



# Optimization of Zn Leaching Recovery from Tire Rubber and High-Purity ZnO Production

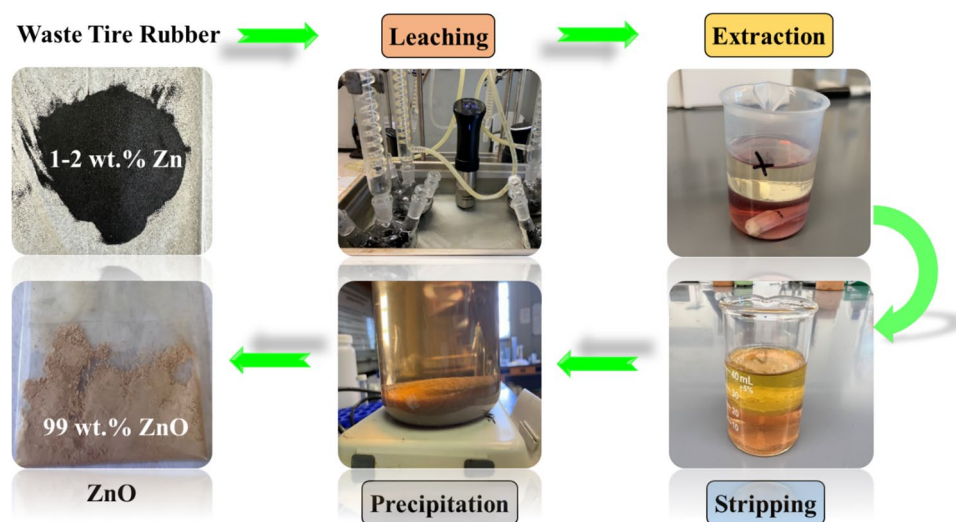
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Received: 16 April 2024 / Accepted: 29 November 2024  
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## Abstract

Waste tire rubber is regarded as a potential source for Zn recovery and recycling. In this study, the occurrence of modes of Zn was first characterized by an electron probe microanalyzer (EPMA), and the result indicated both ZnO and ZnS were present in the tire rubber. The Zn leaching recovery was optimized by response surface methodology, and temperature was identified as the most significant variable. The highest recovery of over 98% was obtained at 90 °C for 400 min when using 2.0 mol/L HNO<sub>3</sub> as the lixiviant. After that, the Zn-containing leach liquor was subjected to solvent extraction for further separation and purification using bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272) and 2-ethylhexylphosphonic mono-2-ethylhexyl (PC88A) as extractants. Various parameters, such as equilibrium pH, extractant concentration, and organic-to-aqueous (O/A) ratio, were investigated to maximize the Zn extraction while minimizing the contamination of impurities. The result indicated that 0.1 mol/L Cyanex 272 exhibited a higher separation factor for Zn over major impurities compared to PC88A under the same conditions. To produce the high-purity ZnO, the Zn-loaded organic phase was subjected to stripping tests, and over 92% of Zn was stripped out with trace amounts of impurities. Finally, the pH value of the stripped solution was increased to precipitate Zn, and a final ZnO product with a purity of over 99% was obtained. This study provided a reference for waste tire rubber management and utilization.

## Graphical Abstract



**Keywords** Waste tire rubber · Acid leaching · Solvent extraction · Zinc oxide

The contributing editor for this article was Nikhil Dhawan.

Extended author information available on the last page of the article

## Introduction

The burgeoning global automobile industry has engendered a remarkable demand for tires, leading to an annual production of 1.5 billion tires [1]. Meanwhile, a significant amount of waste end-of-life tires is generated every year, either by being thrown away or buried [2], although an estimated 86% is recycled or otherwise diverted from landfills in the U.S. [3]. It is estimated that by the year 2030, there will be a need to regularly discard 5 billion tires [4]. Tires encompass a diverse array of constituents, which include various rubber polymers as well as fillers. Additionally, they incorporate stabilizing agents along with cross-linking agents. Furthermore, secondary components are integrated into their composition. It is noteworthy that these diverse components, while serving their intended purposes within tire construction, have the potential to negatively impact the environment and human health [5]. ZnO is normally employed as a catalyst in tire rubber vulcanization, and it may not be covalently bound to polymers [6]. Therefore, ZnO has the potential to be released from waste tire rubber into the environment and cause environmental pollution [7]). It is necessary to consider the recycling of waste tire rubber. Table 1 shows the summary of resource recovery from waste tire rubber.

The recovery of Zn from tires is normally achieved by hydrometallurgical processes, and the effects of various parameters on Zn extraction have been investigated. For example, lower pH values and solid-to-liquid ratios at higher temperatures led to higher recovery of Zn during the leaching process of waste tire rubber [8–13]. However, some impurities, such as Cu, Pb, and Cr, were extracted simultaneously with Zn during the leaching process of waste tire rubber. With the aim of obtaining Zn-containing products with high purity, it is imperative to remove these impurities from the waste tire rubber leachate. However, the pyrometallurgy process necessitates elevated temperatures (at least 950 °C) to achieve the vaporization and subsequent condensation of Zn [14]. This requirement resulted in substantial energy consumption, which can be both economically burdensome and environmentally deleterious due to the resultant greenhouse gas emissions [15]. Currently, lots of work has been done to investigate the reduction of greenhouse gas emissions in various areas [16, 17]. Therefore, compared to pyrometallurgy, hydrometallurgy was more suitable to be selected for metal recovery from a sustainable perspective.

Most of the recent studies focus on metal recovery from secondary resources (e.g., waste streams) with particular emphasis on applying hydrometallurgical techniques [18, 19]. These techniques involve leaching with acids and alkalis to preliminarily release the desired metals,

which is followed by subsequent metal purification using solvent extraction, ion exchange, and/or precipitation methods [20]. In all techniques used for subsequent metal purification, solvent extraction plays a pivotal role in the generation of a high-purity precursor solution, which is subsequently utilized in the production of high-value products of valuable metals (e.g., metal powders, metal oxide powders, or salts) due to its simplicity, selectivity, cost-effectiveness, shorter reaction times, and smooth reaction conditions [21–23]. To get the high-purity Zn product for this study, the Zn-enriched waste tire rubber leachate was purified using solvent extraction.

Previous studies have reported the extraction, separation, and recovery of Zn due to its various applications in numerous industrial areas [24]. Organophosphorus extractants have gained wide utilization in the extraction process owing to their outstanding selectivity in complex formation under specified conditions [25, 26]. Specifically, organophosphorus extractants have found extensive applications in Zn extraction. Baba and Adekola investigated Zn extraction from the leachate obtained after Zn leaching using D2EHPA, achieving a Zn extraction efficiency of 93.42% [25, 26]. Soltani et al. found that 88.5% of Zn was extracted with the 2 stages extraction system composed of 30 vol% D2EHPA as the extractant [27]. The mechanisms of Zn recovery by D2EHPA have been investigated comprehensively. Falco et al. reported that compared to D2EHPA, Cyanex 272 showed better performance in the separation of Zn and Mn [28]. Tanlega and Ibana found that in a nitric acid leach solution, Al and Zn were extracted using Cyanex 272 at a pH value of 1.2 and only 2 mg/kg Co was co-extracted [29]. Nathsarma and Devi found that the separation factor of Zn over Mn was highest with 0.05 mol/L PC88A [30]. The Cyanex 272 and PC88A show better selectivity toward Zn especially in the complex chemical environment. Therefore, in comparison to the extensively studied D2EHPA, this study placed greater emphasis on evaluating the extraction efficiency of Zn from waste tire leachate using PC88A and Cyanex 272.

Most of the published studies focused only on leaching, or solvent extraction for the Zn recovery. In addition, the investigated experimental parameters are limited. The novelty of this study lies in the systematic and comprehensive development of a process for the efficient production of high-purity ZnO from waste tire rubber by an integrated hydrometallurgical process, combining acid leaching, solvent extraction, and precipitation. In this study, the sample was characterized by an electron probe microanalyzer (EPMA) to investigate the Zn-containing phases present in the tire rubber. To optimize the Zn leaching recovery, response surface methodology was conducted to identify the effects of various variables, such as temperature, acid concentration, and time on the leaching process. After reaching the highest Zn recovery,

**Table 1** Resource recovery from waste tire rubber

Sample	Method	Conditions	Results	References
Waste tire rubber	Acid leaching	2 mol/L HNO <sub>3</sub> at 90°C for 400 min	Over 98% of Zn recovery	[11]
Automobile tire waste ashes	Acid leaching, solvent extraction, precipitation	1 mol/L HNO <sub>3</sub> at 23°C for 24 h	Around 70% of Zn recovery with less than 1% Fe co-extraction. 67% of Zn recovery was achieved by the following solvent extraction using tri-n-octylamine	[54]
Brass-coated steel wire in retired tires	Dissolution	20% ammonia, 10% hydrogen peroxide, and a liquid–solid ratio of 10 for 5 min	Nearly 100% of Cu and Zn extraction	[55]
Residue obtained after Zn leaching	Aggregation	Replace fine with Zn leaching residue aggregate in a mortar	A remarkable loss in engineering properties of rubberized mortar when raw waste rubber was utilized, and a decrease in performance was more pronounced in the samples with zinc-extracted waste rubber residue	[56]
Waste tires	Catalytic pyrolysis	Zinc-loaded tire-derived char was used as the cheap catalyst for recovering valuable BTEX (benzene, toluene, ethylbenzene, and xylene products) from waste tires through pyrolysis	The relative content of BTEX reached 54.70% and the cumulative BTEX yield was 10.13 wt. %, increasing by 5.95 times compared to that of non-catalytic conditions	[57]
Waste tires	Pyrolysis	Heat-treated at 1000°C in argon	The pyrolytic char containing 5.1 wt. % zinc and a collection of such obtained ash (10.4% yield) that contains 42 wt. % of Zn	[14]
Waste tire fly ash	Thermal treatment and selective leaching	Heat-treated at 250 °C and water leaching	More than 90% of Zn recovery	[58]
Leachate obtained after leaching in HCl	Solvent extraction	0.032 M Cyanex272, 10 g/L solid concentration, 25°C for 25 min	93.42% Zn extraction and 92% of Zn stripping efficiency	[25, 26]

**Table 2** Concentrations (mg/kg) of major metals in the waste tire rubber

Metal	Mg	Al	Ca	Fe	Zn
mg/kg	566.5	218.9	627.0	130.6	10,389.2

the Zn was separated and purified from the leach liquor by solvent extraction and stripping at the proper conditions, respectively. The Zn enriched in the resulting stripped solution was precipitated by pH value increment for high-purity ZnO production. Findings from these experiments led to an effective route to recover and recycle the Zn from waste tire rubber.

## Materials and Methods

### Materials

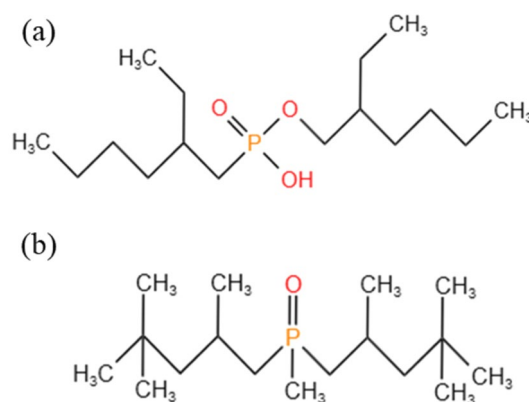
The waste tire rubber with a particle size of around 100  $\mu\text{m}$  was kindly provided by Lehigh Technologies (Tucker, Georgia, USA). Chemical specifications of waste tire rubber were published by the author [11]. Table 2 shows the main metals in the waste tire rubber analyzed after being dissolved in aqua regia ( $V_{\text{HNO}_3}:V_{\text{HCl}} = 3:1$ ). Elemental concentration analysis in solutions was conducted by an inductively coupled plasma emission mass spectrometer (ICP-MS, Thermo Electron iCAP-RQ, Thermo Scientific, USA).

The chemicals used in this study included hydrochloric acid (HCl, 37 wt%), nitric acid ( $\text{HNO}_3$ , 67–70 wt%), 50% w/w sodium hydroxide (NaOH,  $\geq 97$  wt%), and odorless kerosene. All chemicals were purchased from Thermo Fisher Scientific, USA. 2-ethylhexylphosphonic mono-2-ethylhexyl (PC88A; M.W. 299.4) and bis(2,4,4-trimethylpentyl) phosphinic acid (Cyanex 272; M.W. 306.4) were supplied by Solvay America, Inc. All the chemicals were used as received without further purification. The structures of PC88A and Cyanex 272 are shown in Fig. 1. Type I deionized water, with a resistivity of 18.2  $\text{M}\Omega\text{-cm}$  at 25  $^\circ\text{C}$ , was prepared by Direct-Q Water Purification System from Millipore, USA.

### Methods

#### Acid Leaching and Experimental Design

As a strong oxidizing agent,  $\text{HNO}_3$  can oxidize and dissolve the carbon black comprised in the tire rubber, which has been proved by the authors [11]. Therefore,  $\text{HNO}_3$  was employed as the lixiviant in this study to further optimize the Zn leaching recovery. The rationale for using  $\text{HNO}_3$  as the lixiviant was further elaborated in detail in the online



**Fig. 1** The structure of the extractants used in this study: **a** PC88A, and **b** Cyanex 272

supplementary material. The detailed leaching procedures can also be found in the online supplementary material. It is well known that various independent variables can affect the acid leaching process, and therefore, it is necessary to evaluate the significance of these variables on the dependent response. Box-Behnken Design (BBD) of the mathematical Response Surface Methodology (RSM) is an affordable and reliable method to describe the effect of variables as well as their interactions. In this study, temperature (30–90  $^\circ\text{C}$ ), acid concentration (1.0–2.0 mol/L), and time (100–400 min) were chosen as variables, while the Zn leaching recovery was defined as the response. The Design Expert Software (version 13.0) was utilized for designing the experiments and analysis of obtained results. Overall, the experimental design consisted of 17 experiments that the actual and code levels of independent factors are displayed in Table 3.

#### Solvent Extraction

The solvent extraction aims to selectively recover Zn from the leach liquor and avoid the contamination of other metal impurities. The organic phase was prepared by mixing a certain amount of organic extractants into kerosene as a diluent. A 10 mol/L NaOH solution was employed to adjust the pH value during the whole extraction process. To ensure an adequate reaction, the aqueous and organic phases were continuously mixed under magnetic stirring. Following each pH adjustment, the mixture was agitated at 400 rpm for 2 min to stabilize the pH value. After reaching the pre-determined pH value, the mixture was continuously agitated for 20 min to realize equilibrium. Subsequently, the pH value was recorded as the equilibrium one. A portable pH meter (AP110, Thermo Fisher Scientific, USA) was used to monitor the pH value. The resulting mixture was transferred to a separatory funnel and left for 5 min for sufficient disengagement. Elemental concentrations of the aqueous phase

**Table 3** Levels and codes of factors for Box-Behnken design

Variables	Symbol	Unit	Low	High	Values of code
Temperature	A	°C	30	90	- 1 = 30; 0 = 60; 1 = 90
Acid concentration	B	mol/L	1	2	- 1 = 1.0; 0 = 1.5; 1 = 2.0
Time	C	min	100	400	- 1 = 100; 0 = 200; 1 = 400

were measured by ICP-MS. The extraction percentage ( $E_1$ , %) is determined as the quantity of metal extracted into the organic phase in relation to the metal content in the initial feed solution. The distribution ratio ( $D$ ) is defined as the quantity of metal extracted into the organic phase divided by the remaining metal content in the aqueous phase. The separation factor for Zn over other metals ( $\beta_{Zn/M}$ ) is defined as the ratio of the Zn distribution ( $D_{Zn}$ ) to the distribution of any other metals in the leachate ( $D_M$ ). Following the extraction process, the extraction percentage ( $E_1$ , %), distribution ratio ( $D$ ), and separation coefficient ( $\beta_{Zn/M}$ ) were calculated using Eqs. (1)–(3), respectively.

$$E_1 = \frac{[M]_{WTRL} - [M]_{A1}}{[M]_{WTRL}} \times 100 \quad (1)$$

$$D = \frac{[M]_{WTRL} - [M]_{A1}}{[M]_{A1}} \quad (2)$$

$$\beta_{Zn/M} = \frac{D_{Zn}}{D_M}, \quad (3)$$

where  $[M]_{WTRL}$  (mg/L) and  $[M]_{A1}$  (mg/L) denote the metal concentration in the leach liquor obtained from the leaching process and in the raffinate obtained from the extraction test, respectively.

During the extraction process, the effects of organic extractants (Cyanex 272 and PC88A), pH value (1.0–5.0), extractant concentration (0.01–0.2 mol/L), and organic-to-aqueous phase ratio (O/A ratio, 1:5 to 5:1) were investigated to separate and purify the Zn from the leach liquor, with the purpose of high-purity ZnO production.

### Stripping

After the extraction step, the Zn-loaded organic phase was subjected to stripping tests using various concentrations of  $\text{HNO}_3$  (0.5–4 mol/L), while maintaining a fixed O/A ratio of 1:1. After 20 min of stirring at 400 rpm, the separation of aqueous and organic phases was carried out using the same method aforementioned. Elemental concentrations of the stripped solution were analyzed by ICP-MS. The stripping percentage ( $S$ ) is defined by Eq. (4):

$$S = \frac{[M]_{LS}}{[M]_{LO}} \times 100\%, \quad (4)$$

where  $[M]_{LS}$  (mg/L) and  $[M]_{LO}$  (mg/L) are the metal concentrations in the loaded stripped liquor and the loaded organic solution, respectively.

### Precipitation

After the stripping tests, the Zn present in the stripped solution was precipitated by adding 50% (w/w) NaOH dropwise until the pH value reached 12.0. During the precipitation test, the solution was stirred at 400 rpm, and an extra 30 min of stirring was applied to ensure sufficient precipitation after the pH value reached 12.0. After that, the resulting suspension was centrifuged at 5000 rpm for 5 min. The supernatant was diluted 100 times with 5% (v/v)  $\text{HNO}_3$  for elemental determination. The precipitate was rinsed several times with deionized water and then dried at 80 °C for 24 h for further analyses. The metal recovery ( $R$ , %) after the steps of extraction, stripping, and precipitation was calculated by Eq. (5):

$$R = \frac{M_{WTRL} - M_{A2}}{M_{WTRL}} \times 100\%, \quad (5)$$

where  $[M]_{WTRL}$  (mg/L) denotes the metal concentration in the WTRL obtained from the leaching process and  $M_{A2}$  (mg/L) is the metal concentration in the aqueous phase obtained after precipitation.

### Characterization

JEOL JXA-iHP200F field emission electron probe micro-analyzer (EPMA) was employed for the characterization of tire rubber particles. The sample was loaded onto a 1-inch diameter sample holder with a vertical profile not exceeding 1 mm and was coated with carbon using a mini sputter coater. 30 mm<sup>2</sup> energy-dispersive silicon drift detector (SDD) was used for rapid phase identification, and wavelength-dispersive spectrometer (WDS) was used for fast, high-resolution, quantitative chemical analyses of elements.

The precipitate was digested using a microwave digestion system (Multiwave GO Plus, Anton Paar, USA) to evaluate the final product purity. A 50-mL digestion tube was filled with 0.2 g of the sample and 12 mL of aqua regia ( $V_{\text{HNO}_3}: V_{\text{HCl}} = 1:3$ ). The vessel was placed inside the digestion rotor

and subjected to microwave digestion. The digestion was performed at a temperature of 185 °C with a heating rate of 18.5 °C/min for 40 min. After cooling to room temperature, the digestion solution was taken out and centrifuged. The supernatant was diluted 1000 times with 5% (v/v) HNO<sub>3</sub> to ensure the metal concentrations fell into the calibration range of ICP-MS equipment, which was sent for elemental determination.

The obtained ZnO precipitate was characterized by X-ray diffraction (XRD) as well as scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM–EDS) for further characterization. A Bruker D8 Advance XRD (Bruker Corporation, USA) with Cu K $\alpha$  radiation was employed. The X-ray tube operated at 40 kV with a current of 40 mA. The SEM–EDS analysis was conducted by JSM-IT500HR SEM (JEOL, MA, USA) equipped with an Ultim Max EDS detector (Oxford Instruments, Abington, UK). SEM images were obtained in the backscattered electron detector (BED-C) mode with a working distance of 3 mm. EDS mapping was recorded at a resolution of 1024  $\times$  768 pixels at the magnification of 1500 $\times$  with an acceleration voltage of 20 kV, with a 100  $\mu$ s/pixel dwell time.

## Results and Discussion

### Sample Characterization

A previous paper published by the authors demonstrated that ZnO was the dominant Zn-containing phase in tire rubber, and several particles were confirmed to be ZnO exposed or encapsulated within the rubber matrix (Fig. S1 in the online supplementary material [11]). To show the surface chemical composition more intuitively, the tire rubber particles were characterized by EPMA-WDS as shown in Fig. 2. The selected particle had an irregular shape with a maximum dimension of around 25  $\mu$ m. It is seen from Fig. 2b that the Zn concentration varied across the selected tire rubber particle, relating to the physical association characteristics

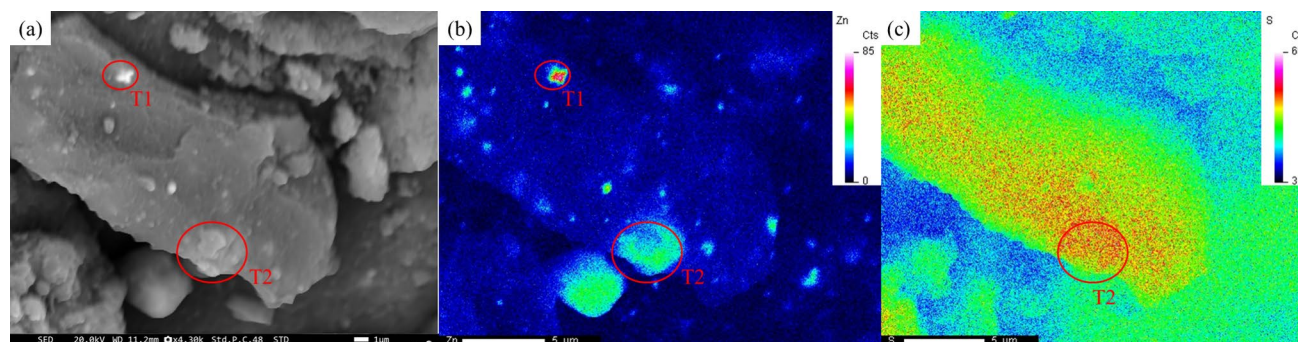
**Table 4** Summary of model statistics for the BBD experiments

Source	Sequential <i>P</i> -value	Adjusted <i>R</i> <sup>2</sup>	Predicted <i>R</i> <sup>2</sup>	Remark
Linear	<0.0001	0.8790	0.7988	
2FI	0.0205	0.9736	0.9351	Suggested
Quadratic	0.1290	0.9589	0.7120	
Cubic		1.0000		Aliased

of Zn-containing particles. The exposed particle in region T1 was evident with a concentrated red area in the Zn elemental mapping, while the S concentration was minimal in the corresponding location (Fig. 2c), indicating a ZnO particle exposed on the surface. The green color located in the T2 region suggested an encapsulated Zn-containing particle, and the relatively higher S concentration shown in the quantitative mapping indicated that this particle was likely a ZnS particle. In addition, the distribution of S was more uniformly dispersed than that of Zn in the tire rubber, indicating the presence of S-containing nanoparticles. Several studies have reported that the ZnS was an important species dispersed across the tire rubber attributing to the incorporation of S and ZnO as additives in the tire manufacturing process [31, 32]. Therefore, it can be concluded that ZnO and ZnS were the major forms of Zn present in the tire rubber. Table 2 shows the elemental composition of the tire rubber, and Zn had the highest concentration (~1 wt%) among the others.

### Optimization of the Zn Leaching Recovery

To optimize the Zn leaching recovery from tire rubber, response surface methodology (RSM) was employed to assess the interactive effects among various conditions. In this study, a total of 17 experiments were designed to evaluate the interactions of temperature (A), acid concentration (B), and time (C). Table S1 in the online supplementary material shows the detailed experimental conditions as well



**Fig. 2** Secondary electron detector (SED) image (a) and the elemental mapping of Zn (b), and S (c) of a selected tire rubber particle

as the response of Zn leaching recovery, and the response was found to range from 3.35 to 91.67%. Statistical analysis shown in Table 4 indicated linear was an inadequate model due to the lower  $R^2$  value [33]. Compared with the quadratic model, 2FI possessed a higher  $R^2$  value of 0.9736, which suggested a better correlation between practical and predicted values of response. In addition, the difference between adjusted  $R^2$  and predicted  $R^2$  should be less than 0.2 [34]. Therefore, the 2FI model is the suggested one for optimization and modeling of the Zn leaching recovery from tire rubber.

The analysis of variance (ANOVA) was conducted to evaluate the significance and accuracy of the suggested 2FI model. As shown in Table 5, the F-value of the model was 41.57, which indicated the predictive regression equation can effectively reflect the relationship between the variables and response. The values of “ $P$ -value” less than 0.05 suggest model terms are significant. While the insignificant terms were used for hierarchy backing. In this study, temperature and time were the most significant terms since the  $P$  values were much lower than those of acid concentration, and the interactive effect of temperature and time. The  $R^2$  of 0.9615 indicated that 96.15% of the response variability in the experimental data can be explained by the 2FI model. The adequate precision shows the signal-to-noise ratio, which is desirable if the value is greater than 4. The suggested model had a ratio of 22.14 implying an adequate signal. All the analysis indicated a significant and accurate model to describe the Zn leaching process. Therefore, the model equation linking the response to independent variables can be given as follows:

$$Y = 33.69 + 33.46A + 7.91B + 11.21C + 3.42AB + 12.42AC + 2.75BC, \quad (6)$$

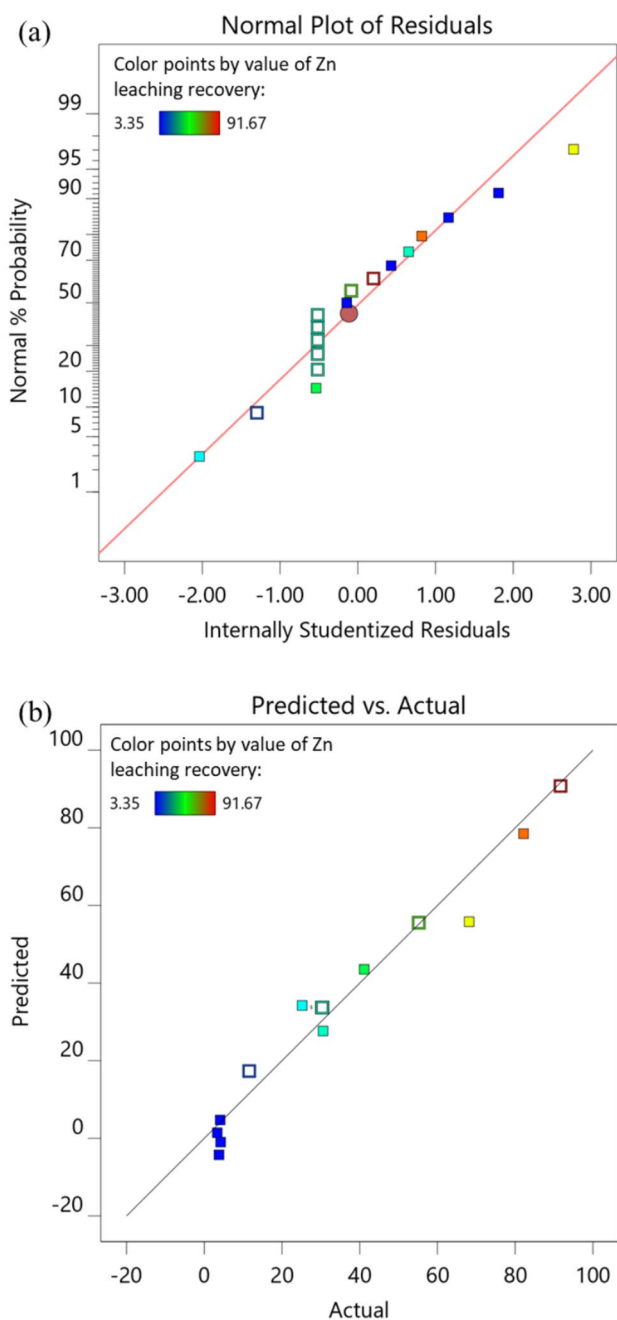
where  $Y$  represents the Zn leaching recovery (%) from tire rubber, as well as  $A$ ,  $B$ , and  $C$  refer to the coded values of temperature, acid concentration, and time, respectively.

It has been reported that the residuals contain information about the lack of fit, which can be used to check the adequacy of the suggested model [35]. The normal plot of residuals was established to diagnose and validate the systematic departures of the suggested model from the assumptions. As shown in Fig. 3a, the normal probability plot for the studentized residuals was approximately linear, suggesting the error terms were normally distributed and independent of each [36]. The predicted values calculated from Eq. (6) are shown in Fig. 3b. It can be clearly seen that the predicted points are in good agreement with the actual values, demonstrating the suggested 2FI model can accurately predict the Zn leaching recovery when the three variables were selected within the studied range.

Three-dimensional (3D) response surface plots derived from the model equation [Eq. (6)] can show the interactions between the independent variables on the Zn leaching recovery from tire rubber [37]. As the suggested model has three independent variables, two factors are set as variables, while keeping the other one constant. Thus, a total of three 3D plots were formed to investigate the influence of two variables on the response. Figure 4a depicts the effect of the interaction between temperature and acid concentration on the Zn leaching recovery at a fixed reaction time of 250 min. It is evident that higher temperature is favorable for Zn releasing from tire rubber. For example, elevating the leaching temperature from 30 to 90 °C, the Zn leaching recovery increased from 4.09 to 82.15% when the acid concentration was fixed

**Table 5** ANOVA result of the 2FI model for Zn leaching recovery from tire rubber

Source	Sum of squares	df	Mean square	F-value	P-value	Remarks
Model	11,155.55	6	1859.26	41.57	<0.0001	Significant
A-Temperature	8956.57	1	8956.57	200.28	<0.0001	Significant
B-Acid concentration	500.86	1	500.86	11.20	0.0074	Significant
C-Time	1004.42	1	1004.42	22.46	0.0008	Significant
AB	46.92	1	46.92	1.05	0.3298	
AC	616.53	1	616.53	13.79	0.0040	Significant
BC	30.25	1	30.25	0.6764	0.4300	
Residual	447.21	10	44.72			
Lack of fit	447.21	6	74.54			
Pure error	0.0000	4	0.0000			
Cor total	11,602.76	16				
$R^2$	0.9615			Adjusted $R^2$		0.9736
Predicted $R^2$	0.9351			Adequate Precision		22.14



**Fig. 3** Relationships between the normal % probability and internally studentized residuals (a); and the actual and predicted values of Zn leaching recovery from tire rubber

at 2.0 mol/L. In addition, increasing the acid concentration can also improve the Zn leaching recovery, but its effect is much weaker than that of temperature. A much steeper response surface shown in Fig. 4c illustrated the significant interaction between temperature and time at a fixed acid concentration (1.5 mol/L), which was in accordance with the ANOVA analysis (Table 5). The Zn leaching recovery increased with the increases in temperature and time, and the

maximum recovery of 91.67% was obtained after 400 min of reaction at 90 °C. It should be noted that the slope of the 3D plot in variable A was steeper than that in variable C, which means the influence of temperature on Zn leaching recovery was more significant than that of time. Similarly, the interactive effect of acid concentration and time on Zn leaching recovery at 60 °C is shown in Fig. 4b, and it can be seen that these two variables have a weaker effect on the response as a result of the flatter surface. Despite the weaker interaction, the time was more significant than acid concentration for Zn leaching recovery due to the steeper slope of the 3D plot. This result indicates the importance of the variables affecting the Zn leaching recovery following the order of temperature > time > acid concentration, which corresponded to the *P* values of the three variables (<0.0001, 0.0008, and 0.0074, respectively). Overall, a combination analysis of ANOVA and 3D plots concluded that the leaching temperature was the most significant variable, and the interaction between temperature and time had a major influence on the Zn leaching recovery from tire rubber.

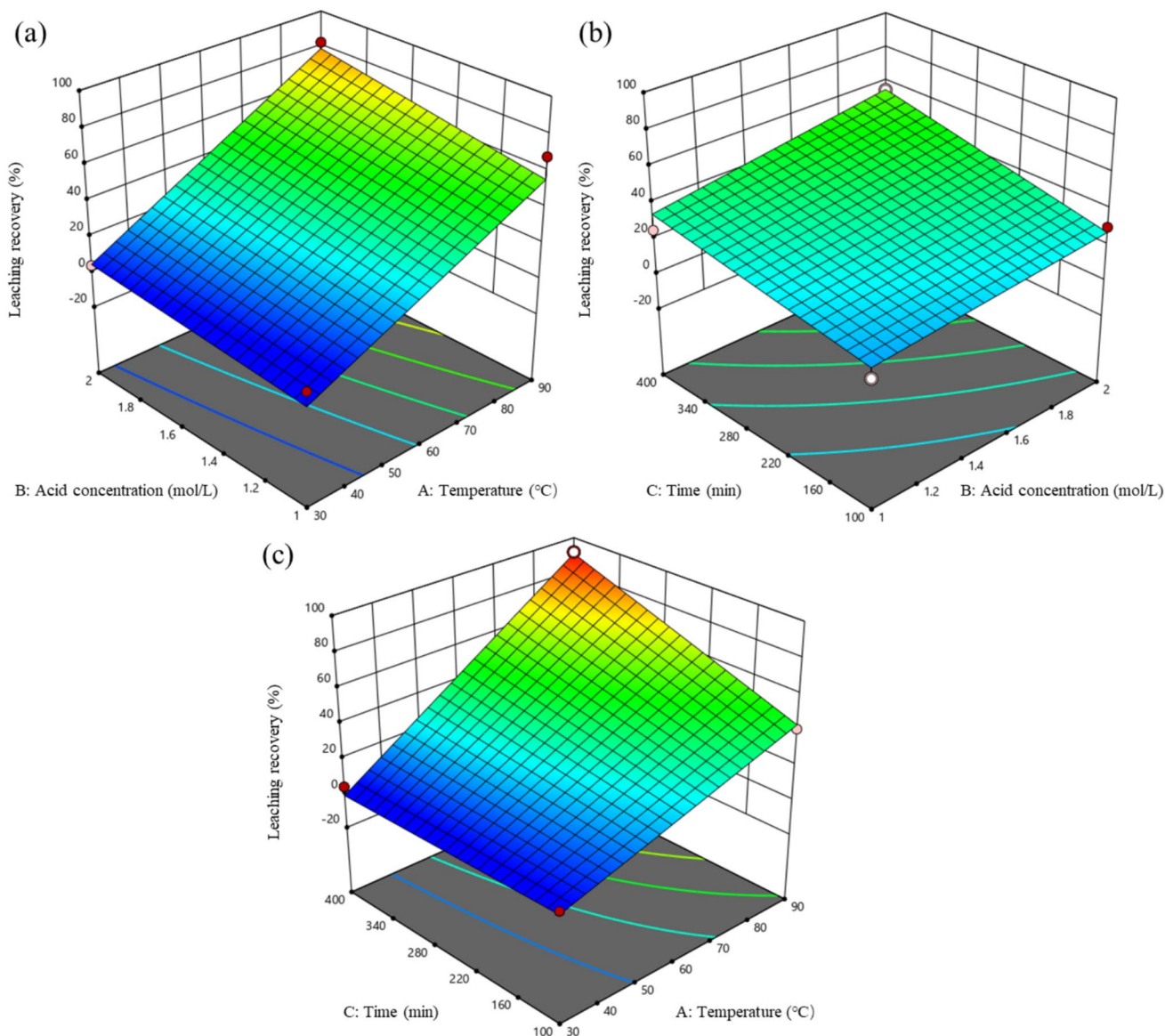
To maximize the Zn leaching recovery, the leaching test of tire rubber was conducted at 90 °C for 400 min using 2.0 mol/L HNO<sub>3</sub> as the lixiviant. The leaching recovery as well as the major metal concentration in the leachate is shown in Table 6. It can be seen that the concentration of Zn in the leachate was around 540 mg/L, and the leaching recovery of Zn reached over 98%, which means almost all the Zn was dissolved into the leachate. Simultaneously, some impurities, such as Mg, Al, Ca, and Fe, were also released from tire rubber. In order to purify the leachate for ZnO production, the impurities should be removed from the solution. Therefore, in this study, solvent extraction, stripping, and precipitation were conducted to produce high-purity ZnO. The leaching result of some trace metals was included in the online supplementary material (Table S2).

### Solvent Extraction

To selectively extract Zn and prevent the contamination of other impurities from the leach liquor, the following sections explored different parameters, including different organic extractants (PC88A, and Cyanex 272), pH values, organic extractant concentrations, and O/A ratios.

### Effect of pH

Figure 5a shows the effect of pH on the extraction of Zn and other major metals from leach liquor using 0.1 mol/L PC88A as the extractant with an O/A ratio of 1:1. It can be seen that almost 98% of Zn can be extracted from the leach liquor at a pH value of 3.0. When increasing the pH from 3.0 to 5.0, it exerted a negligible influence on the Zn extraction efficiency. Poor selectivity was observed for Zn and Al in the pH range



**Fig. 4.** 3D response surface plots showing the effect of the interactions of **a** temperature and acid concentration at time=250 min; **b** acid concentration and time at temperature =60 °C; and **c** temperature

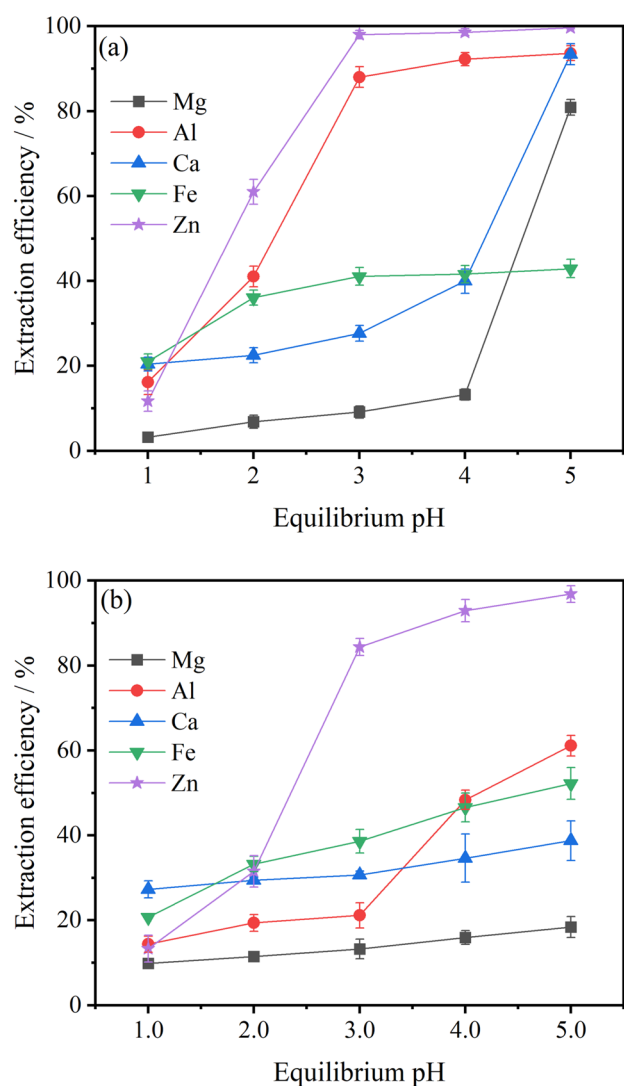
and time at acid concentration =1.5 mol/L on the Zn leaching recovery from tire rubber

**Table 6** The leaching recovery (%) of major metals and the corresponding concentration (mg/L) in the leach liquor

Metal	Mg	Al	Ca	Fe	Zn
Recovery/%	23.62	72.91	48.39	93.72	98.16
Concentration/mg/L	6.69	7.98	15.17	6.12	539.34

from 1.0 to 5.0, indicating that Al can be easily co-extracted with Zn in the PC88A system. As shown in Fig. S2a, b in the online supplementary material, dominant Zn and Al species present in the waste tire leach liquor were Zn<sup>2+</sup> and Al<sup>3+</sup> in the pH range from 1.0 to 5.0, respectively. This phenomenon

indicated that Zn and Al had the potential to be extracted with the pH increase from 1.0 to 5.0. No significant change in the extraction efficiency of Mg and Ca can be found as the pH value increased from 1.0 to 3.0. When pH was less than 3.0, most of the Zn and Al were extracted into the organic phase by forming high stability chelate complexes, increasing the consumption of the deprotonated form generated by PC88A. When increasing pH from 3.0 to 5.0, a significant increase in the extraction efficiencies of Mg and Ca was observed, which escalated from 7.5 to 78.8% and from 26.0 to 94.6%, respectively. Figure S2c, d in the online supplementary material illustrates that the primary species of Mg and Ca in the waste leach liquor are Mg<sup>2+</sup> and Ca<sup>2+</sup> at various pH values,



**Fig. 5** Effect of pH on the extraction of metals using different organic extractants: **a** PC88A, **b** Cyanex 272

which are easily extracted. When increasing pH from 3.0 to 5.0, with nearly 100% extraction of Zn and Al, the produced deprotonated form thereafter can be available for the heterogeneous complexation reaction with other metals, resulting in the increased extraction efficiencies of Mg and Ca [38]. The Fe extraction increased gradually from 22.2 to 40.2% as the pH increased from 1.0 to 3.0. There was a minimal alteration in the extraction rate of Fe after reaching a pH of 3.0. This phenomenon indicated that Fe predominantly existed as  $\text{Fe}^{3+}$

in the waste tire rubber leachate (Fig. S2e in the online supplementary material).

Figure 5b indicates the effect of pH on the extraction of Zn and other metals from the leach liquor using 0.1 mol/L Cyanex 272 as the extractant with an O/A ratio of 1:1. Zn extraction reached over 95% at a pH value of 4.0, indicating a desired condition for Zn extraction using Cyanex 272 in the nitric acid solution system. Moreover, in the Cyanex 272 system, a lower co-extraction efficiency of Al was found compared to that in the PC88A system. The increase of pH values posed a weak effect on the extraction efficiency of Mg and Ca, while Fe extraction efficiency enhanced gradually with the increased pH value from 1.0 to 5.0. In general, at low pH, the extractants, including PC88A and Cyanex 272, predominantly existed in the protonated form (HA). As the pH increased, extractants underwent deprotonation to form anionic forms ( $\text{A}^-$ ), which were effectively coordinated with metal ions [Eqs. (7)–(12)].



$\Delta\text{pH}_{50}$  is defined as the degree of difficulty in separating two different metals, representing the pH at which 50% of metal extraction occurs, and serves as an indicator of the selectivity of an extractant toward a specific series of bivalent metal cations [39]. A smaller  $\text{pH}_{50}$  value indicates a higher level of selectivity exhibited by the extractant for the respective metal cation [40], and it can be calculated in the following Eq. (13):

$$\Delta\text{pH}_{50} = \text{pH}_{50(\text{M1})} - \text{pH}_{50(\text{Zn})}, \quad (13)$$

where  $\text{pH}_{50(\text{M1})}$  and  $\text{pH}_{50(\text{Zn})}$  represent the values of  $\text{pH}_{50}$  for other metals and Zn, respectively.

The results of  $\text{pH}_{50}$  in Table 7 showed that the extraction efficiency of the metals from leach liquor followed the order:  $\text{Zn} > \text{Al} > \text{Ca} > \text{Mg} > \text{Fe}$  in the PC88A system, and  $\text{Zn} > \text{Al} > \text{Fe} > \text{Mg} \approx \text{Ca}$  in the Cyanex 272 system. It is well

**Table 7** Effects of using different organic extractants on  $\text{pH}_{50}$  values of metals

	Metal	Mg	Al	Ca	Fe	Zn
$\text{pH}_{50}$	PC88A	4.6	2.3	4.3	–	1.8
	Cyanex 272	–	4.1	–	4.6	2.4

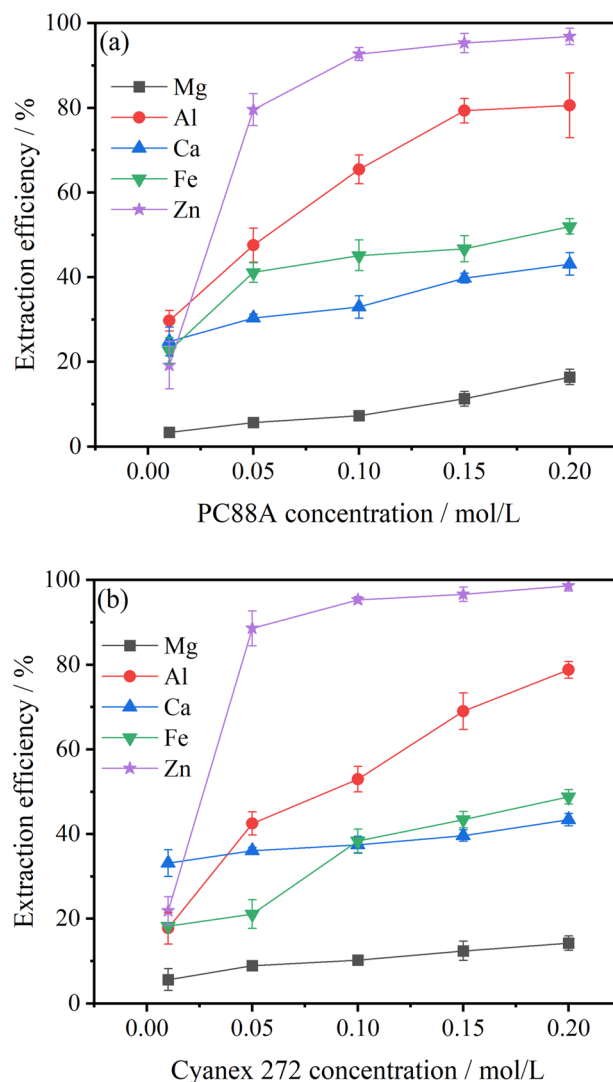
documented in the literature that organophosphorus extractants, PC88A and Cyanex 272, exhibited better performance in selective extracting Zn compared to other elements [41, 42], which is consistent with the results obtained from Table 7. When using PC88A as the extractant in the extraction process, the value of  $\text{pH}_{50}$  for Zn is 1.7, which was lower than that of using Cyanex 272. This result showed that PC88A exhibited higher efficiency in extracting Zn than Cyanex 272 under similar experimental conditions owing to the stronger affinity between Zn and PC88A [43]. Compared to Cyanex 272, the phosphonic acid groups in PC88A, which contain two oxygen atoms available for coordination, exhibit stronger chelation and binding capacities with both  $\text{Zn}^{2+}$  and  $\text{Al}^{3+}$  [44, 45]. In contrast, the phosphinic acid groups in Cyanex 272 preferentially form stronger and more stable complexes with divalent ions such as  $\text{Zn}^{2+}$ , while steric hindrance diminishes its effectiveness in extracting  $\text{Al}^{3+}$  [25, 26]. Based on the results of Table 7, it can be derived that  $\Delta\text{pH}_{50}$  values of Zn and Al were 0.5 and 1.7 using PC88A and Cyanex 272 as extractants, respectively, which were smaller than the  $\Delta\text{pH}_{50}$  values for Zn and other metals. Therefore, when using PC88A and Cyanex 272 as the extractants in the nitric acid solution, it is more difficult to separate Zn and Al relative to the separation of Zn and other metals. In addition, it can be concluded that it was more difficult to selectively separate Al from Zn using PC88A as the extractant compared to Cyanex 272 in the nitric acid solution. In addition to Al, Fe was easily co-extracted using Cyanex 272 during the extraction owing to the relatively low value of  $\Delta\text{pH}_{50}$  for Zn and Fe. Moreover, when using PC88A as the extractant and the feed pH value was lower than 4.0, Fe exhibited a higher tendency to be co-extracted with Zn compared to Ca and Mg. A certain amount of Fe co-extraction in both PC88A and Cyanex 272 systems is because, in addition to Zn, organic extractants like PC88A and Cyanex 272 can form strong organic phase complexes with Fe [46].

Zn can be extracted at a lower pH using PC88A as the extractant compared to Cyanex 272, and the co-extraction of Fe with Zn can be reduced to some extent in the PC88A system. However, it is easier to separate Al, Mg, and Ca from Zn in the Cyanex 272 system compared to the PC88A system. Furthermore, pH 3.0 and pH 4.0 were the optimal pH values when using PC88A and Cyanex 272 for extraction, as the extraction efficiency of Zn was relatively high, and the co-extraction of impurities was minimized. Therefore, to further purify Zn from the leach liquor, the effect of various parameters of the two extractants on the extraction efficiency of Zn continued to be investigated in the following study.

### Effect of Organic Extractant Concentration

The effect of organic extractant concentration in the range of 0.01–0.2 mol/L on the extraction efficiency of Zn and other major metals is shown in Fig. 6. During the extraction,

PC88A and Cyanex 272 were used to selectively extract Zn and minimize the co-extractions of other impurity metals with an O/A ratio of 1:1 at equilibrium pH values of 3.0 and 4.0, respectively. According to Fig. 6, the extraction efficiency of Zn in both PC88A and Cyanex 272 systems increased significantly from 16.3 to 80.0%, and from 21.5 to 88.6%, respectively, when increasing extractant concentration up to 0.05 mol/L. Further increasing the concentrations of the organic extractant from 0.05 to 0.1 mol/L, the extraction efficiency of Zn increased minimally from 86.3 to 88.3%. Given the nearly 90% extraction of Zn at a concentration of 0.1 mol/L for both PC88A and Cyanex 272, minimal enhancement in the extraction efficiency of Zn was observed when further increasing the concentration of the extractants to 0.2 mol/L. It can be found that Al was more easily co-extracted with Zn with increasing organic



**Fig. 6** Effect of organic extractant concentration on the extraction of metals using different organic extractants: **a** PC88A, **b** Cyanex 272

extractant concentrations compared to other impurities, such as Mg, Ca, and Fe, in the nitric acid solution. When using PC88A as the extractant, there was a significant increase in the co-extraction of Al from 27.2 to 79.8% as the extractant concentration increased from 0.01 to 0.15 mol/L, and the Al extraction efficiency increased steadily as the concentration further increased to 0.2 mol/L. In terms of the Cyanex 272 system, there was a continuous increase in Al co-extraction with Zn from 16.2 to 79.7% in the range from 0.01 to 0.2 mol/L. It has been reported that maximum Al extraction from sulfate medium can be achieved in the equilibrium pH range of 3.2–3.6 by using 0.3 mol/L Cyanex 272 as the extractant [47]. In this study, it can also be found that PC88A had the ability to selectively extract Al in the nitric acid solution. As shown in Fig. 6a, when using PC88A as the extractant, the co-extraction of Fe increased significantly from 22.7 to 43.8% with the extractant concentration up to 0.05 mol/L. However, there was only a minor increase in Fe extraction with a further increase of PC88A concentration from 0.05 to 0.2 mol/L. It can be observed from Fig. 6b that a significant increase in Fe extraction occurred by increasing the Cyanex 272 concentration from 0.05 to 0.1 mol/L. A negligible increase was found for Fe extraction when Cyanex 272 concentration increased from 0.1 to 0.2 mol/L. The co-extractions of Mg and Ca grew more smoothly compared to other major metals when increasing the extractant concentration in both PC88A and Cyanex 272 systems, indicating that the change of extractant concentrations exerted a negligible impact on the co-extractions of Mg and Ca. In summary, when using PC88A and Cyanex 272 as extractants, the separation of Al and Fe from Zn should be taken into consideration.

Table 8 shows the distribution coefficient ratios ( $D$ ) of Zn, Al, and Fe, and the separation factors ( $\beta$ ) of Zn/Al and Zn/Fe, as a function of the organic extractant concentration. As shown, extractant concentration had a more profound effect on  $\beta_{Zn/Al}$  and  $\beta_{Zn/Fe}$  in the Cyanex 272 system compared to the PC88A system. When using Cyanex 272

as the extractant, the value of  $\beta_{Zn/Al}$  increased from 1.16 to 13.75 with the elevated concentration range from 0.01 to 0.1 mol/L. After that, the value decreased when the extractant concentration was higher than 0.1 mol/L, indicating that 0.1 mol/L Cyanex 272 was suitable to separate Al from Zn in the nitric acid solution. In terms of Fe co-extraction,  $\beta_{Zn/Fe}$  continuously increased with the rising concentration of Cyanex 272. In general, based on the above discussion, considering maximizing Zn extraction and minimizing the contamination of other impurities, 0.1 mol/L Cyanex 272 was chosen as the optimal operating condition for the selective extraction of Zn from the leach liquor.

### Effect of O/A Ratio

Figure 7 depicts the effect of O/A ratio on the extraction of Zn and other metals using 0.1 mol/L Cyanex 272 at an equilibrium pH value of 4.0. The increase in O/A ratio from 1:5 to 1:1 exhibited a negligible effect on the efficiency of Zn extraction. However, the extraction of Zn decreased from 93.4 to 62.1% with an increasing O/A ratio from 1:1 to 5:1. The decreased phase ratio of Cyanex 272 led to insufficient deprotonated forms that can complex with metal ions, thus resulting in lower extraction efficiency [38]. Additionally, the increase of O/A ratio from 1:5 to 1:2 had a negligible impact on the co-extraction of Al. Nevertheless, Al co-extraction reduced significantly from 73.4 to 30.0% as the O/A ratio increased from 1:2 to 2:1. The co-extraction of Fe gradually decreased with increasing O/A ratio, while the Mg and Ca co-extractions basically remained constant as the O/A ratio increased from 1:5 to 1:2. After that, the extraction efficiencies of Mg and Ca experienced a significant decline from 74.4 to 9.3% and 68.7 to 5.7%, respectively, as the O/A ratio further increased from 1:2 to 1:1. It showed that Cyanex 272 is more appropriate for extracting Zn and Al compared to Mg and Ca. This was due to the fact that an elevated concentration of Cyanex 272 led to the preferential

**Table 8** Effect of extractant concentration on distribution ratio ( $D$ ) and separation factor ( $\beta$ ) of Zn and Al

Extractant	Concentration (mol/L)	$D_{Zn}$	$D_{Al}$	$D_{Fe}$	$\beta_{Zn/Al}$	$\beta_{Zn/Fe}$
PC88A	0.01	0.34	0.58	0.45	0.59	0.75
	0.05	4.62	1.01	1.00	4.56	4.64
	0.10	8.35	2.69	1.18	3.10	7.09
	0.15	17.18	4.68	1.23	3.67	13.94
	0.20	21.48	6.00	1.24	3.58	17.28
Cyanex 272	0.01	0.43	0.37	0.22	1.16	1.92
	0.05	8.85	1.01	0.52	8.85	16.95
	0.10	22.19	1.61	1.01	13.75	21.93
	0.15	26.12	2.24	1.17	11.68	22.40
	0.20	39.53	4.63	1.30	8.53	30.35

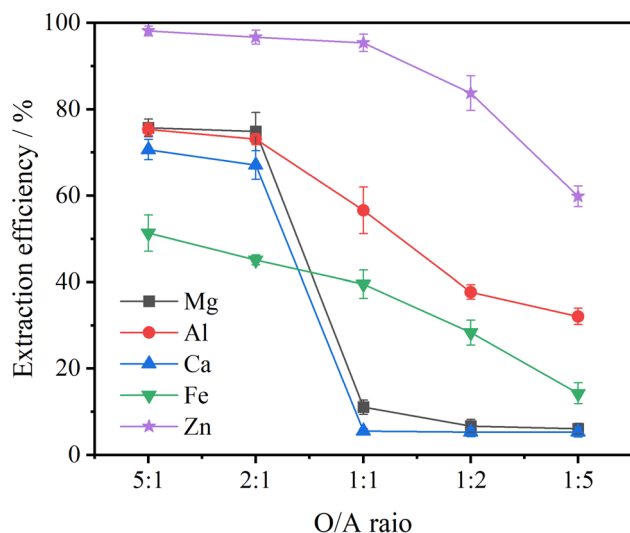


Fig. 7 Effect of O/A ratio on the extraction of metals

extraction of Zn and Al. Considering the nearly complete extraction of Zn as well as the minimized co-extraction of other impurities from the leach liquor, the O/A ratio of 1:1 was applied in the following experiments.

In conclusion, 97.4% Zn can be selectively extracted from the leach liquor when using 0.10 mol/L Cyanex 272 as the extractant and an O/A ratio of 1:1 at a pH value of 4.0. Meanwhile, 9.3% Mg, 57.7% Al, 5.7% Ca, and 42.9% Fe were co-extracted under the optimized conditions.

**McCabe–Thiele Analysis for Zn Extraction** Extraction isotherm was studied to evaluate the extraction capacity, and the McCabe–Thiele diagram was constructed to determine the number of theoretical stages required for the complete extraction of Zn from the waste tire rubber leach liquor [48]. The Zn distribution isotherm was identified by adjusting the O/A ratio between 1:5 and 5:1 using 0.1 mol/L Cyanex 272 at a pH value of 4.0. As depicted in Fig. 8, at an O/A ratio of 1:1, a single-stage extraction process is sufficient to achieve 100% Zn extraction using 0.1 mol/L Cyanex 272 at a pH of 4.0.

### Stripping

Single-stage stripping of the Zn-loaded organic phase was performed with the stripping reagent,  $\text{HNO}_3$ , at an O/A ratio of 1:1 by continuous mixing for 20 min. Different concentrations of  $\text{HNO}_3$  in the range from 0.5 to 4 mol/L were examined for the effective stripping of Zn from the loaded organic phase. The result is shown in Fig. 9. It can be observed that 92.8% of Zn can be stripped using 0.5 mol/L  $\text{HNO}_3$ . The incremental increase in concentrations from 0.5 to 4 mol/L had a negligible impact on the

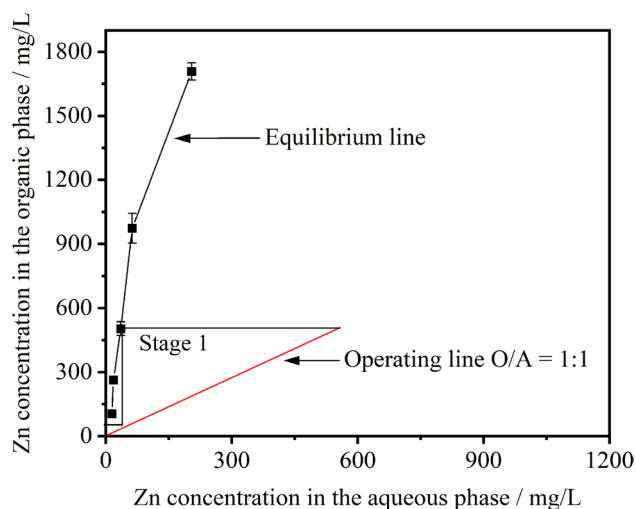


Fig. 8 McCabe–Thiele diagram for Zn extraction from the leach liquor

stripping efficiency of Zn. Fe and Al were easier to strip from the loaded organic phase compared to Mg and Ca. In addition, Fe showed a higher stripping efficiency in the  $\text{HNO}_3$  concentration range from 0.5 to 4 mol/L compared to Al. The  $\text{HNO}_3$  solution showed a significant increase in stripping percentage on Zn and Fe since nitrate ions can be complex with Fe and Zn [49]. When stripping Zn and Fe using  $\text{HNO}_3$  solution, the complexation between nitrate ions and Zn or Fe will disrupt the prior complexation between Zn or Fe and the solvent extractant, facilitating the cation exchange of  $\text{H}^+$  and Zn or Fe [50]. Therefore, compared to Al, Zn, as well as Fe, exhibited greater

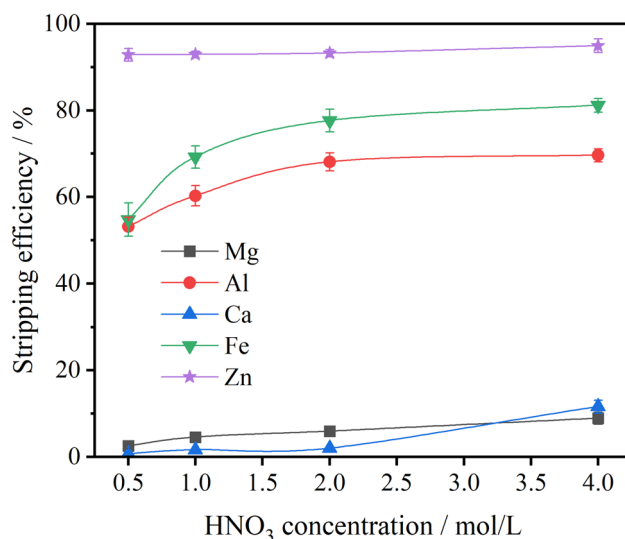
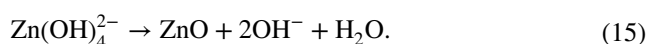


Fig. 9 Effect of  $\text{HNO}_3$  concentration on the stripping efficiency of various metals

potential to be stripped by  $\text{HNO}_3$  solution. Considering the subsequent high-purity ZnO production, 0.5 mol/L  $\text{HNO}_3$  was suitable for the stripping of Zn from the loaded organic phase.

### Precipitation of ZnO

To produce the high-purity ZnO, the stripped solution was subjected to pH increase by adding 50% w/w NaOH solution. The high alkalinity of pH 12.0 was chosen to ensure both the product purity and rapid nucleation rate of ZnO [23, 51]. The reactions are shown in Eqs. (14) and (15):



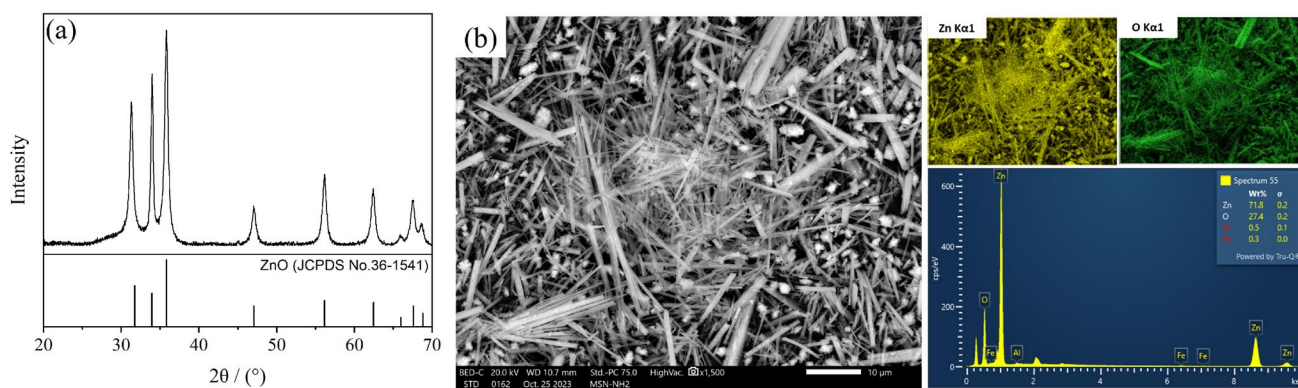
The produced ZnO powder was characterized by XRD and SEM–EDS for purity confirmation. As shown in Fig. 10a, the sharp and high intensity peaks were perfectly indexed to the standard material of ZnO referenced from the JCPDS card No. 36-1541. Figure 10b shows the morphology as well as the EDS spectrum and elemental mapping of the ZnO powder. The ZnO powder is composed of nanowires, nanorods, or needle-like particles with the largest dimension of decades of microns. These crystals aggregated with each other at the end, which formed the typical hexagonal wurtzite structure of ZnO [52]. The EDS elemental mapping confirmed that the constituent elements were homogeneously distributed in the crystal. In addition, the produced precipitate was digested for elemental analysis, and the result indicated that < 0.5% of impurities were co-precipitated with Zn, which was consistent with the elemental identification in the EDS spectrum. Finally, the ZnO product with a purity of over 99% was obtained, and the total recovery of Zn reached around 85%.

### Flowsheet Description

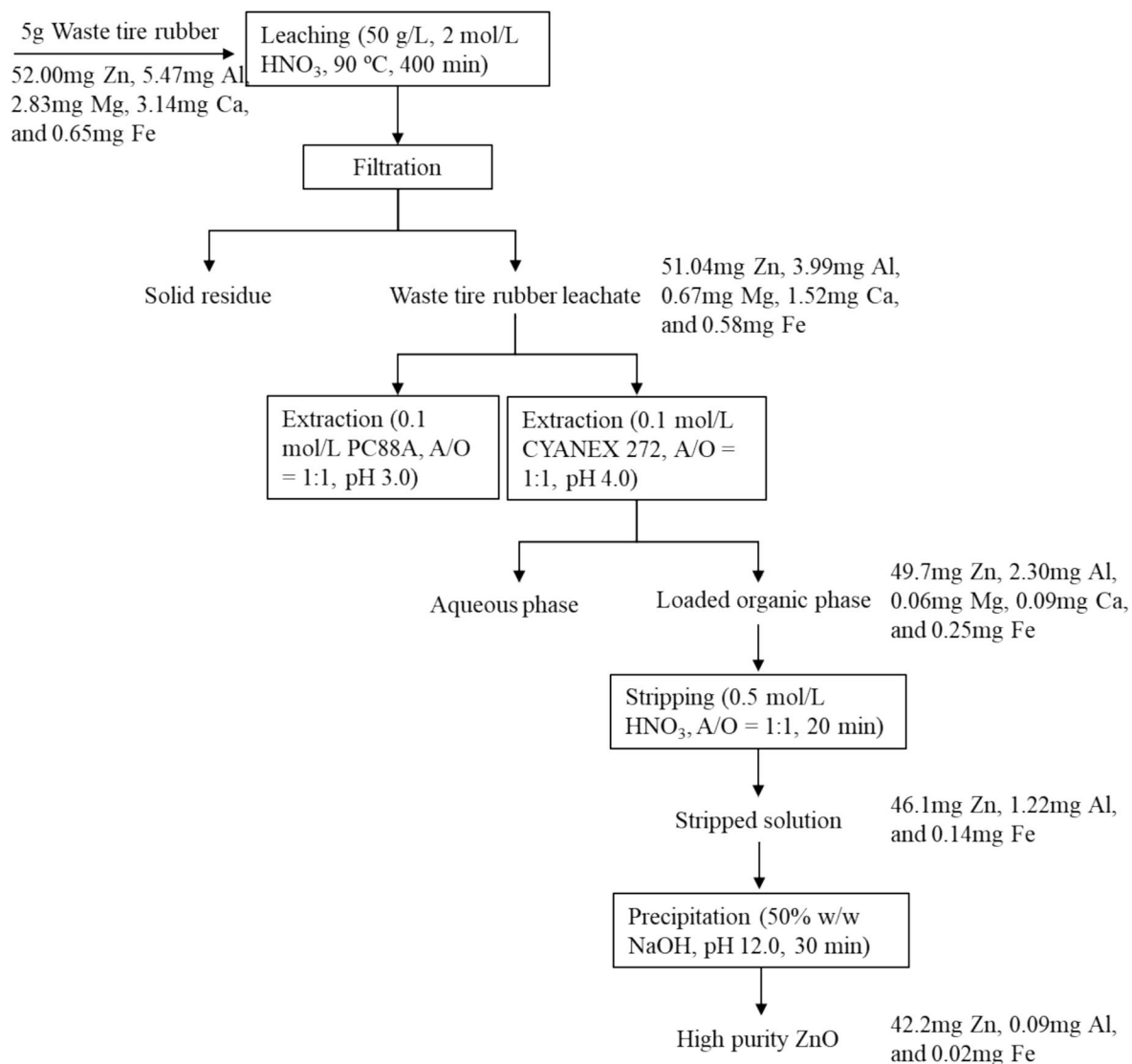
A flowsheet for the production of high-purity ZnO from waste tire rubber is proposed in Fig. 11. Zn recovery from waste tire rubber was investigated by an integrated hydro-metallurgical method, including acid leaching, solvent extraction, and precipitation. The purity of produced ZnO was determined to be over 99% which can be utilized for the manufacture of new tires. However, from the environmentally friendly perspective, how to dispose of the generated leaching residue becomes a challenge for the researchers. To make a comprehensive utilization of waste tire rubber, the leaching residue was used as a partial alternative in rubberized cementitious materials (RCM), and authors found that the strength recovery index and the strength gain of RCM with a partial alternative of leaching residue were increased [53]. Furthermore, pH values of aqueous raffinate achieved after the solvent extraction process were adjusted and reused in the solvent extraction process to reduce environmental impact and improve process sustainability.

### Conclusions

This study mainly focused on the high-purity ZnO production from waste tire rubber. The elemental analysis by EPMA found the presence of both ZnO and ZnS particles, thereby confirming the predominant Zn-containing phase within the tire rubber. To optimize the Zn leaching process, the response surface methodology was conducted with temperature, acid concentration, and time as independent variables, and Zn leaching recovery as the response. The result of the analysis of variance (ANOVA) showed that the temperature was the most influenced variable and a recovery value of 98.16% can be obtained under the following conditions: 90 °C leaching temperature, 2.0 mol/L  $\text{HNO}_3$ , and 400 min of reaction.



**Fig. 10** XRD pattern (a) and SEM–EDS characterization b of the product obtained by precipitation of stripped solution



**Fig. 11** The proposed flowsheet for the production of high-purity ZnO from waste tire rubber

After the release of Zn into the leach liquor, solvent extraction using Cyanex 272 and PC88A as the extractants was performed for further separation and purification. It was found that 97.4% of Zn can be selectively extracted from the leach liquor using 0.10 mol/L Cyanex 272 with an O/A ratio of 1:1 at a pH value of 4.0. In addition, the impurities such as Al and Fe can be easily co-extracted with Zn using both Cyanex 272 and PC88A as the extractants. However, Cyanex 272 had a much higher separation factor of Zn/Al and Zn/Fe, respectively. Therefore, Cyanex 272 was selected for maximizing the Zn extraction with minimal impurity contamination. The number of counter-current stages for Zn extraction was determined by the McCabe–Thiele diagram, and it was revealed that over 99% Zn can be recovered by Cyanex 272 after one

counter-current stage. The stripping tests showed that 92.8% of Zn can be stripped from the loaded organic phase by 0.5 mol/L HNO<sub>3</sub> solution while minimizing the presence of impurities. After that, the ZnO was precipitated from the stripped solution by increasing the solution pH to 12.0. A combination analysis of XRD, SEM–EDS, and elemental composition showed that the purity of ZnO product reached over 99%, with a total recovery of around 85%.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s40831-024-00981-5>.

**Acknowledgements** Funding for this study was provided by the Center for Tire Research under Project SUST-2021-D14-4. The authors would like to express their gratitude to Lehigh Technologies for supplying the

waste tire rubber. The authors thank Jeffrey Parks for performing the ICP-MS analyses.

## Declarations

**Conflict of Interest** The authors declare that they have no conflict of interest.

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