



Effects of Different pH Values on Dissolution and Recovery of Zinc and Manganese from Spent Zinc–Carbon Batteries Using Ascorbic Acids

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Authors' contributions

This work was carried out in collaboration between all authors. All authors read and approved the final manuscript.

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ABSTRACT

The improper disposal of solid batteries containing manganese and zinc has adverse effects from both an environmental and economic standpoint. It would therefore be useful to be able to recover the compounds of zinc and manganese in these batteries so that these materials might either be re-used or properly disposed of.

This research presents the results of the effects of different pH values on the dissolution of zinc and manganese from waste zinc – carbon batteries using mixtures of ascorbic acid and sulfuric acids.

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The waste batteries were manually separated into various components, and the inner cathode and anode electrodes were ground into powder. This was followed by the extraction of 10 g of battery paste with a mixture of 15 g/dm³ ascorbic acid, 0.5 M or 1.0 M H₂SO₄ at different pH values from 2 to 12 (at about 80°C) and an agitation speed of about 20 rpm. The resulting solutions analyzed using atomic absorption spectrophotometry (AAS) showed that the concentration of Mn extracted from the battery was higher than that of Zn at pH's of 2, 4, 6. The concentrations ranged from 1200 – 10000 mg/kg and 200 – 4200 mg/kg for Mn and Zn, respectively. This indicates that more Mn than Zn would be extracted at lower pH than at higher pH values. The extraction of both metals into the solution decreased with increased in pH of the solution mixture and these results are shown to be consistent with a kinetic model. It was also observed that the recovery of metals from the battery was pH dependent and that more was recovered using NaOH rather than KOH solutions.

Keywords: Manganese; zinc; extraction; waste battery; pH values.

1. INTRODUCTION

Though zinc-carbon battery is abundantly available in Nigeria, not much has been reported on the recovery of the valuable components from its wastes after deposition at the expiration of the life-span. This could be attributed to the fact that primary batteries are not secondary rechargeable batteries and lack of the exact method for estimating their recycling efficiency [1]. However, considering the economic and environmental pollution caused by batteries indiscriminate disposal on human being and other living things in the environs [2], there is still need for recycling and recovery of the valuable components or compounds of manganese and zinc from the batteries. Besides, this will enhance effective environmental management [3]. According to Osinanjo et al. [4], zinc-carbon batteries caused more pollution than alkaline batteries due to the presence of more toxic metals such as Pb and Cd.

Manganese toxicity to terrestrial plants has been reported. For instance, manganese caused disorders in some crops, such as crinkle leaf in cotton according to Adams and Wear [5]. Although zinc was considered to be relatively nontoxic [6], manifestations of overt toxicity symptoms have been reported to be nausea, vomiting, epigastric pain, lethargy, and fatigue due to high intake of Zn [7]. According to Nriagu [6], though zinc would not participate in cellular reduction-oxidation cycle, free ionic zinc, Zn²⁺ could be a potent killer of neurons and other cell types.

As part of efforts to reducing the environmental pollution caused by wastes and in compliance with directive for urgent need for recycling of waste batteries, alkaline and zinc-carbon batteries were collected, dismantled, separated

and analyzed for lead, cadmium and copper. The report showed that the pollution caused by the alkaline batteries was less than that of zinc-carbon because the former contain less Pb and Cd than the latter [4]. This necessitates the need to recycle waste zinc-carbon battery. In addition to using materials recovered for secondary applications, recovery technologies must be economical, environmentally effective [8], and purposely achieved the reduction in the volume of the scraps or cases as well as selective separation of the valuable components according to Xu et al. [9] as reported by Bankole et al. [10]. All the three primary components of zinc-carbon batteries such as zinc, manganese dioxide and steel which is the can, could be recovered and reused in new product either as precursors or starting materials. For instance, recycling of Zn and Mn and their compounds was reported by Gęga and walkowiak [8] and more zinc was recovered than manganese. S-M et al. [11] used ammoniacal ammonium carbonate to selectively leach Zn and Mn from spent zinc-carbon batteries and observed that greater percentage of zinc was leached than manganese. Generally, physical and chemical processes are the two categories of processes used in the laboratory and industry to recycle and recover valuable components from all kinds of batteries such as primary and secondary batteries.

The physical processes are generally manual and mechanical separation of the components of batteries. Example is the extraction of electrolyte mixture into organic solvents such as ethanol after manual or mechanical dismantling of batteries, which enhanced reduction in the environmental pollution [12,13]. The chemical processes are mainly hydrometallurgical methods involving acid or base leaching, solvent extraction, chemical precipitation, bioprocess and electrochemical process or combination of the

processes. Jadhav and Hocheng [14] employed a novel leaching system using ferric sulphate hydrate by chemical method to dissolve nickel (Ni) and cadmium (Cd) from spent Ni–Cd batteries and showed that pH among others factors was the optimum condition for the removal of the metals from the waste battery used. Besides, metals could be recycled industrially from waste batteries. This research work aimed at knowing the amount of zinc and manganese that could be recovered from waste zinc-carbon batteries as a function of different pH values.

2. MATERIALS AND METHODS

2.1 Sample Collection

The waste cylindrical zinc-carbon batteries used for this study were collected from three different refuse disposal locations. These were Agege, Lagos State, Agbara area in Ogun State and Ketu Adie-Owe, Ado-Odo Ota, Local Government Area in Ogun State.

2.2 Separation of Battery Components

The waste cylindrical zinc-carbon batteries used contained carbon as graphite, which serves as the positive terminal (anode). Carbon is an important part of the battery construction which does not take part in the electrochemical reaction, but only helps in collecting the current and reducing manganese dioxide. The zinc serves as the negative terminal (cathode), while the electrolyte is generally either ammonium chloride or zinc chloride.

The separation was carried out by first testing the battery voltage to ascertain the need for discharge to avoid accident caused by battery spark. The battery was then manually dismantled, followed by separation of the components like battery plastic, cover and paper films. Magnetic separation of the iron cover from the mixture of black paste, metallic scraps and remaining paper films was done. The mixture of the black paste, manganese oxide, mercury and graphite was grounded together using ceramic mortar and pestle. After grinding, the powder obtained was stored in plastic containers before Zn and Mn metals were extracted from the powder. The flow

chart for the experimental procedures used for the extraction and dissolution of manganese and zinc materials from waste zinc-carbon battery used is shown (Fig. 1).

2.3 Preparation of Chemicals for Recovery of Manganese and Zinc

The solutions used for the recovery included 0.5 and 1.0 M of H₂SO₄ (sulphuric acid, 98 g/mol) prepared with distilled water. Solution of ascorbic acid used was prepared by dissolving 15 g of the ascorbic acid in 1000 cm³ of distilled water. The solutions of 1.0 M of both potassium hydroxide and sodium hydroxide used as the pH adjusters were also prepared.

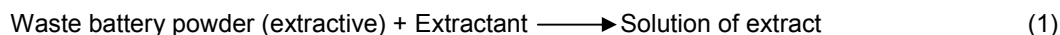
2.4 Extraction of Manganese and Zinc from Waste Zinc-carbon Battery

Mixture of 100 cm³ of 15g/dm³ of ascorbic acid used as a reducing agent, 100 cm³ of 0.5 M H₂SO₄ with 10 g of grounded sample of waste battery was poured into a 500 cm³ borosil flask, followed by the adjustment of the pH of the solution to different values from 2 to 12 by addition of 1M potassium hydroxide. The mixture was then heated in a heating mantle at 80 °C with agitation speed of about 20 rpm for 2 hours.

The steps above were repeated for sulphuric acid (1M H₂SO₄) with the pH values similarly adjusted by addition of potassium hydroxide (1M KOH) solution. Similarly, the pH level of the mixture of 100 cm³ of 15g/dm³ of ascorbic acid, 100 cm³ of 0.5 M H₂SO₄ and 10 g of grounded sample of waste battery was also adjusted to the values from 2 to 8 by addition of 1M NaOH solution. The steps and conditions were maintained to extract both Mn and Zn into the solution mixture. The experimental set-up used for the extraction of the metals from the wastes batteries used is shown in Fig. 2.

2.5 Chemistry of the Dissolution and Recovery of Zn and Mn from the Battery

Extraction is simply a method to remove inorganic or organic soluble components from either a liquid or solid matrix. Therefore, the extraction of both Zn and Mn in this research work can be presented as follows:



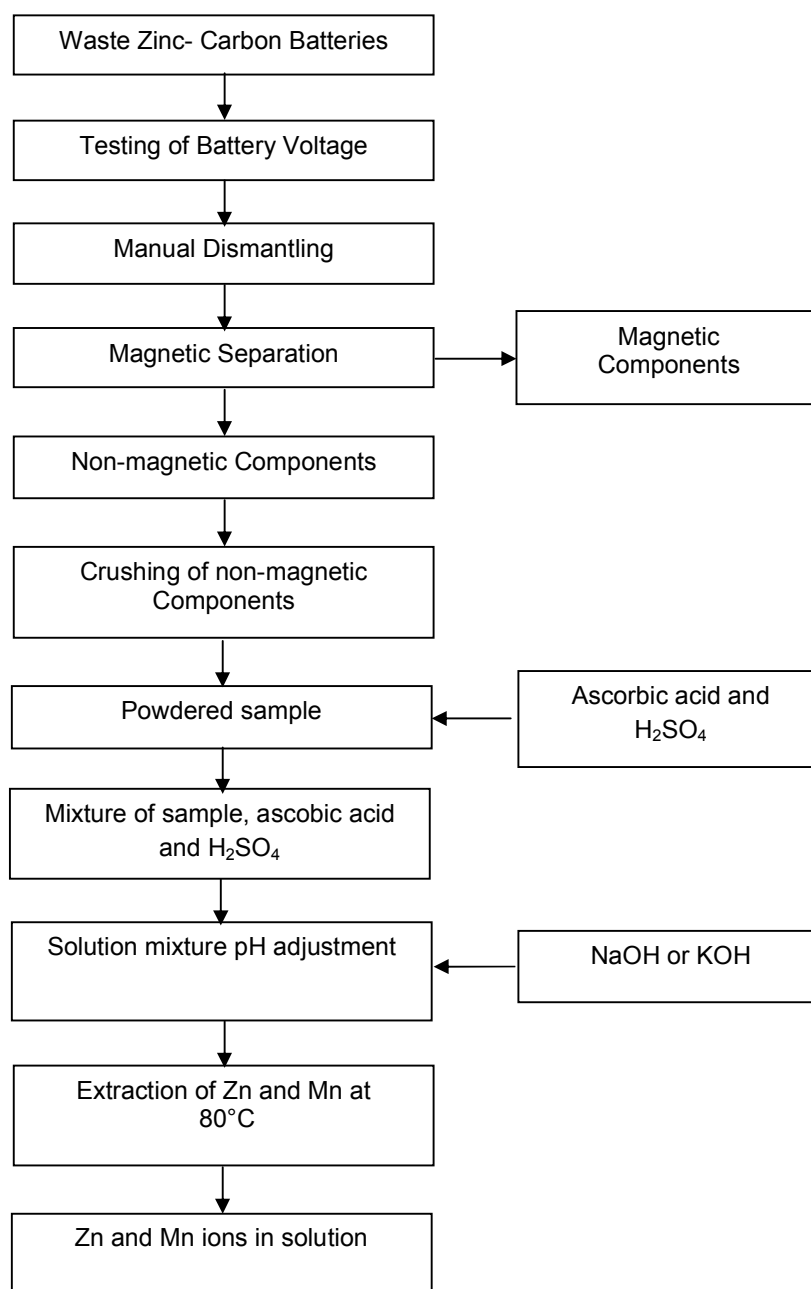
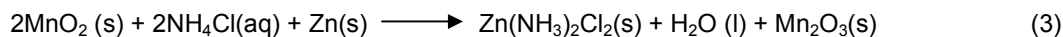


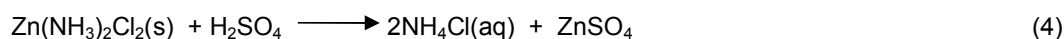
Fig. 1. Flow chart for the extraction of manganese and zinc materials from waste zinc-carbon battery

From the experimental procedures, the proposed chemistries for the recovery of both Zn and Mn can be written according to equations 2 and 3 below.



Considering the overall reduction-oxidation reaction of Zn-C battery given in equation (3), equations (4) and (5) can be proposed as additional chemistries for the quantitative extraction of both Zn and Mn from the powder sample of the waste battery used when H_2SO_4 was added.





Considering Ferella et al. [15] and simple overall reaction reported by Gęga and Walkowiak [8] shown in equation (6), waste battery contains mixture of manganese oxides such as Mn_2O_3 and Mn_3O_4 . Therefore, the chemistry of the dissolution in H_2SO_4 will also produce insoluble MnO_2 as shown in equation (7).

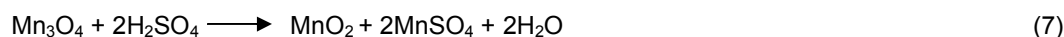
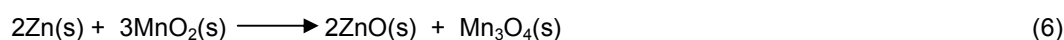


Fig. 2. Experimental set-up for the extraction of manganese and zinc from the waste Zn-carbon batteries

3. RESULTS AND DISCUSSION

3.1 Effects of Different pH Values on Mn and Zn Extraction with 0.5 M H_2SO_4

Fig. 3 showed Zn and Mn extraction as a function of different pH values under the same leaching conditions of 10 g of sample, solution mixture containing 0.5 M H_2SO_4 at 80°C and agitation speed of about 20 rpm for 2 hours. The concentration of Mn extracted from the battery

was higher than that of Zn at the pH from 2 to 8, with the values of Mn ranging from 1200-10000 mg/kg and that of Zn from 200 – 4200 mg/kg. It is evident that more Mn than Zn will be extracted at a lower pH value. At the pH of 6, the amount of Mn and Zn dissolved increased. However, at the pH of 10 and 12, the amounts of Mn and Zn metals extracted were relatively the same and almost constant. Generally, the extraction of both metals into solution decreased with increased in pH of the mixture.

3.2 Comparison of Mn Extracted with Different Concentration of H₂SO₄

Fig. 4 showed Mn extraction as a function of concentrations of sulfuric acid at different pH values under the same leaching conditions of 10 g of sample at 80°C and agitation speed of about 20 rpm for 2 hours. Similar to the report of Ige et al. [16], concentration of acid showed remarkable effects on the dissolution of Mn from the battery. The concentration of Mn extracted with 1M

H₂SO₄ steadily decreased with increased in the pH of the solution mixture more than in 0.5M H₂SO₄. However, Mn generally showed sensitivity to the concentration of H₂SO₄ according to Shin et al. [17]. Significant amount of Mn metal will be extracted from the waste Zn-C battery at lower pH than at higher pH values. This shows that the higher the pH value, the lower the concentration of Mn that would be recovered.

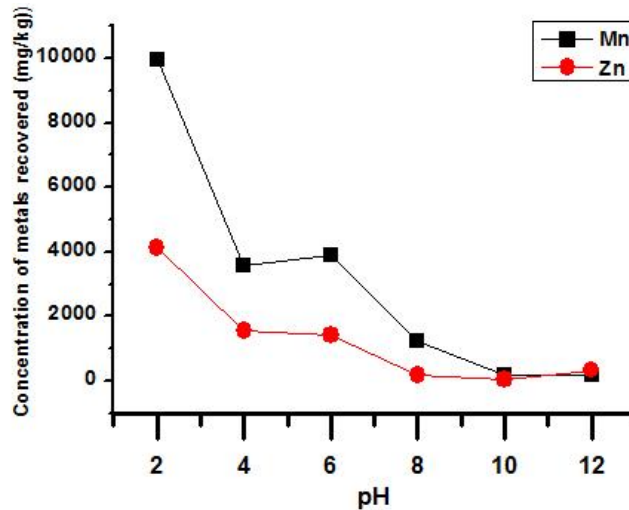


Fig. 3. Concentration of Mn and Zn extracted into solution of 0.5M H₂SO₄ at different pH values adjusted with KOH

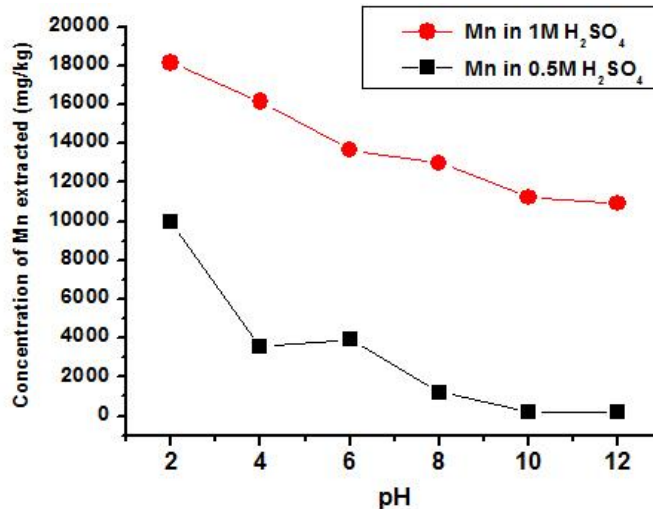


Fig. 4. Concentration of Mn extracted into solution of 0.5M and 1 M H₂SO₄ at different pH values adjusted with addition of KOH

3.3 Comparison of Mn and Zn Extracted with 0.5 M H₂SO₄ in NaOH and KOH

According to Fig. 5, the concentrations of manganese and zinc extracted into the solution, whose pH was adjusted by addition of 1M NaOH were greater than that of addition of 1M KOH even with increased in pH of the solution. Generally, for both NaOH and KOH, the concentrations of Mn were greater than that of Zn. This contradicted the reports by Gęga and Walkowiak [8] and S-M et al. [11], where the recovery of Zn was greater than that of Mn. Fig. 6 showed the representative materials obtained during the extraction at the pH of 4 before and after washing with water and then air-dried at room temperature.

3.4 General Analysis of the Results and Findings

Proposition 1: From the results, the concentration of metals extracted into the solution was inversely proportional to the hydrogen concentration (pH value).

Proposition 2: By proposition 1, it showed that the rate of dissolution of metals decreased with an increased in pH values.

Proof of result:

(1). Observation from the experiment as proposed in 1 showed that if A represents the concentration of metal dissolved and the

hydrogen concentration is designated by p, then the following is actualized:

$$A \propto \frac{1}{p} \Rightarrow A = \frac{k}{p}, \text{ that is, } Ap = k \quad (8)$$

We have, $A_1p_1 = A_2p_2 = A_3p_3 = A_4p_4 = \dots = A_{n-1}p_{n-1} = A_n p_n$.

Here, if the pH value is given, it is easy to calculate the concentration of metal to be extracted by simply using,

$$A_1 = \frac{A_2 p_2}{p_1}$$

By using (8), the approximate constant value could be generated as follows:

$$\frac{1}{n} \sum_{i=1}^n k_i = \frac{1}{n} \sum_{i=1}^n A_i p_i = k. \quad (9)$$

Tables 1 and 2 below could be generated for the extraction of both Zn and Mn into the solution, using Fig. 3 and Fig. 4, respectively.

The average approximate constant for the two metals selected is given by:

$$\frac{5683.33 + 15000.00}{2} = 20683.33/2 = 10341.67 \cong 10342 \text{ mg/kg pH}$$

In general, $Ap = \kappa$, from where, $A = \frac{\kappa}{p}$.

(2). Furthermore, by proposition 2, if time factor t, is involved, then, the known proposition could give rise to the following relationship.

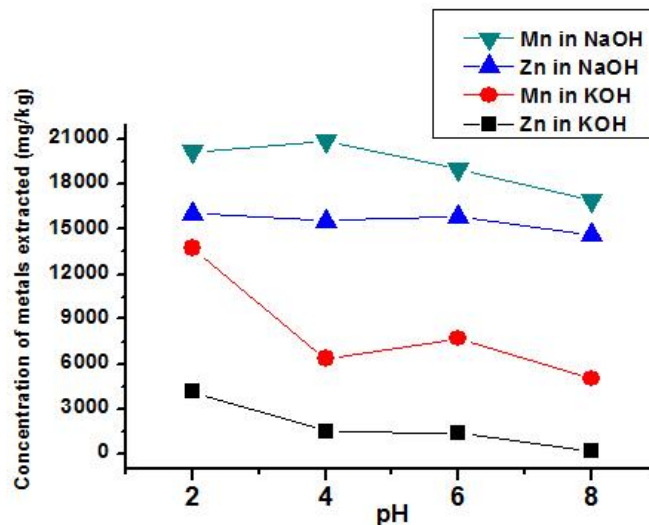


Fig. 5. Concentration of Mn and Zn extracted into solution of 0.5 M H₂SO₄ at varying pH adjusted with both KOH and NaOH

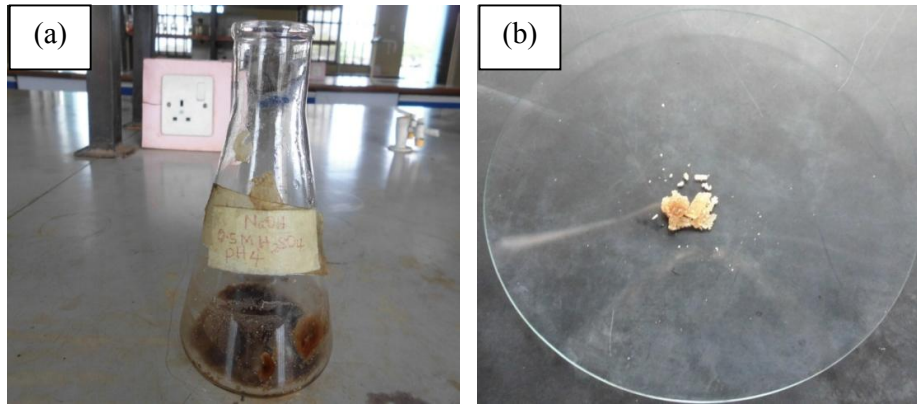


Fig. 6. Extract obtained at pH of 4 (a) before and (b) after washing with water

Table 1. An approximate data generated for Zn from Fig. 3

A	4000	1600	1550	600	500	650	
p	2	4	6	8	10	12	
Ap	8000	6400	9300	4800	5000	7800	$\sum Ap = 34100$

$$k = \frac{34 \cdot 100}{6} = 5683.33 \text{ mg/kg pH}$$

Table 2. An approximate data generated for Mn from Fig. 4

A	10000	3800	4000	1800	800	700	
p	2	4	6	8	10	12	
Ap	20000	15200	24000	14400	8000	8400	$\sum Ap = 90000$

$$k = \frac{90000}{6} = 15000.00 \text{ mg/kg pH}$$

Let the amount of metal be represented by G, then

$$dG/dt \propto 1/p \Rightarrow dG/dt = k/p$$

$$\frac{dG}{dt} \propto \frac{1}{p}, \Rightarrow \frac{dG}{dt} = \frac{k}{p},$$

This means that it is the rate of

$$dG = \frac{k}{p} dt, \text{ so that, } \int_{G_0}^G dX = \frac{k}{p} \int_{t_0}^t dt.$$

$$\Rightarrow [X]_{G_0}^G = \left[\frac{k}{p} t \right]_{t_0}^t$$

$$\Rightarrow G - G_0 = \frac{k}{p} (t - t_0).$$

$$G = \frac{k}{p} (t - t_0) + G_0 \tag{10}$$

Assuming $t_0 = 0$, then (10) becomes $G = \frac{k}{p} t + G_0$.

This equation is of the form, $Y = mX + C$, a linear relationship with slope $m = \frac{k}{p}$ and G_0 (the initial amount) is the intercept, while G is the amount at time, t.

Hence, given that $G = \frac{\kappa}{p}$ from (9),

$G = \frac{G_0}{1 + t_0 - t}$. Here, the amount of metals could be calculated at any given time t.

3.4.1 Observation and general recommendations

For economic importance, substances could be dissolved at a very low pH value, using strong acids like H_2SO_4 . This could enhance the dissolution of metals such as zinc and manganese and separation from impurities.

4. CONCLUSION

The extraction of zinc and manganese from waste zinc-carbon batteries at different pH values from 2 to 12 into the solution mixture of 10 g of battery paste, 15 g/dm³ ascorbic acid and H_2SO_4 at about 80°C and agitation speed of about 20 rpm has been studied. It showed that extraction of Zn and Mn was pH dependent and that the extraction decreased with increased in the pH values. It has been shown that at lower pH, both Zn and Mn could be extracted from the waste Zn-C battery. However, higher concentration of Mn would be extracted than Zn from the waste battery. The metals extracted could be precipitated as useful starting materials for the preparation of other chemical compounds for immediate use in the laboratory. Mathematical

deductions have been proposed based on the experiment and could be employed at different pH values and time for subsequent metal extraction.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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