



Study on Rare Earth Elements Leaching from Magnetic Coal Fly Ash by Citric Acid

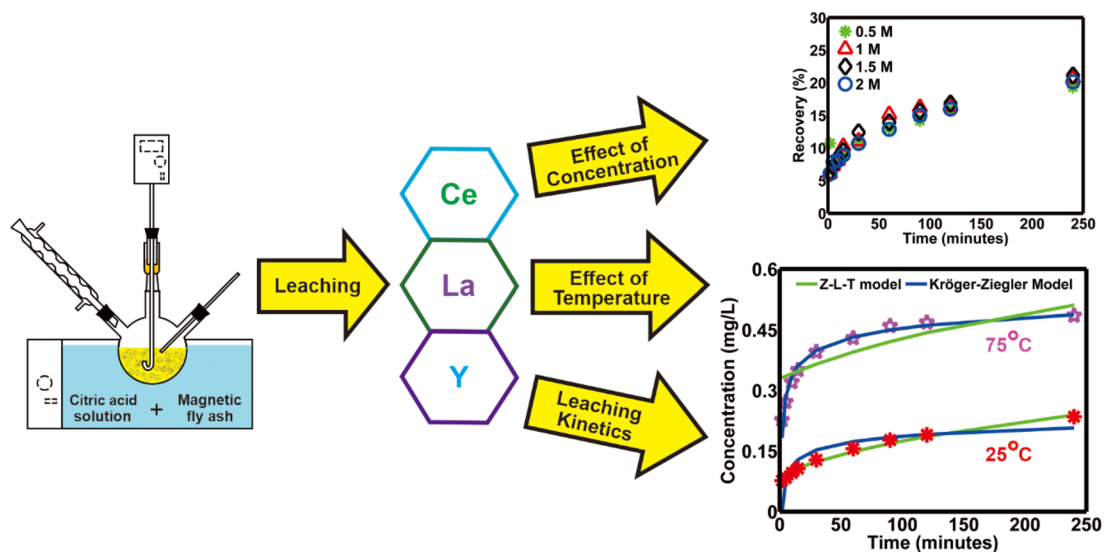
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Abstract

The production of fly ash as a solid waste of coal combustion increases with electricity demand growth in Indonesia. Fly ash is usually discarded in landfills due to its lack of utilization. Poor handling of the material can cause pollution and harm to human health. One potential of fly ash that can be further explored is as an alternative source of rare earth elements. The use of citric acid in the recovery process will be more environmentally friendly. The magnetic phase of fly ash is used as it is more favorable for the leaching process due to the smaller amount of acid-resistant components. This research aims to study the leaching mechanisms, evaluate the effect of temperature and acid concentration, and determine the appropriate kinetics model. Magnetic fly ash of less than $38\ \mu\text{m}$ was leached using 300 mL of citric acid with an S/L ratio of 1:10 at a 400 rpm stirring rate. The leaching experiments were carried out for 4 h and samples were taken at the designated time. Acid concentration of 0.5 M, 1 M, 1.5 M, and 2 M was used, while the temperature was varied from 25 °C, 45 °C, 65 °C, and 75 °C to 90 °C. The results show that acid concentration does not affect La, Ce, and Y recovery. Meanwhile, the temperature has a significant impact where the recovery increases as temperature elevates. Leaching at lower temperatures (25 °C and 45 °C) fits the Z–L–T kinetics model, while at higher temperatures (65 °C, 75 °C, and 90 °C) it follows the Kröger-Ziegler model.

Graphical Abstract



Keywords Magnetic coal fly ash · Rare earth elements · Citric acid · Acid leaching · Leaching kinetics

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Extended author information available on the last page of the article

Introduction

Electricity is a vital need derived from coal, gas, oil, and renewable energy such as wind, biogas, biomass, hydro, and geothermal. In 2018, 56.4% of Indonesia's electricity supply was met with coal as the energy source [1]. The implementation of the Indonesian Government's 35,000 MW electricity program to fulfill rising demand by building new power plants ensures an increase in coal usage in the following years [2]. Meanwhile, coal combustion produces fly ash which is considered limited in utilization and mostly disposed of in landfills [3]. The production of fly ash increases along with electricity demand growth and is predicted to reach 25.92 million tons in 2027 [4, 5]. The generation of fly ash dust containing heavy metals can pollute the environment and potentially harm human health [6].

Fly ash mainly consists of SiO_2 , Al_2O_3 , Fe_2O_3 , and CaO [7]. Fly ash also contains trace elements, such as As, Zn, Se, Pb, and valuable elements like rare earth [8, 9]. A large amount of fly ash is potential to be an alternative source of rare earth elements when the ratio of critical to excessive rare earth, known as C_{outlook} , is at least 0.7 and the percentage of critical elements is in the range of 30–51% [10, 11]. Rare earth elements like La, Ce, and Y are used in various industries, especially in clean technology, including battery, energy-efficient lighting, and catalytic converter [12]. A rare earth monopoly by China, which accounted for 84.7% of total world production, and their export restriction risk worldwide supply [13, 14]. The supply may be insufficient since rare earth demand actually grows over the years [15, 16]. In 2030, China is predicted not to meet 66% of world demand for Ce to be used as Al–Ce alloy in the automotive industry [17]. In addition to that, the need for Ce and La oxide in NiMH batteries is estimated to rise by 2030 [18]. Meanwhile, in accordance with supply risk, essential usage, and lack of substitutes, the availability of Y is also considered critical for several years to come [19].

Rare earth elements can be recovered from their source using the acid leaching method [20, 21]. Previous researchers have worked with inorganic acids such as hydrochloric acid, sulfuric acid, and nitric acid to extract rare earth elements from coal fly ash [22–24]. Unfortunately, these acids produce hazardous gasses like Cl_2 , SO_2 , and NO_x that may harm living organisms and the environment if not managed in a sustainable way [25–27]. An environmentally friendly substance that can be used in place of the inorganic acids is organic acids, one of which is citric acid [28, 29]. Citric acid is naturally non-toxic as it is found in almost all living organisms, biodegradable, and does not release toxic gasses when reacted [30–32].

On an industrial scale, citric acid is produced by *Aspergillus niger* which feeds on carbon sources such as molasses and starch [33]. However, these carbon sources can be replaced by starch-containing agro-industrial wastes which are abundant in Indonesia, like maize, cassava, and sweet potato, to reduce costs [34].

Si-containing components including amorphous aluminosilicates (glass) and SiO_2 are, however, practically resistant to acid attack and disturb the leaching process [35]. Alkali digestion or sintering is usually needed to raise the recovery value [10, 22, 28]. Alkali can break and solubilize amorphous glass that hinders the release of rare earth elements [28]. Digestion using NaOH, for example, produces $\text{REY}(\text{OH})_3$ (hydroxides of rare earth and yttrium) that can be further recovered through the acid leaching process [36]. Another method to increase leaching efficiency is to separate fly ash into phases according to its magnetic properties. Most glass and SiO_2 are considered non-magnetic, while components containing Fe are magnetic [5]. Fe-rich components that are soluble in acid can be obtained by doing magnetic separation, favoring the leaching process [37]. Aside from the characteristic of raw material and the leaching reagent applied into the process, some parameters related to the operating condition, such as acid concentration, time, temperature, and stirring speed, can influence the leaching process [38, 39].

Based on the review, a comprehensive study on REY leaching from the magnetic coal fly ash using citric acid has not been reported. Not only the sustainability aspect at which citric acid can be an alternative for REY leaching from magnetic coal fly ash, but the recovery in a level of appropriate to scale-up also has not been studied. Thus, this study aims to investigate the leaching mechanisms of La, Ce, and Y and to determine the kinetics model. Finalizing this study, parameter design related to the kinetics model fits for La, Ce, and Y extraction from magnetic coal fly ash using citric acid can be obtained for the scale-up process.

Materials and Methods

Materials and Their Characterization

The main material used in this study is magnetic coal fly ash collected from the Tanjung Awar-Awar coal power plant, Tuban Regency, East Java, Indonesia. Magnetic fly ash was obtained after separating fly ash of less than $38\ \mu\text{m}$ in size with a magnetic separator via wet method using an electric current of 2 A. The crystal structure of magnetic fly ash was determined by X-ray diffraction (XRD, X'Pert 3 Powder, PANalytical, Netherland). The analysis was carried out using $\text{CuK}\alpha$ radiation in the 2θ

range from 10° to 80°. Magnetic fly ash's morphology was analyzed via the Secondary Electron Imaging (SEI) method at 20 kV using JSM-6510 LA series of Scanning Electron Microscope (SEM). Surface area and pore size of magnetic fly ash were measured on QuadraSorb Station 1 version 7.01 by nitrogen gas adsorption at 77.3 K using the MultiPoint Brunauer–Emmett–Teller method.

The feasibility of magnetic fly ash as an alternative source of rare earth elements is determined using the value of C_{outlook} and critical rare earth percentage. The C_{outlook} value was calculated using Eq. 1 [11].

$$C_{\text{outlook}} = \frac{(\text{Nd} + \text{Eu} + \text{Tb} + \text{Dy} + \text{Er} + \text{Y})/(\text{Total rare earth elements})}{(\text{Ce} + \text{Ho} + \text{Tm} + \text{Yb} + \text{Lu})/(\text{Total rare earth elements})} \quad (1)$$

Meanwhile, the percentage of critical elements in respect of total rare earth elements was calculated using Eq. 2.

$$\% \text{critical} = \frac{(\text{Nd} + \text{Eu} + \text{Tb} + \text{Dy} + \text{Er} + \text{Y})}{\text{Total rare earth elements}} \times 100\% \quad (2)$$

As a leaching agent, citric acid monohydrate ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$) of analytical grade from Merck with CAS number 5949-29-1 was used. Citric acid monohydrate was dissolved in distilled water produced by water distillation apparatus-type 1032 from Köttermann, Germany, into various concentrations.

For analysis purposes, the standard solution was diluted in pure solvent. The pure solvent used was aqua pro injection obtained from PT Ikapharmindo Putramas. The standard solution used was a rare earth element mix for ICP from Sigma-Aldrich containing Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu of 50 mg/L each in 2% nitric acid solution. Analysis of rare earth elements concentration was carried out using ICP-OES (Optima 8300, Perkin Elmer, USA).

Leaching of Rare Earth Elements

A citric acid solution of 300 mL was put into a three-neck flask. The citric acid solution was then heated in a water bath until the leaching temperature was achieved. As much as 30 g of magnetic fly ash was added to the heated solution. The fly ash was dried before in the oven for an hour at a temperature of 125 °C. The mixture was stirred using a glass stirrer at 400 rpm, while the leaching temperature was kept constant. The leaching experiment was carried out for 4 h. Samples were taken using a syringe at 2, 5, 10, 15, 30, 60, 90, 120, and 240 as much as 3 mL each. The experiment was done at various citric acid concentrations of 0.5 M, 1 M, 1.5 M, and 2 M, as well as various leaching temperatures of 25 °C (room temperature), 45 °C, 65 °C, 75 °C, and 90 °C.

Liquid Sample Preparation

A sample of 3 mL was centrifuged at 4000 rpm for 1 min to separate the liquid and the solid. The liquid was then filtered using a 0.2 nm microfilter to ensure no solids are included when the sample is analyzed. As much as 1 mL of filtered liquid sample was diluted ten times using aqua pro injection before it was analyzed using ICP-OES.

The recovery value of La, Ce, and Y from magnetic fly ash is calculated using Eq. 3.

$$\alpha = \frac{10C_{\text{REE}}V}{mX_0} \quad (3)$$

where α is the recovery value, C_{REE} is the concentration of either La, Ce, or Y from analysis (mg/L), V is the volume of citric acid solution (L), m is the mass of leached magnetic fly ash (kg), and X_0 is the initial content of either La, Ce, or Y in magnetic fly ash (mg/kg).

Results and Discussion

Magnetic Fly Ash Characterization

Material characterization carried out in this study includes analysis using XRD, SEM, and Surface Area Analyzer (SAA). Figure 1 shows magnetic fly ash's diffractogram as a result of XRD analysis.

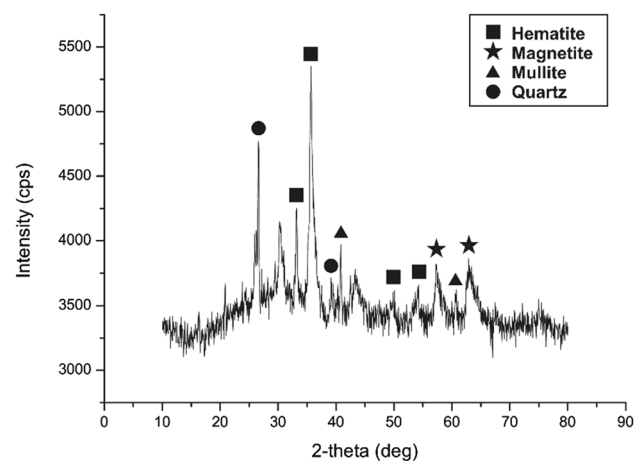
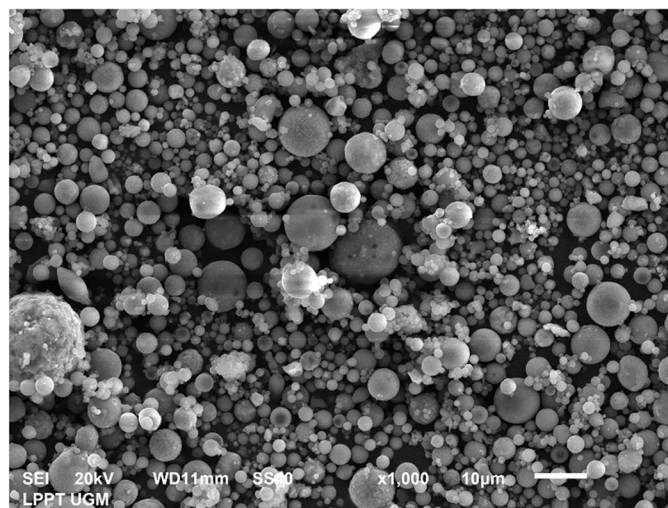


Fig. 1 Diffractogram of magnetic fly ash

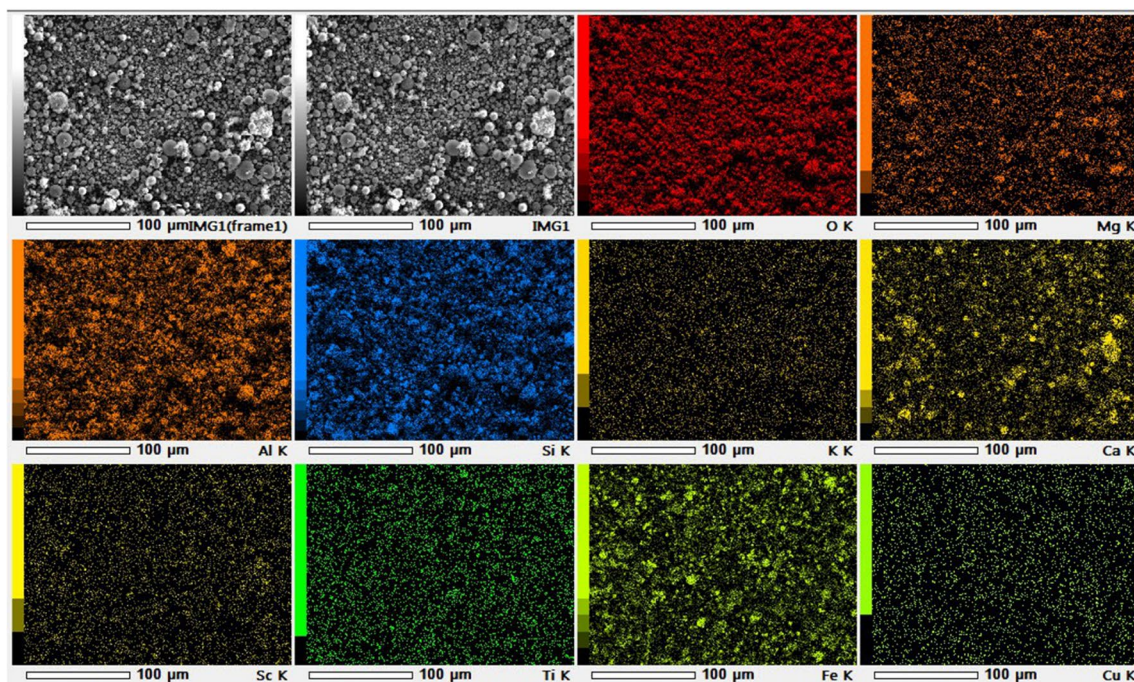
The result agrees with the previous finding as the magnetic fly ash contains quartz (SiO_2), mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$), magnetite (Fe_3O_4), and hematite (Fe_2O_3) [40]. Hematite is observed to have high peak intensity at 2θ values of 35.7° and 33.23° . The sample is also composed of amorphous materials, indicated by a wide hump in 2θ range from 20° to 45° [41]. The amorphous materials are most likely

aluminosilicate glasses and some are modified by cations, like Ca^{2+} , Mg^{2+} , Na^+ , or K^+ [42].

The result of 1000 times magnification of magnetic fly ash by SEM is shown in Fig. 2a. Each particle tends to be round; thus, magnetic fly ash can be assumed as a spherical solid. The mapping of these elements in magnetic fly ash is presented in Fig. 2b. As the magnetic phase mainly consists



(a)



(b)

Fig. 2 **a** SEM of magnetic fly ash particles with 1000 times magnification and **b** elemental map of magnetic fly ash ((from left to right) 1st row: an overview of magnetic fly ash, magnetic fly ash, O map-

ping, Mg mapping; 2nd row: Al mapping, Si mapping, K mapping, Ca mapping; 3rd row: Sc mapping, Ti mapping, Fe mapping, Cu mapping)

Table 1 Composition of major elements as oxides (XRF analysis) in fly ash from Tanjung Awar-Awar coal power plant

Major element (%)	Raw fly ash [43]	Non-magnetic fly ash [28]	Magnetic fly ash [44]
SiO ₂	50.9	53.2	31.5
Al ₂ O ₃	28.7	31.9	21.6
Fe ₂ O ₃	9.04	5.58	31.4
CaO	3.31	3.08	6.34
MgO	2.23	2.11	4.39
Na ₂ O	0.82	0.9	0.53
K ₂ O	0.85	0.99	0.59
Cr ₂ O ₃	0.02	0.01	0.032
TiO ₂	1.04	1.15	0.83
MnO	0.07	0.06	0.17
P ₂ O ₅	0.23	0.24	0.26
SrO	0.07	0.08	0.07
BaO	0.08	0.07	0.1
LOI	1.91	1.09	2.01

Table 2 Elemental composition of rare earth (ICP-MS analysis) in fly ash from Tanjung Awar-Awar coal power plant

Element (ppm)	Raw fly ash [43]	Non-magnetic fly ash [28]	Magnetic fly ash [44]
La	42.3	49	40
Ce	84.9	98.3	83.6
Pr	9.7	11.45	9.69
Nd	37.4	45.2	37.8
Sm	7.7	8.7	7.81
Eu	1.7	1.99	1.93
Gd	7.7	9.35	8.76
Tb	1.3	1.43	1.22
Dy	7.8	9.32	8.1
Ho	1.8	1.8	1.66
Er	5.1	5.74	4.8
Tm	0.8	0.92	0.73
Yb	5.0	6.08	4.5
Lu	0.8	0.95	0.73
Y	46.4	53.2	46.7
ΣREE	260.4	303.43	258.03

of Fe oxides, Fe can be seen in the map to coincide with oxygen. The result of the surface area analyzer reveals that magnetic fly ash has a surface area of 8.185 m²/g and an average pore diameter of 6.025 nm. This low surface indicates that the ash particles are non-porous.

The concentration of major and rare earth elements in raw fly ash, non-magnetic fly ash, and magnetic fly ash from the Tanjung Awar-Awar coal power plant has been analyzed and summarized in Tables 1 and 2. The coal fly ash used was also

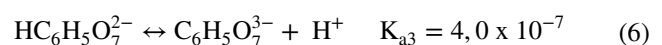
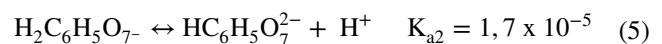
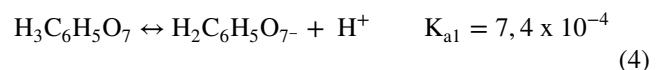
previously analyzed by our group [28, 43, 44]. Major elements were measured as oxides using XRF analysis, whereas rare earth was measured as elemental using ICP-MS due to their far lower concentration. The results appoint that the major metal oxides of fly ash before and after magnetic separation are SiO₂, Al₂O₃, and Fe₂O₃. Magnetic separation significantly increases Fe₂O₃ concentration in magnetic fly ash around 3.5-fold, from 9.04 to 31.4%. The magnetic phase also experiences a rise in CaO concentration, from 3.31 to 6.34%, and MgO concentration, from 2.23 to 4.39%.

On the other hand, the phase declines in SiO₂ and Al₂O₃ concentration, although the ratios to raw fly ash are not as notable as in Fe₂O₃. As much as 31.5% of SiO₂ and 21.6% of Al₂O₃ are still contained from the initial concentration of 50.9% and 28.7%. This is due to the presence of glass fractions containing Fe, Ca, and Mg as a result of fusion from coal combustion, making it possible to be attracted by a magnetic field [42]. The concentration of major elements in the magnetic phase is the complete opposite of the non-magnetic one, where SiO₂ and Al₂O₃ concentration increase, while the concentration of Fe₂O₃, CaO, and MgO experience a decrease.

Rare earth elements do not exist in coal fly ash as minerals; instead, they are distributed in the particles after the combustion process [23]. It is shown in Table 2 that Ce, Y, and La are the three most abundant elements in the magnetic fly ash with a concentration of 83.6 ppm, 46.7 ppm, and 40 ppm, respectively. The feasibility of this material as a rare earth elements source is determined by calculating the value of C_{outlook} and the percentage of critical rare earth. The C_{outlook} value appears to be 1.102 and the critical rare earth is 38.97%. Therefore, magnetic fly ash from the Tanjung Awar-Awar coal power plant can be considered as a potential alternative source of rare earth elements, particularly as the source of Ce, Y, and La.

The Effect of Acid Concentration

Rare earth elements from magnetic fly ash can be leached by citric acid due to the formation of complexes. First, citric acid dissociates into H⁺ ions and their anions [45].



Hydrogen ions then displace the position of rare earth ions and rare earth ions form soluble metal–ligand complexes with anions [46]. The complexation reaction of La, Ce, and

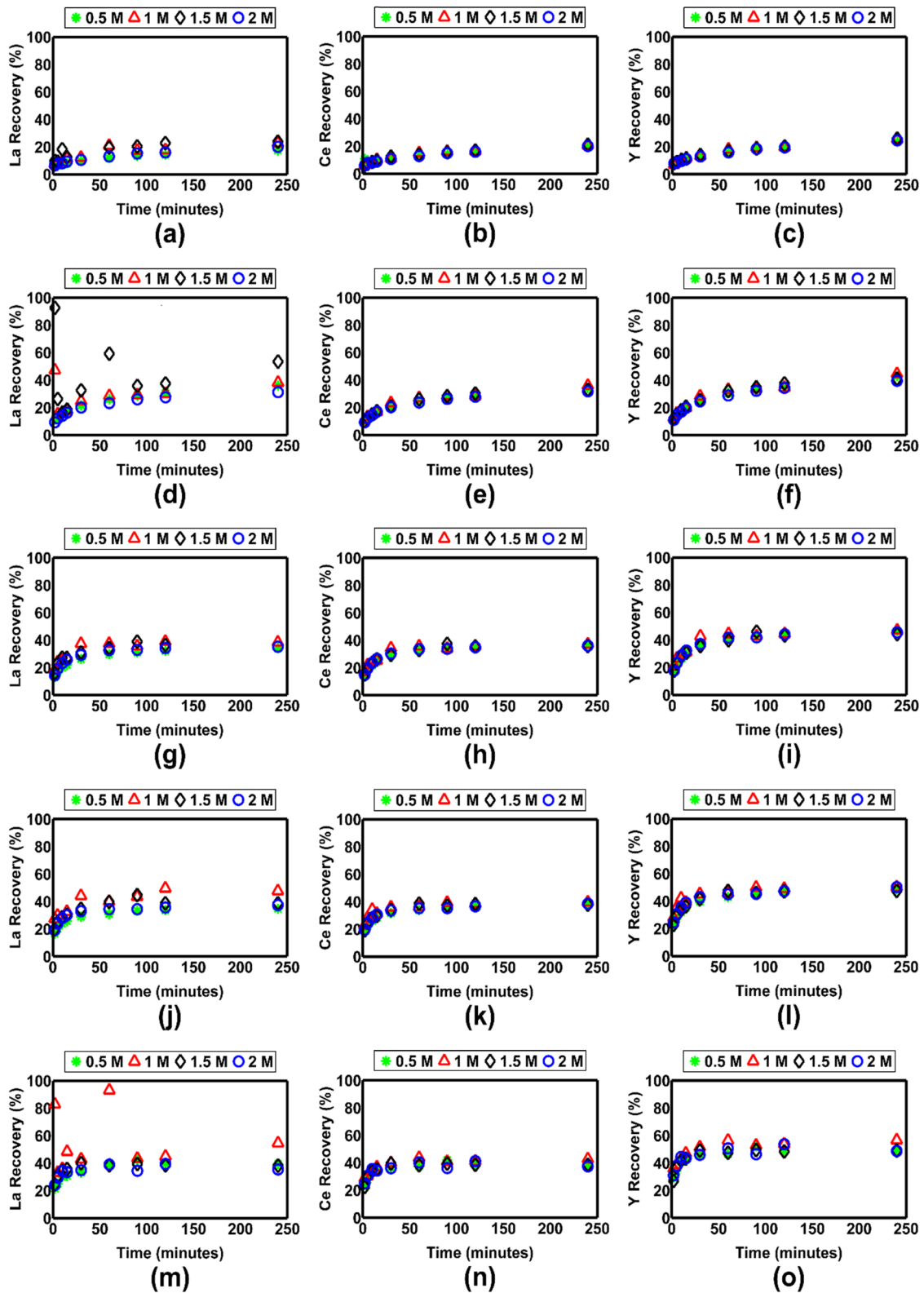
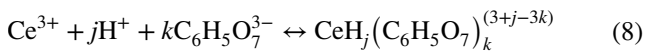
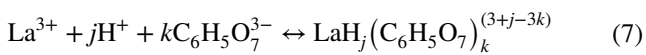


Fig. 3 Recovery of rare earth elements by various citric acid concentrations: **a** La; **b** Ce; **c** Y at 25 °C; **d** La; **e** Ce; **f** Y at 45 °C; **g** La; **h** Ce; **i** Y at 65 °C; **j** La; **k** Ce; **l** Y at 75 °C; and **m** La; **n** Ce; and **o** Y at 90 °C

Y ions by citric acid anions can be derived from general complexation reaction of 3-valence metal [47].



The effect of citric acid concentration in the leaching of La, Ce, and Y in various temperatures is shown in Fig. 3. It is shown from the graphs that the recovery has a slight rise when 1 M of citric acid was used instead of 0.5 M of citric acid, but the rise is not too significant. Furthermore, the recovery of either La, Ce, or Y by various acid concentrations in all temperatures tends to overlap, indicating that acid concentration does not affect La, Ce, and Y recovery.

In the solution, citric acid dissociates according to Eqs. 4, 5, and 6. The increase in citric acid concentration increases the number of anions that have an important role in rare earth leaching. Since the dissociation of citric acid is a reversible reaction, the concentration of H^+ ions and anions can reach a saturation point when a tremendous amount of citric acid is used. This causes the equilibrium to shift to the left so that the concentration of H^+ ions and anions decrease. As a result, the recovery value is lower when a too high concentration of citric acid is used. However, the effect of citric acid concentration is not very significant at lower temperatures.

The Effect of Temperature

The recovery of either La, Ce, or Y in various temperatures gives the same trend as presented in Fig. 4 for a citric acid concentration of 0.5 M. Recovery value increases

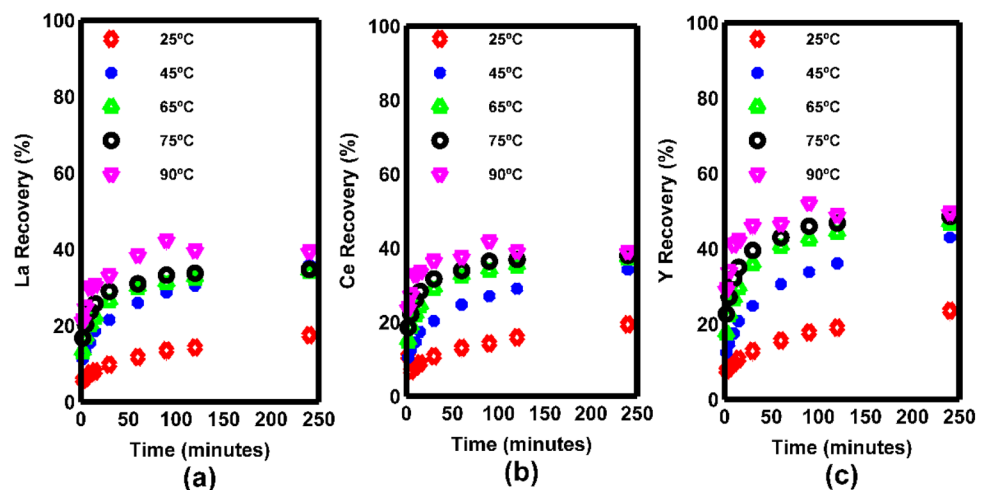
along with the elevation of temperature. Citric acid leach rare earth elements through diffusion and complexation reaction mechanisms. As temperature rises, the kinetic energy of the molecules increases so that the likelihood of intense molecule contact is greater and speeds up the complex formation. The surge in kinetic energy also increases molecular movement, thereby accelerating diffusion in the leaching process.

The rise of La, Ce, and Y recovery is relatively rapid in the early minutes of the leaching process. The increase in recovery value is not significant after 90 min. This trend is mainly found at high-temperature leaching, namely at a temperature of 65 °C and above. Initially, the system is rich in reactants and is far from equilibrium, so that the increase in recovery value occurs rapidly. The longer the leaching process, the amount of reactants becomes less and the system gets closer to equilibrium, thus slowing the increase in recovery value. The use of high temperature elevates the leaching rate making it faster to reach equilibrium.

Leaching Kinetics

The kinetics model is essential for evaluating the rate of leaching and for the scale-up process [48]. It can also be used to explain the leaching phenomenon. The kinetics model for the solid–liquid system can be proposed using assumptions that the solid is spherical, the particles are uniform in size, and the reactant particle is surrounded by the other reactant [49]. In this study, Zhuvralev–Lesokhin–Templeman (Z–L–T) kinetics model and Kröger–Ziegler kinetics model were used. These two models are based on the assumption that diffusion is the stage controlling the kinetics. Z–L–T model uses added assumptions that the diffusion coefficient is constant and that the reactant activity is proportional to unreacted solid $(1 - \alpha)$ [50, 51]. Meanwhile,

Fig. 4 Recovery of **a** La; **b** Ce; and **c** Y by 0.5 M of citric acid at various temperatures



the Kröger-Ziegler kinetics model assumes that the diffusion coefficient is not constant. Instead, it is inversely proportional to reaction time, and that the reactant activity is constant [51, 52]. The Z–L–T model and Kröger-Ziegler model are stated in Eqs. 10 and 11, respectively [52].

$$\left((1 - \alpha)^{-\frac{1}{3}} - 1 \right)^2 = k_{ZLT} t \quad (10)$$

$$\left(1 - (1 - \alpha)^{\frac{1}{3}} \right)^2 = k_{KZ} \ln t \quad (11)$$

where α is either La, Ce, or Y recovery value, k_{ZLT} is the rate constant of the Z–L–T model, k_{KZ} is the rate constant of the Kröger-Ziegler model, and t is leaching time. In practice, data analysis of the kinetics model may give a non-zero intercept since the time $t=0$, which gives the value of $\alpha=0$, is hard to observe [23].

Data fitting from Figs. 5, 6, and 7 indicate that La, Ce, and Y leaching phenomenon from magnetic coal fly ash by citric acid follows two different kinetics models for two groups of temperature. Leaching at low temperatures follows the Z–L–T model, while at high temperatures follows the Kröger-Ziegler kinetics model. The two models are fit

indicated by the R^2 values that are very close to 1 (Table 3). Thus, two models explaining the leaching phenomenon are in accordance with the different trends of recovery values at low-temperature and high-temperature leaching. At low temperatures, namely 25 °C and 45 °C, the recovery values of La, Ce, and Y tend to increase even after 240 min of leaching. On the other hand, at high temperatures, namely 65 °C, 75 °C, and 90 °C, the recovery value initially increases, but tends to be constant after leaching for more than 90 min.

Z–L–T kinetics model assumes that diffusion is controlled by reactant activity, in this case, citric acid. At the beginning of the leaching process, there is a difference in citric acid concentration in the liquid body and magnetic fly ash. This becomes the driving force for citric acid to diffuse into magnetic fly ash. The activity factor of citric acid is still high at the beginning. As citric acid reacts with leachable elements, the concentration becomes less and the activity factor decreases. Since the leaching kinetics tends to be slow at lower temperatures, the decline in citric acid concentration is vivid.

Unlike the Z–L–T model, the Kröger-Ziegler kinetics model assumes that the diffusion coefficient value decreases with time. At first, citric acid can diffuse rapidly

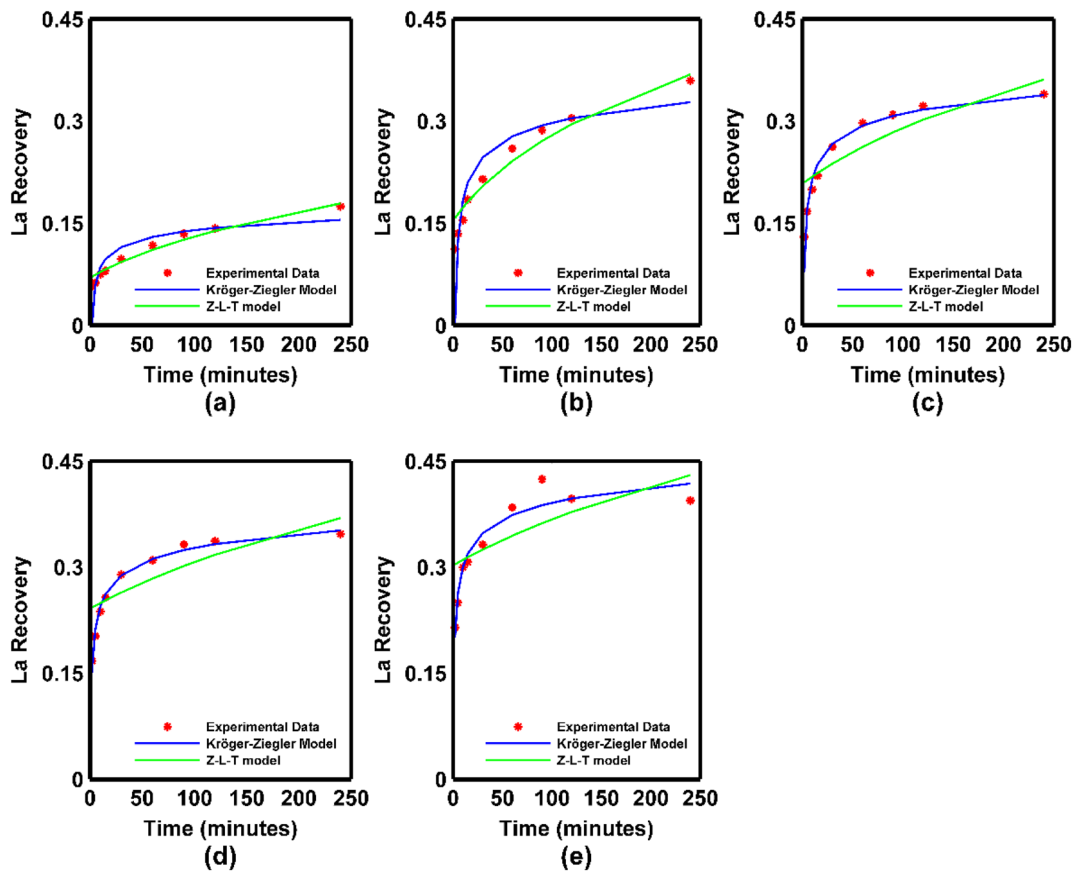


Fig. 5 Plot of Z–L–T and Kröger-Ziegler model to experimental data of La leaching at a 25 °C; b 45 °C; c 65 °C; d 75 °C; and e 90 °C

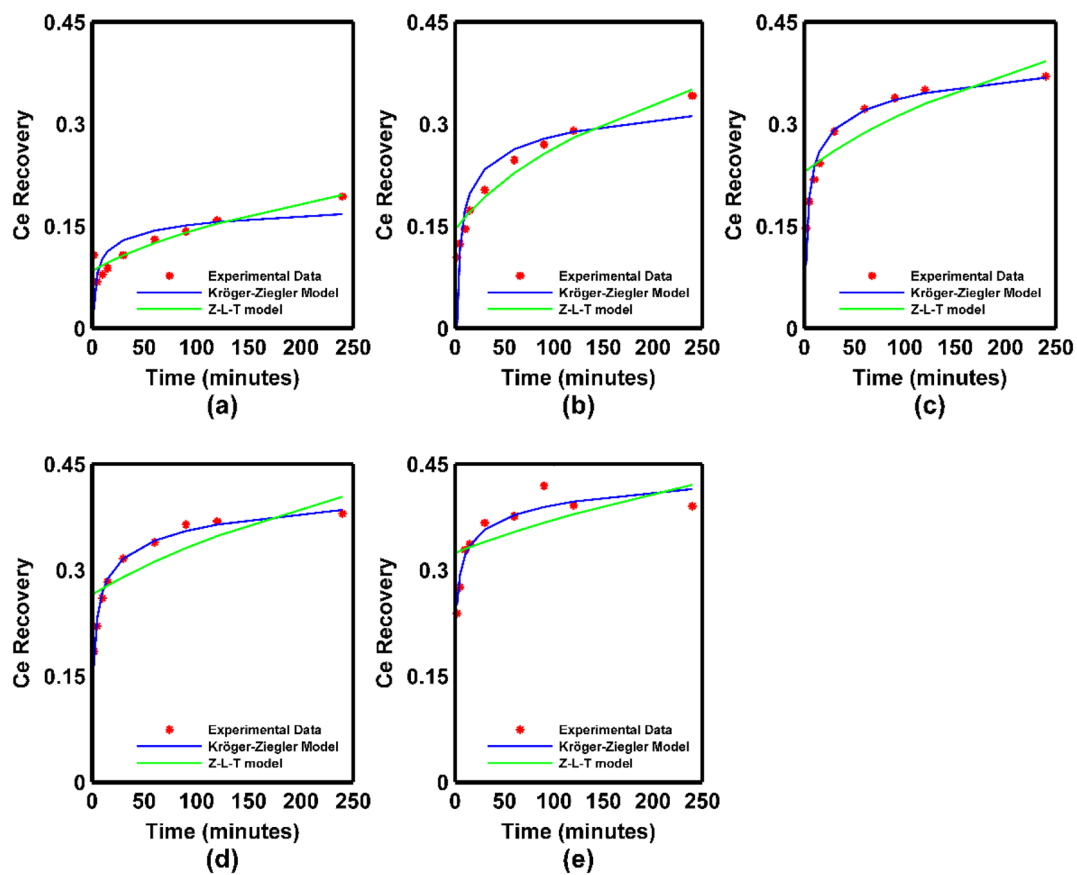


Fig. 6 Plot of Z–L–T and Kröger-Ziegler model to experimental data of Ce leaching at **a** 25 °C; **b** 45 °C; **c** 65 °C; **d** 75 °C; and **e** 90 °C

into magnetic fly ash due to the great driving force and the absence of an ash layer. After the reaction, unleached components such as silica form a layer of ash. This layer grows thicker with leaching time and hinders diffusion; thus, the diffusion coefficient becomes smaller.

Higher temperature favors the leaching rate that, at some point, the system gets very close to equilibrium. The steady recovery value of rare earth elements indicates that citric acid is also constant in concentration. This is where Kröger-Ziegler and Z–L–T kinetics model differ. Citric acid concentration can be considered constant through the leaching process only when the kinetics is fast enough to reach equilibrium, namely at the temperature of 65 °C, 75 °C, and 90 °C.

The value of rate constants indicates an increase in the order of $\text{La} < \text{Ce} < \text{Y}$. It implies that Y is leached more quickly than Ce and La, while La is the hardest to leach. Rare earth elements are usually present in solution in the form of trivalent or having +3 oxidation number [53]. Y^{3+} ion has an ionic radius of 0.9 Å, which is the smallest compared to Ce and La with an ionic radius of 1.01 Å and 1.032 Å, respectively [54]. The small ionic radius results in Y having a greater value of ionic potential. It means

that Y bonds stronger with a citric acid anion to form a metal–ligand complex, thus easier to leach. Besides, the smaller radius also makes it faster for Y to diffuse into the liquid body—the leaching rate decreases in a particular sequence with the rise of the ionic radius.

In this study, the overall recovery values are around 50% for Y and approximately 40% for La and Ce. The values are still comparable with the use of inorganic acids. Hydrochloric acid (HCl), for example, leaches 24.48% of rare earth elements from raw fly ash, but recovers 84.95% of the elements from the desilicated one [55]. Leaching using concentrated HNO_3 yields 44.1% of maximum percent recovery, yet the value increases to more than 75% with Na_2O_2 sinter pre-treatment [10]. Meanwhile, H_2SO_4 leaches 75.25% of rare earth elements after alkali digestion [36]. As for organic acid, citric acid still gives better recovery values than acetic acid. Even after NaOH digestion, acetic acid can only recover as much as 17.38%, 20.58%, and 18.45% of La, Ce, and Y, respectively [28]. According to previous studies, rare earth recovery by citric acid can be potentially increased by treating the fly ash with alkali (NaOH digestion or Na_2O_2 sintering) before leaching.

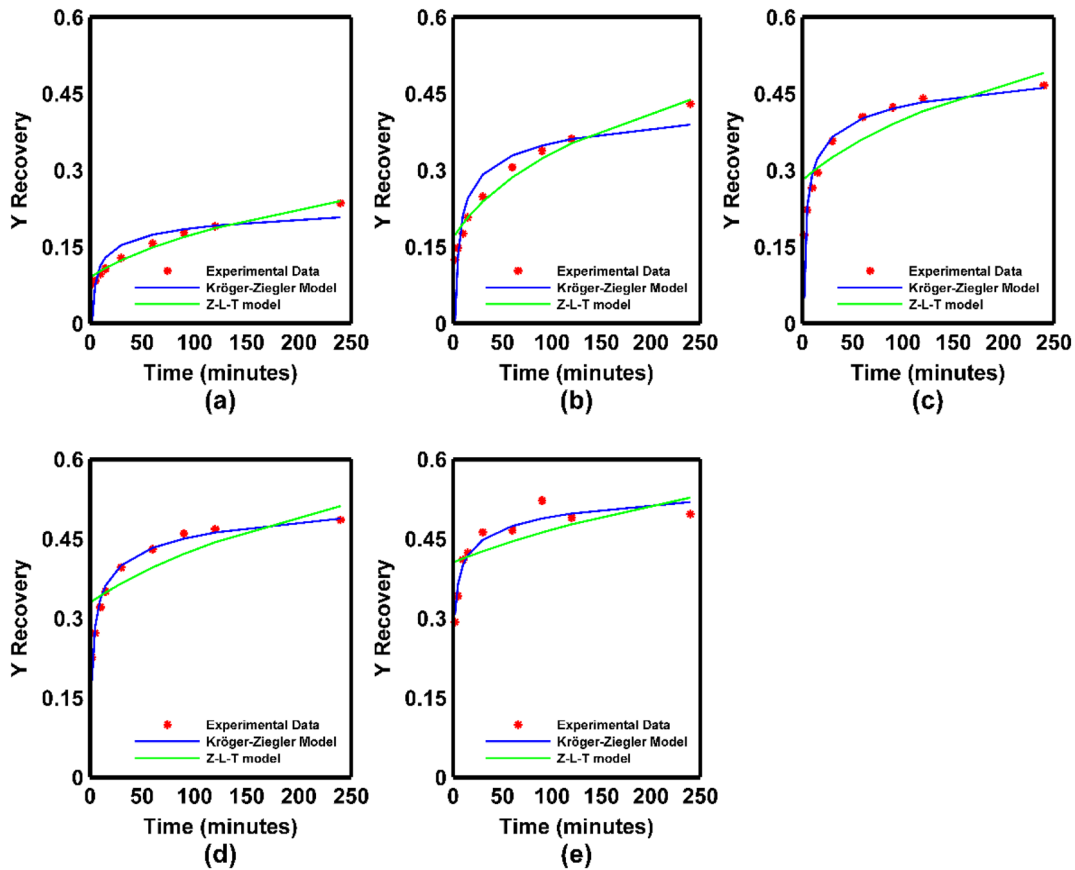


Fig. 7 Plot of Z–L–T and Kröger-Ziegler model to experimental data of Y leaching at **a** 25 °C; **b** 45 °C; **c** 65 °C; **d** 75 °C; and **e** 90 °C

Table 3 Z–L–T and Kröger-Ziegler model parameters

Element	Parameter	Temperature				
		25 °C	45 °C	65 °C	75 °C	90 °C
La	k_{ZLT}	1.682×10^{-5}	1.007×10^{-4}	8.087×10^{-5}	7.653×10^{-5}	1.096×10^{-4}
	R^2	0.9746	0.9642	0.7796	0.7145	0.5253
	k_{KZ}	6.744×10^{-4}	3.496×10^{-3}	3.305×10^{-3}	3.201×10^{-3}	4.629×10^{-3}
	R^2	0.8446	0.8837	0.9802	0.9882	0.8920
Ce	k_{ZLT}	2.005×10^{-5}	8.814×10^{-5}	1.016×10^{-4}	9.893×10^{-5}	8.458×10^{-5}
	R^2	0.9626	0.9625	0.7875	0.7180	0.4504
	k_{KZ}	7.139×10^{-4}	3.124×10^{-3}	3.993×10^{-3}	3.967×10^{-3}	3.832×10^{-3}
	R^2	0.6843	0.8851	0.9805	0.9870	0.8841
Y	k_{ZLT}	3.388×10^{-5}	1.704×10^{-4}	2.089×10^{-4}	2.190×10^{-4}	1.869×10^{-4}
	R^2	0.9853	0.9781	0.8142	0.7641	0.4991
	k_{KZ}	1.269×10^{-3}	5.394×10^{-3}	7.197×10^{-3}	7.465×10^{-3}	7.046×10^{-3}
	R^2	0.8267	0.8658	0.9731	0.9849	0.9031

Conclusion

Magnetic fly ash from the Tanjung Awar-Awar coal power plant mainly consists of SiO_2 , Fe_2O_3 , and Al_2O_3 . The content is not only in the form of crystalline material, but also

in amorphous glass. Magnetic fly ash is spherical material that also contains elements like K, Ca, Mg, Ti, and rare earth elements. The most abundant rare earth elements in the material are Ce, Y, and La. Enough critical elements make magnetic fly ash a potential alternative source of rare earth.

Rare earth elements can be leached from magnetic fly ash by forming soluble metal–ligand complexes with organic acids. Citric acid is one of the organic acids that shows great performance in leaching La, Ce, and Y from magnetic fly ash. The use of various concentrations in the range of 0.5 M to 2 M does not significantly affect the recovery. In contrast, the temperature has a significant effect on rare earth elements recovery where the recovery value increases along with the elevation of temperature from 25 to 90 °C.

Kinetics study on citric acid leaching of rare earth elements from magnetic fly ash shows that the leaching is controlled by diffusion. Z–L–T kinetics model fits the leaching phenomenon at the temperature of 25 °C and 45 °C. The leaching rate is slow; thus, the change in citric acid activity matters most. Meanwhile, leaching at the temperature of 65 °C, 75 °C, and 90 °C gives a faster leaching rate that the system approaches equilibrium and reactant concentration can be considered constant throughout the leaching process. The diffusion also becomes slower with leaching time since a layer of ash that hindered the process is formed. The Kröger-Ziegler kinetics model best describes this phenomenon.

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Declarations

Conflict of interest The authors confirm that there are no conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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