PbSO₄ Leaching in Citric Acid/Sodium Citrate Solution and Subsequent Yielding Lead Citrate via Controlled Crystallization

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Abstract: Lead citrate is a key precursor for the green recycling of spent lead acid battery paste in a citric acid/sodium citrate (CA/SC) solution. In this study, the main paste component, $PbSO_4$, was leached and crystallized to yield lead citrate. Results showed that the leaching of $PbSO_4$ in citric acid/sodium citrate solution was remarkably enhanced by an increase in temperature from 35 °C to 95 °C and an increase in sodium citrate (SC) concentration from 50 to 650 g/L. In comparison, increasing the citric acid/sodium citrate molar ratio inhibited this leaching. Controlled crystallization through cooling the solution or adjusting the pH of the solution can effectively produce lead citrate crystals. The X-ray diffraction patterns of four products obtained in a comparison test were all consistent with $Pb_3(C_6H_5O_7)_2$. However, the scanning electron microscopy analysis suggested that the morphology was distinct from rods to sheets, which were mainly affected by the temperature variation.

Keywords: spent lead acid battery paste; lead citrate; leaching; crystallization

1. Introduction

China is the largest producer and consumer of primary and secondary refined lead around the world. An increasing number of enterprises in China have begun to produce secondary lead using spent lead acid batteries (LAB) as raw materials. However, the proportion of secondary lead production was only 30% of the total lead production in 2013 and is estimated to reach 44% in 2015 and 60% in 2028 [1,2]. There are great opportunities for the secondary lead recycling industry, due to a number of economic and environmental concerns arising from outdated technologies, such as the pyro-metallurgical and hydro-electrometallurgical processes [3,4]. It turns out that, in China, the accumulative lead into the environment has amounted to 19.54 million tons over the past five decades [5]. In consideration of the toxic damage of lead on the human body, more stringent laws and regulations have been promulgated concerning secondary lead production. Therefore, it is essential to develop new sustainable approaches to recycle spent LABs.

Spent lead paste is the main lead-containing part of LABs and consists of four valuable lead components: $PbSO_4$ (~60%), PbO_2 (~28%), PbO (~9%), and Pb (~3%) [6]. Recently, investigators focused on single hydro-metallurgical methods to recover lead from spent lead paste, especially concentrating on the desulfurization of $PbSO_4$ using reagents such as Na_2CO_3, NaCl, and NaOH [7–9]. Kumar et al. [10–13] had developed a novel paste for the recycling method. In this process, the spent

lead paste was treated with citric acid and sodium citrate in aqueous solutions to generate a lead citrate precursor via leaching and crystallization. Lead is finally recovered as an ultra-fine lead oxide powder by the further calcination of the lead citrate precursor at a low temperature. New battery pastes containing this novel powder exhibit excellent electrochemical performance and initial capacity [14–16]. In comparison with traditional processes, this route is substantially advantageous due to reduced cost and less emission of lead containing dust and SO_2 gas. Equipped with additional benefits, including a short process, easy operation, and excellent recovery of lead, this process has already been deemed a promising technique for industrial applications [14].

For this green route, the synthesis of lead citrate by a leaching/crystallization process is the first step and is of great importance. However, the procedures of leaching and crystallization are still not well understood. In particular, when treating the actual spent lead paste, there is the problem of a high cost, mainly originating from excess reagent consumption [13]. In order to yield lead citrate with a satisfactory recovery and expense, a thorough understanding of the leaching and crystallization processes would be essential. As no definitive research has yet been reported, this work focuses on studying the behaviors of leaching and crystallization. The main component of spent lead paste, $PbSO_4$, was used in experiments to investigate the effects of time, temperature, and regent concentration on the lead proportion in filtrate. It is assumed that the findings obtained in this study may lead to a further process optimization for efficient plant operation.

2. Materials and Methods

2.1. Chemicals

In this paper, experiments were carried out using lead sulfate $PbSO_4$ (Sinppharm, Shanghai, China), citric acid $C_6H_8O_7 \cdot H_2O$ (Tianjin Kemiou, Tianjin, China) and sodium citrate $Na_3C_6H_5O_7 \cdot 2H_2O$ (Sinppharm). The size of all lead sulfate powder is smaller than 125 μm. All chemicals used in this study were analytically pure and commercially available.

2.2. Procedures

The citric acid/sodium citrate CA/SC mixed solution was prepared by adding $Na_3C_6H_5O_7 \cdot 2H_2O$ together with $C_6H_8O_7 \cdot H_2O$ into 100 mL of deionized and distilled water. The initial $PbSO_4$/water weight ratio was constant as 1/10 for each experiment. The solution temperature was monitored by a contact thermometer.

The leaching experiment was carried out in a glass beaker immersed in a thermostatic water bath, under mechanic agitation at a constant stirring rate of 250 rpm. The CA/SC mixed solution was prepared and preheated to a specified temperature in advance. After allowing $PbSO_4$ to leach in the solution for a certain time, any remaining solid in the beaker was filtered out. The filtrate was measured for lead concentration via a chemical analysis by titration with ethylene diamine tetraacetic acid (EDTA) [17]. The residue was dried and weighed to verify the accuracy of the data by deducing a lead content balance. The crystallization experiment was performed by cooling the leaching solution at room temperature (20 ± 2 °C) or adjusting the solution composition by varying CA/SC molar ratio. A static aging time of about 12 h during crystallization was provided to allow full crystallization. After being filtrated, washed with deionized water, and dried at 60 °C, the residue was obtained as the final product. Following this, the filtrate was analyzed for lead concentration.

The lead proportion in filtrate was calculated from the lead concentration as follows in Equation (1):

$$\text{Lead proportion in filtrate} = \frac{(C_1 \times V_1)}{(W_0/303)} \times 100\% \tag{1}$$

where W_0 (g) is the mass of $PbSO_4$ sample, 303 is the molecular weight of $PbSO_4$, C_1 (mol·L^{-1}) is the lead concentration in a filtrate solution of the leaching or crystallization procedure, and V_1 (L) is the volume of this filtrate solution.

The pH value of solution was measured by a pH meter (PHS-3C, Rex Electric Chemical, Shanghai, China). X-ray diffraction data was obtained by using a D8 Advance X-ray diffractometer (Cu Kα, 3 KW, BRUKER, Munich, Germany). The morphological study of the product was carried out with a scanning electron microscope (SEM, 4.5 nm, 18–300,000 times, JSM-5510LV, Japan Electron Optics Laboratory Co. Ltd., Osaka, Japan).

3. Results

3.1. PbSO$_4$ Leaching in Citric Acid/Sodium Citrate Solution

In this part, the leaching of PbSO$_4$ in CA/SC mixed solution was determined by varying leaching time, leaching temperature, concentration of SC, and the molar ratio of CA/SC. The pH values were also recorded when changing the concentrations of reagents, in order to indicate the pH variation in the solution. Experiments were carried out at a constant stirring rate of 250 rpm, with an identical initial PbSO$_4$/water ratio of 1/10. These parameters were set up according to previous research. The lead proportion in the filtrate continuously increased with an increase in leaching time. As shown in Figure 1, at constant values of a leaching temperature of 35 °C, an SC concentration of 300 g/L, and a CA/SC molar ratio of 0, the lead proportion in filtrate increased to 99.84% as leaching time was increased to 60 min. Further increasing the leaching time beyond 60 min did not have any significant effect, suggesting that the leaching process was nearly completed. Thus, PbSO$_4$ is considered to be completely converted in the solution within a short duration of 60 min.
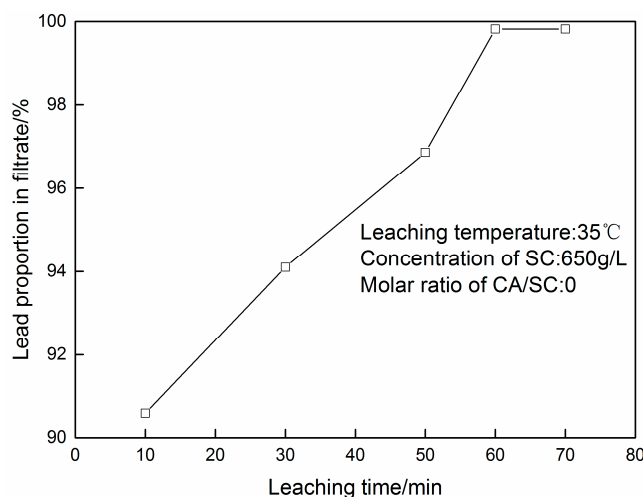

Figure 1. Lead proportion in filtrate with different leaching time (leaching temperature is 35 °C, concentration of SC is 650 g/L, molar ratio of CA/SC is 0).

In order to investigate the effect of temperature on the leaching behavior, the SC concentration was set as 650 g/L and 300 g/L, leaching time was kept to the optimum of 60 min, and the molar ratio of CA/SC was set as 0. As seen in Figure 2, the lead proportion in the filtrate maintained a high level of over 99% when temperature was beyond 35 °C. In the case of a relatively low value of SC concentration as 300 g/L, this revealed that the lead proportion in filtrate increased significantly as temperature rose. Namely, the leaching behavior can be strikingly enhanced by increasing temperature.
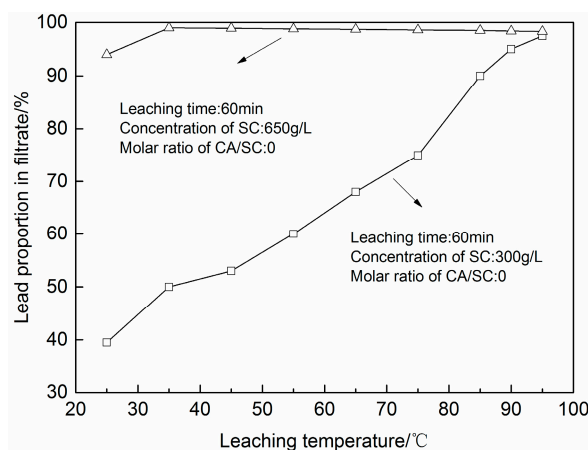
Figure 2. Lead proportion in filtrate with different leaching temperatures (leaching time is 60 min, concentration of SC is 650 g/L or 300 g/L, molar ratio of CA/SC is 0).

Figure 3 shows that the lead proportion in filtrate increased sharply from 21.25% to 99.84% when the concentration of SC was increased from 50 to 650 g/L at the same leaching time of 60 min, a leaching temperature of 35 °C, and a CA/SC molar ratio of 0. The single sodium citrate solution tended to be alkaline due to a series of hydrolytic reactions listed as Equations (2)–(4) [18]. However, in this experiment, the solution pH remained nearly constant between 6.5 and 7.0, which corresponds to thermodynamic analysis from which the optimal pH region for maximizing lead solubility in citrate solution was found to be approximately 6–7 [19]. This phenomenon should be to the result of a prior complex reaction between $PbSO_4$ and $Na_3C_6H_5O_7 \cdot 2H_2O$, which can generate a soluble ionic lead citrate complex. The National Institute of Standards and Technology (NIST) [20] also provides several soluble lead citrate complexes such as $Pb(C_6H_7O_7)^+$, $Pb_2(OH)_2(C_6H_5O_7)_2^{4-}$, $Pb_2(C_6H_5O_7)_2^{2-}$, $Pb(C_6H_5O_7)^-$, $PbH(C_6H_5O_7)_2^{3-}$, $Pb(C_6H_5O_7)_2^{4-}$, and $Pb_2(OH)(C_6H_5O_7)_2^{3-}$. Thus, the leaching behavior of $PbSO_4$ in a single citrate solution can be reinforced by increasing the concentration of sodium citrate.

$$C_6H_5O_7^{3-} + H_2O \rightleftarrows C_6H_6O_7^{2-} + OH^- \tag{2}$$

$$C_6H_6O_7^{2-} + H_2O \rightleftarrows C_6H_7O_7^- + OH^- \tag{3}$$

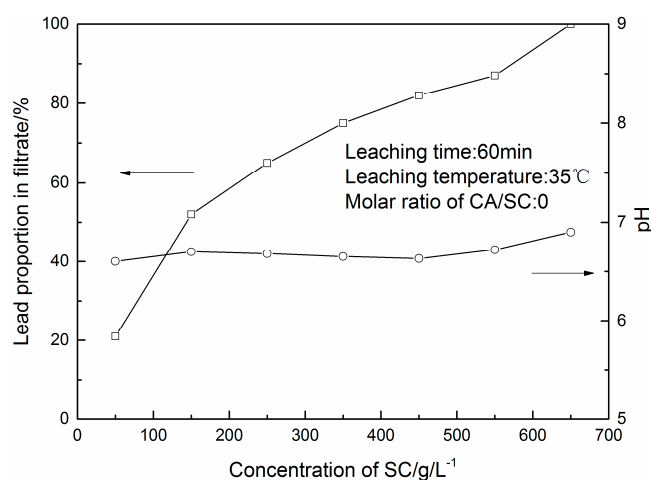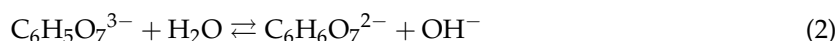$$C_6H_7O_7^- + H_2O \rightleftarrows C_6H_8O_7 + OH^- \tag{4}$$

Figure 3. Lead proportion in filtrate with different concentrations of SC (leaching time is 60 min, leaching temperature is 35 °C, molar ratio of CA/SC is 0).

In contrast with the role of sodium citrate, the addition of citric acid can lead to a decrease in the lead proportion in the filtrate. This experiment was performed at an optimum leaching time of 60 min, an SC concentration of 650 g/L, and a leaching temperature of 35 °C. It can be seen in Figure 4 that the lead proportion in filtrate decreased markedly from 99.84% to 1.95% as CA/SC molar ratio increased from 0 to 0.88, with the pH values of the solution decreasing continuously from 6.87 to 3.32. The solution dissociation reaction of $C_6H_8O_7$ is listed as Equations (5)–(7) [21], with hydrogen ions possibly being generated from a three-step dissociation. It is assumed that, when increasing the molar ratio of CA/SC at a constant SC concentration, namely a higher concentration of citric acid in solution, the generation of H^+ (hydrogen ions) will promote the hydrolytic consumption of $Na_3C_6H_5O_7 \cdot 2H_2O$, due to the natural pH buffering property of the CA/SC solution [22]. However, if the consumption of sodium citrate in hydrolytic reaction dominates, the complex reaction may be weakened or retarded, which would lead to an inhibitory effect on leaching behavior. This explanation can also be supported by the fact that it usually takes more than eight hours to finish the conversion of lead sulfate to lead citrate when treating the actual spent lead paste with excess citric acid [23].
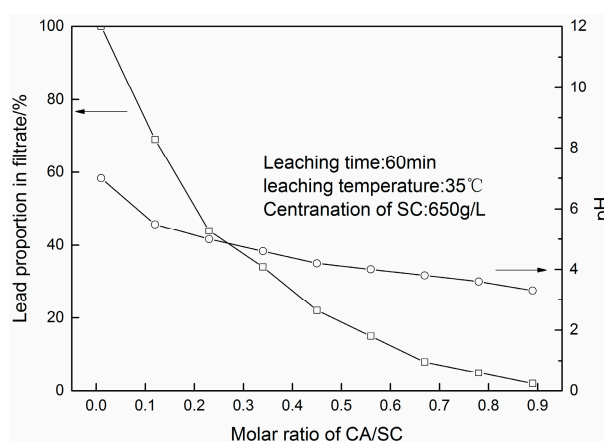
$$C_6H_8O_7 = C_6H_7O_7^- + H^+ \tag{5}$$

$$C_6H_7O_7^- = C_6H_6O_7^{2-} + H^+ \tag{6}$$

$$C_6H_6O_7^{2-} = C_6H_5O_7^{3-} + H^+ \tag{7}$$

Figure 4. Lead proportion in filtrate with different molar ratios of CA/SC (leaching time is 60 min, leaching temperature is 35 °C, concentration SC is 650 g/L).

In summary, the leaching of $PbSO_4$ in CA/SC solutions can be fulfilled at 60 min, with significant enhancement by increasing temperature and SC concentration, whereas increasing the CA/SC molar ratio had the opposite effect. The optimal combined conditions for the leaching of $PbSO_4$ are listed in Table 1.

Table 1. Optimal leaching conditions for $PbSO_4$ in CA/SC solutions.

No.	Time (min)	Temperature (°C)	Concentration of SC (g/L)	Molar Ratio of CA/SC
1	60	25	700	0
2	60	35	650	0
3	60	45	600	0
4	60	55	550	0
5	60	65	500	0
6	60	75	450	0
7	60	85	400	0
8	60	95	300	0

3.2. Lead Citrate Yielded from CA/SC Solution via Controlled Crystallization

Controlled crystallization, such as changing temperature or adjusting solution pH, has been reported to be an effective way to obtain crystals from a saturated solution [24,25]. In this part, lead citrate was obtained from a CA/SC solution by aging at room temperature and adjusting the solution pH through changing the molar ratio of CA/SC. Following this, the lead proportion of lead remaining in solution after filtrating is measured because a satisfied lead recovery is required for practical applications.

The effect of initial temperature on the lead proportion in the filtrate is shown in Figure 5. Results indicate that, at a constant CA/SC molar ratio of 0, the lead proportion in the filtrate decreased with an increase in initial temperature, especially when it was beyond 75 °C. At an initial temperature less than 75 °C, the lead proportion in the filtrate kept exceeding 90%, suggesting that only a few crystals were crystallized from solution. After further increasing the temperature to 95 °C, the conversion rate was only 11.68%. This phenomenon suggests that a large temperature difference is of great benefit to the crystallization of lead citrate, with this effect only being conspicuous if the initial temperature is beyond 75 °C.
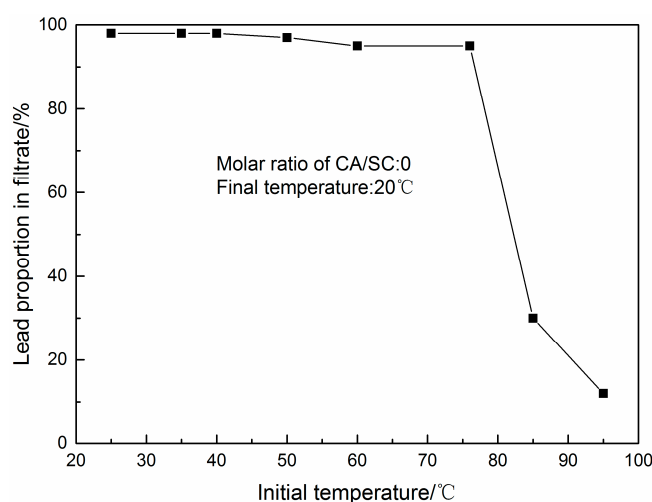

Figure 5. Lead proportion in filtrate with different initial temperatures (molar ratio of CA/SC is 0, final temperature is 20 °C).

Adjusting solution concentrations is also considered to be a potential crystallization method of obtaining lead citrate. The effect of CA/SC molar ratio on the lead proportion in a filtrate was investigated at a constant initial temperature of 35 °C and an SC concentration of 650 g/L. As seen in Figure 6, the lead proportion in the filtrate continues to decrease with an increase in CA/SC molar ratio. When the ratio was 0.92, the lead proportion in the filtrate was only 0.43%, indicating that 99.08% of lead has been converted and recovered as lead citrate. On the other hand, the pH value of solution continuously decreased from 6.87 to 3.28. Increasing the molar ratio of CA/SC leads to more hydrogen ions in solution. It has been reported that outside the pH region below 6, the solubility of lead citrate is severely inhibited. The precipitation of lead citrate from the leach solution may be due to the decrease in the solubility of lead citrate due to the addition of citric acid [21]. Therefore, as an inverse procedure of the dissolution of lead citrate, the crystallization behavior of lead citrate can be considerably promoted with an increase in the CA/SC molar ratio.
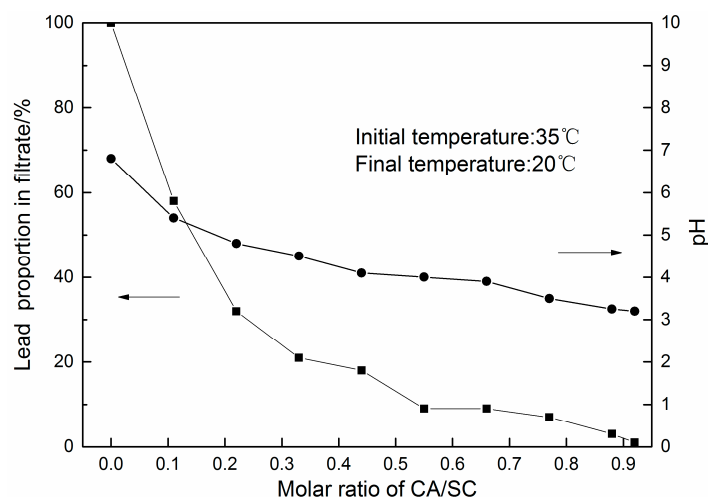
Figure 6. Lead proportion in filtrate with different molar ratios of CA/SC (initial temperature is 35 °C, final temperature is 20 °C).

In summary, controlled crystallization by cooling at room temperature or increasing the molar ratio of CA/SC is considered to be effective in yielding lead citrate from leaching solutions.

3.3. Comparison Test on the Characterization of Lead Citrate

Based on the charge balance theory, the final crystal of lead citrate is supposed to have a potential chemical formula of $[Pb(C_6H_7O_7)_2]_n$, $[Pb(C_6H_6O_7)]_n$, or $[Pb_3(C_6H_5O_7)_2]_n$. To investigate the effect of the above two major factors of temperature and the CA/SC molar ratio on the composition and morphology of the lead citrate, a further comparison test on the characterization of lead citrate was carried out. The experiment was under different synthesis conditions listed in Table 2. As shown in Table 2, there were two different levels for either temperature or molar ratio of CA/SC. The final products produced from $PbSO_4$ were analyzed by X-ray diffraction and SEM.

Table 2. Synthesis conditions to obtain lead citrate crystals in CA/SC solutions.

No.	Initial Temperature (°C)	Molar Ratio of CA/SC
a	35	0.92
b	35	0
c	95	0
d	95	0.92

As shown in Figure 7, the X-ray diffraction patterns of four products were similar to each other, with the exception of a peak at 2θ of around 35° for (c) and (d). This may be related to the fact that this relatively large temperature variation between 35 and 95 °C can possibly lead to a difference in the coordination number of the crystal water. Furthermore, because there is no data on lead citrate in the existing powder diffraction file (PDF), the products could only be compared with $Pb_3(C_6H_5O_7)_2 \cdot 3H_2O$ from the documented paper, and these products were all found to match this very well [13]. Thus, neither temperature nor CA/SC molar ratio would make a difference on the composition of lead citrate, with the chemical formula of final lead citrate being $Pb_3(C_6H_5O_7)_2$.
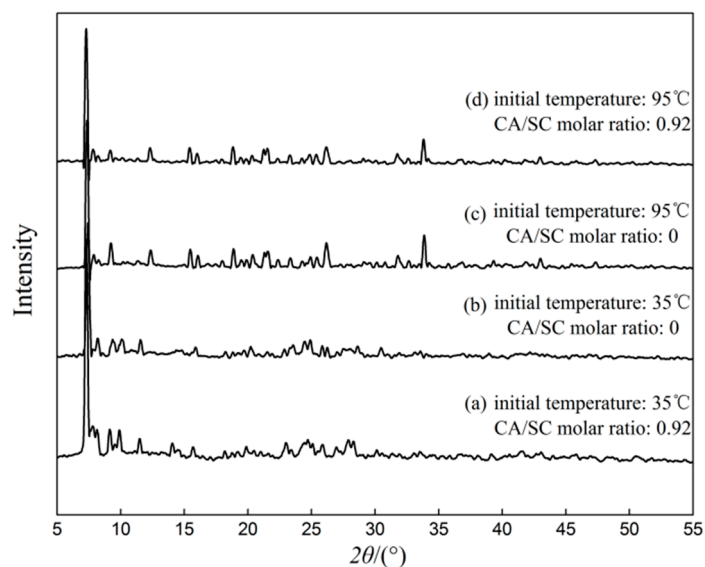
Figure 7. XRD patterns of lead citrate crystals obtained under different synthesis conditions.

SEM images of these four products are shown in Figure 8. There was an obvious distinction in the crystal morphology, as sheets were found for Samples (a) and (b), while rods were found for Samples (c) and (d). The results prove that, under the same CA/SC molar ratio, the shapes of lead citrate considerably differ. Thus, it can be affirmed that the environment temperature would influence the rate of crystal growth. By varying the initial temperature, the crystallization kinetic parameter is dramatically changed, resulting in potential differences in the crystal shape [25]. Therefore, it is obvious that the temperature plays a main role in the eventual morphology of lead citrate.
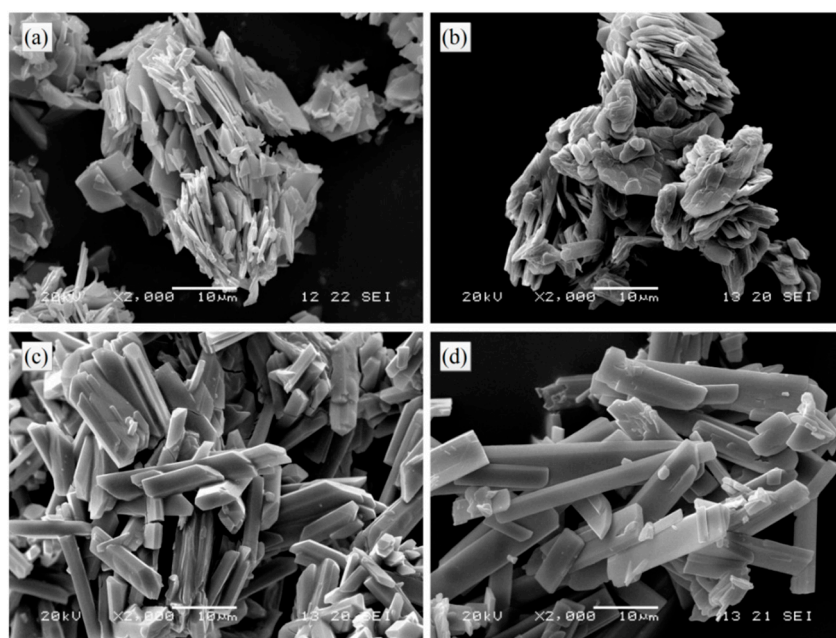

Figure 8. SEM images of lead citrate crystals obtained under different synthesis conditions. (**a**) Initial temperature: 35 °C, molar ratio of CA/SC: 0.92; (**b**) Initial temperature: 35 °C, molar ratio of CA/SC: 0; (**c**) Initial temperature: 95 °C, molar ratio of CA/SC: 0; (**d**) Initial temperature: 95 °C, molar ratio of CA/SC: 0.92.

4. Conclusions

We investigated how leaching $PbSO_4$ in a CA/SC mixed solution is determined by varying leaching time, temperature, concentration of SC, and molar ratio of CA/SC. Results show that, at an optimum leaching time of 60 min, the leaching of $PbSO_4$ in CA/SC mixed solution is significantly enhanced by increasing the temperature and the concentration of SC, while increasing CA/SC molar ratio had the opposite effect.

Controlled crystallization of lead citrate was performed under the optimal leaching conditions. Results showed that both cooling the solution and increasing the CA/SC molar ratio were effective in yielding lead citrate with an excellent recovery of beyond 99%.

Comparison tests on the characterization of the final lead citrate crystal were carried out by X-ray diffraction and SEM analysis. Results revealed that all the products synthesized under different conditions were in the same chemical formula as $Pb_3(C_6H_5O_7)_2$, while distinct morphology of sheets and rods was related to the factor of temperature.

Author Contributions: Dongsheng He and Jiakuan Yang conceived and designed the experiments; Cong Yang performed the experiments; Yuyuan Wu and Xing Liu analyzed the data; Weimin Xie contributed reagents/materials/analysis tools; Cong Yang wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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