An experimental study on hydrometallurgical process for the separation of lead in waste CRTs funnel glass

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Abstract. Waste CRTs display funnel glass contains a lot of lead, and improper disposal of waste CRTs funnel glass is easy to cause greater environmental risks. Three extraction systems of citric acid/sodium citrate, EDTA-2Na, and citric acid/sodium citrate/EDTA-2Na were used to leach the lead in waste CRTs funnel glass. The effect of extraction rate for three extraction systems was investigated. The results showed that the effect of the extraction systems of citric acid/sodium citrate/EDTA-2Na to leaching the lead in waste CRTs could reach more than 80%, which provides a way for the green treatment of waste CRTs.

1. Introduction
Waste cathode ray tube (CRTs) is an important part of WEEE. As far as our country is concerned, the existing number of color TV sets is more than 500 million, and the number of CRTs televisions still accounts for a large proportion. In addition, the number of computer CRTs displays also exceeds 40 million. The amount of waste in the latter will be maintained at a high level for a long time. Statistics show that the number of abandoned CRTs televisions in China will reach 19.5 million in 2020[1]. On the other hand, CRTs funnel glass contains a lot of heavy metal lead. Therefore, How to properly separate the lead in the CRTs funnel glass and find a way to solve the environmental problems caused by waste CRTs is a hot issue for many researchers at present.

In recent years, the main separation and treatment methods of lead in waste CRTs funnel glass are wet extraction and fire melting. Among them, sodium hydroxide, nitric acid, fluosilicic acid, hydrochloric acid and other strong acid and strong alkaline solutions are mainly used as extractants in wet extraction [2, 3]. Although the effect of extraction is good, there are some pollution and safety problems. In fire melting, carbon is often used as reductant, and the lead oxide is reduced to simple substance lead at high temperature for recovery [4, 5]. However, the high energy consumption and harsh process conditions are not conducive to the industrialization of the technology. Therefore, the research on green environmental protection and efficient lead separation technology is particularly urgent. Based on the study of lead leaching characteristics in CRTs funnel glass, the leaching effect of green leaching agent on lead was investigated in this paper, which provides a new idea for hydrometallurgical separation of lead from waste CRTs.

2. Experimental

2.1 Material
Waste CRTs funnel glass was firstly crushed by a hammer grinder, and the particles of 40-80 mesh
were selected as the initial material. Citric acid-sodium citrate, EDTA and its compound weak acid extraction system were chosen as the extractant. The deionized water was used as experimental water.

2.2 Test and analytical instruments
QM-3SP2 planet ball mill was used for mechanical activation. The HJ-6A multi-head magnetic agitator was used in the leaching test. The leaching concentration of lead was measured by PE-2100 atomic absorption spectrophotometer. In addition, XRF-1800 wavelength x-ray fluorescence spectrometer and S-4800 field scanning electron microscope were used to investigate the characteristics of the materials.

2.3 experimental methods
The mass ratio of ball to material was 2:1 and the ball milling speed was set to 400r per min, and the mechanical activation time was chosen in 4h, 8h, 12h and 24h respectively. After ball milling, 2g powder of waste CRTs and 40mL extractant solution were added to the leaching container at a liquid-solid ratio of 20:1 (L/kg). The extraction time was set at 2h, 4h, 8h, 12h, 24h respectively, and extraction temperature was set at 80℃. After the reaction, the 30mL mixture was put into the polyethylene centrifugal tube for high speed centrifugal separation, and the upper clearance was filtered and diluted. After dilution, the concentration of Pb was detected by flame atomic absorption spectrophotometer, and the leaching efficiency of lead was calculated.

3. Results and discussions
3.1 material characteristics
In this experiment, hammer crusher was used to pretreat and tattered waste CRTs funnel glass. Some studies have shown that the particle size formed after crushing is mainly distributed in 40-80 mesh. Therefore, 40-80 mesh waste CRTs funnel glass powder was selected as the initial material.

3.1.1 XRF analysis. The chemical composition of the initial material was qualitatively analyzed by XRF-1800 wavelength X-ray fluorescence spectrometer, and the results were shown in Table 1.

| oxide    | wt% | oxide    | wt% |
|----------|-----|----------|-----|
| SiO₂     | 59.45 | MgO     | 1.91 |
| PbO      | 22.02 | CaO     | 3.20 |
| K₂O      | 8.13  | SrO     | 1.14 |
| Na₂O     | 1.84  | Al₂O₃   | 1.35 |

Note: not listed where oxide mass fraction is less than 1%.

In fact, the lead content of CRTs funnel glass from different sources is different, and its main component is generally more than 20%. Compared with the lowest industrial grade of Pb in the primary lead-zinc ore, normally 0.7-1%, lead in waste CRTs funnel glass has higher recovery value.

3.1.2 SEM analysis. Mechanical Activation Pretreatment of CRTs funnel glass initial material was implemented by QM-3SP2 Planet Ball Mill. The ratio of ball to material was 2:1, and the ball milling speed was 400r/min, and Fig. 1 shows the SEM photos of milled waste CRTs funnel glass after 0h, 4h, 12h, and 24h the milling time respectively.
Fig. 1 SEM photos of milled waste CRTs funnel glass
(a) ball milling 0 h; (b) ball milling 4h; (c) ball milling 12h; (d) ball milling 24h

As can be seen from the SEM photos, the surface of the initial material particles is smooth and dense, and the edges and angles are clear. There is an obvious boundary between particles as shown in figure 1a. With the prolongation of milling time, the diameter of particles decreases sharply. At the same time, the sharp edges and corners gradually disappear, and the proportion of fine particles increases gradually, and loose flocs appear as shown in Fig.1c, the specific surface area of the particles increases, and the contact probability with the extractant is also increased, make the leaching reaction more adequate, and the leaching effect of lead becomes better. The material of ball milling for 24 hours was selected as the initial material of leaching experiment.

3.2 Lead leaching experiment

3.2.1 Citric acid-sodium citrate extraction system. 0.5mol/L extraction solution was prepared in this experiment, which contained six sodium citrate concentration of 0%, 33%, 37.5%, 50%, 67% and 100% respectively. Extraction conditions: The extraction temperature was 80°C and the liquid-solid ratio was 20:1(L/kg). The magnetic stirring speed was 500±10r/min and the leaching reaction time was set to 24 h. The results of lead leaching are shown in figure 2.

Fig 2. Leaching efficiency of citric acid/sodium citrate extraction system for the lead in waste CRTs
Fig. 2 shows that the citric acid-sodium citrate extraction system with different concentration ratios is significantly different in extraction effect of Pb in funnel glass. The highest leaching rate of lead in waste CRTs funnel glass is citric acid-sodium citrate solution containing 37.5% sodium citrate, and the lead leaching efficiency is 40.40%. Sodium citrate containing 67% takes second place, and the leaching rate of lead is 30.03%. The leaching rate of lead in the waste CRTs funnel glass is less than 10% by a single citric acid or sodium citrate solution. It is considered that the leaching reaction of the lead in the waste CRTs funnel glass is mainly the ion exchange reaction between H\(^+\) and Pb\(^{2+}\) in the extractant solution, there is a large amount of H\(^+\) in acidic solution, which makes the possibility of lead ion replacement greatly improved\(^8\). Citrate can react with lead to form a clathrate, which enhances the diffusion strength of lead and promotes the leaching of Pb.

3.2.2 EDTA-2Na extraction system. In this experiment, three concentrations of EDTA-2Na solution were prepared for leaching. The molar ratio of EDTA-2Na to Pb in funnel glass is 1:1, 1:2 and 2:1 respectively. Extraction conditions were as follows: The extraction temperature is 80\(^\circ\)C, the liquid-solid ratio is 20:1(L/kg), and the magnetic stirring speed is 500±10r/min. The extraction results are shown in figure 3.

![Graph showing leaching efficiency of EDTA-2Na extraction system for the lead in waste CRTs](image)

Fig 3. Leaching efficiency of EDTA-2Na extraction system for the lead in waste CRTs

Fig. 3 shows that EDTA-2Na extractant has a significant effect on the extraction of Pb from waste CRTs funnel glass. For the funnel glass material milled for 24 hours, the lead leaching rate in waste CRTs funnel glass increases with the increase of leaching time for 24 hours. When the molar ratio of EDTA-2Na to Pb is 1:1, the extraction effect is the best, and the maximum leaching rate is 47.24%. The extraction of lead by citric acid-sodium citrate extraction system is slightly better than that of citric acid-sodium citrate extraction system. The leaching rate of lead increased obviously at the first twelve hours, the molar ratio of EDTA-2Na to Pb was 2:1, but there was little increase in the leaching rate within 12 hours. EDTA-2Na is a typical weak acid complex, and its leaching mechanism of lead is similar to that of sodium citrate leaching system. The experimental results show that the complexation effect of EDTA on lead is better than that of citrate. However, the possible reason for the poor lead leaching effect caused by excessive EDTA is the enhancement of steric resistance effect.

3.2.3 Complex extraction system of citric acid-sodium citrate and EDTA-2Na. In this experiment, three concentrations of EDTA-2Na complex extraction system solutions were prepared with citric acid-sodium citrate solution containing 37.5% sodium citrate as solvent. The addition of EDTA-2Na was prepared by its molar ratio to the lead in the waste CRTs funnel glass at 1:1, 1:2, 2:1 respectively. The extraction conditions were as follows: extraction temperature 80\(^\circ\)C, liquid-solid ratio 20:1(L/kg), magnetic stirring speed 500±10r/min, extraction time 2, 4, 8, 12, 24 h. The results of lead leaching rate are shown in figure 4.
Fig 4. Leaching efficiency of citric acid/sodium citrate/EDTA-2Na extraction system for the lead in waste CRTs

Fig. 4 shows that the complex extraction system of EDTA-2Na and citric acid-sodium citrate has a significant effect on the extraction of lead from waste CRTs funnel glass. The leaching rate of lead in waste CRTs funnel glass increases with the prolongation of leaching time. When the molar ratio of EDTA-2Na to lead is 1:1, the leaching rate of lead is up to 80.09%, which is obviously better than that of single EDTA-2Na or citric acid-sodium citrate extraction system. Even the worst compound system (the molar ratio of EDTA-2Na to lead is 1:2), the leaching efficiency of lead can reach 60.85%. It is much higher than the two kinds of extraction systems mentioned above. The experimental results show that the citric acid-sodium citrate is easy to form a soluble complex with lead, it promotes the activity and mobility of lead ions. EDTA is easy to form more stable complexes with lead. The compound system can effectively promote the migration and complexation of lead.

4. Conclusion
The main results are as follows: (1) The three leaching systems can enhance the leaching of lead from waste CRTs funnel glass. Under the same conditions, the leaching rate of lead in waste CRTs funnel glass by citric acid-sodium citrate leaching system can reach 40.40%, while the lead leaching rate of the EDTA-2Na leaching system to the waste CRTs funnel glass can reach 47.24%, moreover, the leaching system formed by the combination of the two can realize the leaching of lead from waste CRTs funnel glass more than 80%.(2) The mechanical activation can enhance the extraction and recovery of lead in the waste CRTs funnel glass.(3) The experimental results of this study provide a new idea of green extractant and high efficiency technological process for leaching and separation of lead from waste CRTs funnel glass.

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