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ORIGINAL ARTICLE

Rare earths leaching from Philippine phosphogypsum using Taguchi method, regression, and artificial neural network analysis

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Abstract

The Philippines produce some 2.1–3.2 million t phosphogypsum (PG) per year. PG can contain elevated concentrations of rare earth elements (REEs). In this work, the leaching efficiency of the REEs from Philippine PG with H_2SO_4 was for the first time studied. A total of 18 experimental setups (repeated 3 times each) were conducted to optimize the acid concentration (1–10%), leaching temperature (40–80 °C), leaching time (5–120 min), and solid-to-liquid ratio (1:10–1:2) with the overall goal of maximizing the REE leaching efficiency. Applying different optimizations (Taguchi method, regression analysis and artificial neural network (ANN) analysis), a total REEs leaching efficiency of 71% (La 75%, Ce 72%, Nd 71% and Y 63%) was realized. Our results show the importance of the explanatory variables in the order of acid concentration > temperature > time > solid-to-liquid ratio. Based on the regression models, the REE leaching efficiencies are directly related to the linear combination of acid concentration, temperature, and time. Meanwhile, the ANN recognized the relevance of the solid-to-liquid ratio in the leaching process with an overall *R* of 0.97379. The proposed ANN model can be used to predict REE leaching efficiencies from PG with reasonable accuracy.

Keywords Phosphogypsum · Rare earth elements (REEs) · Leaching · Taguchi method · Artificial neural network

Introduction

The Philippines is one of the largest phosphate fertilizer producers in the Southeast Asia, processing phosphate ore imported from different locations to wet phosphoric acid, an intermediate product in fertilizer production, and phosphogypsum (PG). PG is a powdery byproduct of which roughly 40% are presently used in the cement industry and as soil conditioners in the Philippines. The Mines and Geosciences Bureau of the Philippines is leaving no stone unturned in its quest to locate rare earth elements (REEs) that could support the country's production sector while reducing metal imports from China [1, 2]. Ramirez et al. [3] recently pointed to the approximately 10.1 million t PG that are dry-stacked and accessible in the Philippines as a potential secondary resource of REEs.

Phosphate ore, the main raw material in phosphate fertilizer production is known for its elevated content of valuable trace elements, most notably REEs [4–11] and uranium [12–16]. During wet phosphoric acid production with sulfuric acid as it is done at most phosphate fertilizer plants worldwide, the majority of REEs (> 80%) transfers to the solid PG while most of the uranium (> 80%) transfers to the liquid phosphoric acid [17–20]. There is increased research activity to fully utilize PG stacks worldwide instead of just managing them [21–30]. Not processing PG but stacking the material could result in potential present and future environmental risks [31–37]. Recovering REEs that occur in relevant concentrations in PG [38–43] and ideally also removing actinides from the PG before using the remaining gypsum matrix as an inexpensive raw material in construction seems to be an attractive option [23, 44–47]. Although there have been considerable efforts to determine the concentrations

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and quantities of REEs in Philippine PG [3, 48] no work ever attempted to recover these resources. The present study aims at filling this gap by providing a simple as well as potentially economic process and optimization for REE leaching from Philippine PG that can be upscaled and applied in a next step.

Materials and methods

PG samples and elemental composition

PG samples were collected from 2-m-deep trenches in the tailing ponds of the main fertilizer plant in the Philippines as described in a previous work [3]. Although, the Philippines is one of the largest producers of fertilizer in Southeast Asia it has no domestic source of phosphate rock (PR). The PG in the Philippines is produced from a combination of sedimentary PR imported from China, Egypt, Israel, Jordan, Peru, Tunisia, the USA and Vietnam and igneous PR from Russia and South Africa [49, 50]. There are around 10.1 million t PG in the tailings ponds in the Philippines that have been accumulated since 1984 [48].

Five (5) of the samples with the highest total REE (TREE) concentrations from a previous study of the tailings ponds [3] were pulverized using mortar and pestle, and subsequently mixed to form a composite. To ensure homogeneity, the composite, weighing approximately 10 kg, was mixed in a Thermo Scientific bottle/tube roller for 24 h at 80 rpm. Samples were then sent to a third-party testing laboratory (Intertek Testing Services Philippines, Muntinlupa City, Philippines) for analysis. The laboratory is accredited by the Philippine Accreditation Bureau and also ISO/IEC 17025:2017-certified. Approximately 1 g of the composite was digested using a combination of analytical grade 37% HCl, 70% HNO_3, 50% HF and 69–72% $HClO_4$ and then analyzed for REEs using a combination of Inductively Coupled Plasma Mass Spectrometry (ICP-MS Agilent 7700x) and inductively coupled plasma optical emission spectrometry (ICP-OES Agilent 5100). Blank solutions and certified reference materials (i.e., OREAS 501c, 600, 623 90, and 44P) were used to ensure the accuracy of the results. The detection limits ranged from 0.05 to 0.1 mg kg^{-1}. The REE composition of the PG composite is presented in Table 1.

Table 1 REE composition of the PG composite analyzed by ICP-MS

REE	Concentration (mg kg^{-1})
La	82.7
Ce	132.7
Pr	18.20
Nd	75.5
Sm	15
Eu	3.5
Gd	15
Tb	2.06
Dy	12.3
Ho	2.4
Er	6.9
Tm	0.8
Yb	4.4
Lu	0.50
Y	91.3
TREE	463.26

Table 2 Experimental matrix of the leaching experiment

Leaching steps	Leaching conditions	
Step 1 Varying H_2SO_4 concentration, % vol/vol	1 2.5 5 10	2 h leaching time Ambient temperature 1:5 *S/L* ratio
Step 2 Varying temperature, °C	40 50 60 70	Optimum acid Concentration 2 h Leaching time 1:5 *S/L* ratio
Step 3 Varying time, min	5 15 30 45 60	Optimum acid Concentration Optimum temperature 1:5 *S/L* ratio
Step 4 Varying *S/L* ratio	1:2 1:3 1:4 1:5 1:10	Optimum concentration Optimum time Optimum temperature

REE leaching procedure

The leaching experiments were conducted following the patterns proposed by Al-Thyabat and Zhang [51, 52], Cánovas et al. [41], Lütke et al. [53], Rychkov et al. [54], and Walawalkar et al. [55] for other than Philippine PG. It is well known that PG from different locations shows different trace-element concentrations, so that leaching experiments successfully conducted at one PG location may lead to different results when a different PG stack is considered. The differences can be attributed to the different phosphate ore processed, the different processing conditions, as well as different qualities of the sulfuric acid used for wet-phosphoric acid processing [56]. The REE leaching optimization followed four succeeding steps: (1) optimizing acid concentration (C), (2) optimizing temperature (T), (3) optimizing time (t), and (4) optimizing solid-to-liquid ratio (*S/L* ratio) as summarized in Table 2.

There are a number of acids that are technically promising for leaching of REEs from PG [57–72]. In this work, H_2SO_4 (< 10% vol/vol) was chosen for its comparable leaching efficiency with HCl and HNO_3, low solubility of PG in H_2SO_4 (i.e., resulting PG residue from leaching will enable secondary applications), and most importantly for onsite availability and economic reasons which could be beneficial for large scale extraction of REEs from PG in the Philippines [54].

Step 1: determination of optimum acid concentration

10 g PG was added to 50 mL (1:5 *S*/*L* ratio) of acid of varying concentrations in a 250 mL beaker. The mixture was leached at 380 rpm for 2 h at ambient temperature using 1% to 10% H_2SO_4. This concentration range was used to avoid common ion effect and formation of less soluble bisulfates that could inhibit the leaching of REEs from PG [73].

Step 2: determination of optimum temperature

10 g PG was added to 50 mL (1:5 *S*/*L* ratio) of the optimum acid concentration obtained in Step 1 in a 250 mL beaker. The mixture was leached at 380 rpm for 2 h at temperatures 40 to 80 °C.

Step 3: determination of optimum time

10 g PG was added to 50 mL (1:5 *S*/*L* ratio) of optimum acid concentration in a 250 mL beaker. The mixture was leached at 380 rpm at optimum temperatures obtained in Step 2 and at varying leaching times from 5 to 60 min.

Step 4: determination of optimum *S*/*L* ratio

10 g PG was added to varying volumes of optimum acid concentrations in 250 mL beaker to form 1:2, 1:3, 1:4, 1:5, and 1:10 *S*/*L* ratios. The mixture was leached for 30 min at 380 rpm at optimum temperatures.

The leaching experiment was performed in a hot bath (Fig. 1a). The temperature of the acid was stabilized prior to the addition of the PG. The acid-PG mixture was covered with a watch glass to prevent acid evaporation. After each leaching experiment, the PG and acid mixture was filtered using 125 mm Whatman ™ filter papers (Cat No 1440 125) and washed with 100 mL of distilled water (Fig. 1b). The collected residue was then dried in an oven at 105 °C for 24 h. Each experimental setup was repeated three (3) times which resulted in a total of 54 experiments. Due to the complexity of analyzing metals dissolved in sulfuric acid matrix [74], the dried residues were instead analyzed for REEs by the four-acid digestion method using ICP-MS and ICP-OES.

REE leaching efficiency

The efficiency of the leaching procedure was determined using the following formula:

$$\text{Leaching Efficiency (\%)} = \frac{C_i - C_f}{C_i} \times 100 \quad (1)$$

where C_i and C_f are the REE concentrations in PG composite and PG residue, respectively.

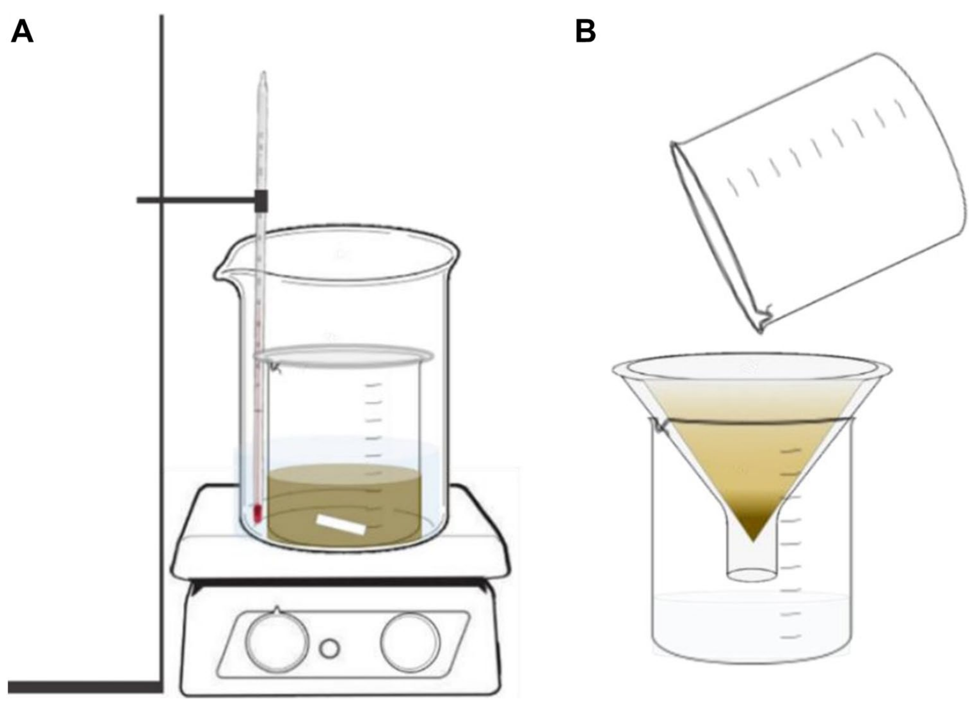

Fig. 1 Experimental setup of the leaching procedure showing the **A** hot bath with the PG and acid mixture, and **B** filtering of the mixture after the leaching experiment

Taguchi method

Taguchi method is an engineering technique used for process optimization which involves system design, parameter design, and tolerance design procedures [75, 76]. The signal/noise (*S*/*N*) ratio is used to examine the response in each experiment and the corresponding variance in the Taguchi method. The *S*/*N* ratio is a measure of deviation of quality characteristics from the ideal values [77]. There are usually three types of S/N ratios:

$$\text{Nominal value is better: } \frac{S}{N} = -10\log\sum_{i=1}^{n}\frac{(y_i - m)^2}{n} \tag{2}$$

$$\text{Smaller value is better}: \frac{S}{N} = -10\log\frac{1}{n}\left(\sum_{i=1}^{n} y_i^2\right) \tag{3}$$

$$\text{Larger value is better}: \frac{S}{N} = -10\log\frac{1}{n}\left(\sum_{i=1}^{n}\frac{1}{y_i^2}\right) \tag{4}$$

where *m* is the desired nominal value, *n* is the number of experiments, and *y* is the experimental result [78].

Multiple linear regression

A simple linear regression evaluates the relationship between the explanatory variable *x* and the response variable *y*. If there are multiple explanatory variables, Multiple linear regression (MLR) is utilized [79, 80]. Regression is normally used to make predictions. MLR assumes that the explanatory and response variables have a linear relationship, that the data has a normal distribution, that there are no extreme values, and that there are no multiple ties between the explanatory variables. MLR also synchronically accounts for the variance of the explanatory variable in the response variables [81].

Stepwise regression

Stepwise regression is also a multivariate modelling technique in which an explanatory variable is added or removed from the linear model at each step. In each step, the variable that increases the R^2 coefficient the most is added to the model [82, 83]. In contrast to MLR, stepwise regression does not incorporate all the explanatory variables into the model but instead evaluates their statistical significance one at a time. It is typically used when investigating numerous explanatory variables. In this work, the regression models were performed in IBM SPSS Statistics version 25.

Artificial neural network (ANN)

Artificial neural network (ANN) is a machine learning technique that is now extensively used in mineral processing to identify complex relationships between input and output data using a series of nonlinear functions [84–86]. Unlike regression, ANN can be trained to learn and recognize patterns between the inputs and outputs [87]. One of the many benefits of using ANN is that it tolerates data noise [88]. ANN has been employed for optimization of leaching and extraction processes of precious metals (i.e., Cu, REEs, etc.) in several studies [75, 86, 88, 89].

ANN is essentially a computer model that simulates the brains learning mechanism. ANN consists of nodes or neurons which are processors that operate in a parallel way. The neurons are arranged in layers including an input layer, one or more hidden layers, and an output layer. The neurons are interconnected to one another through connection links carrying specific weights.

In this work, the feed-forward ANN using back-propagation algorithm was used to model the relationship between the explanatory variables and the REE leaching efficiency using MATLAB R2021b. Back-propagation algorithm is a method of reducing the error between output and input data by altering the weighted connections between neurons [90]. The architecture of the 4-9-5 neural network used in this work is shown in Fig. 2.

Results and discussion

Experimental leaching output

Acid concentration, temperature, time, and *S*/*L* ratio were optimized to maximize the efficiency of REE leaching from PG. The variables used in this work are based on previous experimental works [41, 51–53, 55]. Strong inorganic acids (i.e., HCl, HNO_3, and H_2SO_4) were extensively used for the investigation of REE leaching from other than Philippine PG [91, 92]. H_2SO_4 was also used for leaching experiments from Florida PG by Gaetjens et al. [93] and Liang et al. [94], Russian PG by Lokshin et al. [95, 96], and Brazilian PG by Lütke et al. [53].

We performed a total of 18 leaching setups, repeated 3 times each to guarantee high accuracy of the results. The

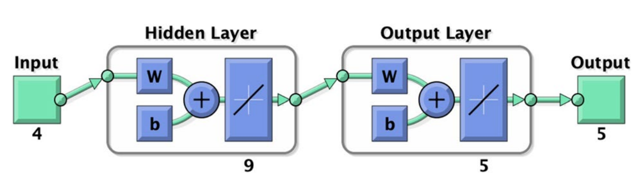

Fig. 2 ANN structure for the optimization of REE leaching from PG in the 4-9-5 form

total experimental design matrix and the obtained REE leaching efficiencies are presented in Table 3. The leaching efficiencies for La, Ce, Nd, Y, and TREE ranged from 17 to 75%, 12 to 72%, 13 to 71%, 14 to 68%, and 14 to 71%. The setup with the highest TREE leaching efficiency was test number 6 which used 10% H_2SO_4, at 50 °C, a leaching time of 120 min, and a 1:5 *S*/*L* ratio.

For all the REEs, the leaching efficiencies followed the same trend in each of the leaching steps as shown in Figs. 3A–D. The efficiency of REE leaching increased with higher acid concentrations (Fig. 3A). This can be attributed to bisulfate formation that causes an increase in Ca^{2+} concentration after the reaction between H^+ with SO_4^{2-} as a result of increased gypsum solubility that controls the REE leaching efficiency since the gypsum hosts the REEs [32]. The temperature has a catalytic effect so that the leaching efficiency increased as the temperature increased from 40 °C to 50 °C ($p < 0.05$) as shown in Fig. 3B. The results for 50 °C to 80 °C are not significantly different ($p > 0.05$), although 50 °C leached the most REEs in the experiment. Generally, leaching efficiencies decrease at higher temperatures due to dissolution of fluoride precipitates which then reacts with the REEs and forms an insoluble precipitate [92]. The majority of the REEs leached from the PG after 15 min (Fig. 3C) although the setup with leaching time of 120 min leached the most REEs. Considering the economics in an industrial scale, we used 30 min for the final step of the optimization procedure. Leaching kinetic studies also show that the maximum REEs were leached from the PG after 20 min [53, 55]. Lastly, the most diluted mixture (1:10 *S*/*L* ratio) leached most of the REEs although the results of 1:3, 1:4, and 1:5 were not very different (Fig. 3D). The slight decrease in leaching efficiency observed for 1:5 is not significantly different ($p > 0.05$) with the results of 1:3 and 1:4. In some cases studied, a decrease in leaching efficiency could be explained with reaching the gypsum solubility limit [55]. In general, it is not desirable to have increased Ca^{2+} concentration in the solution because it can compete with REEs for available binding sites on the leaching agents. This means that if there is an excess of Ca^{2+} ions in the solution, they may bind to the leaching agents instead, which reduces the efficiency of the REE leaching process.

The Pearson correlation coefficients *r* between the independent variables (*C* H_2SO_4, *T*, *t*, and *S*/*L* ratio) and the dependent variables (La, Ce, Nd, Y, and TREE) is shown in Table 4. Among the explanatory variables, C H_2SO_4 has the highest *r* 0.918 to 0.956 ($p < 0.01$), followed by T with *r* 0.681–0.739 ($p < 0.01$). It is noteworthy that t has a negative *r* while the *S*/*L* ratio has a small positive *r*. Both were not significant ($p > 0.05$). Although the variables that should be used in regression models are for $r > 0.3$, we still used t and the *S*/*L* ratio in the regression models.

Determining the optimum leaching conditions using Taguchi method

Although the design of the experiment is not based on the orthogonal array suggested by Taguchi, we still used the

Table 3 Experimental matrix and the resulting La, Ce, Nd, Y, and TREE leaching efficiencies (%)

Te st number	C (%)	T (°C)	*t* (mins)	*S*/*L* ratio (g mL^{-1})	La (%)	Ce (%)	Nd (%)	Y (%)	TREE (%)
1	1	28	120	1:5	16.5 ± 1.1	11.9 ± 1.2	12.9 ± 1.4	13.7 ± 0.6	13.7 ± 0.9
2	2.5	28	120	1:5	30.8 ± 0.7	26.1 ± 0.9	26.5 ± 0.8	30.4 ± 0.8	28.4 ± 0.6
3	5	28	120	1:5	39.7 ± 2.1	35.8 ± 2.3	35.2 ± 2.0	40.3 ± 1.6	37.7 ± 1.9
4	10	28	120	1:5	58.7 ± 4.8	57.6 ± 5.0	52.7 ± 4.2	56.4 ± 3.7	55.9 ± 4.3
5	10	40	120	1:5	62.4 ± 0.7	61.3 ± 0.8	55.9 ± 0.8	58.5 ± 0.8	58.8 ± 0.8
6	10	50	120	1:5	74.6 ± 2.9	72.4 ± 2.5	70.6 ± 3.6	68.2 ± 2.5	71.0 ± 2.9
7	10	60	120	1:5	69.5 ± 5.5	67.6 ± 4.8	64.4 ± 7.1	63.2 ± 4.2	65.6 ± 5.5
8	10	70	120	1:5	64.8 ± 2.7	63.6 ± 2.3	58.4 ± 3.6	59.0 ± 1.9	60.8 ± 2.6
9	10	80	120	1:5	73.3 ± 5.9	70.9 ± 5.5	68.9 ± 7.0	66.1 ± 5.3	69.2 ± 6.0
10	10	50	5	1:5	57.7 ± 2.1	53.8 ± 2.3	49.5 ± 2.2	52.4 ± 1.4	52.9 ± 1.9
11	10	50	15	1:5	62.6 ± 0.2	58.7 ± 0.2	53.6 ± 1.0	56.2 ± 0.8	57.1 ± 0.5
12	10	50	30	1:5	63.0 ± 0.2	59.2 ± 0.5	53.9 ± 0.3	57.1 ± 0.8	57.6 ± 0.5
13	10	50	45	1:5	64.1 ± 0.3	60.4 ± 0.1	55.4 ± 0.3	58.5 ± 0.7	59.0 ± 0.3
14	10	50	60	1:5	63.9 ± 0.9	60.4 ± 0.7	55.3 ± 1.3	57.6 ± 0.8	58.7 ± 0.8
15	10	50	30	1:2	61.4 ± 0.8	59.4 ± 0.8	52.5 ± 0.9	57.5 ± 0.5	57.2 ± 0.7
16	10	50	30	1:3	63.9 ± 0.8	61.7 ± 0.9	55.1 ± 0.6	59.9 ± 1.1	59.6 ± 0.8
17	10	50	30	1:4	64.0 ± 0.2	62.0 ± 0.2	55.5 ± 0.3	59.8 ± 0.6	59.7 ± 0.1
18	10	50	30	1:10	65.5 ± 0.5	63.4 ± 0.4	57.0 ± 0.4	60.8 ± 0.7	61.1 ± 0.5

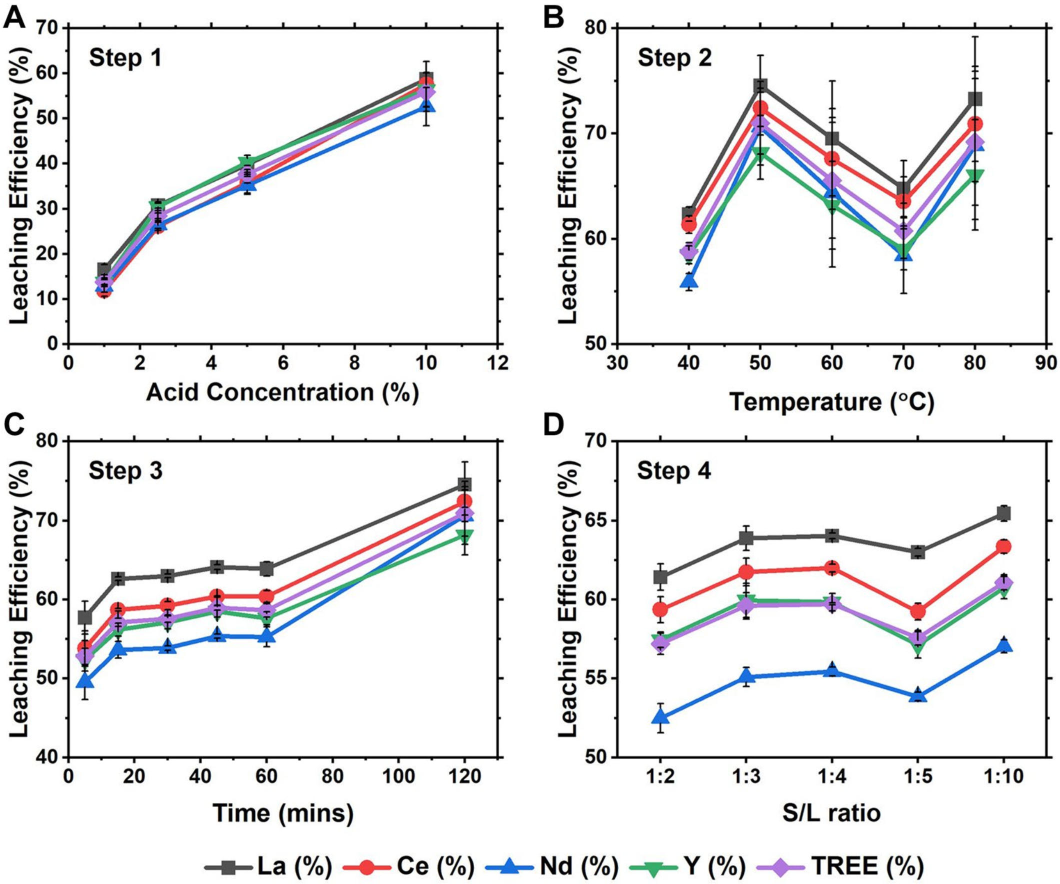

Fig. 3 Effects of **A** acid concentration, **B** temperature, **C** time, and **D** solid-to-liquid ratio on the leaching efficiency of REEs in H_2SO_4

Table 4 Pearson correlation coefficient between the explanatory variables and specific REE leaching efficiency

	C	*T*	*t*	SL ratio
La	0.955*	0.730*	− 0.269	0.053
Ce	0.956*	0.722*	− 0.240	0.063
Nd	0.918*	0.739*	− 0.151	0.014
Y	0.952*	0.681*	− 0.252	0.074
TREE	0.946*	0.720*	− 0.226	0.052

*$p<0.01$ to denote that the correlation is significant at the 99% confidence interval

Taguchi method to determine the optimum combination of variables. The result of the REE leaching efficiency was converted to signal-to-noise (*S*/*N*) ratios. The *S*/*N* ratio is a measure of deviation of quality characteristics from the ideal values [77]. There are three different types of *S*/*N* ratios (i.e., nominal value is better, smaller is better, and larger is better) depending on the data characteristics [78]. In this work, the larger is better type was used building on the work of Brest Kasongo and Mwanat [75]. Thus, the levels of the explanatory variables with the highest average S/N ratios are considered optimal. The result of this method can therefore determine the optimum levels and combination of the variables to maximize REEs leaching from PG. The square of responses, inverse of the square of responses, and *S*/*N* for the REE yield for each of the experiments is shown in Table 5.

The average *S*/*N* ratios of the explanatory variables at different levels for specific REE leaching is shown in Table 6. For all the REEs, the highest average *S*/*N* ratios corresponded to level 4 (10% H_2SO_4) for the acid concentration, level 6 (80 °C) for the temperature, level 3 (30 min—Y and TREE) to level 4 (45 min—La, Ce, and Nd) for the time, and level 1 (1:10) for the *S*/*L* ratio. Therefore, the optimum combination of the variables for the maximum leaching of REEs in PG is 10% H_2SO_4, 80 °C, 30–45 min, and 1:10 for the acid concentration, temperature, time, and *S*/*L* ratio, respectively.

Aside from finding the optimum combination of the variables, the Taguchi method also ranks the variables according to their overall importance to REE leaching efficiency. Also shown in Table 6 are the deltas and ranks of the explanatory variables which compare the relative magnitude of their effects. The delta is the difference between the highest and lowest average S/N ratio of each variable. And for this work, the higher the delta, the greater is the influence

Table 5 Square of responses, inverse square of responses and S/N ratios of the REEs for each experimental setup

Test number	Square of responses					Inverse of the square of responses					*S/N* ratios				
	La	Ce	Nd	Y	TREE	La	Ce	Nd	Y	TREE	La	Ce	Nd	Y	TREE
1	273	141	166	189	188	0.0037	0.0071	0.0060	0.0053	0.0053	24.36	21.48	22.21	22.75	22.75
2	948	681	702	926	807	0.0011	0.0015	0.0014	0.0011	0.0012	29.77	28.33	28.46	29.67	29.07
3	1579	1279	1238	1622	1419	0.0006	0.0008	0.0008	0.0006	0.0007	31.99	31.07	30.93	32.10	31.52
4	3449	3315	2774	3180	3123	0.0003	0.0003	0.0004	0.0003	0.0003	35.38	35.20	34.43	35.02	34.95
5	3888	3763	3124	3420	3457	0.0003	0.0003	0.0003	0.0003	0.0003	35.90	35.76	34.95	35.34	35.39
6	5560	5245	4990	4647	5037	0.0002	0.0002	0.0002	0.0002	0.0002	37.45	37.20	36.98	36.67	37.02
7	4834	4569	4149	3992	4297	0.0002	0.0002	0.0002	0.0003	0.0002	36.84	36.60	36.18	36.01	36.33
8	4195	4039	3412	3480	3692	0.0002	0.0002	0.0003	0.0003	0.0003	36.23	36.06	35.33	35.42	35.67
9	5370	5028	4744	4366	4790	0.0002	0.0002	0.0002	0.0002	0.0002	37.30	37.01	36.76	36.40	36.80
10	3331	2895	2454	2744	2796	0.0003	0.0003	0.0004	0.0004	0.0004	35.23	34.62	33.90	34.38	34.46
11	3923	3446	2878	3159	3263	0.0003	0.0003	0.0003	0.0003	0.0003	35.94	35.37	34.59	35.00	35.14
12	3969	3508	2901	3263	3316	0.0003	0.0003	0.0003	0.0003	0.0003	35.99	35.45	34.63	35.14	35.21
13	4112	3647	3065	3424	3477	0.0002	0.0003	0.0003	0.0003	0.0003	36.14	35.62	34.86	35.35	35.41
14	4081	3647	3055	3322	3440	0.0002	0.0003	0.0003	0.0003	0.0003	36.11	35.62	34.85	35.21	35.37
15	3773	3523	2756	3301	3271	0.0003	0.0003	0.0004	0.0003	0.0003	35.77	35.47	34.40	35.19	35.15
16	4081	3812	3036	3594	3553	0.0002	0.0003	0.0003	0.0003	0.0003	36.11	35.81	34.82	35.56	35.51
17	4102	3843	3075	3581	3567	0.0002	0.0003	0.0003	0.0003	0.0003	36.13	35.85	34.88	35.54	35.52
18	4285	4013	3254	3691	3732	0.0002	0.0002	0.0003	0.0003	0.0003	36.32	36.04	35.12	35.67	35.72

of the variable which assigns their rankings. Based on the delta, the ranking of the variables according to their overall importance to REE leaching in PG is as follows: acid concentration > temperature > time > *S/L* ratio.

Modelling of REE leaching efficiency using MLR

Multiple linear regression (MLR) models the linear association between the independent/explanatory variables (i.e., *C*, *T*, *t*, *S/L* ratio) and the dependent/response (i.e., La_{eff}, Ce_{eff}, Nd_{eff}, Y_{eff}, and $TREE_{eff}$) variables. We used the first order MLR to model the leaching efficiencies of REEs in PG using the explanatory variables. The MLR model used in this work follows the form proposed by Uyanık and Güler [81]:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i \cdot X_i \tag{5}$$

where β_0 is the coefficient of the intercept or the constant and β_i is the slope or the coefficient of the explanatory variable X_i [89]. The significance of the explanatory variable for inclusion in the linear model was validated using *p* values ($p \leq 0.05$) or Sig. For all the REEs, the regression statistics show an R^2 of 0.938–0.961, adjusted R^2 of 0.919–0.949, standard error of 3.534–4.025, and an overall *p* value of 0.000. The coefficients, *p* values, and the 95% confidence intervals of the explanatory variables are shown in Table 7.

Based on these values, the forms of the MLR models for the leaching efficiencies of the specific REEs are:

$$La_{eff}(\%) = 5.889 + 4.701\,C\,H_2SO_4 + 0.194T \tag{6}$$

$$Ce_{eff}(\%) = -1.943 + 5.119\,C\,H_2SO_4 + 0.181\,T + 0.058\,t \tag{7}$$

$$Nd_{eff}(\%) = -1.873 + 4.434\,C\,H_2SO_4 + 0.216\,T + 0.074\,t \tag{8}$$

$$Y_{eff}(\%) = 6.183 + 4.518\,C\,H_2SO_4 + 0.048\,t \tag{9}$$

$$TREE_{eff}(\%) = 2.138 + 4.630\,C\,H_2SO_4 + 0.056\,t \tag{10}$$

The regression models confirmed the results of the Pearson correlation and Taguchi method that the *S/L* ratio is not a particularly important variable in determining the leaching efficiency of REEs. *T* is significant for La_{eff}, Ce_{eff}, and Nd_{eff} whereas t is significant for all except for La_{eff}. For all the REEs, C H_2SO_4 is the most significant variable.

We validated the models using the experimental parameters in Table 3. Using the models, we found very good correspondence between the experimental and predicted values (Fig. 4A) with $r_{\text{Expt-Predicted}}$ ($p < 0.01$) of 0.983, 0.989, 0.990, 0.977, and 0.966 for La_{eff}, Ce_{eff}, Nd_{eff}, Y_{eff}, and $TREE_{eff}$ models, respectively. We also computed the deviation of the predicted values from the experimental values using the % error. The performance

Table 6 Response for signal/noise ratio of the explanatory variables and their corresponding levels

Level	*C*	*T*	*t*	*S/L* ratio
La				
1	24.36	30.37	35.23	36.32
2	29.77	35.90	35.94	34.62
3	31.99	36.12	36.06	36.13
4	36.19	36.84	36.14	36.11
5		36.23	36.11	35.77
6		37.30	33.91	
Delta	11.82	6.93	2.23	1.70
Rank	1	2	3	4
Ce				
1	21.48	29.02	34.62	36.04
2	28.33	35.76	35.37	33.96
3	31.07	35.70	35.72	35.85
4	35.84	36.60	35.62	35.81
5		36.06	35.62	35.47
6		37.01	33.19	
Delta	14.37	7.99	2.53	2.08
Rank	1	2	3	4
Nd				
1	22.21	29.01	33.90	35.12
2	28.46	34.95	34.59	33.50
3	30.93	34.90	34.77	34.88
4	35.11	36.18	34.86	34.82
5		35.33	34.85	34.40
6		36.76	32.91	
Delta	12.91	7.75	1.95	1.62
Rank	1	2	3	4
Y				
1	22.75	29.89	34.38	35.67
2	29.67	35.34	35.00	33.89
3	32.10	35.37	35.42	35.54
4	35.46	36.01	35.35	35.56
5		35.42	35.21	35.19
6		36.40	33.27	
Delta	12.71	6.52	2.15	1.78
Rank	1	2	3	4
TREE				
1	22.75	29.57	34.46	35.72
2	29.07	35.39	35.14	33.93
3	31.52	35.45	35.42	35.52
4	35.58	36.33	35.41	35.51
5		35.67	35.37	35.15
6		36.80	33.28	
Delta	12.83	7.23	2.14	1.78
Rank	1	2	3	4

of each model based on the average % error computed from the 18 experimental tests (Fig. 4B) is in the order of 7.08 ± 3.59% (La_{eff}) < 7.38 ± 9.66% (Nd_{eff}) < 8.17 ± 8.90% (Ce_{eff}) < 11.02 ± 8.48% (Y_{eff}) < 13.53 ± 6.72 ($TREE_{eff}$).

Modelling of REE leaching efficiency using stepwise regression

Leaching efficiency of TREEs can also be affected by an interaction among the different parameters. To determine such effects, we developed a first order multiple linear regression model with interaction effects between the explanatory variables using stepwise regression. The model follows the general form of:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i \cdot X_i + \sum_{i=1}^{k-1} \sum_{j=i+1}^{k} \beta_{ij} \cdot X_i \cdot X_j + \sum_{i=1}^{k-2} \sum_{j=k+1}^{k-1} \sum_{l=j+1}^{k} \beta_{ijl} \cdot X_i \cdot X_j \cdot X_k \tag{11}$$

where k is the number of explanatory variables [89]. A total of 18 interactions were analyzed including C H_2SO_4, T, t, S/L, C H_2SO_4·C H_2SO_4, C H_2SO_4·T, C H_2SO_4·t, C H_2SO_4·S/L, T·T, T·t, T·S/L, t•t, t·S/L, S/L·S/LI, C H_2SO_4·T·t, C H_2SO_4·T·S/L, C H_2SO_4·t·S/L, and T·t•S/L. The stepping method criteria used for inclusion in the model is the probability of F (entry ≤ 0.05 and removal ≥ 0.10). The coefficients, p values, 95% confidence interval, and other relevant statistics of the stepwise regression models of the possible interactions between the explanatory variables are presented in Table 8. For each of the REEs, two regression models were produced but the second model was selected for its non-multicollinearity such that Tolerance > 0.1 and VIF < 10 [89].

Among these possible interactions, we found that only C H_2SO_4 is significant for modelling the leaching efficiencies of all the REEs. The stepwise regression verifies the previous result of the MLR that the S/L ratio and its possible interaction with the other explanatory variables is not significant for the REE leaching efficiency from PG. And like the previous MLR models, there were very high accuracies in the regression models with R^2 = 0.936–0.960, adjusted R^2 = 0.928–0.955, a standard error of 3.3121–3.7875, and an overall p value of 0.000–0.011.

The analytical forms of the leaching models based on the interaction between the explanatory variables are therefore:

$$La_{eff}(\%) = 14.686 + 4.613\, C\, H_2SO_4 \tag{12}$$

Table 7 First order MLR model of the explanatory variables

Model		Unstandardized coefficients		Standardized coefficients	t	Sig	95.0% Confidence interval for B		Correlations			Collinearity statistics	
		B	Std. error	Beta			Lower bound	Upper bound	Zero-order	Partial	Part	Tolerance	VIF
Coefficients (La_{eff})													
1	(Constant)	5.889	5.052		1.166	0.265	− 5.024	16.803					
	C	4.701	0.441	0.897	10.664	0.000	3.748	5.653	0.955	0.947	0.629	0.492	2.035
	T	0.194	0.082	0.184	2.382	0.033	0.018	0.370	0.730	0.551	0.141	0.585	1.711
	t	0.041	0.021	0.131	1.926	0.076	− 0.005	0.087	− 0.269	0.471	0.114	0.755	1.325
	S/*L* ratio	− 0.045	0.112	− 0.024	− 0.397	0.698	− 0.287	0.198	0.053	− 0.109	− 0.023	0.930	1.075
Coefficients (Ce_{eff})													
1	(Constant)	− 1.943	4.943		− 0.393	0.701	− 12.622	8.735					
	C	5.119	0.431	0.927	11.868	0.000	4.187	6.051	0.956	0.957	0.650	0.492	2.035
	T	0.181	0.080	0.162	2.264	0.041	0.008	0.353	0.722	0.532	0.124	0.585	1.711
	t	0.058	0.021	0.174	2.764	0.016	0.013	0.103	− 0.240	0.608	0.151	0.755	1.325
	S/*L* ratio	− 0.011	0.110	− 0.005	− 0.096	0.925	− 0.248	0.227	0.063	− 0.027	− 0.005	0.930	1.075
Coefficients (Nd_{eff})													
1	(Constant)	− 1.873	5.629		− 0.333	0.745	− 14.034	10.289					
	C	4.434	0.491	0.890	9.027	0.000	3.373	5.495	0.918	0.929	0.624	0.492	2.035
	T	0.216	0.091	0.215	2.378	0.033	0.020	0.412	0.739	0.551	0.164	0.585	1.711
	t	0.074	0.024	0.248	3.120	0.008	0.023	0.126	− 0.151	0.654	0.216	0.755	1.325
	S/*L* ratio	− 0.057	0.125	− 0.033	− 0.454	0.657	− 0.327	0.213	0.014	− 0.125	− 0.031	0.930	1.075
Coefficients (Y_{eff})													
1	(Constant)	6.183	5.211		1.187	0.257	− 5.074	17.411					
	C	4.518	0.455	0.960	9.937	0.000	3.536	5.501	0.952	0.940	0.673	0.492	2.035
	T	0.095	0.084	0.100	1.131	0.278	− 0.087	0.277	0.681	0.299	0.077	0.585	1.711
	t	0.048	0.022	0.169	2.166	0.049	0.000	0.095	− 0.252	0.515	0.147	0.755	1.325
	S/*L* ratio	0.004	0.116	0.002	0.033	0.974	− 0.246	0.254	0.074	0.009	0.002	0.930	1.075
Coefficients ($TREE_{eff}$)													
1	(Constant)	2.138	5.170		0.413	0.686	− 9.032	13.307					
	C	4.630	0.451	0.920	10.264	0.000	3.656	5.605	0.946	0.943	0.645	0.492	2.035
	T	0.169	0.083	0.167	2.025	0.064	− 0.011	0.349	0.720	0.490	0.127	0.585	1.711
	t	0.056	0.022	0.184	2.543	0.025	0.008	0.103	− 0.226	0.576	0.160	0.755	1.325
	S/*L* ratio	− 0.024	0.115	− 0.014	− 0.208	0.838	− 0.272	0.224	0.052	− 0.058	− 0.013	0.930	1.075

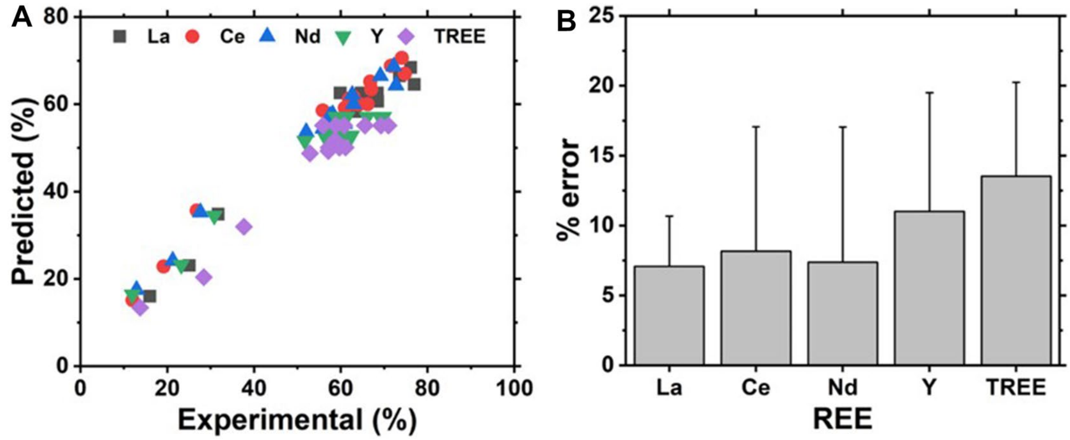

Fig. 4 **A** Comparison of the experimental REE leaching efficiencies and predicted REE leaching efficiencies using the MLR model, and the **B** the deviation of the predicted values from the experimental values using the % error

$$Ce_{eff}(\%) = 9.517 + 4.820\, C\, H_2SO_4 \tag{13}$$

$$Nd_{eff}(\%) = 11.703 + 3.989\, C\, H_2SO_4 \tag{14}$$

$$Y_{eff}(\%) = 14.785 + 4.157\, C\, H_2SO_4 \tag{15}$$

$$TREE_{eff}(\%) = 12.804 + 4.324\, C\, H_2SO_4 \tag{16}$$

Validation of the model showed a very high correlation between the experimental and predicted values (Fig. 5A) with $r_{Expt\text{-}Predicted}$ ($p < 0.01$) = 0.914, 0.915, 0.918, 0.970, and 0.946 for La, Ce, Nd, Y, and TREE, respectively. Meanwhile, the average % error of the models is in the following order: Y (6.54 ± 9.24%) < L (7.58 ± 5.61%) < Ce (8.81 ± 6.63%) < TREE (8.89 ± 7.23%) < Nd (10.75 ± 8.03) as shown in Fig. 5B.

The regression models consistently eliminate the significance of the *S*/*L* ratio. This makes sense since the leaching efficiency only increased by 3–5% as the mixture became more diluted in Step 4 of the experimental procedure (Fig. 2D). Unlike the previous regression model, the stepwise regression of possible interaction between the parameters eliminated the significance of T and t in the leaching of REEs. To validate the role of the *S*/*L* ratio that may probably not observe linear patterns, the ANN was used to find hidden patterns that the regression models were not able to identify.

Modelling of REE leaching efficiency using ANN

The modelling was carried out using a 4-9-5 architecture based on the recommendation by the improved version of the Kolmogorov theorem called the Kolmogorov Mapping Neural Network Existence Theorem. This theorem recommends a three-layer neural network composing of n inputs, $2n+1$ hidden layers, and m outputs [97]. Thus, the 4-9-5 ANN architecture corresponds to 4 neurons in the input layer, 9 neurons in one hidden layer, and 5 neurons in the output layer. The *nntool* was used to perform the computation in MATLAB R2021b. By default, this tool uses 70% of the data for training, 15% for validation, and 15% for testing.

The Levenberg–Marquardt backpropagation algorithm that updates the values of weights according to the Levenberg–Marquardt optimization was used to train a feedforward ANN. In a backpropagation algorithm, the network continues until convergence or a maximum number of iterations is reached [98]. The *pureline* function was used as the activation function in the ANN structure. The number of epochs was set at an initial of 100 but the training process stopped after 3 iterations. The training stops when the model with the lowest root mean squared error on single test points is found. The correlation coefficient *R* for the training of the final model was 0.98073. The *R* values for the testing and the overall model were 0.98039 and 0.97379, respectively. The results are shown in Figs. 6A–C. The leaching efficiencies of REEs from PG can be predicted at very high accuracy using ANN. In contrast to the results of the regression models, the ANN was able to accurately predict REE leaching efficiency with very high R values even after considering the *S*/*L* ratio.

Conclusions

This work investigated for the first time, the leaching efficiency of the REEs from Philippine PG with H_2SO_4 and optimized the relevant parameters: acid concentration > temperature > time > solid-to-liquid ratio using Taguchi method, regression, and ANN analysis. A TREEs leaching efficiency of 71% (La 75%, Ce 72%, Nd 71% and Y 63%) was realized and it could be shown that the modelling approaches

Table 8 Stepwise regression model of the interaction effects with significant p ($p < 0.05$) including their coefficients, p values, and the 95% confidence intervals

Model		Unstandardized coefficients		Standardized coefficients	t	Sig	95.0% Confidence interval for B		Correlations			Collinearity Statistics	
		B	Std. error	Beta			Lower bound	Upper bound	Zero-order	Partial	Part	Tolerance	VIF
Coefficients (La_{eff})													
1	(Constant)	14.623	3.573		4.093	0.001	7.049	22.197					
	C	5.005	0.387	0.955	12.924	0.000	4.184	5.826	0.955	0.955	0.955	1.000	1.000
2	(Constant)	14.686	2.749		5.342	0.000	8.826	20.547					
	C	4.613	0.319	0.880	14.473	0.000	3.934	5.292	0.955	0.966	0.823	0.874	1.144
	$C\,T\,t$	0.000	0.000	0.211	3.467	0.003	0.000	0.000	0.523	0.667	0.197	0.874	1.144
Coefficients (Ce_{eff})													
1	(Constant)	9.444	3.752		2.517	0.023	1.490	17.398					
	C	5.275	0.407	0.956	12.972	0.000	4.413	6.137	0.956	0.956	0.956	1.000	1.000
2	(Constant)	9.517	2.615		3.640	0.002	3.944	15.091					
	C	4.820	0.303	0.873	15.900	0.000	4.174	5.466	0.956	0.972	0.816	0.874	1.144
	$C\,T\,t$	0.000	0.000	0.233	4.236	0.001	0.000	0.000	0.542	0.738	0.217	0.874	1.144
Coefficients (Nd_{eff})													
1	(Constant)	11.609	4.566		2.542	0.022	1.929	21.289					
	C	4.570	0.495	0.918	9.233	0.000	3.520	5.619	0.918	0.918	0.918	1.000	1.000
2	(Constant)	11.703	2.990		3.914	0.001	5.329	18.076					
	C	3.989	0.347	0.801	11.508	0.000	3.250	4.728	0.918	0.948	0.749	0.874	1.144
	$C\,T\,t$	0.000	0.000	0.329	4.723	0.000	0.000	0.000	0.613	0.773	0.307	0.874	1.144
Coefficients (Y_{eff})													
1	(Constant)	14.732	3.308		4.453	0.000	7.719	21.745					
	C	4.482	0.359	0.952	12.500	0.000	3.722	5.242	0.952	0.952	0.952	1.000	1.000
2	(Constant)	14.785	2.742		5.393	0.000	8.941	20.629					
	C	4.157	0.318	0.883	13.081	0.000	3.480	4.835	0.952	0.959	0.826	0.874	1.144
	$C\,T\,t$	9.027E-05	0.000	0.195	2.880	0.011	0.000	0.000	0.508	0.597	0.182	0.874	1.144
Coefficients ($TREE_{eff}$)													
1	(Constant)	12.733	3.749		3.396	0.004	4.785	20.681					
	C	4.761	0.406	0.946	11.716	0.000	3.899	5.622	0.946	0.946	0.946	1.000	1.000
2	(Constant)	12.804	2.732		4.687	0.000	6.981	18.626					
	C	4.324	0.317	0.859	13.654	0.000	3.649	4.999	0.946	0.962	0.804	0.874	1.144
	$C\,T\,t$	0.000	0.000	0.245	3.891	0.001	0.000	0.000	0.550	0.709	0.229	0.874	1.144

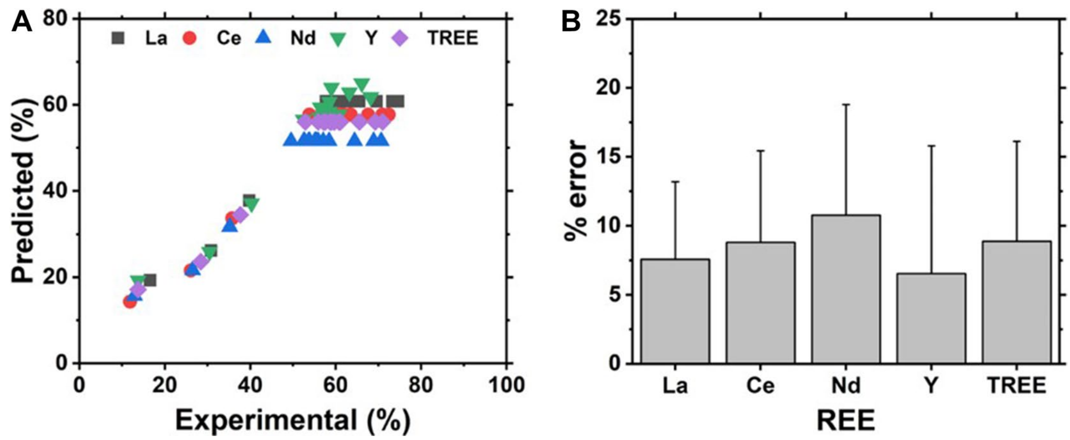

Fig. 5 **A** Comparison of the experimental TREE leaching efficiency and predicted TREE using the stepwise regression model of interaction effects, and the **B** the deviation of the predicted values from the experimental values using the % error

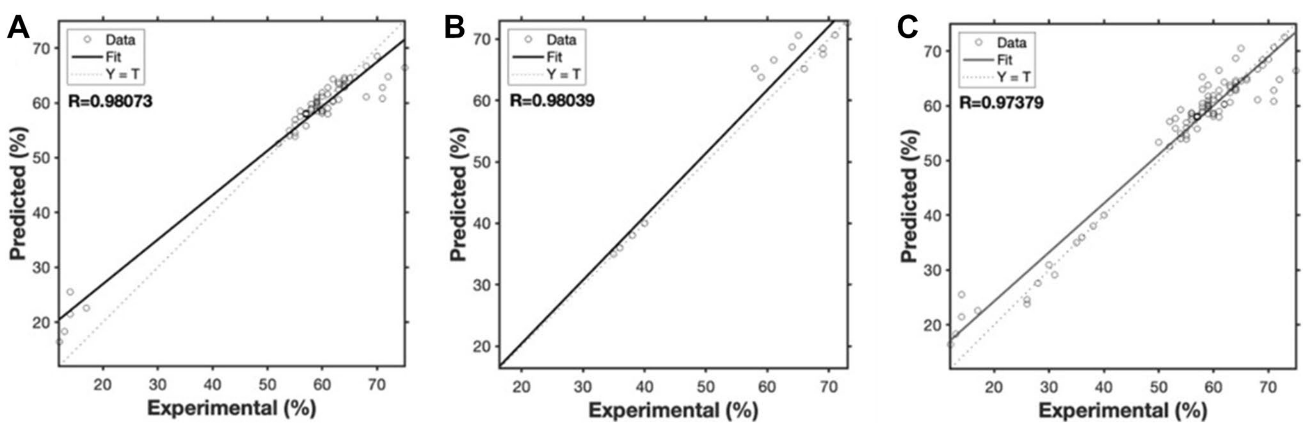

Fig. 6 Leaching efficiency predicted by the neural network in the **A** training, **B** testing, and **C** the overall model versus the experimental leaching efficiency showed very high R using the 4-9-5 ANN architecture

are powerful tools to predict and optimize the leaching efficiencies of REEs from Philippine PG. The experiments described here, though very successful, were all conducted at laboratory scale, and it is recommended to conduct larger pilot plant scale experiments next, to better understand the potential of REE recovery from Philippine PG on larger scale.

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