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Optimization of intensified leaching and selective recovery of Y and Eu from waste cathode ray tube phosphor

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ABSTRACT

The optimization study of rare earth elements (REEs) leaching from electronic waste is imperative for industrialscale development with cost- and energy-efficient processing. Response surface methodology (RSM) with the principle of central composite design (CCD) was utilized to optimize the Y and Eu leaching process from waste cathode ray tube (CRT) phosphor in subcritical water extraction. The analysis of variance (ANOVA) demonstrated that acid concentration and leaching temperature had a significant effect on the leaching efficiency of Y and Eu in subcritical water extraction. The obtained optimum conditions of Y and Eu leaching from waste CRT phosphor were 1.15 mol/L H₂SO₄ solution as the leaching agent, 166 ± 1 °C, for 27 min in subcritical water at a 20 g/L of solid to liquid (S/L) ratio. The experiment under optimum conditions resulted in 99.07 % and 99.62 % leaching efficiency of Y and Eu, respectively, which had a relative error of less than 1 % from the value predicted by the model. Selective separation of Y and Eu from the leaching solution was carried out as well and it resulted in 87.72 % and 95.11 % recovery of Y and Eu, respectively. The recovery product consists mainly of REE(PO₄). This study could be the alternative process for electronic waste utilization as the secondary resources of valuable rare metals promoting the circular economy.

1. Introduction

Lanthanides as known as rare earth elements (REEs) play an important role in green and high-technology developments, which is why they are also called "the vitamin of modern industry" and "the seed of technology" due to their irreplaceable properties (Balaram, 2019; Dushyantha et al., 2020; Tran et al., 2022). The high demand for REEs in green applications (batteries for electric cars, and wind turbines) (Kouhail et al., 2022) and advanced technologies (optical, catalytic, magnetic, and luminescence) (Zuo et al., 2019) contrasts with their high supply risk due to their limited distribution in the Earth's crust and difficulties in extraction due to their low concentration in the ore, hence, they are considered critical elements (Massari and Ruberti, 2013; Watari, 2020; Deng et al., 2022). According to the U.S. Geological Survey (Cordier, 2023), the largest REE reserves are still owned by China with total reserves of 44 million tons, followed by Vietnam with 22 million tons, Russia and Brazil with 21 million tons each, while,

Indonesia has potential treasure trove of rare earth metals with estimated reserves of around 300,000 tons, and the exploration of REE in Indonesia is believed to reveal a big potential resource (Setiawan, 2018). However, there is still no information regarding the domestic production and use of REEs in Indonesia. About 90 % of the world's REE supply and trade are currently dominated and controlled by China due to the imbalanced REE reserves (Depraiter and Goutte, 2023) and it leads to instability and shortage (Gómez et al., 2023). Therefore, the extraction of REEs from secondary resources is of paramount importance to meet future raw material needs (Dhawan and Tanvar, 2022), to promote the circular economy and the sustainability of critical metals (Marra et al., 2019; Ahn et al., 2019; Spooren et al., 2020). There are various secondary resources of REEs such as phosphogypsum (PG) (Hakkar et al., 2021), fly ash (FA) (Fu et al., 2022), and electronic waste (e-waste) such as phosphors in LEDs, cathode ray tubes, fluorescent lamps (S. Zhang et al., 2017), magnets in wind turbines, electric motors (Ahirwar and Tripathi, 2021), and used batteries (Sethurajan et al., 2019). The REEs

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Table 1

Studies of Y and Eu leaching from waste CRT	phosphor.
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Extraction conditions	Extraction efficiency	Reference
Roasting at 800 °C for three hours + a pretreatment of 5 M NaOH for 7 h followed by leaching at a 5 g/L, 0.1 M Sodium pyrophosphate ($Na_4P_2O_7$) at rt*, pH 6	Y, Eu, Sm, and Ce of 58, 90, 90 and 87 %, respectively, were	(Alvarado- Hernández et al., 2019)
Selective roasting with addition of ZnSO ₄ at 750 °C for 30 min followed by water leaching at 25 °C for 24 h	Y = 93.4 %; $Eu = 94.9$ %	(Önal and Binnemans, 2019)
3 M H ₂ SO ₄ , 4 vol% H ₂ O ₂ ,55 °C, and 1 h	Y and Eu reached 99 %	(Yin et al., 2018)
Roasting at 850 °C for 20 min followed by 1) leaching at rt* using acetic acid, 10 mL g ⁻¹ for 2 h, then 2) leaching at 90 °C using methane sulphonic acid; 10 mL g ⁻¹ for 24 h	About 90 wt% of Y and Eu was dissolved with	(Forte et al., 2019)
400 mL of 0.4 M H ₂ SO ₄ , 60 mL of 30v/v % H ₂ O ₂ at 80 °C for 20 min and L/S ratio 23	Y and Eu = around 90–95 %	(Miskufova et al., 2018)
Microwave-assisted leaching at 400 W for 60 min, using 2 mol L − 1 of H ₂ SO ₄ at 10 g/L	Y and Eu were 78.07 % and 100 %,	(Lie et al., 2019)
Closed-vessel microwave leaching 10 g/L of solid concentration, 2 mol·L – 1 of H ₂ SO ₄ solution, 125 oC, 30 min of leaching time	Y and Eu was 86.67 % and 100 %	(Lie and Liu, 2021a)
0.5 M sulfuric acid (H ₂ SO ₄) at 65 °C; a 10 g/L of solid to liquid ratio within 12 h of conventional extraction.	Y and Eu were 28.15 % and 35.92 %, respectively, when	(Lin et al., 2018)
Subcritical water extraction at 125 °C using 0.75 M of H ₂ SO ₄ , a 10 g/L of solid to liquid ratio for 30 min	$\begin{array}{l} Y = 97.51 \ \%; \ Eu = 100 \\ \% \end{array}$	(Lin et al., 2018)
Supercritical CO_2 extraction along with a small volume of tributyl- phosphate-nitric acid (TBP- HNO ₃) as the chelating agent at 40 °C, 31 MPa, 3 h, 0.2 g/mL (sample to adduct ratio), and 750 rpm	More than 70 % Y and Eu extraction and	(Zhang et al., 2022)
Optimal conditions from RSM and ANOVA optimization: 1.15 mol/ L H ₂ SO ₄ solution as the leaching agent, 166–167 °C, for 27 min in subcritical water at 10 bars, a 20 g/L of solid to liquid (S/L) ratio	Above 99 % of Y and Eu	This study

*room temperature.

Table 2

The major metal content of waste CRT phosphor by aqua-regia digestion analysis.

Element	Zn	S	Y	Pb	Fe	Eu
Content (mg/g)	$\begin{array}{c} 81.22 \\ \pm \ 0.76 \end{array}$	$\begin{array}{c} 61.64 \\ \pm \ 0.84 \end{array}$	$\begin{array}{c} 44.98 \\ \pm \ 0.25 \end{array}$	$\begin{array}{c} 41.43 \\ \pm \ 0.77 \end{array}$	$\begin{array}{c} 15.25 \\ \pm \ 0.45 \end{array}$	$\begin{array}{c} 3.21 \\ \pm \ 0.01 \end{array}$

Table 3

Leaching conditions of Y and Eu from waste CRT phosphor using H₂SO₄ solution.

Parameter	Code	Coded level				
		-1.68	-1	0	1	1.68
Acid concentration (mol/L)	А	0	0.25	0.75	1.25	1.59
Temperature (°C)	В	83	100	125	150	167
Time (min)	С	3.18	10	20	30	36.82

concentration in the phosphor of a cathode ray tube (CRT) is quite high as a fluorescent component of the tube television (Lin et al., 2018), and it is also reported that 4.5 g of REEs per 500 kg of a discarded CRT can potentially be recovered (Pindar and Dhawan, 2021). The production of waste tube television is still increasing in developing countries such as Indonesia and Thailand, and accounts for a large portion of e-waste in both countries; 16.8 % of e-waste in Indonesia in 2020 (Mairizal et al., 2021) and 24 % of e-waste in Thailand in 2019 (Mangmeechai, 2022). However, only about 26 % of CRT waste is recycled worldwide due to limited knowledge about the recycling process and investigation of practical approaches (Pindar and Dhawan, 2021). Therefore, the development of practical technology for the recovery of rare metals from e-waste, especially from waste CRT phosphor, is inevitable.

The effective leaching of Y and Eu from waste CRT phosphor has been investigated using subcritical water extraction (SWE) with H_2SO_4 solution as a leaching agent that provided a lower co-dissolution of impurities (Lin et al., 2018). The extraction yield of rare metals could be enhanced by the intensive subcritical water condition of a temperature of about 100–374 °C and of a pressure of 1–22.1 MPa (Constantine et al., 2022; Möller et al., 2011). Yao et al. (Yao et al., 2018) reported above 85 % extraction efficiency of REEs from nickel metal hydride battery has been achieved using supercritical CO₂ extraction at 35 °C, 31 MPa for 2 h. Therefore, subcritical water extraction is still preferable for practical application since it facilitates the intensive dissolution of REEs from ewaste at mild operational conditions.

The optimization of REEs leaching from waste CRT phosphor is essential for energy and environmental reasons, besides, the significant effect of operational parameters on the leaching efficiency of REEs should be well investigated. This is also an essential step to improve the experimental study of the proposed technology for practical application at a large scale (Cheng et al., 2023; Ferreira et al., 2021). This study aims to investigate the optimum conditions and the influential factors of Y and Eu leaching from waste CRT phosphor using statistical methods of response surface methodology (RSM) and analysis of variance (ANOVA) (Padh et al., 2023). Several critical parameters such as leaching agent concentration, leaching temperature, and time were used as factors in designing the experiments. According to the literature study in Table 1, the application of RSM in the optimization of Y and Eu leaching from waste CRT phosphor in a subcritical reactor has not yet been reported. Moreover, the selective separation of Y and Eu from the acidic leaching solution was also conducted by precipitation with phosphate ions for the comprehensive REEs recovery process (Constantine et al., 2022; Zhang et al., 2022). Utilization of waste CRT phosphor as a raw material for modern mining of rare metals, Y and Eu, could be a solution and an innovation for sustainable technology and circular economy by converting waste into valuable and high-value products.

2. Methodology

2.1. Materials

Waste CRT phosphor powder as Y and Eu resource was supplied by FGD Recycling Industrial Co. Ltd, a recycling company in Taichung, Taiwan. It was dried at 50 °C for 7 days to remove the moisture content. Then it was sieved through 100 mesh of sieve to remove the coarse waste glass and to obtain the uniform particle size which is less than 150 μ m. HCl (37 wt%) was from Acros Organic - UK and HNO₃ (65 wt%) was from Panreac - Spain for aqua-regia digestion. The concentrated sulfuric acid (98 % w/w) was purchased from Smart Lab - Indonesia, it was diluted to a mild concentration (0.25–1.25 mol/L) and used as a leaching agent of REEs in waste CRT phosphor. High purity standard solutions with 1000 mg/L of Y and Eu (Merck - Germany) were used for measuring the Y and Eu content in inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo 7000) at a wavelength of 371.029 and 381.965 nm, respectively. For the recovery process, sodium hydroxide, NaOH, and disodium hydrogen phosphate anhydrous

Table 4

Run	Α	В	С	% leachin	g	Run	Α	В	С	% leachin	g
				Y	Eu					Y	Eu
1	-1	1	-1	69.73	67.30	31	1	-1	-1	27.83	25.29
2	1.68	0	0	90.26	89.16	32	1	1	$^{-1}$	93.10	91.34
3	0	1.68	0	92.21	88.85	33	1	$^{-1}$	1	41.66	40.61
4	$^{-1}$	1	1	78.95	76.71	34	0	0	0	68.74	67.88
5	1	1	1	89.21	87.45	35	0	0	0	68.96	67.78
6	$^{-1}$	1	1	77.95	76.91	36	1	$^{-1}$	$^{-1}$	26.98	25.59
7	0	-1.68	0	7.38	6.43	37	0	-1.68	0	7.79	6.99
8	$^{-1}$	$^{-1}$	$^{-1}$	7.85	7.25	38	0	1.68	0	92.21	88.85
9	0	0	1.68	81.51	80.42	39	0	0	0	66.69	65.66
10	1	$^{-1}$	1	40.86	39.62	40	0	0	0	72.95	72.04
11	0	0	0	71.58	70.74	41	1	1	-1	93.73	91.53
12	$^{-1}$	$^{-1}$	1	9.24	8.74	42	1	1	1	89.21	87.45
13	0	0	0	70.95	70.04	43	0	0	1.68	79.51	78.42
14	-1.68	0	0	1.01	0.89	44	1	1	-1	93.10	91.34
15	0	0	0	71.42	70.29	45	0	0	0	70.01	69.75
16	$^{-1}$	$^{-1}$	1	9.24	8.74	46	0	0	-1.68	48.85	47.30
17	$^{-1}$	1	1	78.95	76.71	47	0	0	0	69.96	68.97
18	1.68	0	0	90.26	89.16	48	-1.68	0	0	0.97	0.86
19	1	$^{-1}$	$^{-1}$	27.42	24.79	49	0	0	0	70.01	69.75
20	0	1.68	0	92.21	88.85	50	0	0	0	72.95	72.04
21	1.68	0	0	90.26	89.16	51	$^{-1}$	$^{-1}$	-1	7.64	6.96
22	0	0	0	69.74	68.78	52	0	0	-1.68	47.88	46.49
23	$^{-1}$	1	$^{-1}$	70.64	68.43	53	0	0	0	69.96	69.24
24	-1.68	0	0	1.31	1.16	54	0	0	0	68.63	67.22
25	0	0	0	69.93	69.29	55	1	$^{-1}$	1	40.89	39.81
26	0	0	-1.68	49.12	48.43	56	$^{-1}$	1	$^{-1}$	69.73	67.53
27	0	0	0	69.42	69.29	57	$^{-1}$	$^{-1}$	1	9.24	8.74
28	0	-1.68	0	8.19	7.09	58	0	0	1.68	79.51	78.42
29	$^{-1}$	$^{-1}$	$^{-1}$	7.25	6.85	59	0	0	0	71.73	70.49
30	1	1	1	89.21	87.45	60	0	0	0	67.68	66.23

Table 5

Regression analysis of RSM and ANOVA for Y leaching.

Term	Coef	SE	T-	F-	P-	Significance
		Coef	Value	Value	Value	
Constant	70.08	1.99	35.29		0.000	Significant
Linear						
Α	17.25	1.32	13.09	171.39	0.000	Significant
В	28.40	1.32	21.55	464.55	0.000	Significant
С	5.34	1.32	4.05	16.44	0.000	Significant
Square						
AA	-8.68	1.28	-6.77	45.85	0.000	Significant
BB	-7.16	1.28	-5.58	31.13	0.000	Significant
CC	-2.07	1.28	-1.61	2.59	0.114	Not
						significant
2-Way						
Interaction						
AB	-2.23	1.72	-1.30	1.68	0.201	Not
						significant
AC	-0.08	1.72	-0.05	0.00	0.964	Not
						significant
BC	-1.36	1.72	-0.79	0.63	0.432	Not
						significant

*Model summary: S = 8.4326; R² = 0.9355; R²_{adj} = 0.9239; R²_{pred} = 0.8965.

Na₂HPO₄, were purchased from Sigma Aldrich - Germany. All chemicals were used without any further purification. The diluent for all chemicals used was deionized water.

The total Y and Eu content in waste CRT phosphor powder was determined using the aqua-regia digestion method according to standard procedure NIEA S321.63B. The mixture from aqua-regia digestion was filtered to obtain a solution which then was diluted with deionized water and analyzed in ICP-OES for Y and Eu content. The determination of Y and Eu using aqua-regia was repeated three times and the average value was taken. The total metal content of waste CRT phosphor is listed in Table 2.

Tab	le 6	
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Regression	analysis	of RSM a	and ANOV	A for Eu	leaching.

Term	Coef	SE Coef	T- Value	F- Value	P- Value	Significance
Constant	69.21	1.99	34.75		0.000	Significant
Linear						
А	17.00	1.32	12.86	165.46	0.000	Significant
В	27.85	1.32	21.08	444.19	0.000	Significant
С	5.48	1.32	4.15	17.21	0.000	Significant
Square						
AA	-8.63	1.29	-6.71	45.00	0.000	Significant
BB	-7.65	1.29	-5.94	35.34	0.000	Significant
CC	-2.20	1.29	-1.71	2.92	0.093	Not
						significant
2-Way						
Interaction						
AB	-1.89	1.73	-1.10	1.20	0.278	Not
						significant
AC	0.01	1.73	0.01	0.00	0.995	Not
						significant
BC	-1.43	1.73	-0.83	0.69	0.411	Not
						significant

*Model summary: S = 8.4575; $R^2 = 0.9335$; $R_{adj}^2 = 0.9216$; $R_{pred}^2 = 0.8934$.

2.2. Experiment: Leaching of Y and Eu from waste CRT phosphor using H_2SO_4 solution

Leaching of rare metals is carried out in a 290-mL subcritical reactor made of stainless steel (SS316) as described in our previous studies (Lie et al., 2020, 2021) at a certain temperature, pressure, and time, the concentration of solvent acid was varied to obtain the optimum conditions of rare metal leaching process. Waste CRT phosphor powder and H₂SO₄ solution were mixed as 20 g/L suspensions in a silicate glass chamber of SWE. The S/L ratio of 20 g/L was chosen according to the preliminary study, it required a mild concentration of acid. Initial pressure was set at 10 bars using N₂ gas and it was increased as



Fig. 1. The effect of the interaction of acid concentration and temperature on the leaching efficiency of a) Y and b) Eu.

temperature increased. The reactor was heated at 100; 125; and 150 $^{\circ}$ C, respectively. The leaching time counting when the desired temperature achieved was ranged from 10 to 30 min. The leaching mixture was filtered through a 0.22 µm membrane (mixed cellulose ester, Advantech). The leaching solution was collected and the metal content was analyzed using ICP-OES, while, the residue was dried at 60 $^{\circ}$ C for 3 days and characterized in XRD and SEM-EDX. The leaching efficiency was calculated based on the Y and Eu concentration (mass) in the leaching solution divided by the total concentration (mass) in the waste CRT phosphor used, respectively.

2.3. Response surface methodology (RSM)

The RSM was used to design the experiments, develop models by considering the relationship among the important parameters, and process optimization based on the mathematical and statistical techniques (Movahhedi et al., 2023). In this study, the effects of leaching agent concentration, SWE temperature, and leaching time were investigated. Central composite design (CCD) was used as the type of design of the experiment with three continuous factors and triple replicates to improve precision. CCD is commonly used for studying the second-order response surface model in environmental processes, functional prediction of both linear and quadratic interaction of influencing factors with a considerably efficient number of experiments including various combinations of the high and low levels of the factors as well as at a distance of from the center point (Banihashemi et al., 2019; Karimifard and Alavi Moghaddam, 2018). Three equidistant values (-1; 0; 1) with two extreme points (low: -1.68; and high: 1.68) were used to represent each variable as seen in Table 3. The design of the experiment of REEs leaching from waste CRT phosphor at a constant solid-to-liquid ratio, 20 g/L, is demonstrated in Table 4. The analysis of variance (ANOVA) was performed after obtaining the experiment results based on the experimental design, it aims to investigate the influencing factors and the mathematical model of the leaching process of REEs from waste CRT phosphor using H₂SO₄ in SWE, according to the following model:

$$y = b_0 + \sum_{i}^{k} b_i x_i + \sum_{i}^{k} b_{ii} x_i^2 + \sum_{i}^{k} \sum_{j}^{l} b_{ij} x_i x_j$$
(1)

Where y is the predicted response value (%); b_0 is a constant; b_i is a linear coefficient; b_{ii} is a quadratic coefficient; b_{ij} is the interaction coefficient; x_i and x_j are the independent variables (Baghalian Nejad et al., 2020; Ferreira et al., 2021). The optimum conditions were also investigated. The experimental responses were statistically analyzed using the Minitab 20 software and the predicted values of the responses were obtained from the full quadratic model described above.

2.4. Rees recovery from leaching solution

According to our previous study (Lie and Liu, 2021b), it has been shown that the REE content in leaching solution can be selectively separated as REE(PO₄) precipitate at low pH. The leaching solution



Fig. 2. The effect of the interaction of acid concentration and time on the leaching efficiency of a) Y and b) Eu.

obtained at optimum condition was collected, about 50 mL of leaching solution was taken and the pH was increased to 1 and 2, respectively, using 3 mol/L of NaOH solution. The mixture was then heated at 50 °C and kept stirred at 100 rpm for 2 h. The precipitation agent, 1 mol/L of Na₂HPO₄ solution, was added slowly with a molar ratio of REE⁺³ and PO₄⁻³ ions at 1:10. The precipitates and supernatant were separated by centrifuge with triple rinsing using distilled water. The precipitates were dried at 60 °C for 3 days and characterized using XRD and SEM-EDX. The REE content in the supernatant was analyzed by ICP-OES.

3. Results and discussions

3.1. Statistical analysis and optimization

The REEs leaching from waste CRT phosphor was conducted with 20 g/L of solid-to-liquid ratio (S/L) using various acid concentrations of H_2SO_4 solution in subcritical water extraction at a specific temperature for a certain period as coded as -1, 0, and 1 according to Table 3. Central composite design with 3 factors and 3 replicates full factorial resulted in 20 base runs and 60 total runs with 1 base block, 1 total block, and alpha of 1.68. There were also 24 cube points, 18 center points in cube, and 18 axial points. The results of each experiment were

recorded as the responses in Table 4. The interactions of each variable and the statistical model in the leaching process of Y and Eu from waste CRT phosphor were determined by the analysis of variance (ANOVA) as seen in Tables 5 and 6. The empirical models were developed to estimate the leaching efficiency of Y and Eu from waste CRT phosphor using H_2SO_4 solution as a leaching agent in SWE using RSM which are presented in Eq. (2) and Eq. (3).

$$Y (\%) = 70.08 + 17.25(A) + 28.40(B) + 5.34(C) - 8.68(A)^2 - 7.16(B)^2 - 2.07$$

(C)² - 2.23(AB) - 0.08(AC) - 1.36(BC) (2)

Eu (%) =
$$69.21 + 17.00(A) + 27.85(B) + 5.48(C) - 8.63(A)^2 - 7.65(B)^2 - 2.20(C)^2 - 1.89(AB) - 0.01(AC) - 1.43(BC)$$
 (3)

Where A is the value of coded acid concentration, B is the value of coded temperature, and C is the value of coded time. The models represent the effect of each factor and their interactions on the REEs leaching. The positive or negative effect of each parameter is shown by the positive or negative value of coefficients in the models. Based on the statement, it can be seen that the single factor had a positive effect, while the factors of quadratic terms and interactions had a negative effect.

The summary of ANOVA results has also been shown in Tables 5 and 6, the P-values of less than 0.05 for the selected reduced cubic model



Fig. 3. The effect of each factor and the interactions on the leaching process of Y and Eu.

indicate the statistically significant model. The linear or single parameters of leaching including acid concentration, temperature, and time have statistically significant effects as well as the quadratic terms of acid concentration and temperature. While the quadratic term of time and the interactions of all variables do not contribute significantly to the model. Compared to the pure error, the P-value of lack of fit on Y and Eu leaching in the ANOVA was higher than 0.05 which is not significant, ensuring the good quality of the fit of the model. The values of R^2 from the models of leaching efficiency of Y and Eu are 0.9355 and 0.9335, respectively, implying that the models fit the experimental data of REE extraction in SWE well and are useful for optimization purposes. A good model fitting is also shown by a small difference between R_{adi}^2 and R_{Pred}^2 in the range of 0 to 0.2 (Chang et al., 2020; Jiang et al., 2017). The difference between adjusted R^2 and predicted R^2_{Pred} at present work is only about 0.028 for both Y and Eu leaching. Therefore, it can be concluded that the RSM models for Y and Eu leaching adequately fit the experimental data.

The experimental results were calculated statistically to see the response of leaching efficiency to the change of variables including acid concentration, temperature, and reaction time. Fig. 1 shows the effect of acid concentration and temperature using 20 g/L of S/L ratio in SWE for 20 min. Increasing the acid concentration and leaching temperature increased the leaching efficiency of Y and Eu. It is clearly shown that the leaching efficiency of Y and Eu increased significantly when increasing the leaching temperature from 100 °C to 150 °C. The results imply that the dissolutions of Y and Eu from waste CRT phosphor described in Eq. (4) and (5) are an endothermic process that is enhanced at a higher temperature. According to the previous characterization of waste CRT phosphor, Y and Eu were present in the form of oxysulfide in the sample powder. The maximum leaching efficiency of Y and Eu was obtained at the white light on the chart, about 100 % of the leaching efficiency of Y and Eu was at around 150 °C and 1 mol/L of acid concentration. Increasing the acid concentration by more than 1 mol/L reduced the leaching efficiency of Y and Eu which might be attributed to the formation of REE sulfate salt whose solubility decreased at a high concentration of H_2SO_4 (Lokshin et al., 2007).

$$Y_2O_2S + 6H^+ \rightarrow 2 Y^{3+} + H_2S + 2 H_2O$$
 (4)

$$Eu_2O_2S + 6H^+ \rightarrow 2 Eu^{3+} + H_2S + 2 H_2O$$
 (5)

The effect of leaching time at various acid concentrations on the leaching efficiency of Y and Eu from waste CRT phosphor at a fixed leaching temperature of 125 °C is demonstrated in Fig. 2. Leaching time has no significant effect on the leaching efficiency of Y and Eu, this is probably because the diffusion process of Y and Eu occurred during the heating process to reach a certain temperature in the SWE reactor, and then the leaching process of Y and Eu become equilibrium after reaching desired temperature. According to the experimental data that were analyzed, the effect of each parameter of REE leaching in SWE from waste CRT phosphor can also be seen from the pareto chart in Fig. 3. The temperature is the most influential parameter for REE leaching, followed by acid concentration, the quadratic acid, the quadratic temperature, and leaching time. The factors with a standardized effect value of less than 2.01 were not considered important parameters. Fig. 4 shows the effect of leaching temperature and time on the leaching efficiency of Y and Eu at a hold value of acid concentration, 0.75 mol/L. It is seen that ANOVA indicates the positive effect of temperature on Y and Eu extraction, however, leaching time does not show a significant effect. The interaction of each parameter with the others such as AB (acid concentration and temperature), BC (temperature and time), and AC (acid concentration and time) do not have a significant effect on the REEs leaching process.

3.2. The optimum condition of Y and Eu leaching in SWE

Response surface methodology was used to determine the optimum condition of Y and Eu leaching from waste CRT phosphor using SWE with the fixed S/L ratio of 20 g/L. The results of the leaching efficiency of Y and Eu from the experiment at certain conditions of each parameter from DOE were statistically used as the response. The optimization of the leaching process of Y and Eu is demonstrated in Fig. 5, the optimum SWE conditions are 1.13 mol/L of H₂SO₄ concentration at 167 °C for 27.3 min for 100 % leaching of Y, while, 1.15 mol/L of H₂SO₄ concentration at 166.2 °C for 27 min for 100 % leaching of Eu. The optimization indicates that the optimum conditions of Y and Eu leaching in SWE using H₂SO₄ solution are identical which might be attributed to the same crystal structure in Y₂O₂S: Eu³⁺, therefore those optimum conditions were used in the experiment with 3 replicates to validate the model predictions. Results showed that 99.07 % \pm 0.12 of Y and 99.62 % \pm



Fig. 4. The effect of the interaction of temperature and time on the leaching efficiency of a) Y and b) Eu.

0.27 of Eu were successfully leached out from waste CRT phosphor which is in good agreement with the model predicted values. The experimental results were in the range of 95 % confidence interval (CI) that validated the model estimated values. The optimization using RSM resulted in the complete (>99 %) leaching efficiency of Y and Eu from waste CRT phosphor using mild acid concentration and temperature in subcritical water extraction as seen in Table 1.

The remaining amount of residue obtained after the leaching process under the optimum conditions was 57.95 \pm 0.15 wt% of the original sample of waste CRT phosphor. The metals in the waste CRT phosphor were in the form of sulfide, oxide, and oxysulfide, therefore, the reduction of solid sample weight during the leaching process was also affected by the dissolution of the oxide compounds besides sulfide and oxysulfide compounds. Fig. 6 compares the XRD pattern of waste CRT phosphor and the leaching residue under the optimum condition. The main compounds existing in the original sample of waste CRT phosphor were ZnS, Y₂O₂S, Eu₂O₂S, and PbSO₄. The XRD pattern of leaching residue confirmed that Y and Eu were completely dissolved into the leaching solution, and the remaining compounds were ZnS which is difficult to dissolve in mild concentrations of acid solution, and PbSO₄ which is insoluble in H₂SO₄ solution. The SEM images of waste CRT phosphor and leaching residue in Figure S1 show no significant difference in the morphology of waste CRT phosphor after being subjected to subcritical conditions.

3.3. The recovery of Y and Eu from leaching solution

The Y and Eu content in the leaching solution was separated using precipitation with NaHPO₄ as the precipitation agent. Phosphate ions can induce the formation of an insoluble compound of REE(PO₄) with REE ions in the aqueous solution at low pH. The initial pH value of the acidic leaching solution was around 0; however, according to our previous study (Constantine et al., 2022), the REEs started to form a precipitate of REE(PO₄) at a pH value higher than 1. However, there were no precipitates formed when molar ratio less than 10 at pH 2. Therefore, the precipitation of REE(PO₄) in the leaching solution of waste CRT phosphor was carried out at pH 2 by adding the 3 M of NaOH solution using molar ratio of total REEs to PO_4^{-3} used of 1:10 at 50 °C for 2 h settling. It resulted in 87.72 % and 95.11 % recovery of Y and Eu, respectively, from the leaching solution as the dark brown precipitates. The recovery product was characterized in XRD and SEM. The XRD pattern in Fig. 7 shows that it contained YPO₄, Y₃Al₅O₁₂, Eu(PO₃)₂, and EuSO₄ which also confirmed the formation of insoluble compounds of REEs and phosphate. The morphology based on SEM characterization of the precipitates in Fig. 8a shows the irregular shape of agglomerated nanoparticles. Fig. 8b demonstrated the elements in the precipitates as analyzed by EDS, it supported the XRD result that it contained of Y, Eu, Al, P, and O while C is from the carbon tape of SEM analysis and Na was the minor impurities of the recovery product.



Fig. 5. The optimum conditions of Y and Eu leaching from RSM.





Fig. 7. The XRD pattern of recovery product.

Fig. 6. The XRD pattern of waste CRT phosphor and leaching residue under the optimum conditions.

REEsPO₄ precipitates.

3.4. The potential of scaling-up SWE

The simple yet effective recovery process of REEs from waste CRT phosphor has been described in the flowsheet (Fig. 9). The complete leaching of REEs from waste CRT phosphor could be obtained using the optimum condition of leaching in SWE. The optimum leaching condition for 20 g/L of solid sample to leaching solution ratio is using 1.15 mol/L of H₂SO₄ solution at 167 °C for 27 min in a subcritical reactor. Furthermore, the separation and purification of Y and Eu from the leaching solution containing various metal ions could be conducted by the selective precipitation using Na₂HPO₄ as a precipitation agent at low pH (pH 2) with a 1:10 M ratio of REEs⁺³ to PO₄⁻³ ions in the precipitation process at 50 °C which could obtain more than 87 % REEs recovered as

The potential of REE recovery from e-waste lies in the industrial scale-up. The scaling-up process could be much more efficient by incorporating the pilot scale studies to obtain quality data and determine the scale-up factor. Some scaling-up studies of SWE in the pilot scale on various applications have been investigated and they showed similar results compared with the lab-scale SWE reactor. The continuous or batch process of SWE could be applied as reported by Colorado et al., a continuous lab-scale subcritical water reactor for cellulose hydrolysis at 350 to 420 °C, pressure of 100 to 136 atm and suspension flowrates of up to 6.4 mL/min could successfully produce 85.4 % reducing sugar



Fig. 8. A) The SEM image and b) EDS results of recovery product.



Fig. 9. Flowsheet of REEs recovery from waste CRT phosphor.

(Colorado et al., 2019). Pilot-scale extraction of polyphenols from spent black tea by semi-continuous SWE has also been evaluated (Rajapaksha and Shimizu, 2022). Recently, the upscaling subcritical extraction of red algae residue from a 500-mL-subcritical reactor in the lab into a 5-L-pilot scale subcritical reactor obtained the comparative extraction yield, and it also confirmed the feasibility of the scaling-up process of the subcritical reactor for extraction (Trigueros et al., 2023). Another study by Ko et al., 2016, also demonstrated the potential of subcritical water extraction implementation on an industrial scale, they obtained similar extraction yields of flavonoids from satsuma mandarin peel using subcritical conditions under laboratory (117.8 mg/g) and pilot scale (113.4 mg/g) (Ko et al., 2016). Besides, (Yuan et al., 2023) also stated that better results of bioactive components extraction had been obtained on the pilot scale compared with on the laboratory scale due to the greater feedstock homogeneity and equipment parameters. According to those studies, there are some key parameters for scaling up the SWE such as heating rate, temperature control, feedstock homogeneity, mixing rate, as well as the commercial applicability of SWE to the other reactions which need to be evaluated carefully. Hence, the scaling-up of SWE for REEs leaching using the optimal conditions by RSM is strongly recommended for further study.

4. Conclusions

Optimization of the leaching process of Y and Eu from waste CRT phosphor in SWE has been investigated using response surface methodology with a central composite design. Analysis of variance (ANOVA) showed that temperature had the greatest influence on the leaching efficiency of Y and Eu, followed by acid concentration and time. Complete leaching (100 %) of Y and Eu could be achieved under the optimum conditions, 1.15 mol/L $\rm H_2SO_4$ solution, at 167 $^\circ C$ for 27 min in SWE with an initial pressure of 10 kg/cm² and a 20 g/L of S/L ratio. Recovery of REEs (Y and Eu) from the leaching solution has been also conducted using the selective precipitant, Na₂HPO₄ at pH 2, molar ratio 1:10 of REEs to phosphate ions, and 50 °C for 2 h. This resulted in a recovery of 87.72 % and 95.11 % of Y and Eu, respectively, with the formation of insoluble REE(PO₄). This process optimization in leaching Y and Eu from waste CRT phosphor followed by selective recovery could be a potential alternative for industrial-scale implementation for the green circular economy of critical metals.

CRediT authorship contribution statement

Jenni Lie: Writing – review & editing, Writing – original draft, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. Hardy Shuwanto: Visualization, Validation, Software. Hairus Abdullah: Visualization, Validation, Resources. Felycia Edi Soetaredjo: Supervision, Data curation. Suryadi Ismadji: Supervision, Data curation. Christian Julius Wijaya: Validation, Software. Chintya Gunarto: Validation, Software.

Declaration of competing interest

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.

Data availability

The data that has been used is confidential.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mineng.2024.108620.

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