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Recovery of gallium from waste light emitting diodes by oxalic acidic leaching

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ABSTRACT

Recovery of gallium from light emitting diodes (LEDs) is receiving great attention due to both high content of gallium and potential risk of environmental pollution. In this study, a novel environment-friendly route was proposed for efficient recovery of gallium from surface mounted device (SMD) of LEDs by using organic acid. Reduction of non-metallic components, selection of lixiviants, optimization of leaching parameters, and possible mechanism of gallium were investigated. Results showed that pyrolysis could reduce non-metallic components effectively, and 22% weight loss was achieved at 733 K. Selection of lixiviant experiments indicated that 83.42% gallium could be extracted from SMD LEDs by oxalic acid, which was much higher than that of 79.89% by hydrochloric acid, 70.62% by citric acid, and 71.69% by DL-malic acid. Further investigation revealed that 90 °C of leaching temperature, $10\ \mathrm{g\ L^{-1}}$ of pulp density, 0.7 M of oxalic acid and 48–75 µm of particle size were the optimum conditions for effective gallium leaching by oxalic acid. After optimization, the gallium recovery efficiency reached as high as 90.36% in 60 min. Such efficient gallium leaching came from the higher dissociation constant of oxalic acid and the formation of ferrous oxalate which would promote the generation and maintenance of H^+. Hence, oxalic acid could be a promising lixiviant for efficient recovery of gallium from SMD LEDs.

1. Introduction

The global waste electrical and electronic equipment (WEEE) consumption was increasing speedily during the previous decades (Afroz et al., 2013; Cucchiella et al., 2015; Wang and Xu, 2014). As known, WEEE contains various valuable materials, such as metals, glass, plastics and other materials (Chan et al., 2007; Kumar et al., 2017; Sun et al., 2017). The US Environmental Protection Agency has made a list of seven major benefits to recover metals from WEEE in comparison with original ores, such as saving in energy and reduction in pollutions (Cui and Forssberg, 2003). Therefore, WEEE was also called urban mine and could be recognized as one of the main sources of metal resources (Isildar et al., 2018; Van et al., 2016).

Previously, electrochemical technology, supercritical technology, vacuum metallurgical separation, bio-metallurgical approach, etc. (Rocchetti et al., 2013; Zhu et al., 2011) were widely used in WEEE recycling. However, the literatures mainly concentrated on recycling of common metals such as copper, iron, aluminum and lead (Xiang et al., 2010; Yazici and Deveci, 2013). There were only few reports on the recycling of precious and rare metals.

Light emitting diodes (LEDs), a new kind of electronic device, are widely used as distributed sources of lighting, and the key substances in their chips are gallium nitride (GaN), gallium phosphide (GaP) and indium gallium nitride (InGaN). Surface mounted device LEDs (SMD LEDs) are one of the LEDs which are easy to be recycled due to small size and simple structure so that SMD LEDs are collected in this study. In China, the scale of LED industry reached ¥ 761.5 billion at steady growth of 19% in 2018 and less than 5% LED waste was recycled properly (Kim and Schubert, 2008; Lim et al., 2011). It was considered that the initial content of gallium in waste LEDs was $2.077\ \mathrm{mg\ kg^{-1}}$ (Zhan et al., 2015; Rahman et al., 2017; Ruiz-Mercado et al., 2017). Gallium existed in LED chips was viewed as a strategic resource in USA, EU, Japan and China (Fröhlich et al., 2017; Poledniok, 2008; Xu et al., 2007). However, significant gallium losses arose in primary production and in waste management. It was estimated that about 93% of the total gallium potential was lost in the production process and only less than

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5% of the LED waste was recycled properly (Ueberschaar et al., 2017). The gallium content is about 60 ppm in bauxite, however is up to 100 ppm in the waste LEDs (Font et al., 2007). With the development of gallium-contained equipment and the worsening of gallium resource starvation, it is important to develop efficient approaches to recover gallium from waste LEDs.

Currently, several methods have been proposed to recycle rare and precious metals from Ga-contained wastes. For example, vacuum metallurgy separation was considered as an efficient method to recover gallium and indium from waste LEDs (Zhan et al., 2015). Swain investigated the gallium recovery from LEDs waste by hydrochloric acidic leaching, and the gallium leaching efficiency reached 64.62% under the optimal conditions, verifying the possibility of gallium leaching by cost-efficient methods (Swain et al., 2015b). Further, Swain achieved a gallium leaching efficiency of 73.68% by the procedures of mixing LEDs waste with Na_2CO_3, ball milling, annealing and hydrochloric acidic leaching (Swain et al., 2015a). However, more efforts should be made to realize gallium recovery in green and high-efficient approaches.

Relevant researches showed that novel lixiviants for organic acids (Li et al., 2012, 2013; Li et al., 2015) could be applied in efficient recovery of lithium and cobalt from waste lithium ion batteries (LIBs) (Bahaloo-Horeh and Mousavi, 2017; Chen et al., 2011; Sun et al., 2018) due to its easy treatment and energy-saving compared with HCl, H_2SO_4 and HNO_3 leaching. It was reported that 540 ton carbon dioxide, 1.365 ton sulfur dioxide, 130 kg phosphate, 98 kg ethane and 2 kg antimony would generate for recycling of waste LIBs per 100 tons of residue by sulfuric acid (Rocchetti et al., 2013). From the economic point view, hydrometallurgical process for waste mobile phones by sulfuric acid would generate 6.14 ton sludge and 1.63 ton tailing in recycling of one ton powder (Innocenzi et al., 2017). Hence, organic acid might be an alternative in hydrometallurgical process for producing the less air pollutants and solid waste.

As organic acids are produced by microorganisms, they are not considered as potential environmental pollutants. As known, oxalic acid is a kind of metabolite of organisms, which is widely distributed in plants, animals, and fungi. Furthermore, it is a common organic acid and can be dissolved in warm water easily. Interestingly, if oxalic acid was employed in the gallium leaching from waste SMD LEDs, gallium and iron can be leached into the solution while ferrous ions in solution can be precipitated as ferrous oxalate directly. The separation process between gallium and iron can be achieved efficiently in the leaching process. Hence, metals leaching by organic acid can provide a new idea and prospects for metals recovery in complex WEEE due to selective leaching ability and less secondary pollution.

Herein, a novel environment-friendly route was proposed for the efficient recovery of gallium from SMD LEDs using oxalic acid. Firstly, the effect of pyrolysis on the reduction of non-metallic components was investigated. Then, effect of various organic acids as lixiviants on gallium leaching efficiency was investigated and compared with that of inorganic acid. Thirdly, single-factor experiment and orthogonal experiment were conducted to optimize the leaching parameters. Finally, possible mechanisms of efficient gallium leaching were discussed.

2. Materials and methods

2.1. Materials

Surface mounted device 2835 light emitting diodes (SMD 2835 LEDs) were collected from YUHAI renewable resource recycling Co., Dongguan, P.R. China. Chemicals including hydrochloric acid and oxalic acid were all analytical grade and purchased from Aladdin, Shanghai, P.R. China.

2.2. Experimental design

Fig. 1 presents the treatment process for the SMD LEDs. Firstly, the waste SMD LEDs was used to investigate the effect of pyrolysis on the removal of non-metallic composition. The samples were weighed and then put into a heating chamber (Tube furnace, LG0512 K, ZKAB, P.R. China) with the nitrogen gas flowing for 15 min until no air in the space. Then, the furnace was heated to 733 K at a rate of 5 K/min. 60 min later, the weight loss was determined by weighing the cooled product.

After that, samples were subjected to prepare particles with different size. Briefly, the outputs were crushed (Grinder, 800Y, Kemanshi, P.R. China)to disaggregate the metal frameworks. Then, ball-milling (Planetary ball mill, PM100, RETSCH, Germany) was used to get rare-metal-rich particles (RMRPs) with smaller size under the rotate speed of 450 rpm within 15 min. After that, the RMRPs were screened and five different particle sizes were generated, i.e. 13–25 μm, 25–48 μm, 48–75 μm, 75–150 μm, and 150–270 μm.

Four kinds of acids, i.e. hydrochloric acid, oxalic acid, citric acid, and malic acid were used to leach RMRPs for further screening the candidate lixiviant. Leaching experiments was carried out by only changing the kinds of acids and keeping other conditions unchanged, namely acid concentration of 0.5 M, pulp density of 10 g L^{-1}, leaching temperature of 70 °C, particle size of 48–75 μm, and leaching time of 60 min. Leaching efficiencies of four lixiviants for key elements including gallium, iron and copper were analyzed to determine the best lixiviant.

Single factor experiments were conducted to determine the optimal leaching conditions, such as concentrations of acid, pulp density, leaching temperature, and particle size. In order to study the influence of acid concentration, pulp density, temperature and particle size, a group of experiments was carried out at the concentration of 0.1 M, 0.2 M, 0.5 M, and 0.7 M (Solubility of oxalic acid is 95.2 g L^{-1} under 20 °C which converted into 0.7 M.), pulp density of 10 g L^{-1}, 20 g L^{-1}, 30 g L^{-1}, 40 g L^{-1} and 50 g L^{-1}, temperature of 30 °C, 50 °C, 70 °C and 90 °C, and particle size of 13–25 μm, 25–48 μm, 48–75 μm, 75–150 μm, and 150–270 μm.

To optimize the leaching parameters, Orthogonal Design Expert II software was used to design 16 screening tests for reducing test times and getting the most significant parameters. Based on the results of the screening tests, the most significant parameter in gallium leaching process was determined. Then, an optimization test was carried out to verify the effect of the selected conditions on the selective leaching of gallium.

After the leaching test, solid/liquid separation was employed to get the leached residue and the precipitation was then characterized using X-ray diffraction (XRD) to explore the leaching mechanism.

2.3. Analytical methods

The thermal gravimetric analysis (TGA, NETZSCH TG 209 F1 Libra, Germany) examination of waste LEDs was conducted under nitrogen atmosphere. Contents of metals before leaching and after leaching were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Agilent, US). The RMRPs and leaching precipitation were characterized by XRD (Philips, Netherland). The concentration of metal ions in the leachate was measured by Atomic Absorption Spectroscopy (AAS, Shimadzu, Japan). In addition, scanning electron microscopy (SEM, Oxford, UK) was carried out to analyze the surface morphology of the particles before and after leaching.

3. Results and discussion

3.1. Reduction of non-metallic components by pyrolysis

The characteristic of TGA-DTA for waste LEDs was shown in Fig.2. It shows that a remarkable weight loss could be observed during 673–773 K. There is a peak at 733 K that represents the highest pyrolysis rate. The final weight loss attained to 22% at 973 K, however,

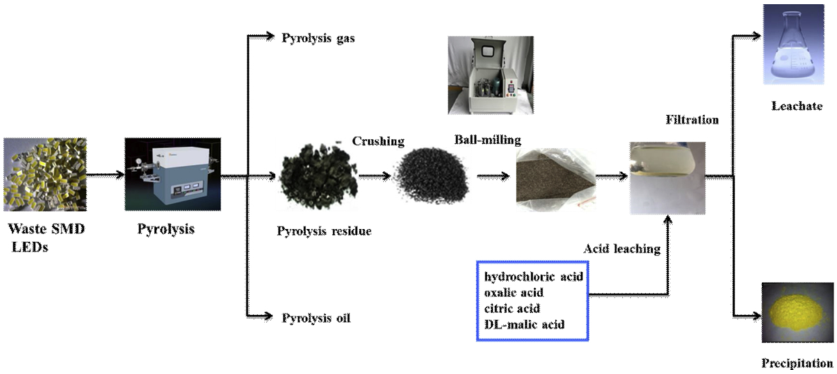

Fig. 1. Flow chart of the recycling process for waste SMD LEDs.

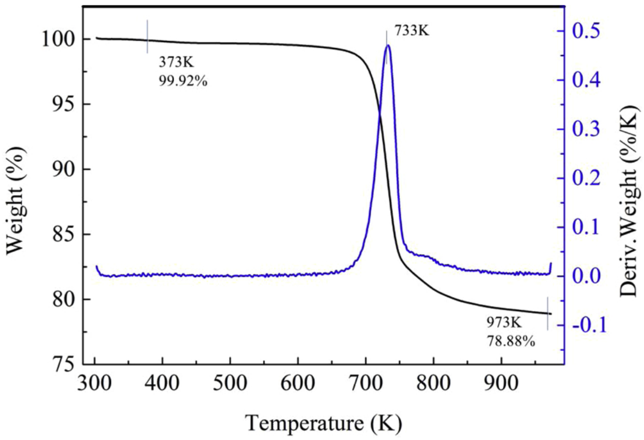

Fig. 2. Effect of pyrolysis of the waste SMD LEDs on DTA-TGA curves.

nearly 20% weight loss achieved below 773 K. Zhan et al. reported that when the pressure of gas was almost 0 Pa, the decomposition temperatures were 600–630 K accordingly and the highest pyrolysis rate achieved at 731.59 K (Zhan et al., 2015). In this study, the temperature with the high weight loss were 656–763 K and the highest pyrolysis rate achieved at 733 K which was slightly higher than that of the previous report. Therefore, the experiment of pyrolysis was utilized at 733 K in this study. The decomposition reaction of GaN are as follow.

$$2\ GaN \rightarrow 2Ga(l) + N_2(g) \tag{1}$$

Wang et al. reported that waste LEDs were major consist of plastic and resin which accounted for a great part of weight (Wang and Xu, 2014). The organics could be decomposed to oils or residues through pyrolysis. Pyrolysis was adopted for the reduction of these organics and the effect of volume reduction for waste SMD LEDs reached nearly 22%. The pyrolyzed residues were mainly comprised of chips, carbon dross, and metal frameworks (Zhan et al., 2015). After pyrolysis, ball-milling and screening, the content of gallium, iron and copper in RMRPs were concentrated significantly (Table 1).

3.2. Selection of lixiviants

According to the hard-soft-acid-base (HSAB) interaction theory, hard acid preferred to combine with hard base however soft acid preferred to combine with soft base. Ga^{3+} is hard acid and Cl^-, NO_3^-, SO_4^{2-} are hard base which follow the order $Cl^- > NO_3^- > SO_4^{2-}$(Swain et al., 2015b). Therefore, HCl is consider to be the best lixiviant in inorganic acids. That is why we choose HCl as the representative of inorganic acids. Besides, oxalic acid, citric acid, and DL-malic acid is selected as organic acid for the experiment.

Table 1
The content of gallium, iron and copper in waste SMD LEDs and RMRPs.

Element	Waste SMD LEDs (mg/kg)	RMRPs (mg/kg)
Ga	22.65	116.43
Fe	657879.3	851008.23
Cu	13930.7	20039.95

Different 0.5 M lixiviants including hydrochloric acid, oxalic acid, citric acid, and DL-malic acid were used for the RMRPs leaching. As demonstrated in Fig.3, gallium leaching efficiency followed the order of oxalic acid (83.42%) > hydrochloric acid (79.89%) > DL-malic acid (71.69%) > citric acid (70.62%) after 60 min. On the other hand, iron leaching efficiency followed the order of DL-malic acid (98.89%) > hydrochloric acid (97.37%) > citric acid (87.31%) > oxalic acid (6.7%). Also, copper leaching efficiency was very low by these four lixiviants.

In theory, iron generated ferrous oxalate precipitation through the reaction with oxalic acid so that the iron leaching efficiency by oxalic acid was much low. Furthermore, copper is difficult to react with low concentration acids. It implies that oxalic acid has prominent selective leaching ability to other metals which created an enabling environment for the latter recovery of gallium. Besides, the formation of ferrous oxalate precipitation would facilitate the dissociation of oxalic acid and promote the generation of H^+ which would not show up in the reaction of hydrochloric acid, citric acid, and DL-malic acid. It might be the reason why the leaching efficiency of oxalic acid is better than that of other acids. Therefore, oxalic acid was considered to be the best lixiviant for the further study.

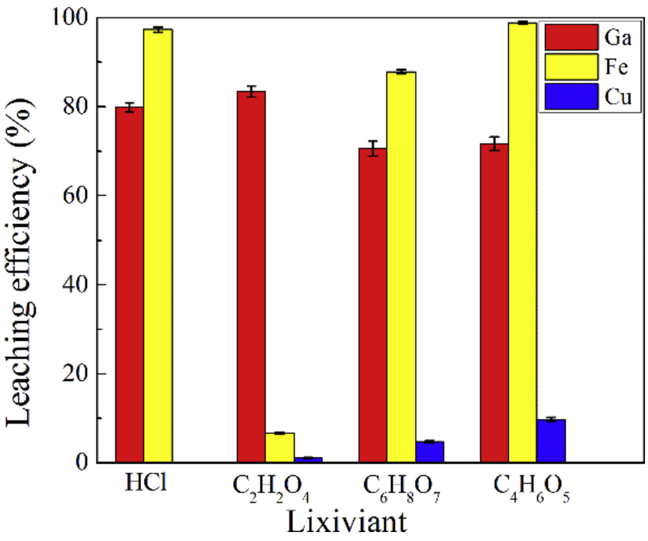

Fig. 3. Effect of four lixiviants on the key metals leaching efficiencies.

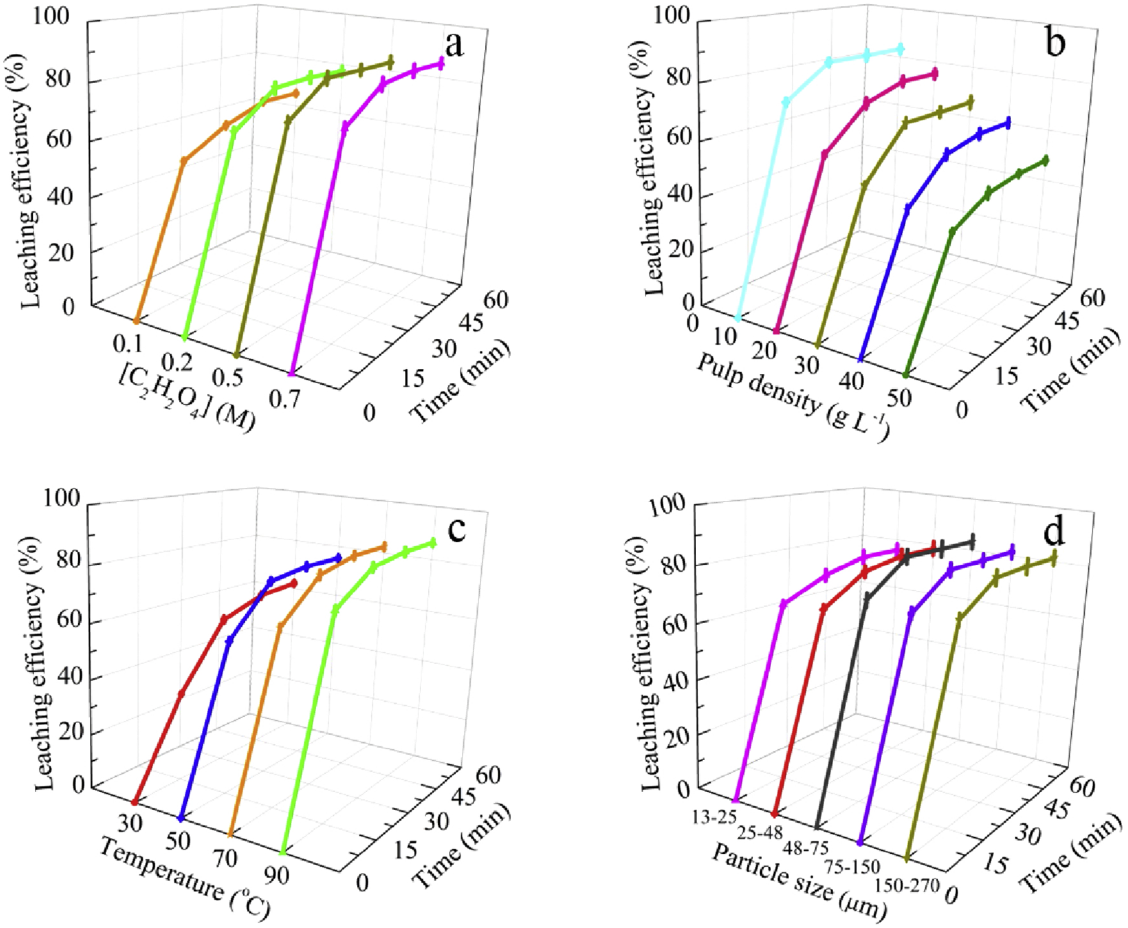

Fig. 4. Effect of different parameters on leaching efficiencies over time (a) effect of oxalic acid concentration; (b) effect of pulp density; (c) effect of temperature; (d) effect of particle size.

3.3. *Effect of leaching conditions*

3.3.1. *Effect of acid concentration*

Effect of oxalic acid concentration on the leaching efficiencies of the RMRPs was investigated. The concentration of oxalic acid ranged from 0.1 to 0.7 M, keeping all other parameters unchanged, i.e. pulp density 10 g L^{-1}, temperature 70 °C, and particle size 48–75 μm. Fig. 4(a) showed effect of leaching efficiencies over time and oxalic acid concentrations. Generally, gallium leaching efficiency increased with the rise of acid concentration and got stable beyond 45 min which ranged from 64.08% to 85.67%. The maximum leaching efficiency was achieved by 0.7 M oxalic acid. Hence, 0.7 M oxalic acid was utilized in further studies.

It is well known that the concentration of H$^+$ played an important role on metals leaching (Li et al., 2014). Oxalic acid dissociates in two steps (Golmohammadzadeh et al., 2017):

$$H_2C_2O_4 \leftrightarrow HC_2O_4^- + H^+ \ K_{a1} = 5.6 \times 10^{-2} \quad (2)$$

$$HC_2O_4^- \leftrightarrow C_2O_4^{2-} + H^+ \ K_{a2} = 1.5 \times 10^{-4} \quad (3)$$

DL-malic acid dissociates in two steps:

$$H_2C_4H_4O_5 \leftrightarrow HC_4H_4O_5^- + H^+ K_{a1} = 4.0 \times 10^{-4} \quad (4)$$

$$HC_4H_4O_5^- \leftrightarrow C_4H_4O_5^{2-} + H^+ K_{a2} = 9.0 \times 10^{-6} \quad (5)$$

Citric acid dissociated in three steps:

$$H_3C_6H_5O_7 \leftrightarrow H_2C_6H_5O_7^- + H^+ K_{a1} = 7.4 \times 10^{-4} \quad (6)$$

$$H_2C_6H_5O_7^- \leftrightarrow HC_6H_5O_7^{2-} + H^+ K_{a2} = 1.7 \times 10^{-5} \quad (7)$$

$$HC_6H_5O_7^{2-} \leftrightarrow C_6H_5O_7^{3-} + H^+ \ K_{a3} = 4.0 \times 10^{-7} \quad (8)$$

Obviously, it could be observed that oxalic acid could produce more H$^+$ because of higher dissociation constant. In comparison to citric acid and DL-malic acid, oxalic acid should be a better lixiviant. This is consistent with the results obtained from the selection experiments. In addition, a higher acid concentration in leaching reaction generally means that the H$^+$ release is more and rapid (Cui et al., 2019). It is necessary to control the H$^+$ concentration and decrease the acid consumption from nontarget substances (Swain et al., 2015b).

3.3.2. *Effect of pulp density*

Effects of pulp density on gallium leaching efficiencies in the range of 10 g L^{-1} to 50 g L^{-1} were studied. The leaching efficiencies were shown as a function of pulp density in Fig. 4(b). It indicated that gallium leaching efficiencies were rising rapidly in the first 30 min. Gallium leaching efficiencies ranged from 48.12% to 83.42% in their stable point. At pulp density of 10 g L^{-1} had highest gallium leaching efficiency. The figure demonstrated that the leaching of gallium decreased as rise of pulp density.

Pulp density is an important condition which enable to use less materials and achieve higher recovery. With the increase of pulp density, insufficient lixiviant might be the limited factor which could not provide sufficient H$^+$ to leach gallium from the waste LEDs (Chandraprabha et al., 2002; Tipre and Dave, 2004). Another reason for the low leaching yield was impurities such as iron and zinc which might lead to the decrease of oxalic acid concentration. It was known that the concentrations of H$^+$ played an important part in metals leaching however decreasing of oxalic acid concentration would lead to the lack of H$^+$.

3.3.3. Effect of temperature

Effect of temperature was also investigated by 0.5 M oxalic acid, keeping pulp density at 10 g L^{-1} for 60 min. Fig. 4(c) indicated that gallium leaching efficiencies was 86.36% when the temperature was set at 90 °C. The gallium leaching efficiency increased with rising of temperature. As temperature varying from 30 to 90 °C, leaching efficiency of gallium achieved from 62.15% to 86.36%. Hence, 90 °C was considered as an optimal condition.

As reported by kinetics of heterogeneous reactions, leaching efficiency decreased at the lower temperature for gallium, iron, and copper. Torres found that this phenomenon might attribute to the effect on the reaction dynamics or a modification of the thermodynamic conditions in the solution (Torres et al., 2018). Obviously, higher temperature could provide enough energy for the reaction system, promote releasing of H^+, and improve reaction efficiency. However, the lixiviants started to vaporize above 90 °C. As decreasing of acid concentrations, metal leaching efficiencies would reduce which was in accord with the data from the temperature experiments.

3.3.4. Effect of particle size

Effect of particle size on the gallium leaching efficiencies from the waste LEDs was investigated. Experiments were carried out by changing the particle size with 13–25 μm, 25–48 μm, 48–75 μm, 75–150 μm and 150–270 μm. In Fig. 4(d), gallium leaching efficiencies ranged from 75.93% to 83.42% as particle size varying from 13 to 25 μm to 150–270 μm in their stable state. Maximum gallium leaching efficiency achieved 83.42% at 48–75 μm particle size.

It was considered that the improvement of leaching efficiency could attribute to the effect of the particle size. In theory, by reducing particle size, the specific surface area of the particle would be rising and the leaching efficiency increased. Zhu et al. considered that extent of the particle–particle collision would increase as reduction of particle size below a critical level which might cause diverse particle size showed different leaching results (Zhu et al., 2011). More importantly, the existence of rest metals in particles which were more active than gallium might be the main inhibition factor. It is reported that for smaller particle size, the reaction rate could increase, and the complex metal molecules formed on the reaction zone surface caused steric hindrance to the desorption of product as well.

3.4. Process optimization

In order to optimize the effect of acid concentration, pulp density, temperature and particle size on gallium leaching efficiency, each influencing factor was divided into four levels (Table S1), and 16 experiments were designed subsequently by Orthogonal Design Expert II (Table S2).

According to the results obtained from the tests, Orthogonal Design Expert II software was used to design and make statistical analysis of 16 experiments. According to the order of range values shown in Table 4, $R_C > R_B > R_D > R_A$. It could be inferred that the most influential factor of gallium leaching efficiency was pulp density, followed by temperature, acid concentration and particle size. As shown in Table 4, $K_{A2} > K_{A3} > K_{A4} > K_{A1}$, $K_{B4} > K_{B3} > K_{B2} > K_{B1}$, $K_{C1} > K_{C2} > K_{C3} > K_{C4}$, $K_{D4} > K_{D3} > K_{D2} > K_{D1}$. Namely, the superior factors for leaching should therefore be $A_2B_4C_1D_4$, i.e., particle size of 48–150 μm, temperature of 90 °C, pulp density of 10 g L^{-1} and the oxalic acid concentration of 0.7 M.

As demonstrated in Table 4, it was clearly that pulp density and temperature played the most important part in leaching process. According to the selective values obtained from Table S4, optimized leaching tests were carried out and results were demonstrated in Fig. 5. It revealed that 90.36% of gallium, 6.56% of iron and 1.2% of copper could be recovered using 0.7 M oxalic acid, pulp density of 10 g L^{-1}, particle size of 48–150 μm, and temperature of 90 °C within 60 min. Compared to the results obtained from single-factor experiment, leaching efficiency increased significantly and selective leaching was achieved which was convenient for further recovery of gallium.

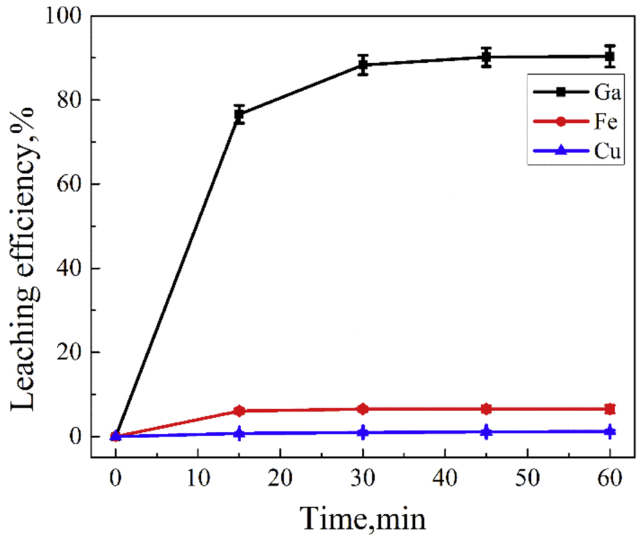

Fig. 5. Leaching efficiencies of gallium, iron and copper as function of time under the optimum conditions.

3.5. Possible mechanism

After the leaching, yellow precipitation could be clearly observed after a standing time of 10 min. As ferrous oxalate is yellow crystalline solid poorly soluble in water, the precipitation was qualitatively characterized using XRD. Fig. 6 shows the XRD pattern of the yellow precipitation. The diffraction peaks in the figure indicated that the precipitation was ferrous oxalate, i.e. FeC_2O_4.

$$H_2C_2O_4 \leftrightarrow HC_2O_4^- + H^+ \tag{9}$$

$$HC_2O_4^- \leftrightarrow C_2O_4^{2-} + H^+ \tag{10}$$

$$2\ Ga + 6H^+ \leftrightarrow 2Ga^{3+} + 3H_2\uparrow \tag{11}$$

$$Fe + H_2C_2O_4 \leftrightarrow FeC_2O_4\downarrow + H_2\uparrow \tag{12}$$

The leaching reaction of waste LEDs and oxalic acid follows the following steps: 1) the dissolution of oxalic acid; 2) the leaching

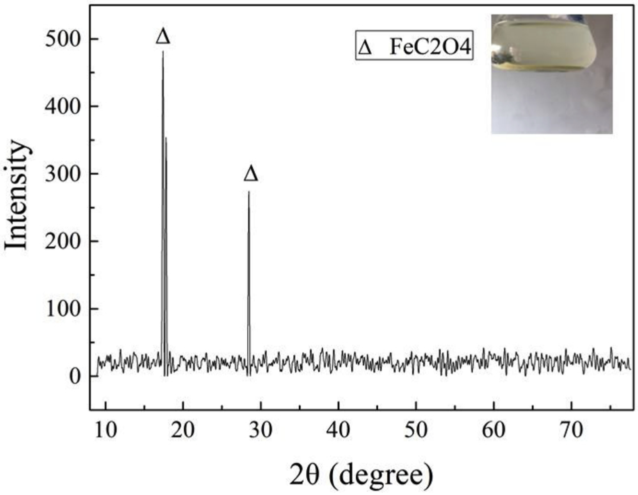

Fig. 6. XRD pattern for the yellow precipitation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

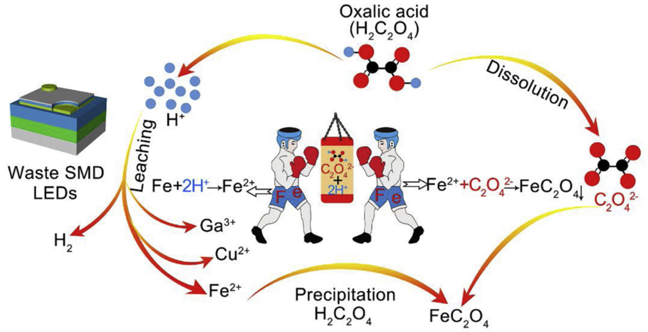

Fig. 7. Possible mechanism of gallium leaching from waste SMD LEDs by oxalic acid.

reaction of gallium and iron with oxalic acid; 3) the precipitation reaction of iron and oxalic acid. It is known that iron was nearly active as gallium and both of them could consume the hydrogen ions (H^+). However, the formation of ferrous oxalate precipitation through the reaction with oxalic acid would promote the generation of H^+ which would not show up in the reaction of hydrochloric acid, citric acid, and DL-malic acid. Therefore, iron played a complex role in the reaction. The reaction of iron with oxalic acid might be the reason why the leaching efficiency of oxalic acid is better than that of hydrochloric acid (Fig. 7).

It is well known that the hydrogen ions (H^+) concentration significantly influenced the efficiency of metal leaching. Among the three kinds of substances of oxalic acid, citric acid and DL-malic acid, oxalic acid had the highest dissociation constant and it could produce more H^+ than the other two under the same concentration which could maintain the H^+ concentration at a stable range. Besides, the formation of ferrous oxalate precipitation promoted the releasing of H^+ so that the leaching efficiency of oxalic acid was higher than that of hydrochloric acid. Consequently, oxalic acid appeared to be the most appropriate reagent in the four acids.

According to previous reports, organic acids played a noteworthy role in metal leaching through acidolysis and complexation mechanisms (Golmohammadzadeh et al., 2018). In acidolysis process, H^+ leach the metals and mobilize them into the solution and in complexation process, the organic acids stabilize the metallic ions by either complex or chelating formation (Horeh et al., 2016). The multiple mechanisms facilitate gallium leaching.

3.6. Discussion

It is urgent to propose a new approach to recover gallium from WEEE in green and efficient means. In this study, a novel method was proposed for gallium leaching by organic acid from waste LEDs. The experimental results showed that the leaching efficiency by the proposed method was higher than that by other methods, indicating its promising application to the recovery of rare metals from WEEE. Also, oxalic acid which is easy to obtain shows low toxicity and easy treatment compared with H_2SO_4, HCl, and HNO_3. Furthermore, it has not been reported about the recovery of gallium by organic acidic leaching to our best knowledge.

It was reported that hydrochloric acidic could achieve a gallium leaching efficiency of 64.62% from LED waste under optimum conditions (Swain et al., 2015b). Further, the combination of ball milling, annealing and hydrochloric acidic increased the gallium leaching efficiency to 73.68% with Na_2CO_3 under optimum conditions (Swain et al., 2015a). In this research, we proposed a novel leaching method of pyrolysis-ball milling-oxalic acidic for gallium recovery from waste LEDs where a gallium leaching efficiency of 90.36% was achieved under the optimal conditions (temperature of 90 °C, pulp density of 10 g L^{-1}, acid concentration of 0.7 M, particle size of 48–150 μm). Recently, it was considered that $C_2O_4^{2-}$ ions could form precipitates with many metal ions such as Ca^{2+}, Sr^{2+}, and Fe^{2+} which improve the ability of selective leaching (Cui et al., 2019). In addition, in a specific complex leaching system from waste LEDs, oxalic acid leaching has great advantages for H + ions release rate to reduce acid consumption. In summary, the novel route in this paper provided possibility for metals recovery in complex WEEE system.

However, more efforts should be made to further improve the leaching efficiency. As described above, iron played a complex role in the reaction. It both consumed some of the H^+ and promoted the releasing of H^+. If it is possible to seek a substance that could promote the releasing of H^+ and would not consume H^+, the gallium leaching efficiency would further increase. On the other hand, reductant could apply to ensure the formation of ferrous oxalate. SEM was performed to examine the surface morphology of the particles before and after the leaching. Fig. S1(a) (b) shows that the particles had a rough surface before the leaching. However, a clean and smooth surface was observed after the leaching, as indicated from Fig. S1(c) (d). As a result, it was reasonable to conclude that oxalic acid had significant effect on the LED particles in metal recovery process. However, gallium probably existed inside the particle so that the lixiviant could not leach the gallium entirely. Therefore, further work should focus on seeking an alternative, reductant and making gallium exposed as much as possible.

4. Conclusions

A novel method was proposed in this research to efficiently leach gallium from waste SMD LEDs. The experimental results showed that the pyrolysis could reduce the organic components by 22% and concentrate the involved metals. Compared with hydrochloric acid, citric acid and malic acid, the oxalic acid adopted in this work showed the best gallium leaching ability and the selective leaching of other metals. Metal leaching efficiency increased with the increase in oxalic acid concentration and temperature, however decreased with the increase in pulp density. After the orthogonal optimization, the gallium leaching efficiency reached 90.36% at the temperature of 90 °C, pulp density of 10 g L^{-1}, oxalic acid concentration of 0.7 M and particle size of 48–75 μm within 60 min. The efficient gallium leaching from waste SMD LEDs by oxalic acid could possibly be attributed to the high dissociation constant of oxalic acid and the large amount of H^+ released in the presence of ferrous ions, which could form ferrous oxalate precipitation and boost the dissociation of the oxalic acid. In summary, the novel method of pyrolysis-ball milling-organic acidic leaching proposed in this work was suitable for the high-efficient gallium leaching from waste SMD LEDs.

Declaration of interest

None.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.resconrec.2019.04.002.

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