RECYCLE LEAD FROM USED LEAD–ACID BATTERY BY HYDROMETALLURGICAL PROCESS

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TÓM TẮT

NGHIÊN CỨU THU HỒI CHÌ TỪ PIN CHÌ - AXIT BẰNG PHƯƠNG PHÁP NGÂM CHIẾT

Trong nghiên cứu này, sử dụng quy trình tái chế bột chì từ pin chì – axit đã qua sử dụng bằng cách ngâm chiết với axit lactic, natri xitrat và hyđrô peoxit. Quá trình ngâm chiết với tỷ lệ lỏng/rắn là 10 (mL/g), thuốc thử gồm 40 ml axit lactic (3 mol/L), 15 ml natri xitrat (1 mol/L) và 15 ml hidro peoxit (pha từ H_2O_2 30% với tỷ lệ 1/4) thời gian ngâm chiết là 10 giờ. Kết quả nghiên cứu cho thấy hiệu suất thu hồi chì đạt trên 90%, chì xitrat hình thành được kết tinh lại ở nhiệt độ phòng trong thời gian 12 giờ với độ tinh khiết đạt 99,9%.

Từ khóa: *Bột chì từ pin chì – axit, ngâm chiết, chì xitrat, kết tinh lại.*

1. INTRODUCTION

Nowadays, there are still many debates about limiting the use of lead-acid batteries (LABs), the main reason being concerns about the effects of lead on humans and the environment [1]. Nevertheless, the use of LABs continues to grow and retain some benefits over Li-ion batteries (LIBs) in the future due to the following reasons: (i) the lower cost in not only mining and refining of lead but also the production of LABs as compared to those of lithium, (ii) the outstanding longevity and power density of the LABs, and (iii) the more safety, transportation, and handling of LABs[2]. In addition, the recycling rate of lead from LABs is high (up to 99%), while the recycling rate of LIBs is only 5% [3], and lead is reused in devices up to 80% [4]. According to the design of a typical LAB, it consists of 64% lead, 28% H_2SO_4 acid, 5% polypropylene, and 3% other metals (such as antimony) [5]. In used LABs, lead mainly exists in the form of lead paste ($PbSO_4$ and $PbO.PbSO_4$ components) with a content of 60%[6]. Therefore, recycling of used LABs is a new concern for the whole society. In addition to economic benefits, it also has environmental significance to minimize impacts on humans. Recycling and reusing lead are highly developed, especially in low- and middle-income countries [6]. While developing countries have owned safe and effective technological processes to recover lead from waste, the lead recycling process in most underdeveloped ones is poorly managed and uncontrolled, resulting in a high leakage of lead pollution in the environment [7]. It is estimated that nearly 1 million people are affected by lead pollution from LAB recycling in the South America and South Asia regions [8]. Used LABs are commonly recycled by physical separation, sulfur removal, smelting, and lead refining [9]. The furnaces are installed with filtration systems to remove sulfur before smelting. This sulfur separation step minimizes pollution and significantly reduces temperature loss during smelting and manufacturing costs. Chemicals, such as NaOH and Na_2CO_3, are often added to reduce sulfur. However, CO_2 emissions as a secondary pollutant are still generated due to the use of coal or coke during the lead refining process. Therefore, new technology to recover lead from used LABs has been developed to replace metallurgical ones[10]. In addition, the use of organic acid solutions and organic acid salts in lead recovery from used LABs has also been researched [11]. Lead was collected in the form of a complex and then heated to obtain ultra-fine lead oxide powder that can be used directly in the production of new batteries. The utilization of organic acids and organic acid salts offers an ecologically sustainable technique for recycling lead-acid batteries. This process conserves energy, restricts the release of SO_x and CO_2 gases, and minimizes the dispersion of lead dust particles, in contrast to conventional metallurgical procedures [12 - 15].

In this article, the recovery of lead oxide powder was studied by leaching lead-containing paste from used LABs with lactic acid and sodium citrate salt.

2. EXPERIMENT

2.1. Chemicals

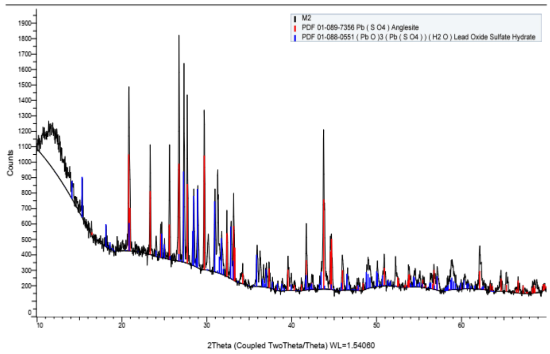

Figure 1. Structural analysis of waste lead powder samples.

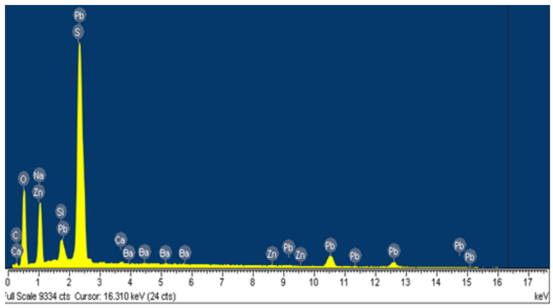

Figure 2. Results of analysis contents of waste lead powder.

- Lead powder was taken from the lead paste of the used lead-acid batteries (Dong Nai batteries) by mechanical and thermal pre-treatment. The structure and chemical compositions of included $PbSO_4$, PbO_2, PbO, Pb, and some other metals were demonstrated in Figures 1 and 2. The total content of lead metal (Pb) accounted for 90.20%, whereas those of antimony and other metals were 9.4% and 0.4%, respectively. This composition was similar to the previous report[16].

- Sodium citrate ($Na_3C_6H_5O_7.2H_2O$), lactic acid ($C_3H_6O_3$), and hydrogen peroxide (H_2O_2) were analytical purity.

2.2. Method

10 g of used lead powder (obtained from lead paste) was dissolved in a 250-mL beaker containing 3 M lactic acid ($C_3H_6O_3$) solution. The solution was

stirred at 400 rpm and heated at 60°C for 1 hour. $Na_3C_6H_5O_7$ with a concentration of 1 mol/L and H_2O_2 (H_2O_2 solution was diluted by 30% H_2O_2 solution with H_2O_2:H_2O ratio of 1/4) were added and kept stirred for the following 8 hours (experimental conditions were shown in table 1). At the end of the reaction, the lead powders were completely dissolved to form $Pb_3(C_6H_5O_7)$. The insoluble was filtered out, and the solution was cooled to room temperature. The citrate lead was recrystallized for 12 hours before being filtered to obtain pure citrate lead. The following reactions describe the process step-by-step:

$$PbO + 2HL \rightarrow PbL_2 + H_2O \quad (1)$$

$$PbO_2 + 2HL + H_2O_2 \rightarrow PbL_2 + 2H_2O + O_2 \quad (2)$$

$$3PbL_2 + 2Na_3C_6H_5O_7 \rightarrow Pb_3(C_6H_5O_7)_2 + 6NaL \quad (3)$$

$$3PbSO_4 + 2Na_3C_3H_6O_7 \rightarrow Pb_3(C_6H_5O_7)_2 + Na_2SO_4 \quad (4)$$

where HL was lactic acid

Experimental conditions to evaluate the influence of liquid/solid ratio (g/mL) were given in Table 1, whereas that of lactic acid concentration was shown in Table 2.

Table 1: The influence of liquid/solid ratio on lead recovery efficiency

Chemicals	Liquid/solid ratio (mL/g)			
	5	8	10	12
$C_3H_6O_3$ 3 mol/L (ml)	15	30	40	50
$Na_3C_6H_5O_7$ 1 mol/L (ml)	10	20	25	35
H_2O_2 7.5 w% (ml)	15	15	15	15

Table 2: The influence of lactic acid concentration on recovery efficiency

Chemicals	$C_3H_6O_3$ concentration (mol/L)			
	1	2	3	4
$C_3H_6O_3$ (ml)	40	40	40	40
$Na_3C_6H_5O_7$ (1 mol/L) (mL)	25	25	25	25
H_2O_2 7.5 % (mL)	15	15	15	15

Lead recovery efficiency was calculated by the following equation (Equation 5)

$$H(\%) = \frac{lead\ content\ after\ filtered}{initial\ lead\ content} \quad (5)$$

The structure and composition of lead powder samples were analyzed by X-ray diffraction (XRD) and X-ray scattering (EDS) methods at the Institute of Materials Science, Vietnam Academy of Science and Technology.

Lead content was analyzed by Agilent 7800 ICP – MS equipment (USA) at the Institute of Geology, Vietnam Academy of Science and Technology.

3. RESULTS AND DISCUSSION

3.1. Effect of liquid/solid ratio on lead recovery efficiency

The yield of pure citrate lead recovery from this process depended on the volume of reagent solution added during the reaction, as shown in Figure 3.

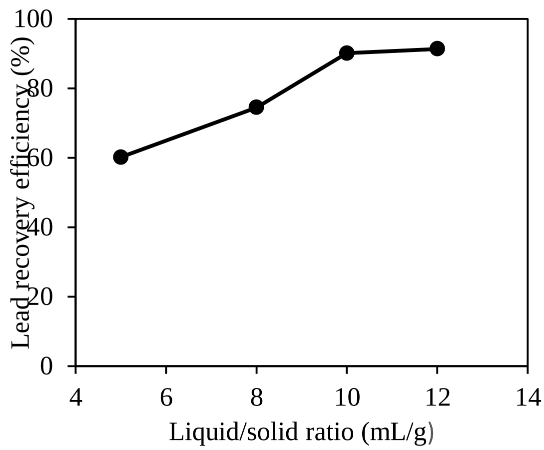

Figure 3: Effect of liquid/solid ratio on efficiency

Figure 3 shows the proportion of lead recovery efficiency with the liquid/solid ratio or the quantity of reagents, including lactic acid, sodium citrate, and hydrogen peroxide. The lead recovery efficiency dramatically increased from about 60% to 90.12% as the liquid/solid ratio increased from 5 to 10. Further growth of the amount of reagent only resulted in a marginal improvement of lead recovery to 91.34%. This was because the reaction of lactic acid and sodium citrate with lead compounds had occurred and reached saturation [15]. In this process, lead citrate ($Pb_3C_6H_5O_7$) existed in solution with temperatures ranging from 60 ^oC to 80 ^oC and easily crystallized at room temperature [17].

3.2. Effect of time on recovery efficiency

Figure 4 demonstrates that the efficiency of lead recovery is influenced by the reaction time due to the sluggish reaction between lead compounds and lactic acid and sodium citrate.

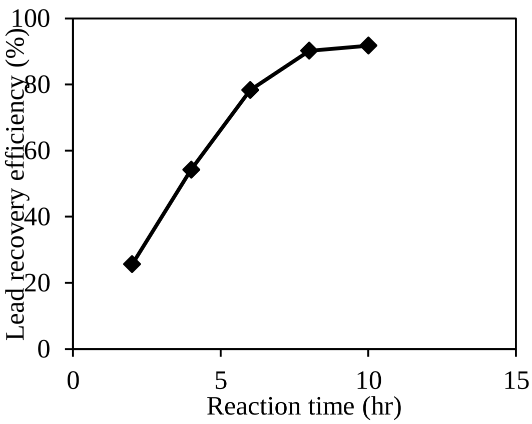

Figure 4. Effect of reaction time to lead recovery efficiency

Lead recovery efficiency gradually increased over time (Figure 4). The efficiency was only reached 25.65% after 2 hours. When the reaction time was increased to 8 hours, the efficiency reached 90.22% and exhibited an insignificant change as the reaction was extended to 12 hours. The long reaction was due to a step-by-step reaction. The lead compounds, such as PbSO4 and PbO, initially reacted with lactic acid. Subsequently, lead lactate was generated and reacted with sodium citrate to produce the citrate lead complex ($Pb_3C_6H_5O_7$). Thus, the reaction time to recover lead from the lead powder of used lead-acid batteries was 10 hours with an efficiency of 90.22%

3.3 Effect of lactic acid content on lead recovery efficiency

Lead recovery efficiency depended on both the lactic acid concentration and the formation of the complex with sodium citrate, and is shown in Figure 5.

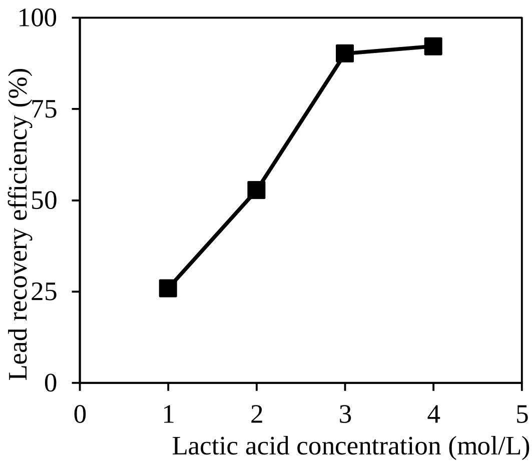

Figure 5. Effect of lactic acid concentration on lead recovery efficiency

The content of lead citrate in the solution depended on the reaction between the compounds in the lead powder and lactic acid. When the lactic acid concentration increased from 1 mol/L to 3 mol/L, the lead content in the solution also increased from 25.92% to 90.21%. However, similar to the liquid/solid ratio, a further increase in lactic concentration to 4 mol/L exhibited an insignificant lead recovery efficiency. It can be seen that the reactions were mostly completed with a lactic acid concentration of 3 mol/L; hence, this concentration was chosen for later lead recovery. Meanwhile, H_2O_2 in the reactions acts as an agent to dissolve PbO_2 and Pb in the waste lead powder of LABs [15].

3.4. Recrystallization of citrate lead

The citrate lead solution was heated and concentrated until the precipitation appeared. The process was stopped, cooled to room temperature, and left for 12 hours to recrystallize citrate lead ($Pb_3C_6H_5O_7.2H_2O$)[19]. Following the filtration process, the recovered lead citrate crystals were analyzed to assess the lead content in the final product. In addition, ultra-high lead oxide powder could be formed from this intermediate product [12]. The metal compositions were analyzed by the ICP-MS method of citrate lead, and the results are shown in Table 3 and Figure 6.

During the crystallization process to recover lead citrate, a portion of lead citrate remained in solution (10%)[15]. The final product had a high purity of up to 99.9%. Otherwise, there was a small amount of Sb (0.09%) and other metals (0.01%).

Table 3: The composition of included metals in citrate lead

No.	Unit	Content (%)
1	Pb	99,9
2	Sb	0,09
3	Other metals	0,01

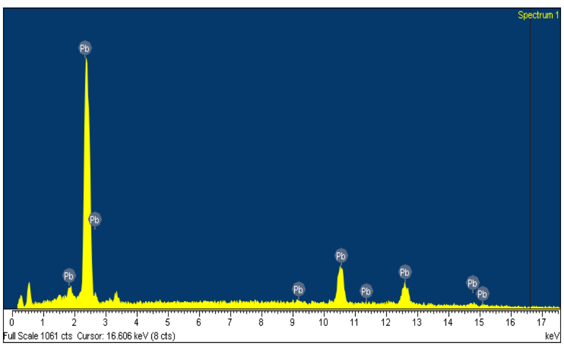

Figure 6. Results of metal compositions in citrate lead.

4. CONCLUSION

This research proposed a process to recover lead from the lead powder of used lead-acid batteries by using lactic acid and sodium citrate with the presence of 7.5% H_2O_2. The separation process with a liquid/solid ratio of 10, lactic acid concentration of 3M, and separation time of 10 hours gave a recovery efficiency of 90.22%. The crystallizing process of the lead citrate product at room temperature after 12 hours obtained the final product with purity up to 99.9%.

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