Thermal Science and Engineering (2021) Volume 4 Issue 1
doi:10.24294/tse.v4i1.1510

ORIGINAL RESEARCH ARTICLE

Thermodynamic study on lead leaching from sodium citrate

Lina Constanza Villa[1], Wilmer Saldarriaga Agudelo[2], Néstor Ricardo Rojas[3*]

[1] *Maestría en Ingeniería-Materiales y Procesos. Universidad Nacional de Colombia, Sede Medellín, Colombia.*

[2] *Doctorado en ciencias químicas - Universidad del Valle. Universidad Nacional de Colombia, Sede Medellín, Colombia.*

[3] *Doctorado en ciencia y tecnología de los materiales. Universidad Nacional de Colombia, Sede Medellín, Colombia. E-mail: nrrojasr@unal.edu.co*

ABSTRACT

Lead-acid batteries account for 60% of the world's electrical energy storage batteries. About 50% of global lead consumption comes from recycled and reused materials. Currently, pyrometallurgical methods account for more than 90% of lead recovery technology; however, these processes are criticized due to sulfur dioxide emissions from the decomposition of lead sulfate at elevated temperatures, in addition to particulate emissions. Lead recovery by recycling batteries by hydrometallurgical processes has been investigated as an alternative to pyrometallurgical processes. In the present work, a thermodynamic analysis of lead leaching with sodium citrate was performed. The thermodynamic analysis was based on the study of three stability diagrams constructed with Medusa® software. Leaching tests were carried out to get to know the system, corroborate the thermodynamic analysis performed, and study the behavior of the system. The results obtained show that it is possible to extract 100% lead with a leaching agent concentration of 0.25 M, a 1:1 solid-liquid ratio, and 25 ℃.

Keywords: Sodium Citrate; Lead Hydrometallurgy; Recycling of Materials; Thermodynamics

ARTICLE INFO

Received: 12 March 2021
Accepted: 10 April 2021
Available online: 16 April 2021

1. Introduction

Lead-acid batteries account for about 60% of batteries sold worldwide. About 50% of lead consumption worldwide is derived from recycled and reused materials. One of the advantages of lead recovery from industrial waste is lower energy consumption, as it uses only 35% to 40% of the energy that would be used to produce lead from mineral ores[1].

The most widely used method in the lead recycling industry uses pyrometallurgical processes, which represent more than 90% of the lead recovery technology. Although these methods are fast, they are also potentially polluting, mainly due to the emission of sulfur dioxide when decomposing lead sulfate and the emission of particulate matter[2]. It directly influences the deterioration of the ozone layer and is critical in the generation of acid rain, causing problems for the environment and human health[1]. Due to the above, the idea of developing a technical alternative to mitigate these environmental impacts arises.

In recent decades, in order to reduce secondary contamination from vapors and dust caused by the pyrometallurgical lead recovery process, lead recovery methods such as hydrometallurgical processes have been proposed[3]. However, these latter processes should be further investigated because they present primary problems such as inefficient desulfurization in an aqueous solution and low solubility of lead compounds in organic solvents[2].

The design of a hydrometallurgical process for lead must take into account the appropriate conditions for desulfurization, leaching and precipitation of lead and/or possible lead compounds, which is essential for the efficiency of the process. Research on the subject has found several advantages compared to traditional processes, such as no emission of sulfur dioxide gas and lead particulate matter, as well as lower energy consumption and recovery of ultrafine lead[4].

In this paper, a thermodynamic analysis of the leaching agent sodium citrate ($Na_3C_6H_5O_7$-$2H_2O$)[5,6] was developed for the extraction of lead obtained from recycled car batteries. The work was carried out through the use of mechanical techniques for the processing of materials, in conjunction with chemical processes implemented in hydrometallurgy. These results, it is expected to contribute to knowledge for the use of the metal recycling industry in our country.

2. Materials and methods

Automotive batteries were collected, based on a commercial analysis, and were selected from the brands that are most commonly in the market. The sulfuric acid contained in the battery was neutralized with sodium carbonate. Subsequently, the internal cells of the battery were extracted to dry them at room temperature. A total of 50 g were taken from each of the electrodes, 100 g in total as an initial sample. The sample was mechanically treated through a Braun Direct Driven Pulverizer UD32, with a speed of 400 rpm. It allowed a homogeneous size reduction. However, to achieve the desired particle size, the material was macerated and then quartered, obtaining a particle size passing mesh N°200 (75 microns) with a sieve of the ASTM-E-11 series. A Varian Spectra AA 220FS atomic absorption spectrometer was used to determine the lead content in the different stages of the investigation. For the acid digestion of the initial sample, prepare a 100 mL solution (aqua regia) to maintain a 1:3 ratio of nitric acid to hydrochloric acid (25 mL HNO_3 and 75 mL HCL). In the solution, 0.121 g of the initial sample already prepared and sieved was dissolved. The solution was stirred at a speed of 300 rpm at a temperature of 350 °C until the solution volume reduces 50 mL. The next step was the cooling of the solution only with agitation and then filtering under vacuum and gauging in a 100 mL flask with the addition of deionized water. The morphological and chemical characterization of the working material was carried out with Phenom Pro X equipment of the Phenom-World brand, which integrates an energy dispersive spectroscopy (EDS) that allows identifying the elements and the chemical composition of the sample. To determine the predominant phases in the sample and the chemical composition of the solid lead-acid battery material, it use the D_8 Advance X-ray diffraction equipment. The thermodynamic analysis was carried out using Medusa® software. According to the characterization performed on the material, the following conditions were set in the program[5], 0.04 M of lead (Pb^{2+}), 0.01 M of sulfate ion, 1 M concentration for the leaching agent, and room temperature (25 °C). The choice of sodium citrate as a leaching agent is based on its low cost and low environmental impact.

The leaching agent complexes lead sulfate ($PbSO_4$) and lead oxide (PbO), in which lead is found as Pb^{2+}. The other existing species such as lead dioxide (PbO_2) and metallic lead Pb^0 do not complex with the leaching agent, so it is necessary to first add a reducing agent which was hydrazine (N_2H_4)[7], which reduces the Pb^{4+} of PbO_2 to Pb^{2+} and finally an oxidizing agent, hydrogen peroxide (H_2O_2), which oxidizes Pb^0 to an oxidation state of Pb^{2+}, in order to form complexes with sodium citrate.

Finally, leaching tests were carried out to learn about the system, corroborate the thermodynamic analysis performed. The working conditions established were as follows: solid-liquid ratio 1:1, 10:1 and 30:1; concentration of the leaching agent: 0.25 M, 0.5 M and 1 M; pH = 7; solution volume 0.1 L; temperature 25 °C; agitation 300 rpm; leaching time 3 hours, reducing agent-oxidizing agent N_2H_4-H_2O_2.

3. Analysis of results

Based on the acid digestion performed and the result of the atomic absorption spectrophotometry, it was found that the lead content in the analyzed battery is 85.6%, therefore, the metal concentration in 1 g of working sample is 0.04 *M Pb* (see calculations in **Annex 1**).

Scanning electron microscopy (SEM) analysis showed that the particle size of the working material is less than 75 μm, as observed in **Figure 1**, and that this material is composed of sulfates and lead oxides, based on the elements found by EDS in the sample and observed in **Figure 2**.

In the X-ray diffractogram (**Figure 3**) it was observed that the predominant phase is lead sulfate ($PbSO_4$) with a concentration of approximately 50.9%, followed by lead dioxide (PbO_2) with a concentration of approximately 36.4%. Metallic lead (Pb) is found at a concentration of 6.1%, and finally lead oxide (PbO) was determined at a concentration of 2.4%.

To perform the thermodynamic analysis, three diagrams were constructed: pourbaix diagrams for the Pb citrate-S-H_2O system, species fraction of the Pb-SO_4-sodium citrate system, and solubility of lead and sulfate ion in the presence of sodium citrate, which is shown below.

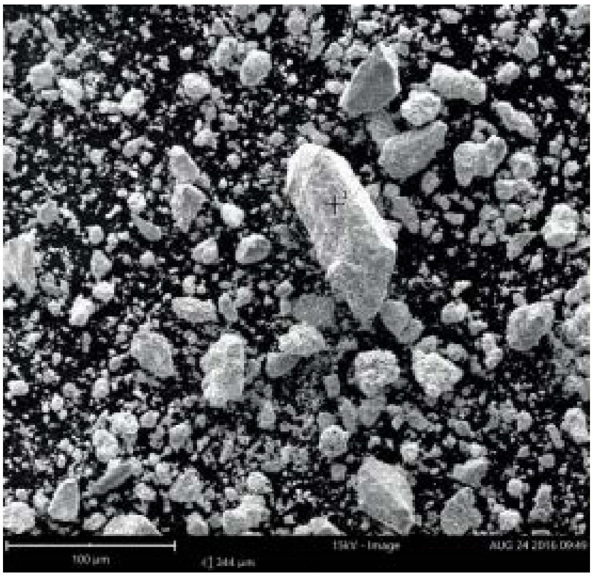

Figure 1. SEM image of the working sample.

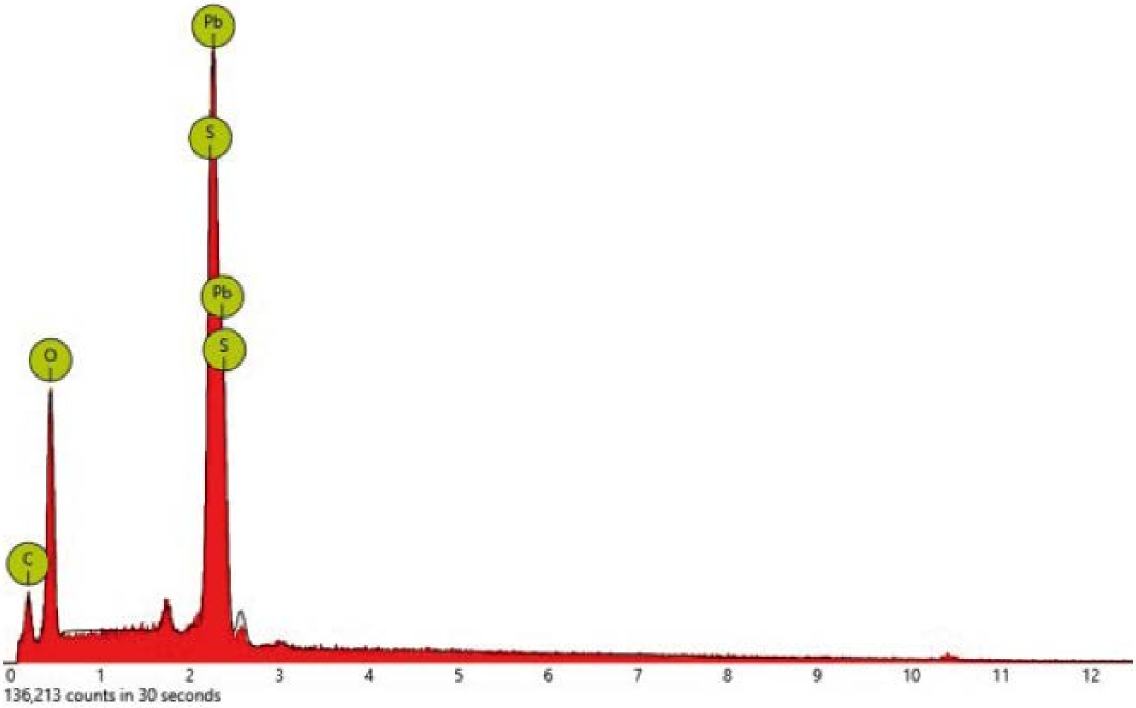

Figure 2. EDS micrographic analysis of the working sample.

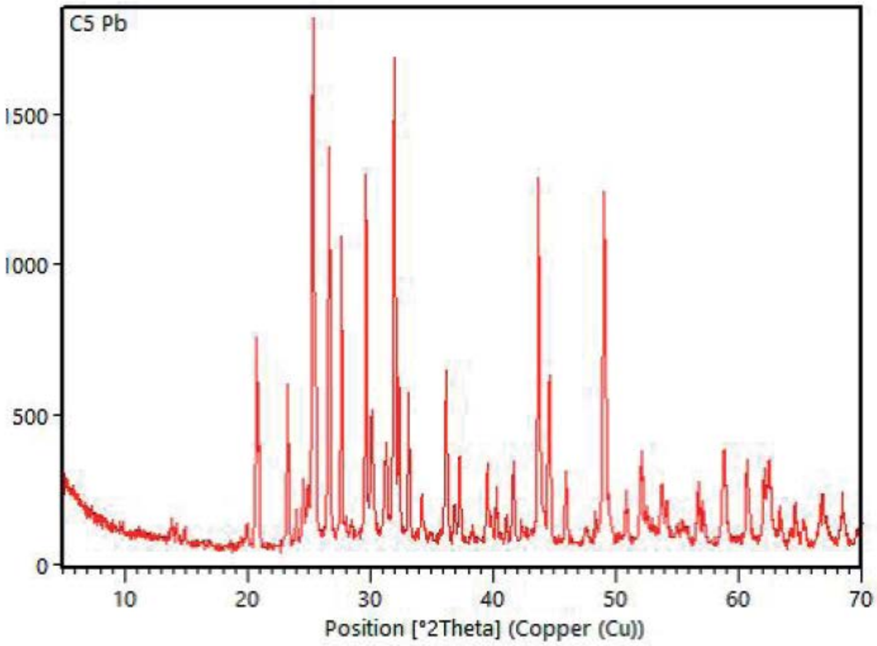

Figure 3. X-ray diffractogram of the sample.

Figure 4 shows the Pourbaix diagram of the Pb-Citrate-S-H_2O system at 25 °C, in which it is observed that within the range of water stability and pH between 5 and 8.5 lead forms two kinds of soluble complexes with citrate Pb(cit)$^-$ and pb(cit)$_2^{4-}$. At pH values lower than 5, precipitation is determined first of a Pb-citrate complex, and then of sulfate $PbSO_4$. At pH higher than 8.5, precipitation of hydroxide $Pb(OH)_2$ is established. For the whole pH working range, PBS sulfide can be obtained from both soluble and insoluble species with the variation of the electric potential.

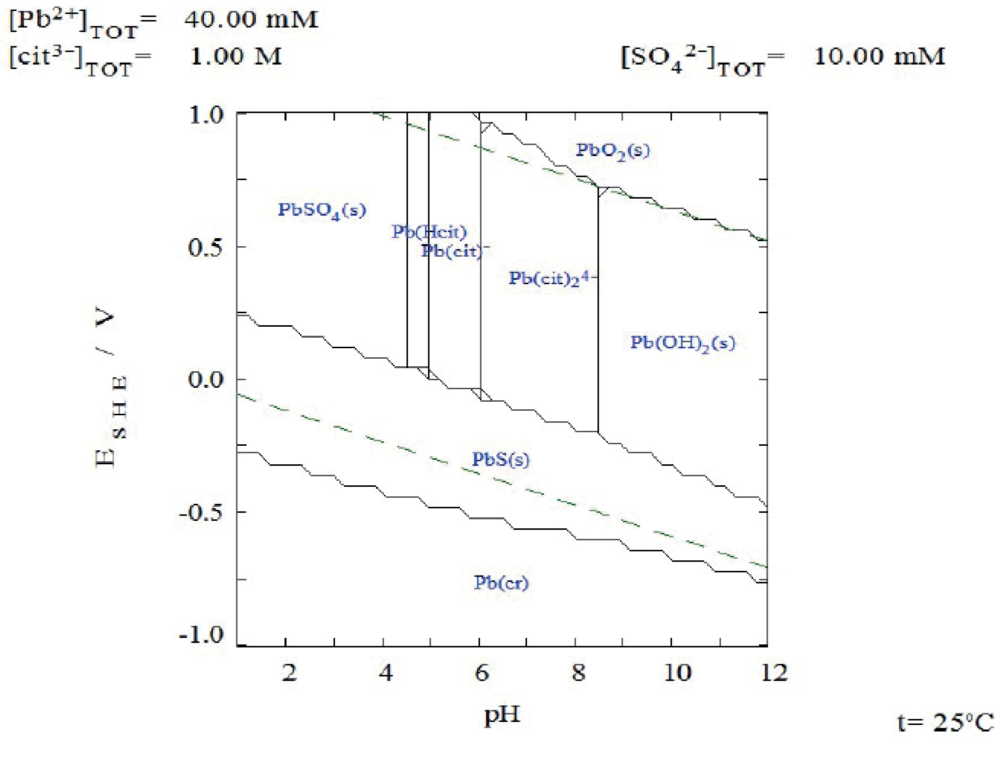

Figure 4. Pourbaix diagram for the Pb-citrate-S-H_2O system in the presence of sodium citrate. Medusa® Software.

Figure 5 shows the species fraction diagram; and concerning the two complexes also found in the Pourbaix diagram, a relative presence for $Pb(cit)_2^{4-}$ of 60% at pH 7.5 is determined, while for the $Pb(cit)^-$ species its presence is only 30% at pH 5.5. The other species that appear in the solution could be obtained by adding hydrazine as a reducing agent and oxidizing with hydrogen peroxide. However, their presence in the system would be less than 30%. The solubility diagram in **Figure 6** shows that Pb is soluble in citrate from acid pH up to pH 8, where its presence decreases. While the sulfate ion is soluble at basic pH up to pH 5, pH from which its solubility decreases.

Based on the above diagrams for a leaching pH range between 5 and 8, it is theoretically possible to leach lead with sodium citrate in the presence of sulfur and obtain $Pb(cit)^-$ and $pb(cit)_2^{4-}$ at a temperature of 25 °C.

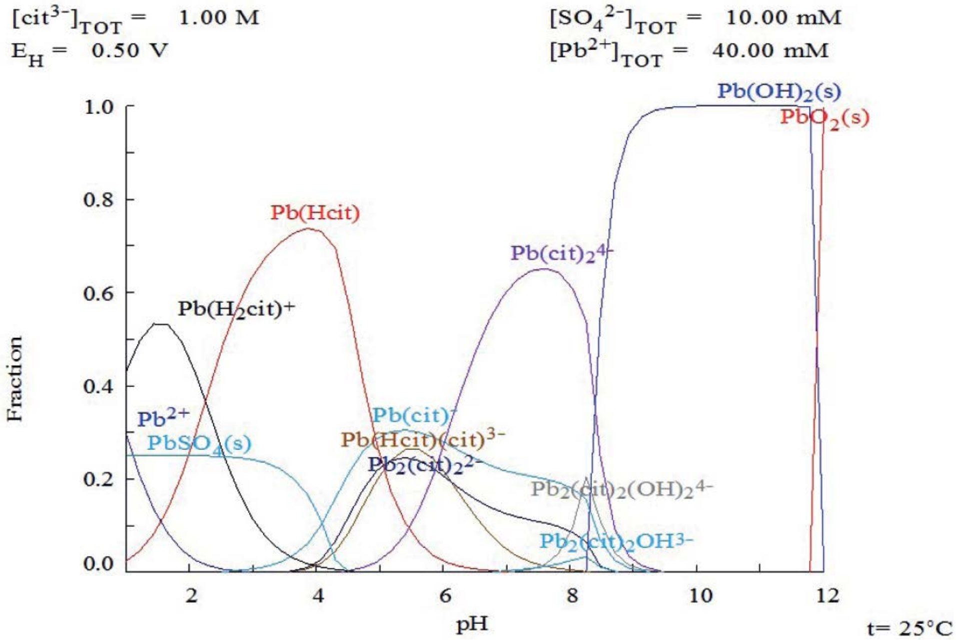

Figure 5. Species fraction plot of the Pb^{2+} system in the presence of sodium citrate. Medusa® software.

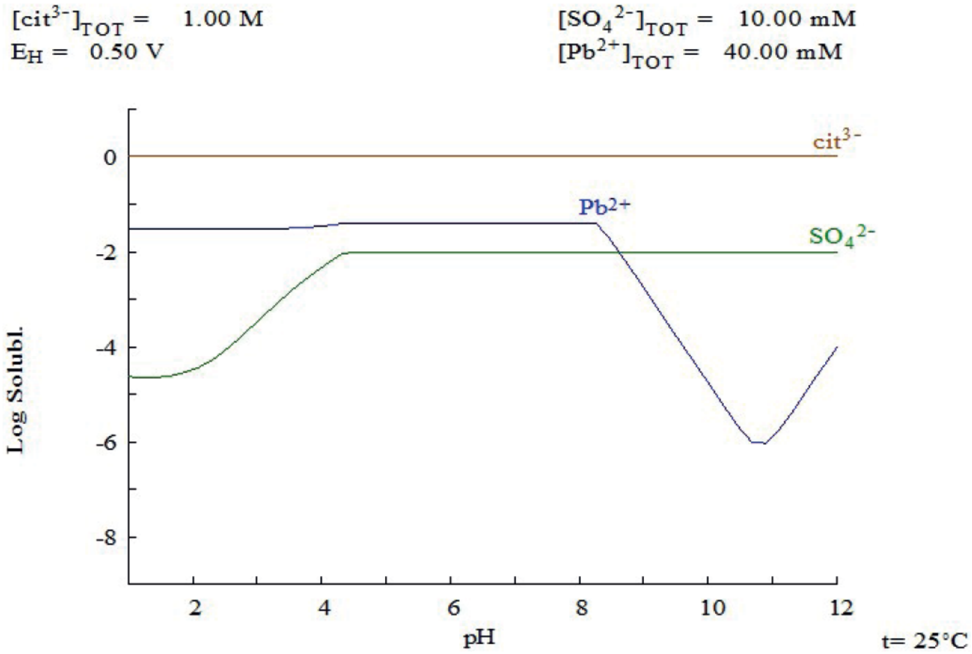

Figure 6. Pb^{2+} solubility diagram in sodium citrate. Medusa® software.

The following three graphs show the results of the sodium citrate leaching kinetic tests. **Figure 7** shows that for a low suspension with a 1:1 solid-liquid ratio and a low concentration of leaching agent (0.25 M), 100% metal extractions are obtained in 138 minutes of leaching. When the concentration of leaching agent increases, the extraction decreases to 80%, which is still an industrially attractive value. The above results indicate that the ionic activity is higher at low concentrations compared to the characteristics of a solution with high concentrations. If the consumption of sodium citrate dominates the hydrolytic reaction, the complex reaction can be weakened or slowed down. It would lead to an inhibitory effect on the behavior of the leaching agent[6,8].

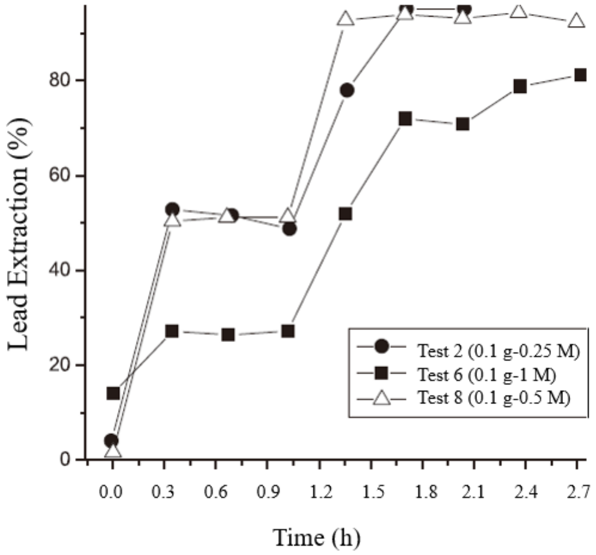

Figure 7. Lead extraction kinetics for a constant mass of 0.1 g in 0.1 L and citrate concentration 0.25, 0.5 and 1 M.

Figure 8 shows a decrease in metal extraction and a lower influence of the leaching agent concentration in the hydrometallurgical process; the highest extraction (90%) was obtained for a 10:1 solid-liquid ratio at 0.25 and 0.5 M citrate; while for a 1 M citrate concentration, 85% was obtained. It is determined that for these solid concentrations the concentration of the leaching agent is not very relevant. Finally, **Figure 9** shows the lowest metal extraction and no influence of the leaching agent concentration. All leachates with the highest 3:1 solid-liquid ratio were between 20 and 25% metal extraction, with less favorable conditions industrially. Low metal extractions at high suspended solids concentrations may again be due to an inhibitory effect on the behavior of the leaching agent; the controlling mechanism of the reaction may also play a role, it is possible that at low concentrations of leaching agent the process is controlled by mass transfer, however, at high concentrations, the mechanism is different[9].

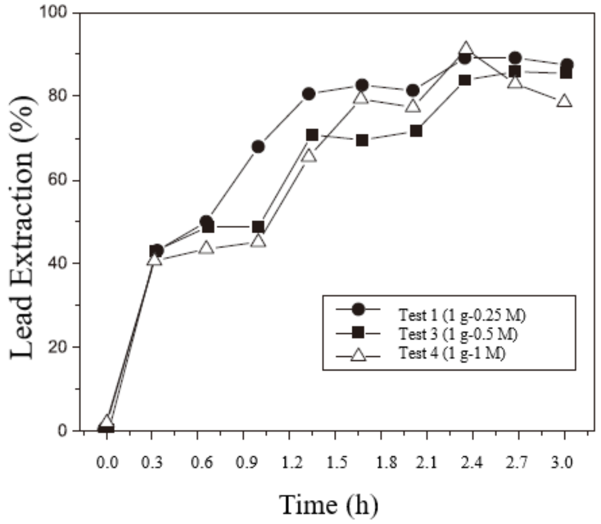

Figure 8. Lead extraction kinetics for a constant mass of 1 g in 0.1 L and citrate concentration 0.25, 0.5 and 1 M.

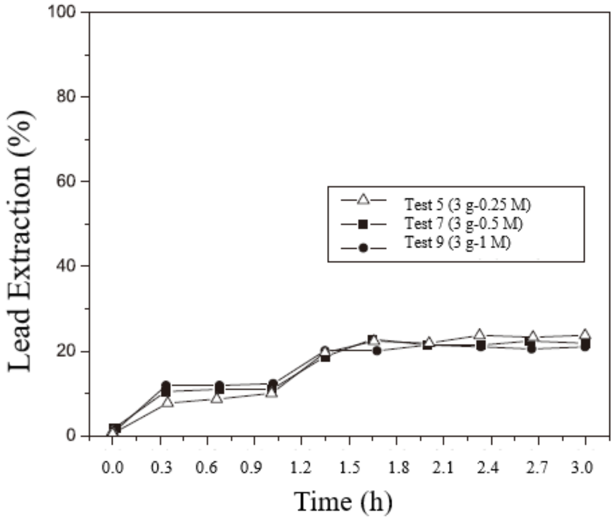

Figure 9. Lead extraction kinetics for a constant mass of 3 g in 0.1 L and citrate concentration 0.25, 0.5 and 1 M.

4. Conclusions

The stability diagrams analyzed show that it is thermodynamically possible to leach lead with sodium citrate to obtain $Pb(cit)^{-}$ and $Pb(cit)_2^{4-}$, at pH between 5 and 8 and temperature of 25 °C. Kinetic studies indicate recoveries of 100 and 90% for citrate concentrations of 0.25 and 0.5 M respectively, at 25 °C and a 1:1 solid-liquid ratio. A hydrometallurgical process is technically possible as a real alternative for lead recycling from spent lead-acid batteries, because with this process, there are no sulfur dioxide or particulate emissions to the environment.

Conflict of interest

The authors declared no conflict of interest.

References

1. Smaniotto A, Antunes A, Filho I, *et al*. Qualitative lead extraction from recycled lead-acid batteries slag. Journal of Hazardous Materials 2009; 172(2–3): 1677–1680. doi: 10.1016/j.Jhazmat.2009.07.026.
2. Sonmez M, Kumar R. Leaching of waste battery paste components. Part 1: Lead citrate synthesis from PbO and PbO_2. Hydrometallurgy 2009; 95(1–2): 53–60. doi: 10.1016/j.Hydromet.2008.04.012.
3. Pan J, Zhang C, Sun Y, *et al*. A new process of lead recovery from waste lead-acid batteries by electrolysis of alkaline lead oxide solution. Electrochem Commun 2012; 19: 70–72. doi: 10.1016/j.elecom.2012.03.028.
4. Zhu X, Li L, Sun X, *et al*. Preparation of basic lead oxide from spent lead acid battery paste via chemical conversion. Hydrometallurgy 2012; 117–118: 24–31. doi: 10.1016/j.hydromet.2012.01.006.
5. Puigdomenech I. MEDUSA, HYDRA and INPUT-SED-PREDOM. Stockholm, Sweden: Royal Institute of Technology. 2004. Available from: https://sites.google.com/site/chemdiagr.
6. He D, Yang C, Wu Y, *et al*. $PbSO_4$ leaching in citric acid/sodium citrate solution and subsequent yielding lead citrate via controlled crystallization. Minerals 2017; 7: 93–103. doi: 10.3390/min7060093.
7. Zarate-Gutierrez R, Lapidus G. Anglesite ($PbSO_4$) leaching in citrate solutions. Hydrometallurgy 2014; 144–145: 124–128. doi: 10.1016/j.hydromet.2014.02.003.
8. Ajibola O, Jimoh BO. Agitation leaching recovery of lead and zinc from complex sulphide ore deposit using HF, HCL and H_2SO_4. Advances in Applied Science Research 2014; 5(3): 68–72. Available from: https://www.primescholars.com/articles/agitation-leaching-recovery-of-lead-and-zinc-from-complex-sulphideore-deposit-using-hf-hcl-and-h2so4.pdf.
9. Seidel A, Zimmels Y. Mechanism and kinetics of aluminum and iron leaching from coal fly ash by sulfuric acid. Chemical Engineering Science 1998; 5(22): 3835–3852. doi: 10.1016/S0009-2509(98)00201-2.

Appendix 1. Determination of lead concentration in the working sample.

Acid digestion of the initial sample: The result of the digestion performed to determine the lead content in the sample was 85.6 ppm for 0.1 g of head sample in 0.1 L of solution:

$$85.6 \text{ ppm} \times \frac{10 \text{ ml solution}}{1 \text{ ml sample}} = 856 \text{ ppm total digestion } 0.1 \text{ L}$$

$$856 \text{ mg/L} \times 0.1 \text{ L} = 85.6 \text{ mg Pb}$$

$$\text{Quality} = 0.1 \text{ g} = 100 \text{ mg}$$

$$\%\text{Pb} = \frac{\text{mg digestion}}{\text{mg sample}} \times 100\% = \frac{85.6 \text{ mg Pb}}{100 \text{ mg sample}} \times 100\% = 85.6\% \text{ Pb}$$

The result of the atomic absorption spectrophotometry shows that the lead (Pb) content of the analyzed battery is 85.6%.

According to this result, the molar concentration of lead was determined:

$$1\ M \text{ Pb} = 207.2 \text{ g/L Pb}$$

$$856 \text{ mg Pb} \times \frac{1 \text{ g Pb}}{1000 \text{ mg Pb}} = 0.856 \text{ g Pb}$$

$$0.856 \text{ g Pb} \times \frac{1 \text{ mol Pb}}{207.2\ g \text{ Pb}} = 4.13 \times 10^{-3} \text{ mol Pb}$$

$$\text{Molar amount in 1 g sample} = \frac{4.13 \times 10^{-3} \text{ mol Pb}}{0.1 \text{ L}} = 0.04\ M \text{ Pb}$$