. The leaching experiments in the present work were carried out based on the information given by Mahros [18]. He reported that maximum leaching of zinc and manganese from the bulk of the spent batteries is achieved by mixing with HCl or H_2SO_4 solution for 2 h at 60 °C. The effect of solid/liquid (S/l) ratio of different acids (2 M) on the leaching of Zn(II) and Mn(II), for 2 h at 50 °C, is given in Table 1. From this table, it is clear that decreasing the S/l ratio increases the leaching of both metals up to 1/5 followed by gradual decrease with higher acid volumes. Leaching with sulfuric gave much better leach percent than hydrochloric acid in case of zinc, whereby HCl gave slightly higher leaching for Mn than H_2SO_4. In both cases, leaching of zinc was much higher than that of Mn. The effect of sulfuric acid molarities on the leach of Zn and Mn was investigated using solid:liquid ratio of 1:5. In Table 2, the results obtained indicate that maximum leaching of both Zn(II) and Mn(II) is reached at H_2SO_4 concentration between 2 and 3 M. The recovery of Zn is around 90% of the total zinc in the black powder matrix, whereby that of Mn is only 7.5%. Higher H_2SO_4 concentration does not contribute much to the % leached of both cations.

The effect of temperature was further investigated using 2 M H_2SO_4 at an S/l ratio of 1/5 and the results indicated that a slight increase in the leaching of Zn(II) and Mn(II) was obtained when the temperature increased from 25 to 50 °C. Higher temperature did not affect the amount of leached metal ions.

Based on the above results, the best operating conditions for leaching Zn(II) and Mn(II) from the dried black paste are the use of 2 M H_2SO_4 at S/l ratio of 1/5, temperature 50 °C and 2 h reaction time.

The low leaching % of Mn by the two acids used can be related to the chemical products of the black paste of the spent batteries. During discharge of the batteries, ZnO or $Zn(OH)_2$ and MnOOH, Mn_2O_3 or Mn_3O_4 are formed depending on the discharge conditions. X-ray diffraction [18] of the black paste showed that zinc

Table 1
Effect of solid:liquid ratio on leaching of Zn(II) and Mn(II) from the dry black paste powder

Solid:liquid ratio (g/ml)	% Zn leached of dry paste (paste composition, 12.2% Zn)		% Mn leached of dry paste (paste composition, 37.4% Mn)	
	H_2SO_4, 2 M	HCl, 2 M	H_2SO_4, 2 M	HCl, 2 M
1:3	7.6 (62.3%)	6.0 (49.2%)	1.8 (4.8%)	2.1 (5.6%)
1:4	9.1 (74.6%)	6.8 (55.7%)	2.1 (5.6%)	2.3 (6.2%)
1:5	10.7 (86.6%)	8.3 (68.0%)	2.5 (6.7%)	2.7 (7.2%)
1:6	10.4 (85.2%)	8.5 (69.6%)	2.2 (5.9%)	2.2 (5.9%)
1:7	10.0 (81.2%)	8.8 (71.1%)	1.9 (5.1%)	2.0 (5.3%)
1:8	9.0 (73.8%)	7.7 (63.1%)	1.6 (4.3%)	1.6 (4.3%)
1:9	8.4 (68.8%)	6.9 (56.6%)	1.4 (3.7%)	1.4 (3.7%)
1:10	6.9 (58.6%)	4.1 (33.6%)	1.2 (3.2%)	1.2 (3.2%)

Temperature: 50 °C for 2 h using 2 M sulfuric or hydrochloric acid solutions. Values between parentheses indicate % metal extracted from the dry paste powder.

Table 2
Effect of sulfuric acid concentration on the leaching of Zn(II) and Mn(II) from dry black paste of spent batteries

Metal	Paste composition (wt.%)	Sulfuric acid concentrations			
		1 M	2 M	3 M	4 M
Zn	12.2	9.2% (75.4%)	10.7% (87.8%)	11.2% (91.8%)	10.9% (89.3%)
Mn	37.4	1.6% (4.2%)	2.5% (6.7%)	2.8% (7.5%)	3.0% (8.0%)

Temperature: 50 °C for 2 h, solid:liquid ratio, 1:5. Values between parentheses indicate % metal extracted from the dry paste powder.

is combined with manganese dioxide to form a zinc-manganese compound of the chemical formula $(Zn_2Mn_4O_8 \cdot H_2O)$. Leaching of manganese from the aforementioned compounds was partially leached by the acids used in this work. The partial leaching of Mn under our experimental conditions is an advantage as it facilitates the extraction of Zn with high chemical purity.

The experimental results obtained for Zn leaching in the present work are more or less similar to that reported by Salgado et al. [7]. However, they reported higher leaching percent for Mn. Very recently, Avraamides et al. [19] obtained more than 90% leaching of Zn and Mn using 0.1–1.0 M sulfuric acid under a flow of sulfur dioxide gas as reducing agent. They found that the leaching rates depend on the sulfur dioxide flow rate, particle size, acid concentration and agitation. Thus, the SO_2/H_2SO_4 leaching offered higher Zn and Mn dissolution at faster rates even at a low temperature and low acid concentration.

3.2. Solvent extraction investigations

Investigations on the extraction of Zn(II) and Mn(II) from a synthetic acid solution were carried out. In this respect, the effect of CYANEX 301 concentration on the extraction of 0.15 M Zn(II) and 0.1 M Mn(II) from 2 M H_2SO_4 medium was investigated in the range 0.1–0.75 M and it was found that the distribution ratio of both metals increases linearly with the extractant concentration, Fig. 1. The slope of both lines is almost

equal to two indicating the participation of two CYANEX 301 molecules in the extracted metal species. The Zn/Mn separation factor ($S_{Zn/Mn} = D_{Zn}/D_{Mn}$) calculated at different CYANEX 301 concentrations, in the investigated range, was found to be nearly constant with an average value of 47.8, Fig. 1.

The effect of sulfuric acid concentration on the extraction of 0.15 M Zn(II) and 0.1 M Mn(II) was separately studied. As shown in Fig. 2, increasing H_2SO_4 concentration slightly decreased the extraction of zinc and increased the manganese extraction. The Zn/Mn separation factor calculated at different sulfuric acid concentrations and presented in Fig. 2 decreased from 315.3 to 48.5 when the extraction was performed from 0.05 and 2 M sulfuric acid, respectively. On the other hand, increasing the hydrogen ion concentration in the range 0.3–2 M, while keeping constant $[SO_4^{2-}]$ at 2 M, by adding appropriate amounts of sodium sulfate to the solution, was found to decrease linearly the distribution ratios of both metals, Fig. 3. Slopes of about −2 indicate the release of two hydrogen ions through the extraction of Zn and Mn. In addition, the separation factor shown in Fig. 3, does not nearly change with the change in pH of the aqueous solution through the investigated range, with an average value of 48.0.

The increasing tendency of the extraction behaviour was almost the same for both metals as organic/aqueous phase ratio increased from 1/4 to 4/1, with higher increase in favour of Zn,
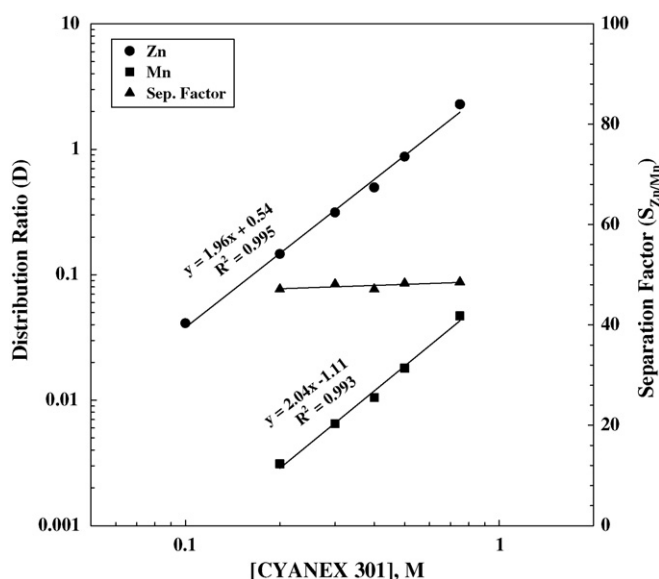

Fig. 1. Effect of CYANEX 301 concentration on the extraction of 0.15 M Zn(II) and 0.1 M Mn(II) from sulfuric acid medium at O/A ratio = 1.
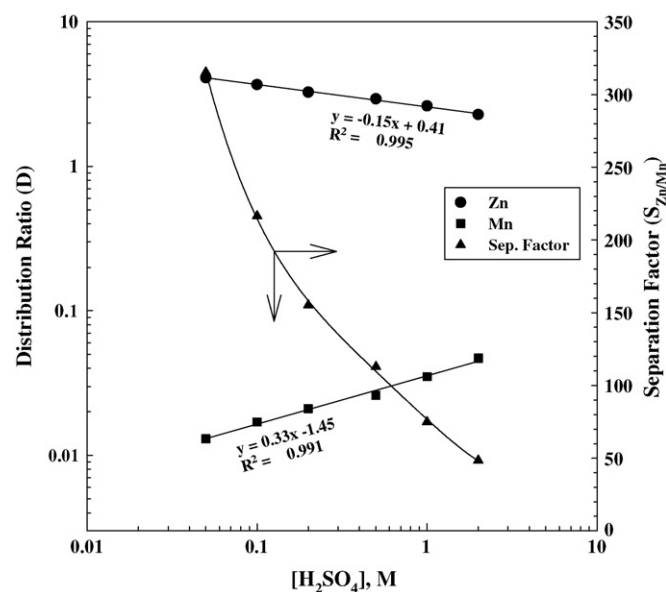
Fig. 2. Effect of sulfuric acid concentration on the extraction of 0.15 M Zn and 0.1 M Mn by 0.75 M CYANEX 301 in kerosene at O/A ratio = 1.
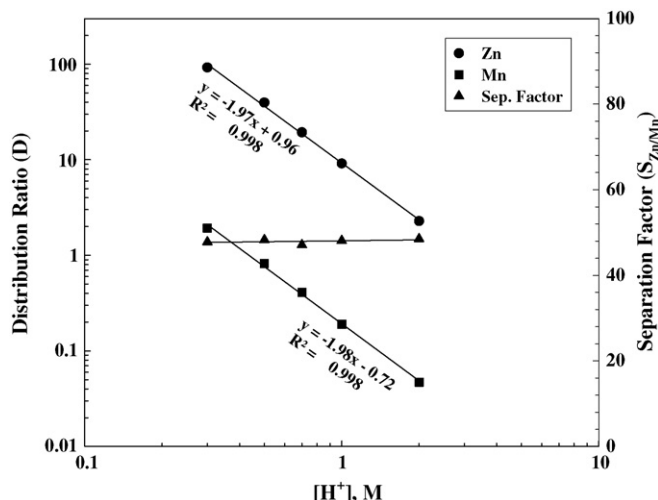
Fig. 3. Effect of hydrogen ion concentration of the aqueous medium on the distribution ratio of Zn(II) and Mn(II) extracted by 0.75 M CYANEX 301 in kerosene from sulfuric acid medium at O/A ratio = 1.

Fig. 4. This reflected on the separation factor ($S_{Zn/Mn}$), which was found to increase with the increase of the O/A ratio. However, the increase in phase ratio not only increases the Zn/Mn separation, but also increases the amount of Mn in the extracted organic solution. Therefore, 1:1 ratio used throughout the present work was for economic reason.

3.2.1. Extraction equilibrium

Considering that CYANEX 301 is present as dimer in the aliphatic diluents [20], and based on the results obtained, the extraction equilibrium of Zn(II) and Mn(II) may be represented by

$$M^{2+} + 2\overline{(HA)_2} \rightleftharpoons \overline{M \cdot A_2(HA)_2} + 2H^+ \tag{3}$$
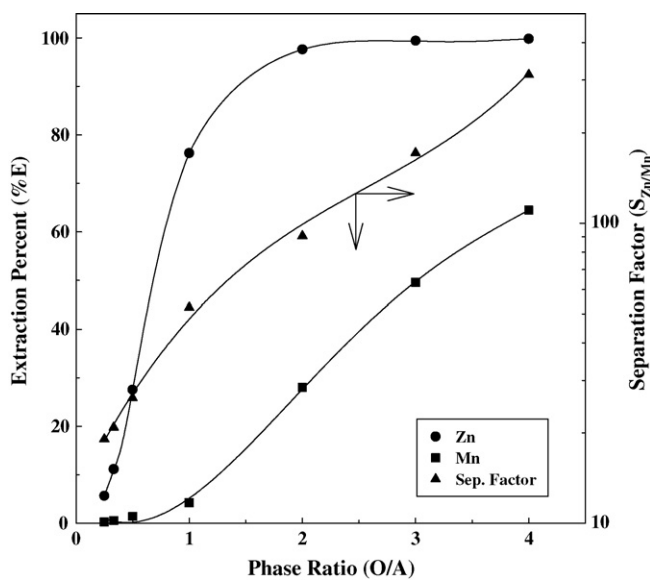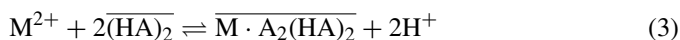

Fig. 4. Effect of phase ratio (organic/aqueous) on the extraction of 0.15 M Zn(II) and 0.1 M Mn(II) from sulfuric acid medium by 0.75 M CYANEX 301 in kerosene.

where $\overline{(HA)_2}$ represents CYANEX 301 in kerosene, M^{2+} refers to Zn(II) or Mn(II) ions and bars stand for the organic phase species.

Therefore, the extraction constant of the above equations is given by

$$K_{ex} = \frac{[\overline{M \cdot A_2(HA)_2}][H^+]^2}{[M^{2+}][\overline{(HA)_2}]^2} \tag{4}$$

or

$$K_{ex} = \frac{D[H^+]^2}{[\overline{(HA)_2}]^2} \tag{5}$$

The average calculated extraction constants for Zn(II) and Mn(II) extraction systems were found to be 16.9 ± 0.78 and 0.37 ± 0.02, respectively, which confirm the difference in the extraction results towards both metal ions using sulfuric acid.

3.2.2. Effect of temperature

The increase of temperature in the range 15–45 °C decreased the extraction of both zinc and manganese from 2 M H$_2$SO$_4$ solution by 0.75 M CYANEX 301 in kerosene as shown in Table 3. The Van's Hoff equation [21] used to calculate the enthalpy change (ΔH) associated with the extraction of these metals is

$$\log K_{ex} = -\frac{\Delta H}{2.303RT} + C \tag{6}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}) and C is a constant.

The plot of log K_{ex} versus $1/T$ for the extraction of both metals gave straight lines as illustrated in Fig. 5. The negative values of the enthalpy change for Zn and Mn extraction calculated from the slopes of the linear relations were found to equal -14.5 and -13.6 kJ mol^{-1}, respectively. This indicates the exothermic nature of the extraction process for both metals.

3.2.3. Stripping procedure

By applying the above extraction system on a solution containing both 0.15 M Zn(II) and 0.1 M Mn(II) in sulfuric acid medium, the extraction percent was found to be 76% and 4%, respectively. Using O/A phase ratio equals to 1 and at 25 °C, hydrochloric acid was found to be efficient stripping agent for zinc, where the stripping percent was 92% when using 5 M HCl

Table 3
Effect of temperature on the distribution ratio of 0.15 M Zn(II) and 0.1 M Mn(II) extracted from 2 M H$_2$SO$_4$ solution by 0.75 M CYANEX 301 in kerosene

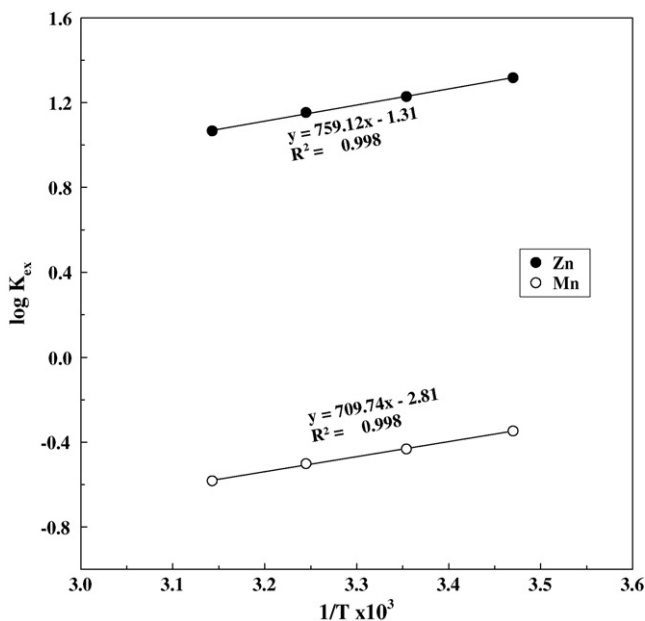| Temperature (°C)	Distribution ratio (D)	
	Zn(II)	Mn(II)
15	2.43	0.068
25	2.25	0.041
35	2.11	0.027
45	1.96	0.016

Fig. 5. Effect of temperature on the equilibrium constant (K_{ex}) of the extraction of 0.15 M Zn(II) and 0.1 M Mn(II) by 0.75 M CYANEX 301 in kerosene from 2 M H$_2$SO$_4$ medium.

Fig. 7. McCabe–Thiele diagram for the extraction of 0.15 M zinc from 2 M H$_2$SO$_4$ solution using 0.75 M CYANEX in kerosene at O/A ratio = 1 and 2.

and almost 0% in case of Mn, Fig. 6. Distilled water recovered about 50% of manganese from the organic phase in one stage while Zn was almost not stripped under the used experimental conditions.

In order to extend the extraction and separation method for application on the solution resulting from leaching of the spent batteries and to predict the number of the theoretical stages required for zinc extraction, a McCabe–Thiele diagram was constructed for O/A ratio = 1 or 2, Fig. 7. To construct the diagram,
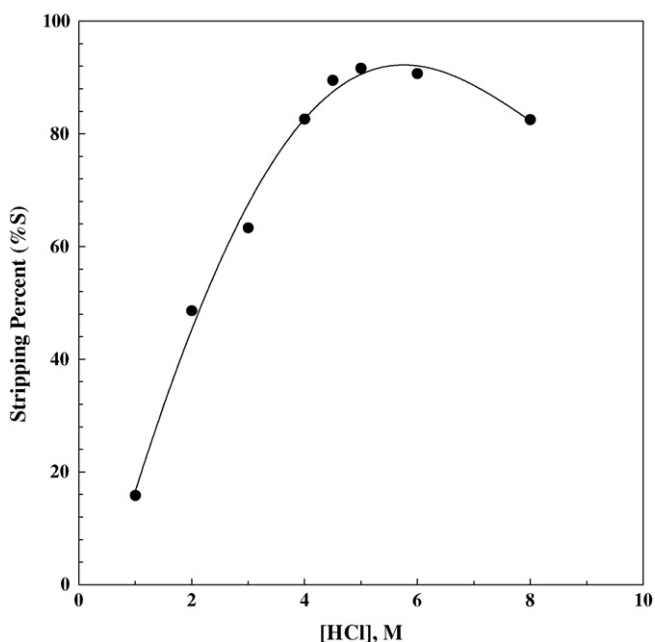

Fig. 6. Effect of hydrochloric acid concentration on the stripping of 0.114 M Zn(II) from loaded organic phase at A/O ratio = 1.
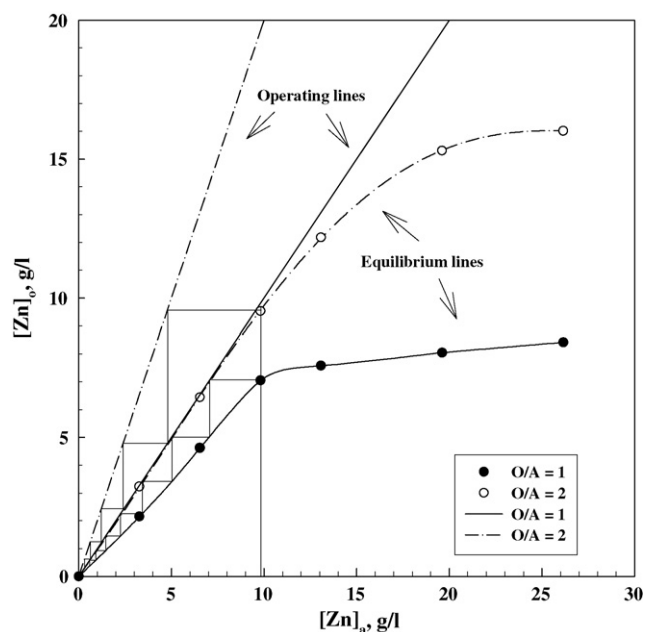
the extraction isotherm which represents the relation between Zn(II) concentration initially found in aqueous phase and its concentration in organic phase was first drawn. A vertical line was then drawn from the concentration of Zn(II) in the feed solution on the *X*-axis. The operating line was next inserted, the slope of which is equal to the phase ratio (O/A = 1 or 2) to be used. Finally, starting from the point where the vertical line from the zinc content of the feed meets the operating line, and drawing a horizontal line to the extraction isotherm and then the vertical line to the operating line.

From this figure, it is clear that at O/A ratio 1:1, the complete extraction of 0.15 M Zn(II) with 0.75 M CYANEX 301 is reached after seven extraction stages, while at O/A ratio 2:1, five extraction stages were sufficient for complete extraction of zinc. On the other hand, the bench scale experiments on the stripping of Zn from the loaded organic solution with 5 M HCl showed efficient stripping after two stages.

Thus, the obtained experimental results show that the extraction of zinc in one stage (76%) by CYANEX 301 from sulfuric acid medium is better than that previously obtained (52.6%) by CYANEX 272 [7] while the extraction percent of manganese is almost the same with the two extractants. Furthermore, the average separation factor (48.0) is comparable to that obtained by Salgado et al. [7] which is equal to 47.7.

3.3. Separation of Zn and Mn from leached black paste solutions

Batch experiments on the leached solution of these batteries were carried out to test the efficiency of the proposed method for the extraction and separation of Zn and Mn from spent MnO$_2$-Zn cell batteries. The spent black paste resulting from the spent dry cells dried in a drying oven for 2 h and subjected to a grinding

step provided a fine powder, and improved the leaching efficiency. Leaching and extraction procedures were carried out by treating 10 g of this powder with 50 ml of 2 M H_2SO_4 solution with continuous stirring at 50 °C, filtering and then analyzing the filtrate for Zn(II) and Mn(II) concentration. The solution shaken with 0.75 M CYANEX 301 in kerosene at 1:1 phase ratio for seven successive extraction stages, showed that extracted Zn and Mn are 98% and 7%, respectively. The total organic phase was separated and treated two times with 5 M HCl for stripping of zinc. The stripping percent for Zn was about 99% while Mn was nearly not stripped.

The process commonly used in the existing plants adopts an initial heat treatment followed by grinding, which intermix the components of the batteries and complicates the recovery process and needs a large scale plant [22]. In the presented method, the extraction and separation of zinc and manganese from sulfate medium using CYANEX 301 is affected by the variation in pH of the leach solution. Devi et al. [9] also found that the extraction and separation of Zn and Mn with the sodium salt of CYANEX 272 is pH dependent. In addition, there is a potentially economic advantage by using CYANEX 301, which is a commercial extractant.

4. Conclusions

- Leaching of Zn and Mn from the black paste resulted from the spent batteries with 2 M H_2SO_4 or HCl solutions using different liquid to solid ratios indicated that H_2SO_4 is relatively more efficient for leaching of Zn than HCl where a maximum value of leaching was obtained at liquid/solid ratio of 5. In case of Mn leaching, 2 M H_2SO_4 or HCl solution produced more or less similar leaching results.

- A slight increase in the leaching of Zn(II) and Mn(II) was obtained when the temperature increased from 25 to 50 °C. Higher temperature had nearly no effect on the amount of leached metal ions.

- Zn(II) and Mn(II) can be extracted by CYANEX 301 dissolved in kerosene from sulfuric acid solution. Increasing the acid concentration slightly increased the extraction of Mn(II) while it decreased the extraction of Zn(II). In both cases, Zn is highly extracted than Mn.

- Slope analysis indicated that the extracted metal species is $\overline{M.A_2(HA)_2}$, where M refers to Zn(II) or Mn(II) ion and HA = CYANEX 301 molecule.

- Increasing the temperature was found to decrease Zn(II) and Mn(II) extraction.

- Selective stripping of Zn(II) from the loaded organic phase was successfully performed using 5 M HCl solution.

- The extraction and stripping procedures successfully applied on the true solution resulting from the leaching of alkaline spent batteries show efficient and selective separation of zinc from manganese.

- The proposed method is simple, efficient and could be useful in a small-scale plant for Zn and Mn recovery from exhausted zinc-manganese dioxide batteries.

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