Leaching Recovery of Rare Earth Elements from Calcination Product of a Coal Coarse Refuse Using Organic Acids

Bin Ji, Qi Li, Wencai Zhang

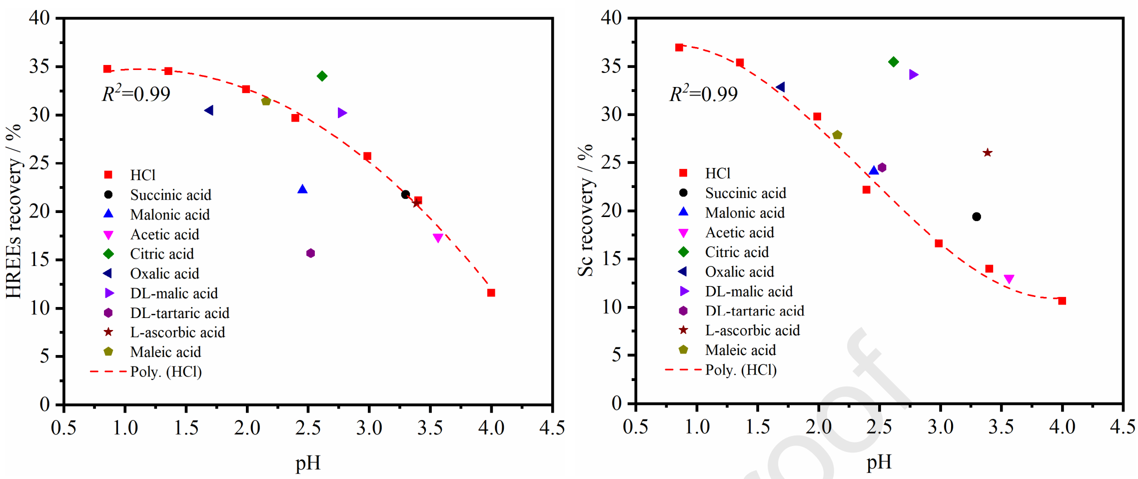
PII: S1002-0721(20)30473-7
DOI: https://doi.org/10.1016/j.jre.2020.11.021
Reference: JRE 907

To appear in: *Journal of Rare Earths*

Received Date: 26 August 2020
Revised Date: 11 November 2020
Accepted Date: 29 November 2020

Please cite this article as: Ji B, Li Q, Zhang W, Leaching Recovery of Rare Earth Elements from Calcination Product of a Coal Coarse Refuse Using Organic Acids, *Journal of Rare Earths*, https://doi.org/10.1016/j.jre.2020.11.021.

Different types of organic acids were used as lixiviants to leach rare earths from the calcination product of a coal coarse refuse. At the same pH, citric acid and DL-malic acid were found to provide the highest recoveries of heavy rare earths and scandium.



Leaching Recovery of Rare Earth Elements from Calcination Product of a Coal Coarse Refuse Using Organic Acids

Bin Ji, Qi Li, Wencai Zhang*

Department of Mining and Minerals Engineering, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, USA

Abstract: Due to the increasing criticality of rare earth elements (REEs), it has become essential to recover REEs from alternative resources. In this study, systematic REEs leaching tests were performed on the calcination product of a coal coarse refuse using hydrochloric acid and different types of organic acid as lixiviants. Experimental results showed that the recovery of REEs, especially heavy REEs (HREEs) and scandium (Sc), were improved by using selected organic acids. Citric acid and DL-malic acid afforded the best leaching performances; whereas, malonic acid, oxalic acid, and DL-tartaric acid were inferior to hydrochloric acid. Results of zeta potential measurements and solution chemical equilibrium calculations showed that malonic acid was more likely adsorbed on the surface of the calcined material compared with citric acid and DL-malic acid. The adsorption may reduce the effective concentration of malonic species in solution and/or increase the amount of REEs adsorbed on the surface, thereby impairing the leaching recovery. Compared with light REEs (LREEs), a stronger adsorption of the HREEs on the surface was observed from electro-kinetic test results. This finding explained why organic acids imposed a more positive impact on the leaching recovery of HREEs. By complexing with the HREEs, organic acids can keep the metal ions in solution and improve the leaching recovery. The adsorption of Sc^{3+} on the surface was the lowest compared with other REEs. Therefore, rather than complexing, the organic anionic species likely played a function of solubilizing Sc from the solid, which is similar to that of hydrogen ions.

Keywords: Rare earth elements, Coal refuse, Acid leaching, Organic acids

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

*Corresponding author: W. Zhang

E-mail address: wencaizhang@vt.edu; Telephone Number: +1-(540) 231-8110

1. Introduction

Rare earth elements (REEs) are a group of 15 elements referred to as the lanthanide series in the periodic table of elements. Scandium (Sc) and yttrium (Y) are normally included in this categorization because of their similar properties and occurrence in the same ore bodies as the lanthanides [1]. REEs are generally classified into two sub-groups according to their atomic weights and locations in the periodical table [2,3], namely light rare earth elements (LREEs) and heavy rare earth elements (HREEs). Promethium (Pm) is produced by radioactive decay and considered as the only element listed in the periodical table without stable isotopes [4,5]. The global production of REEs was 210000 metric tons of REO in 2019 [6]. Fig. 1 shows REEs production by different countries. REEs have been coded as critical materials by several international institutions and governments due to their supply risks and importance to the clean energy industry, advanced military applications, and many commodity items in high-tech industries [3,7–9]. The criticality of REEs has led to increasing interests and studies in the recovery from alternative resources, such as waste electrical and electronic equipment, permanent magnets, and lamp phosphors [3,10,11].

Fig. 1. The distribution of global REO production in 2019.

In recent years, many studies have been completed focusing on the recovery of REEs from coal-based materials [12–20]. As reported by Luttrell et al.[19] , more than 80% of REEs associated with run-of-mine coals report to refuse streams after coal preparation. Therefore, coal refuse is more suitable to be used as a feedstock for REEs recovery compared with other coal-based materials. Physical and hydrometallurgical approaches usually provided low recoveries of REEs from coal refuse [19]. Therefore, calcination treatment prior to acid leaching has been used with encouraging results being obtained [22,23]. For example, REEs recovery from a coal refuse was improved from around 20% to 90% by two hours of calcination at 600 ℃ using 1.2 mol/L HCl as the lixiviant [22]. However, this acid concentration level is too high to make the overall recovery and purification process economically viable [12]. The contradiction is that REEs recovery was reduced when using HCl solutions of a lower concentration, such as 6×10^{-3} mol/L [22]. One potential solution is using organic acids to replace inorganic acids.

Organic acids, especially the low molecular weight organic acids, have been applied for leaching REEs from both conventional rare earth ores and secondary resources [24–27]. Acetic acid, malonic acid, citric acid, tartaric acid, succinic acid, and malic acid have been used to improve the leaching recovery of REEs from an ion-adsorption type rare earth clay [28]. It was found that without pH adjustment, the extraction of REEs can be improved from around 9.6 to 10.7 mmol/kg by adding 1×10^{-3} mol/L of the organic acids. The enhancement of metal leaching in the presence of organic acids is likely due to three mechanisms: (1) protons dissociated from organic acid molecules increase the acidity of leaching systems; (2) organic species affect the saturation state of leach solutions with respect to mineral solids; and (3) organic species change the speciation of metal ions in solution [29].

In this study, acid leaching tests were performed on the calcination product of a coal coarse refuse material using different types of organic acids. Hydrochloric acid was also utilized for comparison purposes. The advantages of the organic acids over HCl were evaluated based on leaching test results. Interaction mechanisms between the organic acids and the solid were investigated through electro-kinetic tests and solution chemical equilibrium calculations. A comprehensive understanding of REEs recovery from calcined coal refuse using organic acids was achieved.

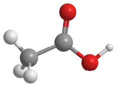
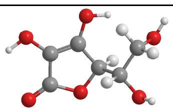
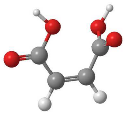
2. Material and methods

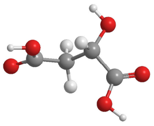
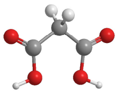
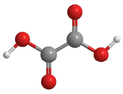
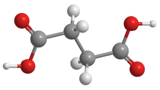
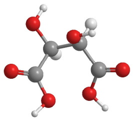
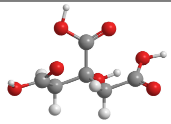
2.1 Materials

The sample used in this study was collected from the feed of a coal preparation plant, which processed coals originating from the Baker (Western Kentucky No. 13) seam located in western Kentucky, USA. The sample was dry-screened to obtain the plus 1 cm fraction, which was then density-fractionated using a dense medium of 2.2 specific gravity (SG). The medium was prepared by mixing fine-grained magnetite with tap water. The 2.2 SG sink fraction was collected and rinsed several times to remove entrained magnetite particles. The resultant sample was then air-dried and crushed to a top size of 0.18 mm using a crusher and a hammer mill, which was used as a feed for this study. The 2.2 SG sink material represents coarse refuse fraction of the run-of-mine coal.

Both organic and inorganic (hydrochloric) acids were used as lixiviants for the rare earth leaching recovery tests for comparison purposes. Details about the organic acids used in the experiments are shown in Table 1. All the organic acids were of ACS grade, while the hydrochloric acid was of trace metal grade. Hydrochloric acid and sodium hydroxide solutions of 1 mol/L were employed as pH regulators. All the chemicals were purchased from Thermo Fisher Scientific, USA. The water used in this study was deionized water with a resistivity of 18.2 MΩ·cm (Type I water per the ASTM D1193-06 standard).

Table 1. Type, formula, pKa (25 □), and structure of the organic acids used in this study.

Type	Organic acid	Formula	pKa1	pKa2	pKa3	Structure
Monocarboxylic	Acetic	$C_2H_4O_2$	4.76	-	-	
Dicarboxylic	L-Ascorbic	$C_6H_8O_6$	4.17	11.57	-	
	Maleic	$C_4H_4O_4$	1.83	6.07	-	

	DL-malic	$C_4H_6O_5$	3.40	5.11	-	
	Malonic	$C_3H_4O_4$	2.80	5.70	-	
	Oxalic	$C_2H_2O_4$	1.23	4.19	-	
	Succinic	$C_4H_6O_4$	4.22	5.70	-	
	DL-tartaric	$C_4H_6O_6$	3.22	4.37	-	
Tricarboxylic	Citric	$C_6H_8O_7$	2.79	4.30	5.65	

2.2 Methods

2.2.1 Calcination test

Calcination of the coarse refuse was performed in a muffle furnace (Model number: EW-33858-80) manufactured by Cole-Parmer, USA. For each batch of calcination, 50 g of the sample was divided into 10 crucibles (approximately 5 g per crucible), which were placed into the furnace. Temperature in the furnace was elevated from room temperature to 600 ℃ at a ramping rate of 10 °C/min. Calcination of the material at 600 ℃ lasted for two hours, after which the furnace was automatically cooled to room temperature. Calcined material in the crucibles was collected and uniformly mixed, which was used as a feed for the acid leaching tests.

2.2.2 Acid leaching test

Acid leaching tests were performed to assess the advantages of using organic acids as lixiviants to extract REEs from the calcined coarse refuse. Fig. 2 shows a schematic of the experimental setup that was used for the leaching tests. Leaching reaction occurred in a three-neck round bottom flask of 1000 mL maximum volumetric capacity, which was fitted with a thermometer, condenser, and glass stopper. The setup minimized water loss resulted from evaporation during the experiments. Leaching characteristics of REEs using HCl solutions of different concentrations were first investigated. Lixiviant screening tests were then conducted using the different types of organic acids listed in Table 1 with a dosage of 0.05 mol/L. Leaching temperature of all tests was maintained at 75 ℃ using a water bath and a hot plate. This temperature has been consistently used in the authors' prior studies relevant to REEs extraction from coal and coal refuse [22,23,30,31]. For each test, 2.5 g solid was mixed with 250 mL lixiviant solution, and the resultant slurry was mixed at 500 r/min using a magnetic stir.

During leaching reaction, representative samples were collected from the slurry to evaluate the leaching behavior of REEs at different time intervals from the start of the leaching process up to a total period of 2 h (i.e., 5, 15, 30, 60, 90 and 120 min). Immediately upon collection, the samples were subjected to solid-liquid separation using a high-speed centrifuge at 5000 r/min for 10 min. Elemental concentration of the supernatant was measured using inductively coupled plasma optical emission spectrometry (ICP-OES). After reaction, the remaining slurry in the flask was filtered using 2.5 µm pore size filter paper. The filtrate was collected for volumetric measurement. The filter cake was thoroughly rinsed using deionized water, and then dried at 60 °C for 12 h. The residual solid was weighed after drying. REEs concentration in both the filtrate and solid residue was analyzed. Elemental content (E_f, mg/kg) of the feed solid was back calculated using the following equation:

$$E_f = 100 \times (C_s \times m_s + C_l \times V_l) \times \frac{m_i}{m_i - m_m} \tag{1}$$

where C_s and C_l represent REEs concentration in the solid residue (mg/kg) and the filtrate (mg/L), respectively; m_s (kg) weight of the solid residue; V_l (L) volume of the filtrate; m_i (kg) weight of the total leaching slurry; and m_m (kg) total weight of all the representative slurry samples collected during the leaching process. The difference between the back-calculated contents and the values measured directly using ICP-OES was within ±5%, indicating minor experimental error.

The fraction of REEs in the feed that was extracted into solution during the leaching process was referred to as leaching recovery (R_i, %). The recovery was calculated using the following equation:

$$R_i = \frac{C_i \times V}{E_f \times 0.0025} \times 100\% \tag{2}$$

where C_i is REEs concentration (mg/L) in the leachate collected during the leaching reaction, V volume of the feed solution (0.25 L), and E_f (mg/kg) back-calculated elemental content in the feed solid. Three duplicates were performed under the same experimental conditions, and the standard variances in the REEs recoveries were less than 3%.

Fig. 2. Schematic of the experimental setup used for the acid leaching tests.

2.2.3 Electro-kinetic test

Electro-kinetic tests were performed to study the interactions between organic acids and solid surface as well as rare earth metal ions in solution. In addition to the acids showing good extraction performance, an ineffective organic acid was also selected for comparison purposes. Zeta potentials were measured using Zs90 Zeta spectrometer (Nano series, Malvern Instruments, UK). For each measurement, 0.04 g of solid was added into 40 mL organic acid solution of a desired concentration, which was prepared by dissolving a predetermined amount of organic acid in 1×10^{-3} mol/L KCl. Prior to the addition of solid, HCl and/or NaOH solutions of 1 mol/L were added to adjust pH of the organic acid solution to predetermined values. The slurry was conditioned through magnetic stirring, and during the conditioning process, slurry pH was regularly monitored and regulated to maintain constant. After conditioning for 12 min, the slurry was stood for 6 min to allow relatively coarse particles to settle. The supernatant was then collected and transferred to a capillary cell for zeta potential measurement. Each test was repeated three times, and the average values were reported. Experimental errors were presented as error bars. All measurements were performed at room temperature (25 ± 1°C).

2.2.4 Solution chemical equilibrium calculation

Generally, when metallic cations (e.g., Sc^{3+}) and/or organic acids (e.g., citric acid, DL-malic acid) are added to an aqueous system, reactions such as hydration, dissociation, and complexation will occur. Each reaction is determined by a thermodynamic reaction constant, based on which the distribution of species at a given pH can be calculated. In this study, solution chemical equilibrium calculations were performed using Visual MINTEQ 3.1[32], which is a freeware chemical equilibrium model maintained by Jon Petter Gustafsson at KTH, Sweden. Results and findings from the calculations were leveraged to understand the leaching mechanisms of REEs from the calcined material using organic acids as the lixiviant.

2.2.5 Sample characterization

All solid samples were digested per a modified ASTM D6357-11 method [33]. The samples were first calcined at 750 □ for 2 h to completely remove the organic matter. Then, 0.1 g calcined material was mixed with 20 mL of aqua regia and 20 mL of hydrofluoric acid in a digestion tube of 50 mL capacity. A hot block maintained at 130 □ was used for sample digestion. After 5 h of digestion, acid liquid in the tube was completely evaporated and the solid material was converted into precipitates. After that, 10 mL of nitric acid and 30 mL of deionized water were added into the tube to dissolve the precipitates, and the hot block temperature was adjusted to 110 °C. The precipitates were dissolved when the solution volume was evaporated to around 10 mL. The digestion tube was then extracted from the hot block and cooled to room temperature. Finally, adjusting the volume to 20 mL by adding deionized water. Elemental contents of the digestion solutions and the liquid samples produced from the experimental tests were measured using ICP-OES manufactured by Thermo Fisher Scientific, USA. A continuing calibration blank (CCB) solution and a continuing calibration verification (CCV) solution were measured periodically during the ICP analysis for quality control.

Mineralogical characterization of the raw and calcined coarse refuse was performed using X-ray diffraction (XRD). A Bruker-AXS D8 DISCOVER diffractometer configured in a parallel-beam geometry with Cu-Kα radiation was used for the characterization. XRD patterns were recorded over a 2θ range of 5°–70° with a step size of 0.02°. XRD patterns were analyzed and processed using MDI JADE 6.0 software.

3. Results and discussion

3.1 Sample characterization

Ash content of the coarse refuse sample was 86.49%. After calcination at 600 ℃ for 2 h, the associated organic matter was completely removed. As shown in Table 2, the content of total REEs in the calcined material was 364 mg/kg, which is over five times higher than the average content of World coals (68.5 mg/kg) [34]. Mineralogical changes of the coarse refuse before and after calcination were characterized by XRD analysis. As shown in Fig. 3, quartz was the most dominant mineral in both the raw and calcined material. Diffraction peaks of kaolinite, pyrite and muscovite were also observed in the pattern of the raw material. However, after calcination, the diffraction peaks of kaolinite and pyrite disappeared, while diffraction peaks corresponding to hematite appeared. This phenomenon is attributable to the conversion of pyrite to hematite as a result of the thermal decomposition in an oxidizing environment [35]. The interlayers of kaolinite start to dehydrate and disintegrate by breaking Al–OH bonds when temperatures exceed 400 ℃ [36,37]. Crystalline kaolinite was completely transformed into amorphous meta-kaolinite when calcination temperature reached 600 ℃. The dehydration and disintegration of kaolinite have been correlated to the improved leachability of REEs per the authors' prior studies [22,23,31]. However, the leaching characteristics of REEs from calcined coal refuse using organic acids as lixiviants have not been investigated to date.

Table 2. REEs contents (mg/kg) of the calcined sample (TREEs, LREEs, and HREEs represent total, light, and heavy REEs, respectively).

TREEs	LREEs	HREEs	Sc	Y	La	Ce	Pr	Nd	Sm
364	299	64.4	21.8	27.6	60.7	128.3	15.1	58.4	14.6
Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
2.4	11.1	1.6	8.5	0.9	5.2	1.0	4.3	1.8	

Note: LREEs include La through Sm plus Sc; HREEs include Eu through Lu plus Y.

Fig. 3. X-ray diffraction patterns of the coarse refuse before and after calcination (Q – quartz, M – muscovite, P – pyrite, K – kaolinite, H – hematite).

3.2 Leaching behavior of REEs using inorganic acid

Leaching recovery of REEs from the calcined material was first investigated using HCl of different concentrations as the lixiviant. Since the complexing affinity of chloride for REEs is negligible, the leaching behavior of REEs in a HCl solution is primarily determined by its acidity. Fig. 4 shows the effect of hydrochloric acid concentration on the leaching recovery of REEs as a function of reaction time. Rapid increases in the recovery of both the LREEs and HREEs occurred in the first few minutes of leaching reactions, which indicate that certain portion of the REEs were associated with easy-to-leach mineral forms, such as metal oxides [23]. After 60 min of leaching, the recovery was barely changed, in particular the systems with more concentrated HCl solutions.

Rising the concentration of HCl from 0.0025 to 0.05 mol/L, TREEs recovery increased from around 15% to 60%. However, from 0.05 to 0.25 mol/L, the recovery only increased by less than 10% (Fig. 4 and Fig**.** ***5***). The recovery of individual REEs displayed the same trend, suggesting no significant increases in the recovery can be obtained by using HCl concentrations of greater than 0.05 mol/L (Fig. S1). Therefore, improvements in the recovery were more effective in a medium acidity range. This fact rationalizes the application of organic acids to leach the REEs, since the majority of organic acids have relatively weak acidities.

Fig. 4. Effects of HCl concentration on the leaching recovery of TREEs (a), LREEs (b), HREEs (c), and Sc (d).

Fig. 5. Leaching recovery of REEs after two hours of reaction as a function of HCl concentration.

3.3 Leaching behavior of REEs using organic acids

Screening tests were performed to identify the most efficient organic acid for recovering REEs from the calcined coal coarse refuse. As shown in Fig. 6, approximately 50%–60% of REEs were extracted after two hours of reaction using 0.05 mol/L maleic acid, citric acid, oxalic acid, and DL-malic acid; whereas the other organic acids of the same dosage only provided less than 40% recovery. The recovery was barely increased after 60 min of reaction for the majority of the organic acids, except succinic acid and acetic acid. The dissociation of hydrogen ions is likely involved in the leaching kinetics. As shown in Table 1, succinic acid and acetic acid have relatively higher pKa1 values; thus, hydrogen ions are more difficult to dissociate from these two acids. As a result, a longer time is required to reach equilibrium [28,38].

Fig. 6. REEs leaching recovery with different types of organic acid at a concentration of 0.05 mol/L.

As Fig. 4 and Fig**.** ***6*** show, two hours of leaching time is sufficient for the leaching processes to reach equilibrium. Therefore, in order to compare the leaching performances of organic and inorganic acids, recovery values obtained after two hours of reaction were plotted against corresponding slurry pH (i.e., pH measured at the end of reaction). As shown in Fig. 7(a-c), when different concentrations of HCl were employed as the lixiviant, TREEs, LREEs, and HREEs recoveries increased with decreases in pH, and the data points can be well fitted using quadratic equations. Per the trend of the fitted curves, it can be observed that when pH was less than 2.0, REEs recovery was barely changed. This phenomenon corroborated the conclusion reached in Section 3.2 that greater increases in the recovery were obtained in a medium acidity range. Changes in the recovery of Sc were better fitted using a cubic equation (Fig. 7(d)). For relatively high acidities (pH < 2.0), the increase in Sc recovery was less than medium acidities (pH > 2.0). Therefore, the conclusion still applies to Sc.

As shown in Fig. 7, LREEs recovery values obtained using organic acids fall on or under the fitted curves. However, selected organic acids, such as citric acid and DL-malic acid, provided HREEs and Sc recovery values above the fitted curves. Around 5% increase in HREEs recovery was obtained in the pH range of 2.0–3.0 (Fig. 7(c)). Larger increases in recovery of around 10%–15% were achieved for Sc (Fig. 7(d)). The different effects of the organic acids on the leaching recovery of individual LREEs and HREEs can be observed from Fig. S2. The comparisons between HCl and organic acids suggested that organic acids, particularly citric acid and DL-malic acid, are advantageous over HCl in terms of the leaching recovery of HREEs and Sc. However, the comparisons were based on a premise that the inorganic and organic leaching systems reached the same pH at the end of reaction. As shown in Fig. 8, within the pH range of the studied HCl and organic acid concentrations, in order to reach the same final pH, the initial pH of HCl leaching systems shall be lower than organic acid leaching systems. Therefore, stronger acidic conditions were provided in the HCl leaching systems, especially at the beginning of the reactions.

Fig. 7. Leaching recovery of TREEs, LREEs, HREEs, and Sc after two hours of reaction as a function of pH using 0.05 mol/L organic acids and different concentrations of HCl.

The leaching function of HCl is primarily realized based on hydrogen ions dissociated from the acid molecules (i.e., acidity). However, for organic acids, acidity together with complexing ability collectively contribute to the dissolution of metal ions from solids. In order to evaluate the effect of the complexing ability associated with organic acids, acid leaching tests were performed using HCl and organic acids. The same concentration of 0.05 mol/L was applied, while the initial pH of all systems was adjusted to 3.0 by adding pH regulators. Moreover, during the leaching processes, the slurry pH was regularly monitored and adjusted to stabilize at the initial value. This experimental procedure ensured that the same acidity was provided for all the lixiviants. Therefore, the impact of the complexing ability of organic acids can be evaluated.

As shown in Fig. 9, when pH was fixed at 3.0, the majority of the investigated organic acids provided higher recoveries of both LREEs and HREEs compared with HCl. Around 65% of LREEs and 32% of HREEs were leached after two hours of reaction with citric acid; whereas, under the same experimental conditions, HCl only leached around 45% of LREEs and 20% of HREEs. Therefore, it can be concluded that complexing ability of the organic acids prompted leaching recovery of the REEs. This conclusion agreed with findings from prior studies reported in the literature [39,40]. The increase in the recovery of LREEs at pH 3.0 is larger than HREEs (20% vs 12%). However, the results shown in Fig. 7 suggested that organic acids imposed a more positive impact on the recovery of HREEs. The contrast can be explained by the fact that at pH 3.0, the fraction of extractable HREEs was less than that of LREEs. The maximum fraction of extractable REEs can be represented using recovery values obtained under strongly acidic conditions (e.g., pH 1.0). As shown, only 35% of HREEs were leached at pH 1.0 with HCl, which is closer to the recovery at pH 3.0 compared with LREEs (35% to 20% versus 75% to 45%). Therefore, the conclusion that organic acid contributed more to the leaching recovery of HREEs still holds.

Fig. 8. Initial and final pH of the organic and HCl leaching systems (Dotted line represents equivalent initial and final pH).

Among the organic acids, oxalic acid provided the strongest acidity (i.e., the lowest pH); however, the corresponding REEs recovery was lower than several other organic acids, such as maleic acid and citric acid. This phenomenon is likely due to the low solubility of rare earth oxalates, leading to the formation of rare earth oxalate precipitates during the leaching process [41,42]. Slurry pH of the systems with malonic acid and DL-tartaric acid were slightly lower than DL-malic acid; whereas, a higher recovery was obtained using DL-malic acid. As shown in Table 1, malonic acid is the next higher homologue of oxalic acid, and the two chemicals have similar molecular structures [43]. Therefore, the lower recovery using malonic acid may be due to the same reason as oxalic acid. Moreover, malonic acid may have a stronger adsorption capacity on the particle surface of the calcined materials, which likely causes negative impacts on the recovery in two aspects: (1) REEs leached from the solid may be tied around the solid surface due to complexation with the adsorbed malonic acid species; and (2) the effective concentration of malonic acid was reduce due to the adsorption. Similar explanations are likely applicable to DL-tartaric acid. It can be observed from the comparisons between Fig. 7 and Fig. 9 that as pH increased to 3.0, REEs recovery values were reduced to nearly null when oxalic acid and DL-tartaric acid were used as the lixiviant. Therefore, the negative effects associated with precipitation and surface adsorption were amplified at higher pH.

Fig. 9. Recovery of LREEs (a) and HREEs (b) using different acids of 0.05 mol/L concentration with pH being fixed at 3.0.

3.4 Zeta potential results and solution chemical equilibrium calculations

Acid leaching test results showed that REEs leaching performances obtained using the different types of organic acids contrasted. For example, higher recoveries of HREEs and Sc were obtained using citric acid and DL-malic acid compared with HCl (Fig. 7). However, a few organic acids, such as malonic acid, are disadvantages to HCl even with the same acidity being utilized (Fig. 9). Theoretically, organic acids are expected to be more efficient than mineral acids since they have both acidity and complexing ability [44,45]. Therefore, in addition to these two factors, other phenomena might occur during the leaching processes, which impaired the recovery.

As reported in the literature, adsorption of organic acids on mineral surface can occur through physical and/or chemical interactions [46]. Therefore, electro-kinetic tests were performed in this study to evaluate the relationship between organic acid adsorption and REEs leaching efficiency. As shown in Fig. 10(a), in the absence of organic acids, zeta potential of the calcined material gradually decreased with the increase in pH, and the point of zero charge (PZC) occurred at around pH 2.2. Declines in zeta potential were observed in the presence of 0.05 mol/L citric, DL-malic, or malonic acids. Moreover, the three acids caused left-shifts of the PZC, which indicates that specific adsorption of the organic species on the surface of the calcined material occurred.

In the pH range of 1.0 to 4.0, the surface of calcined material carried more negative charges after interacting with malonic acid as compared to citric acid and DL-malic acid of the same concentration (0.05 mol/L). Moreover, as shown in Fig. 10(b), the same phenomenon occurred in a wide concentration range of 1×10^{-4} mol/L to 3 mol/L. The three organic acids primarily occurred as undissociated molecules and first-order dissociation anions in the pH range of 1.0 to 4.0 (Fig. 11). Therefore, combining the results of zeta potential measurements and species distribution calculations, it can be concluded that the amount of organic acid species adsorbed on the calcined material surface follows the order of malonic acid > citric acid > DL-malic acid. Therefore, more citrate and malate species complexed with rare earth cations and stayed in solution, however malonic species preferred to stay on the surface, resulting in less REEs and/or less effective malonic species in solution. This conclusion is in accordance with the fact that citric acid and DL-malic acid provided higher recoveries of HREEs and Sc compared with malonic acid (Fig. 7 and Fig. 9).

As pH increases, organic acid molecules gradually dissociate into anionic species, which are less likely adsorbed onto surfaces carrying negative charges due to electrostatic repulsion. This mechanism caused decreases in the negative charge on both the citric acid and DL-malic acid conditioned surfaces in the pH range of 4 to 5 (Fig. 10(a)). For the malonic acid conditioned surface, the decrease occurred in a higher pH range of approximately 4.8 to 6.2. This contrast between malonic acid and the other two organic acids is likely due to: (1) malonic acid has a stronger adsorption capability on the surface; (2) in the pH range of 4 to 5, less malonic species occur as high-valence anions, such as divalent organic anions (Fig. 11). Fig. 10 also shows that when pH is above 6.0, zeta potential of the calcined material is relatively insensitive to organic acids. This suggests that the adsorption of organic species on the surface is very low because of electrostatic repulsion, which is unfavorable to adsorption.

Fig. 10. Effects of organic acids on the zeta potential of the calcined coal coarse refuse. (a) Zeta potential as a function of pH; (b) Zeta potential as a function of organic acid concentration.

Fig. 11. Species distribution of citric acid (a), DL-malic acid (b), and malonic acid (c) as a function of pH (0.05 mol/L total concentration, 25 ℃).

Electro-kinetic test results showed that citric acid and DL-malic acid preferred to stay in solution compared with malonic acid (Fig. 10). By complexing with citric acid and DL-malic acid, the adsorption of leached HREEs and Sc on the solid surface was reduced, resulting in increases in leaching recovery (Fig. 7). However, the adsorption of the REEs on the calcined material surface needs to be confirmed to validate the explanation. As shown in Fig. 12, negative charge on the surface of the calcined material was reduced in the presence of Ce^{3+}, Y^{3+}, and Sc^{3+}. Moreover, the rare earth metal ions caused right shifts of the PZC, in particularly at a higher concentration of 1×10^{-4} mol/L (Fig. 12(b)). Therefore, specific adsorption of the rare earth metal ions occurred, and the conclusion was validated. Furthermore, larger decreases were obtained when adding Y^{3+} compared with Ce^{3+}, suggesting that HREEs have a stronger adsorption capability on the calcined material surface compared with LREEs. This finding is in accordance with the leaching test result that the organic acids imposed a more positive impact on the leaching recovery of HREEs. The adsorption of HREEs on the surface was likely reduced through complexation and staying in solution with the organic acids.

As shown in Fig. 12, compared with Ce^{3+} and Y^{3+}, Sc^{3+} led to minimum decreases in the surface charge, suggesting the lowest adsorption of Sc^{3+}. However, citric acid and DL-malic acid caused largest increases in the recovery of Sc relative to the other REEs. Therefore, rather than reduced adsorption, the positive effect of the organic acid on Sc leaching recovery is likely due to other reason(s). As the results shown in Fig. 7(d), around 35% of Sc was leached with 0.05 mol/L citric acid and DL-malic acid, which is nearly the same as that obtained using HCl with lower pH (2.5 versus 1.0). Given the electro-kinetic test result that Sc adsorption on the calcined material surface is minimal, the organic anionic species likely played a function of prompting the solubilization of Sc from the solid, which is similar to that of hydrogen ions.

Fig. 12. Effects of different concentrations of REEs on the zeta potential of the calcined material: (a) 1×10^{-5} mol/L; and (b) 1×10^{-4} mol/L.

4. Conclusions

Acid leaching tests were performed on the calcination product of the coarse refuse fraction of a run-of-mine coal originating from the Baker seam located in western Kentucky, USA. Different types of organic acids, including succinic acid, malonic acid, acetic acid, citric acid, oxalic acid, DL-malic acid, DL-tartaric acid, ascorbic acid, and maleic acid, were used as the lixiviants. Moreover, hydrochloric acid was also used for comparison purposes. The impact of hydrochloric acid concentration on REEs recovery was first evaluated, and it was found that rapid increases in the recovery occurred in a medium acidity range (e.g., pH 2.0–3.0). This finding rationalized the utilization of organic acids since they normally have lower acidities relative to mineral acids. With the same pH at the end of leaching, higher recoveries of HREEs and Sc were obtained using citric acid and DL-malic acid compared with HCl. Acid leaching tests with slurry pH being fixed at 3.0 showed that both HREEs and LREEs recoveries were improved by using organic acids. These findings suggested that the complexing ability of organic acids, especially citric acid and DL-malic acid, contributed to the leaching recovery of REEs, in particular HREEs and Sc.

Among the investigated organic acids, malonic acid, oxalic acid, and DL-tartaric acid were found to be less efficient compared with the other organic acids and hydrochloric acid. Electro-kinetic test results showed that more malonic species were adsorbed on the surface of the calcined material compared with citric acid and DL-malic acid. The stronger adsorption may lead to two phenomena resulting in the lower REEs recoveries: (1) REEs cations may be tied around the solid surface by the adsorbed malonic species; and (2) effective concentration of malonic species in solution was reduced. The explanations are likely applicable to the inferior performances of oxalic acid and DL-tartaric acid. Moreover, REEs precipitation with the organic acids might also occur during the leaching processes, which may also impair the leaching recovery.

Compared with Ce^{3+}, a stronger adsorption of Y^{3+} on the surface was observed based on electro-kinetic tests. This finding corroborated the conclusion that organic acids imposed a more positive impact on the leaching recovery of HREEs. The adsorption of Sc^{3+} on the surface was lowest compared with other REEs. Therefore, rather than complexing, the organic anionic species likely played a similar function as hydrogen ions, namely solubilizing Sc from the solid.

References

1. Balaram V. Rare earth elements: A review of applications, occurrence, exploration, analysis, recycling, and environmental impact. Geosci Front. 2019;10(4):1285.

2. Massari S, Ruberti M. Rare earth elements as critical raw materials: Focus on international markets and future strategies. Resour Policy. 2013;38(1):36.

3. Binnemans K, Jones PT, Blanpain B, Gerven TV, Yang YX, Walton A, et al. Recycling of rare earths: A critical review. J Clean Prod. 2013;51:1.

4. Zhang WC, Rezaee M, Bhagavatula A, Li YG, Groppo J, Honaker R. A review of the occurrence and promising recovery methods of rare earth elements from coal and coal by-products. Int J Coal Prep Util. 2015;35(6):295.

5. Elkina V, Kurushkin M. Promethium: To Strive, to Seek, to Find and Not to Yield. Front Chem. 2020;8:1.

6. Sangine E. Mineral Commodity Summaries 2020.; 2020. https://pubs.usgs.gov/periodicals/mcs2020/mcs2020.pdf.

7. Chu S. Critical Materials Strategy. DIANE Publishing; 2011.

8. DoI US. Final List of Critical Minerals 2018. Fed Regist. 2018;83(97):23295.

9. European Commission. Report on critical raw materials for the Eu. 2015.

10. Di Piazza S, Cecchi G, Cardinale AM, Carbone C, Mariotti MG, Giovine M, et al. Penicillium expansum Link strain for a biometallurgical method to recover REEs from WEEE. Waste Manag. 2017;60:596.

11. Sun XC, Yuan K, Zhang YW. Advances and prospects of rare earth metal-organic frameworks in catalytic applications. J Rare Earths 2020;38(8):801.

12. Honaker RQ, Zhang WC, Werner J, Noble A, Luttrell GH, Yoon RH. Enhancement of a Process Flowsheet for Recovering and Concentrating Critical Materials from Bituminous Coal Sources. Mining, Metall Explor. 2020;37(1):3.

13. Honaker RQ, Groppo J, Yoon RH, Luttrell GH, Noble A, Herbst J. Process evaluation and flowsheet development for the recovery of rare earth elements from coal and associated byproducts. Miner Metall Process. 2017;34(3):107.

14. Zhang WC, Honaker RQ. Rare earth elements recovery using staged precipitation from a leachate generated from coarse coal refuse. Int J Coal Geol. 2018;195:189.

15. Lin RH, Howard BH, Roth EA, Bank TL, Granite EJ, Soong Y. Enrichment of rare earth elements from coal and coal by-products by physical separations. Fuel 2017;200:506.

16. Wang Z, Dai SF, Zou JH, French D, Graham IT. Rare earth elements and yttrium in coal ash from the Luzhou power plant in Sichuan, Southwest China: Concentration, characterization and optimized extraction. Int J Coal Geol. 2019;203:1.

17. Pan JH, Nie TC, Vaziri Hassas B, Rezaee M, Wen Z, Zhou C. Recovery of rare earth elements from coal fly ash by integrated physical separation and acid leaching. Chemosphere 2020;248:126112.

18. Vass CR, Noble A, Ziemkiewicz PF. The Occurrence and Concentration of Rare Earth Elements in Acid Mine Drainage and Treatment By-products: Part 1—Initial Survey of the Northern Appalachian Coal Basin. Mining, Metall Explor. 2019;36(5):903.

19. Zhang WC, Noble A, Yang XB, Honaker R. A Comprehensive Review of Rare Earth Elements Recovery from Coal-Related Materials. Minerals 2020;10(5):451.

20. Huang Z, Fan M, Tian H. Rare earth elements of fly ash from Wyoming's Powder River Basin coal. J Rare Earths 2020;38(2):219.

21. Luttrell GH, Kiser MJ, Yoon RH, Noble A, Rezaee M, Bhagavatula A, et al. A Field Survey of Rare Earth Element Concentrations in Process Streams Produced by Coal Preparation Plants in the Eastern USA. Mining, Metall Explor. 2019;36(5):889.

22. Zhang WC, Honaker R. Calcination pretreatment effects on acid leaching characteristics of rare earth elements from middlings and coarse refuse material associated with a bituminous coal source. Fuel 2019;249:130.

23. Zhang WC, Honaker R. Characterization and recovery of rare earth elements and other critical metals (Co, Cr, Li, Mn, Sr, and V) from the calcination products of a coal refuse sample. Fuel 2020;267:117236.

24. Goyne KW, Brantley SL, Chorover J. Rare earth element release from phosphate minerals in the presence of organic acids. Chem Geol. 2010;278(1-2):1.

25. Lazo DE, Dyer LG, Alorro RD, Browner R. Treatment of monazite by organic acids I: Solution conversion of rare earths. Hydrometallurgy. 2017;174:202.

26. Qu Y, Li H, Wang XQ, Tian WJ, Shi B, Yao MJ, et al. Bioleaching of major, rare earth, and radioactive elements from red mud by using indigenous chemoheterotrophic bacterium Acetobacter sp. Minerals 2019;9(67):1.

27. Reed DW, Fujita Y, Daubaras DL, Jiao YQ, Thompson VS. Bioleaching of rare earth elements from waste phosphors and cracking catalysts. Hydrometallurgy 2016;166:34.

28. Wang L, Liao CF, Yang YM, Xu HB, Xiao YF, Yan CH. Effects of organic acids on the leaching process of ion-adsorption type rare earth ore. J Rare Earths 2017;35(12):1233.

29. Wang XX, Li QM, Hu HF, Zhang TL, Zhou YY. Dissolution of kaolinite induced by citric, oxalic, and malic acids. J Colloid Interf Sci. 2005;290:481.

30. Zhang WC, Noble A. Mineralogy characterization and recovery of rare earth elements from the roof and floor materials of the Guxu coalfield. Fuel. 2020;270:117533.

31. Zhang WC, Honaker R. Enhanced leachability of rare earth elements from calcined products of bituminous coals. Miner Eng. 2019;142(13):105935.

32. Gustafsson JP. Visual MINTEQ 3.0 user guide. KTH, Department of Land and Water Resources, Stockholm, Sweden.

33. ASTM. ASTM D6357 - 11 Test Methods for Determination of Trace Elements in Coal, Coke, & Combustion Residues from Coal Utilization Processes by Inductively Coupled Plasma Atomic Emission, Inductively Coupled Plasma Mass, & Graphite Furnace Atomic Absorption Spec. 2011:8.

34. Ketris MP, Yudovich YE. Estimations of Clarkes for Carbonaceous biolithes: World averages for trace element contents in black shales and coals. Int J Coal Geol. 2009;78(2):135.

35. Music S, Popović S, Ristić M. Thermal decomposition of pyrite. J Radioanal Nucl Chem Artic. 1992;162(2):217.

36. Brindley GW, Nakahira M. The KaoIinite-Mullite Reaction Series: I, A Survey of Outstanding Problems. J Am Ceram Soc. 1959;42(7):311.

37. Rocha J, Klinowski J. Solid-state NMR studies of the structure and reactivity of metakaolinite. Angew Chemie Int Ed English. 1990;29(5):553.

38. Adeleke R, Nwangburuka C, Oboirien B. Origins, roles and fate of organic acids in soils: A review. South African J Bot. 2017;108:393.

39. Hopfe S, Konsulke S, Barthen R, Lehmann F, Kutschke S, Pollmann K. Screening and selection of technologically applicable microorganisms for recovery of rare earth elements from fluorescent powder. Waste Manag. 2018;79:554.

40. Antonick PJ, Hu ZC, Fujita Y, Reed DW, Das G, Wu LL, et al. Bio- and mineral acid leaching of rare earth elements from synthetic phosphogypsum. J Chem Thermodyn. 2019;132:491.

41. Chi R, Xu Z. A Solution Chemistry Approach to the Study of Rare Earth Element Precipitation by Oxalic Acid. Metall Mater Trans B 1999;30:189.

42. Han KN. Characteristics of precipitation of rare earth elements with various precipitants. Minerals 2020; 10, 178.

43. Doreswamy BH, Mahendra M, Sridhar MA, Prasad JS. Structural studies on praseodymium malonate hydrate. J Mol Struct. 2003;659:81.

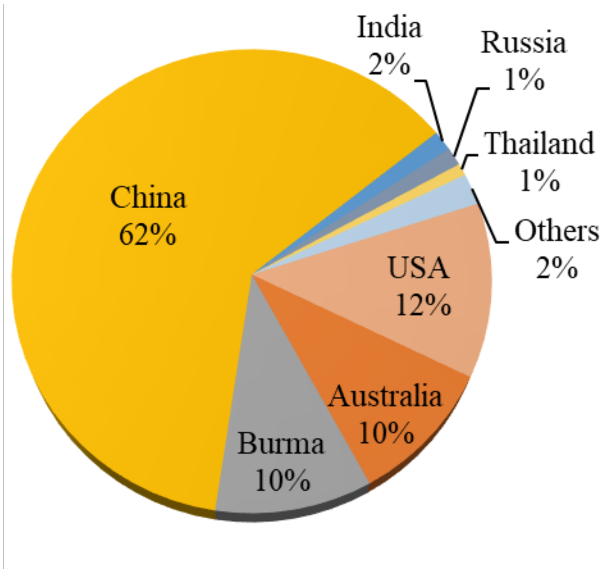
44. Bahaloo-Horeh N, Mousavi SM. Enhanced recovery of valuable metals from spent lithium-ion batteries through optimization of organic acids produced by Aspergillus niger. Waste Manag. 2017;60:666.

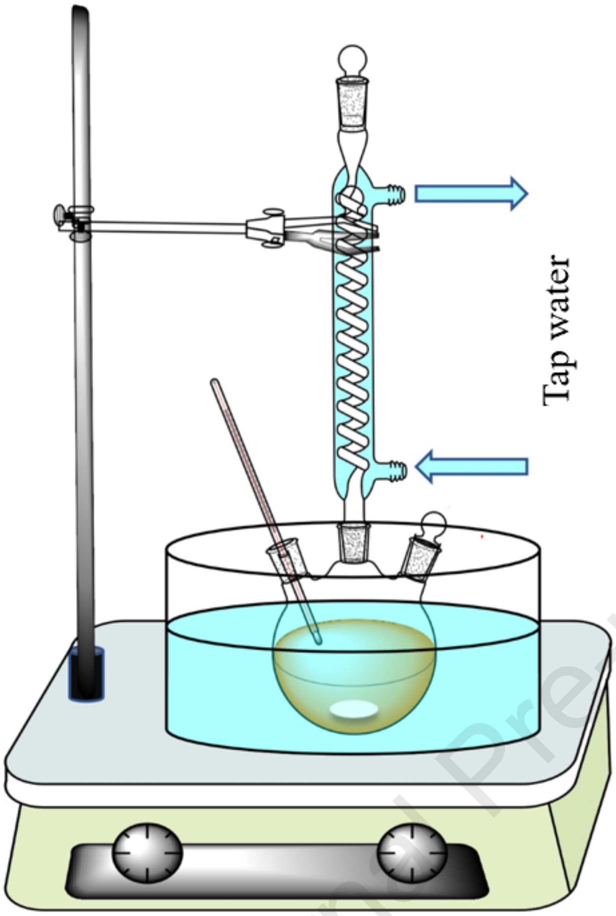
45. Reed DW, Fujita Y, Daubaras DL, Jiao Y, Thompson VS. Bioleaching of rare earth elements from waste phosphors and cracking catalysts. Hydrometallurgy 2016;166:34.

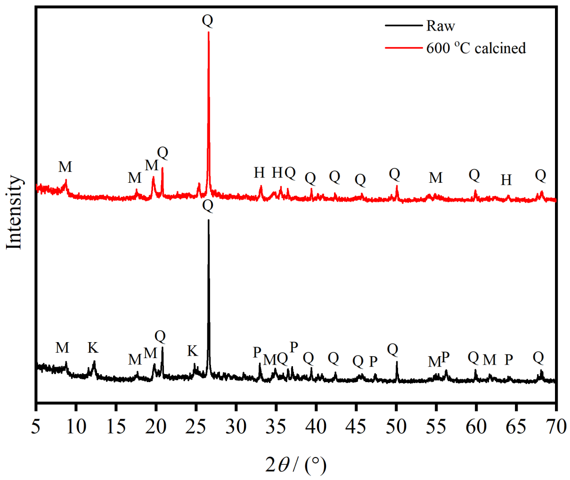
46. Xu RK, Li JY, Ji GL. Effect of Low Molecular Weight Organic Anions on Adsorption of Aluminum by Variable Charge Soils. Water Air Soil Pollut. 2005;168(1):249.

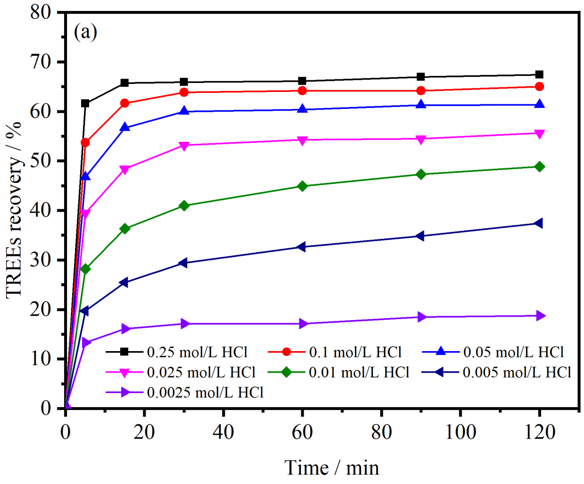
Graphical abstract:

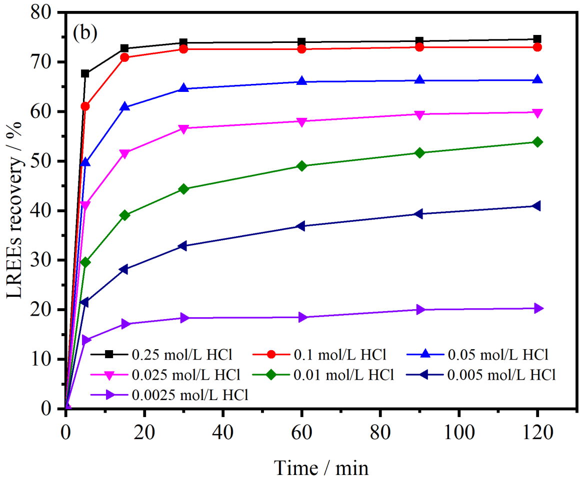
Different types of organic acids were used as lixiviants to leach rare earths from the calcination product of a coal coarse refuse. At the same pH, citric acid and DL-malic acid were found to provide the highest recoveries of heavy rare earths and scandium.

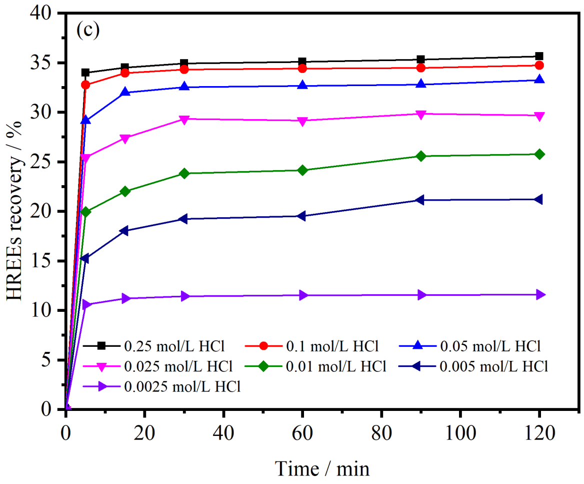

India
2%
Russia
1%
Thailand
1%
Others
2%
China
62%
USA
12%
Australia
10%
Burma
10%

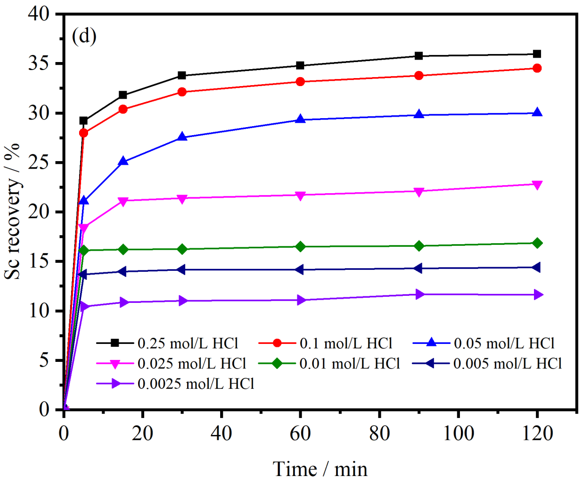

Tap water

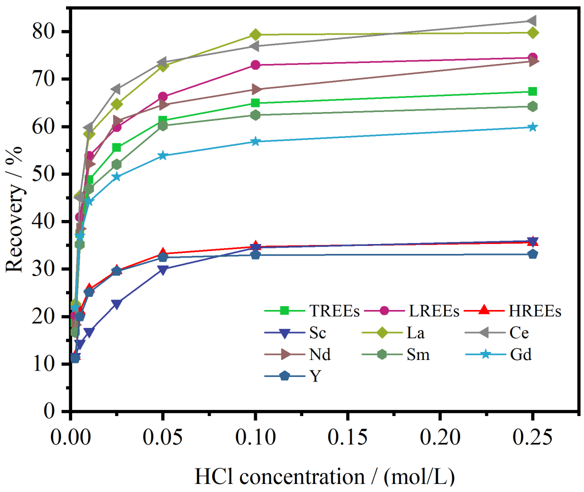

Raw
600 °C calcined
Intensity
M
M
M
Q
Q
H
H
Q
Q
Q
Q
Q
M
Q
H
Q
Q
M
K
M
M
Q
K
P
M
Q
P
Q
Q
Q
P
Q
M
P
Q
M
P
Q
5
10
15
20
25
30
35
40
45
50
55
60
65
70
2θ / (°)

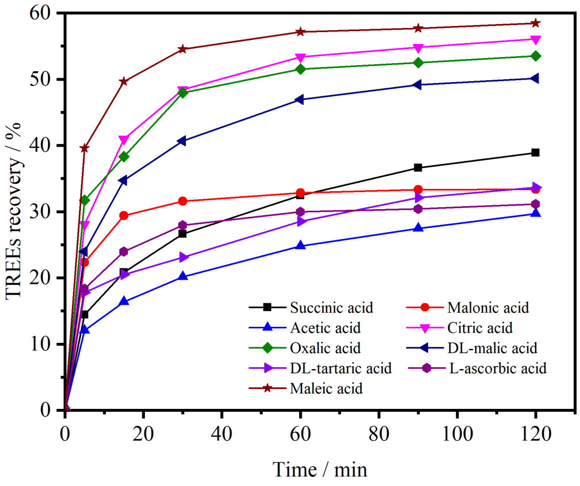

(a)
TREEs recovery / %
Time / min
0
10
20
30
40
50
60
70
80
0
20
40
60
80
100
120
0.25 mol/L HCl
0.1 mol/L HCl
0.05 mol/L HCl
0.025 mol/L HCl
0.01 mol/L HCl
0.005 mol/L HCl
0.0025 mol/L HCl


(b)
LREEs recovery / %
Time / min
0
10
20
30
40
50
60
70
80
0
20
40
60
80
100
120
0.25 mol/L HCl
0.1 mol/L HCl
0.05 mol/L HCl
0.025 mol/L HCl
0.01 mol/L HCl
0.005 mol/L HCl
0.0025 mol/L HCl

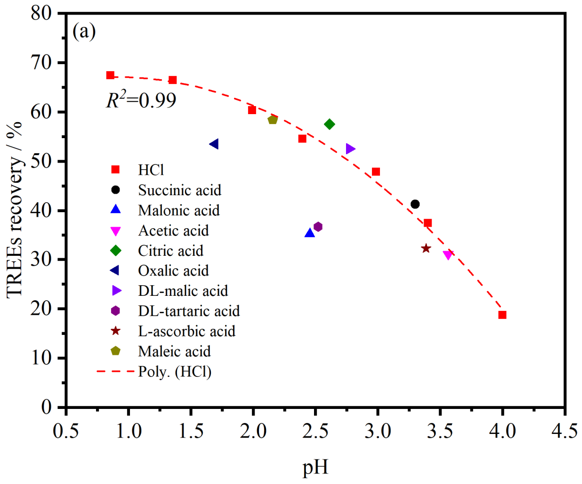

(c)
HREEs recovery / %
Time / min
0
5
10
15
20
25
30
35
40
0
20
40
60
80
100
120
0.25 mol/L HCl
0.1 mol/L HCl
0.05 mol/L HCl
0.025 mol/L HCl
0.01 mol/L HCl
0.005 mol/L HCl
0.0025 mol/L HCl

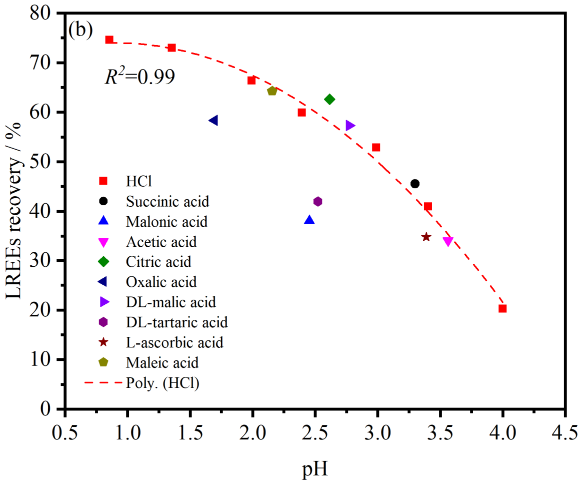

(d)
Sc recovery / %
Time / min
0
5
10
15
20
25
30
35
40
0
20
40
60
80
100
120
0.25 mol/L HCl
0.1 mol/L HCl
0.05 mol/L HCl
0.025 mol/L HCl
0.01 mol/L HCl
0.005 mol/L HCl
0.0025 mol/L HCl

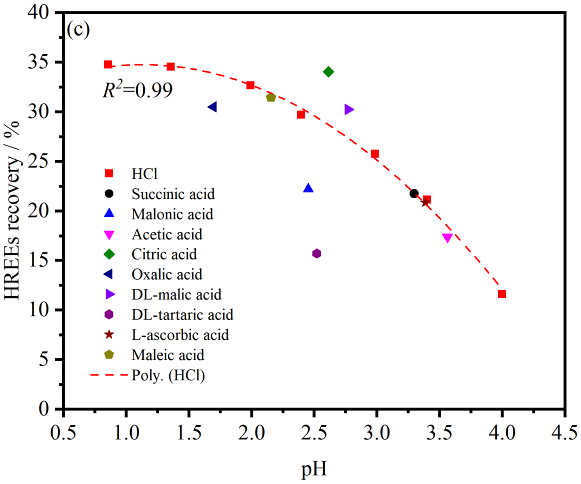

Recovery / %
0
10
20
30
40
50
60
70
80
0.00
0.05
0.10
0.15
0.20
0.25
HCl concentration / (mol/L)
TREEs
LREEs
HREEs
Sc
La
Ce
Nd
Sm
Gd
Y

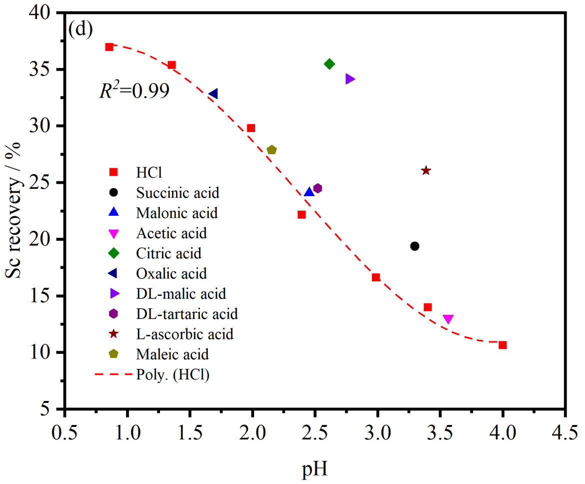


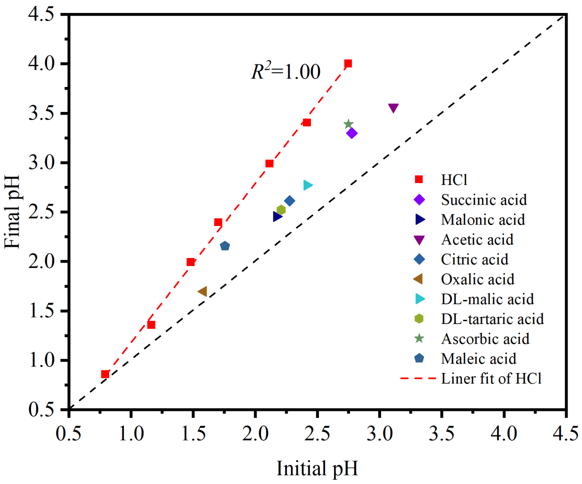
TREEs recovery / %
Time / min
0
10
20
30
40
50
60
0
20
40
60
80
100
120
Succinic acid
Malonic acid
Acetic acid
Citric acid
Oxalic acid
DL-malic acid
DL-tartaric acid
L-ascorbic acid
Maleic acid

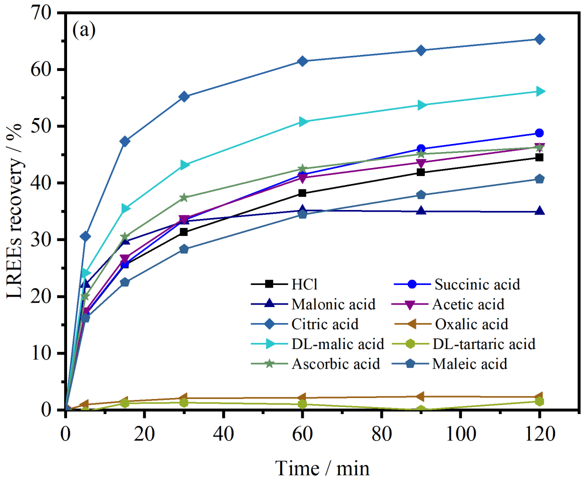

(a)
R^2=0.99
HCl
Succinic acid
Malonic acid
Acetic acid
Citric acid
Oxalic acid
DL-malic acid
DL-tartaric acid
L-ascorbic acid
Maleic acid
Poly. (HCl)
TREEs recovery / %
pH
0
10
20
30
40
50
60
70
80
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5

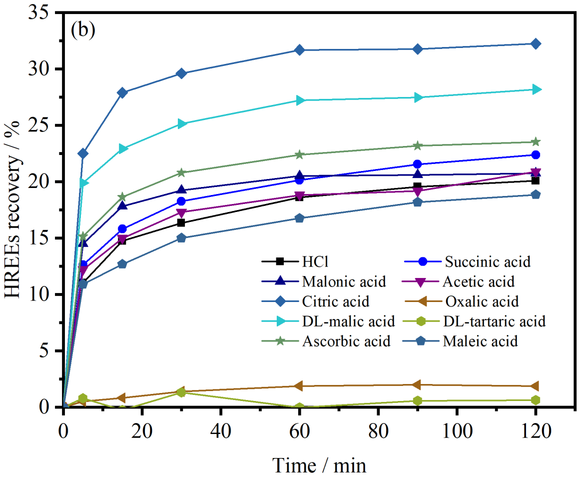

(b)
R²=0.99
LREEs recovery / %
pH
0
10
20
30
40
50
60
70
80
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
HCl
Succinic acid
Malonic acid
Acetic acid
Citric acid
Oxalic acid
DL-malic acid
DL-tartaric acid
L-ascorbic acid
Maleic acid
Poly. (HCl)

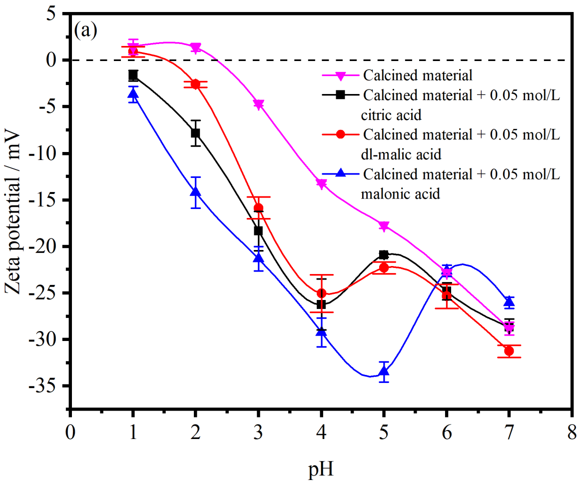

(c)
R^2=0.99
HREEs recovery / %
pH
0
5
10
15
20
25
30
35
40
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
HCl
Succinic acid
Malonic acid
Acetic acid
Citric acid
Oxalic acid
DL-malic acid
DL-tartaric acid
L-ascorbic acid
Maleic acid
Poly. (HCl)

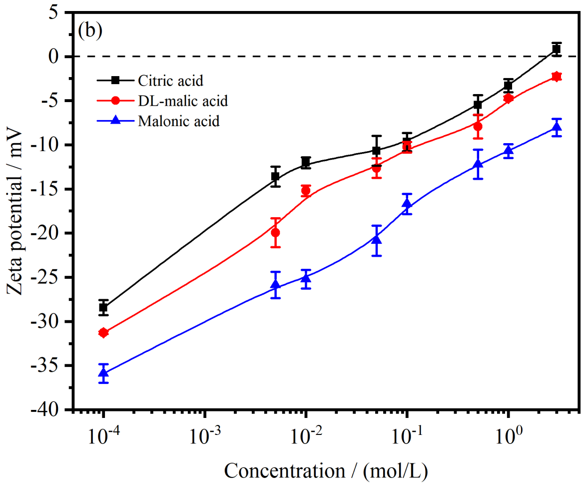

(d)
R^2=0.99
Sc recovery / %
pH
40
35
30
25
20
15
10
5
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
HCl
Succinic acid
Malonic acid
Acetic acid
Citric acid
Oxalic acid
DL-malic acid
DL-tartaric acid
L-ascorbic acid
Maleic acid
Poly. (HCl)

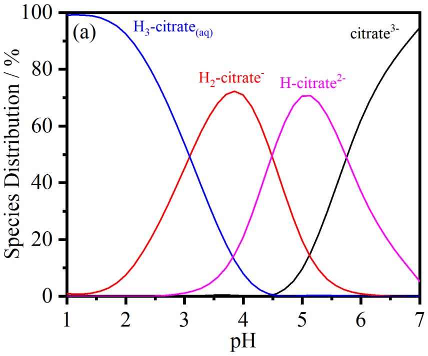

R^2=1.00
HCl
Succinic acid
Malonic acid
Acetic acid
Citric acid
Oxalic acid
DL-malic acid
DL-tartaric acid
Ascorbic acid
Maleic acid
Liner fit of HCl
Final pH
Initial pH
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5

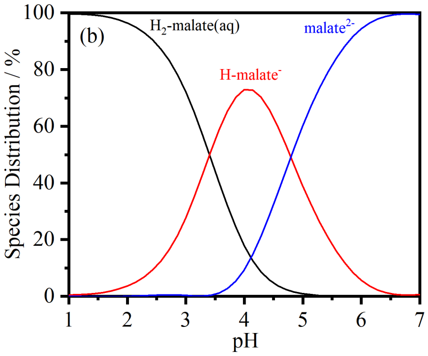

(a)
LREEs recovery / %
Time / min
0
10
20
30
40
50
60
70
0
20
40
60
80
100
120
HCl
Malonic acid
Citric acid
DL-malic acid
Ascorbic acid
Succinic acid
Acetic acid
Oxalic acid
DL-tartaric acid
Maleic acid

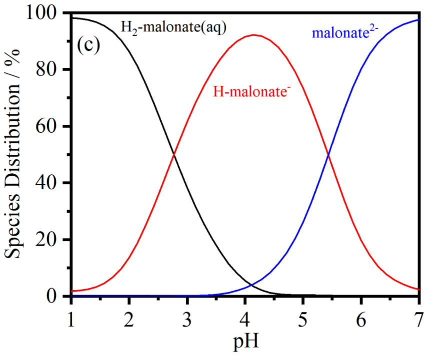

(b)
HREEs recovery / %
Time / min
0
5
10
15
20
25
30
35
0
20
40
60
80
100
120
HCl
Succinic acid
Malonic acid
Acetic acid
Citric acid
Oxalic acid
DL-malic acid
DL-tartaric acid
Ascorbic acid
Maleic acid

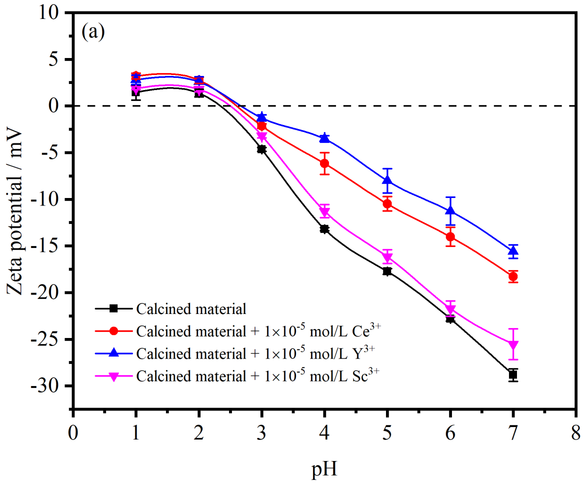

(a)
Calcined material
Calcined material + 0.05 mol/L citric acid
Calcined material + 0.05 mol/L dl-malic acid
Calcined material + 0.05 mol/L malonic acid
Zeta potential / mV
pH
5
0
-5
-10
-15
-20
-25
-30
-35
0
1
2
3
4
5
6
7
8

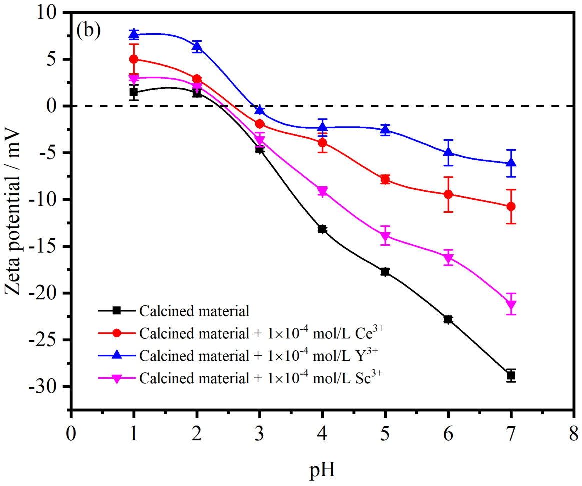

(b)
Citric acid
DL-malic acid
Malonic acid
Zeta potential / mV
5
0
-5
-10
-15
-20
-25
-30
-35
-40
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
Concentration / (mol/L)


(a)
H_3-citrate$_{(aq)}$
H_2-citrate$^-$
H-citrate^{2-}
citrate^{3-}
Species Distribution / %
100
80
60
40
20
0
1
2
3
4
5
6
7
pH


(b)
H$_2$-malate(aq)
H-malate$^-$
malate^{2-}
Species Distribution / %
0
20
40
60
80
100
1
2
3
4
5
6
7
pH


(c)
H$_2$-malonate(aq)
H-malonate$^-$
malonate^{2-}
Species Distribution / %
0
20
40
60
80
100
pH
1
2
3
4
5
6
7


(a)
Zeta potential / mV
pH
10
5
0
-5
-10
-15
-20
-25
-30
0
1
2
3
4
5
6
7
8
Calcined material
Calcined material + 1×10^{-5} mol/L Ce^{3+}
Calcined material + 1×10^{-5} mol/L Y^{3+}
Calcined material + 1×10^{-5} mol/L Sc^{3+}


(b)
Zeta potential / mV
10
5
0
-5
-10
-15
-20
-25
-30
pH
0
1
2
3
4
5
6
7
8
Calcined material
Calcined material + 1×10^{-4} mol/L Ce^{3+}
Calcined material + 1×10^{-4} mol/L Y^{3+}
Calcined material + 1×10^{-4} mol/L Sc^{3+}

- HREE and Sc recovery was improved by using citric acid and DL-malic acid
- Complexing ability of organic acids contributed to the recovery of total REEs
- Malonic, oxalic and DL-tartaric acids were inferior to other organic acids and HCl
- Leaching mechanisms with organic acid as the lixiviant were revealed

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: