FEASIBILITY OF THE CENTRAL COMPOSITE ROTATABLE DESIGN IN COPPER EXTRACTION EXPERIMENTS FROM PRINTED CIRCUIT BOARDS OF TABLETS

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Declarations of interest: none

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Abstract

Tablets entered the Brazilian market in 2010, selling as many as 36,000 units by 2017, but it is estimated that in 2015, this number already amounted to 248 million units worldwide. Unlike other e-waste, tablet waste production is more recent, and very little is known about its composition and recycling paths. Studies using the Central Composite Rotatable Design (CCRD) method to evaluate the recycling of e-waste can be used as an optimized option for the evaluation of e-waste recycling options, replacing the experiments that involve the Full Factorial Design (FFD) method. The goal of this study was to evaluate the applicability of the CCRD method in acid leaching of copper from printed circuit boards (PCB) of tablets by analyzing two variables: liquid solid ratio and concentration of HNO_3. The methodology initially involved the characterization of PCBs. Then, the optimum copper extraction conditions were evaluated through acid leaching using HNO_3, and the extraction was followed by comparative statistical analysis of the CCRD and FFD methods. The copper concentration in tablet PCBs was about 25% w/w, and the optimum copper extraction conditions (90%) were 56g/L (solid/liquid ratio) and 1M HNO_3 concentration. Statistical analysis showed that copper extraction by the CCRD method reached 85%, and the S/L ratio was the most influential in copper extraction. The generated mathematical models were statistically significant, demonstrating that the CCRD method can be applied to copper extraction studies from PCB.

*Keywords***:** printed circuit boards, tablets, acid leaching, Full Factorial Design, Central Composite Rotatable Design.

1. Introduction

Waste Electrical and Electronic Equipment (WEEE) can be defined as any type of electro-electronic equipment that is damaged, obsolete, or has reached the end of its useful life, which has been increasingly generated worldwide [1-3].

In 2014, United Nations University (UNU) reported a global generation of 41.8 million tons of WEEE [4], reaching 50 million tons in 2018 [5]. Of the total reported for 2014, 3 million tons were related to waste Technology Information and Communication (TIC) equipment, such as notebooks, tablets, and smartphones. Introduced in Brazil as of 2010, tablet sales volume in the country increased 800% from 2010 to 2014 [6], becoming rapidly obsolete as also observed for other TIC equipment.

The high volume of tablet sales in replacement of notebooks is possibly due to increased mobility, adequate screen size, resolution, and internet access [7, 8]. Thus, Martinho et al. [7] pointed out that the volume of tablet sales was approximately 248 million units in 2015.

Although the volume of tablets that have reached the end of their useful life is not as expressive as that of desktops, smartphones, and notebooks, their representativeness in the world scenario calls attention to the need for their disposal management. The environmental liability that will grow in the coming years, along with other types of e-waste, is notable.

Recycling of WEEE warrants the extraction of metals from printed circuit boards (PCB) that have economic potential, due to the presence of metals such as copper, precious metals, and other metals that are considered "critical" [8]. Despite the well-known heterogeneity of PCB, copper is commonly found in greater quantities and, on average, reaches 20% by mass of PCBs [1] with concentration varying in the range of 100 to 350g/kg [9-12].

According to Fowler [13], metals and/or metal compounds are recovered from PCBs at varying degrees of efficiency, depending on their value. In the case of copper, which has lower market value when compared to precious metals, the extraction is justified by the concentration found, in addition to minimizing the extraction of non-renewable natural resources from primary sources [12, 14, 15].

To recover metals present in PCBs, pyrometallurgical and hydrometallurgical processes are traditionally used [11, 16-20]. In these studies, the Full Factorial Design (FFD) method is usually used for experimental planning. According to Mendonça [21], the factorial design is an experimental procedure and analysis of observations when there are two or more factors that can influence the outcome of the response variable. However, in experiments using FFD, the number of treatments is generally high, since they involve all possible combinations between the levels of the investigated factors.

In order to optimize experiments for minimizing costs and operational times, the Central Composite Rotatable Design (CCRD) experimental planning method consists of a set of procedures, statistical and mathematical, that can be applied in the study of the interrelationships between one or more responses (dependent variables) with numerous factors (independent variables) [22].

The use of CCRD to optimize and model variables that can be influenced by different responses of experiments is described in several researches from different areas. For example, Núñez-Gómez et al.

[23] performed acid mine drainage remediation with shrimp and aquaculture farming waste and reported that the CCRD was an “economical way of obtaining the maximum amount of information in a short period of time with the fewest number of experiments”. Furthermore, Azizi et al. [24] in the leaching process to extracting Mn from a low-grade manganese ore. Only 28 experiments were conducted to determine the optimum conditions for the leaching process with the highest Mn recovery, the lowest consumption of chemical materials, and minimum time and temperature using the following ranges: sulfuric acid dosage of 1%−9%; oxalic acid dosage of 27.5−57.5 g/L; time of 45−105 min; and temperature of 55−95 °C.

Javed et al. [25] applied CCRD in the experimental optimization of HNO_3 leaching of copper from old AMD Athlon processors, also a type of e-waste, in order to investigate the effect of ultrasonic irradiation from 0 to 300 W on the leaching of copper at temperature range of 25°C to 50°C. The results indicated that the optimum conditions (20% of nitric acid, 48.89°C of temperature and 5.52 W of ultrasound power) were achieved by using ten sets of conditions and was confirmed by 95% confidence interval of predicted response.

In view of the above, the aim of this paper was to analyze the applicability of the CCRD method in a copper leaching study for printed circuit boards of tablets with two independent variables: HNO_3 concentration and solid/liquid ratio.

2. Material and methods

25 obsolete tablets of different models obtained between August/2015 and June/2016 were used, and the PCBs were manually removed. Then, the experimental procedure was performed in 3 stages: i) Characterization of the PCBs of obsolete tablets; (ii) Nitric acid leaching for copper recovery; iii) Analysis of interfering factors in copper leaching using FFD and CCRD methods, as detailed below.

2.1. Stage 1 - Characterization of obsolete tablets PCB

In the first stage, tablet PCBs were characterized by mechanical processing and sample acid digestion. The mechanical processing involved the reduction of the size and the comminution of the slabs, which was carried out in the Laboratory of Tests of Civil Construction Materials (LEMAC) and in the Laboratory of Environmental Characterization of Residues (LACAR) of the Federal University of Espírito Santo, Brazil.

A manual guillotine of the Metalúrgica Schultz brand was used to reduce the size of the PCBs. For this, the PCBs were cut into sizes of approximately 1x1cm (Fig. 2), using technical paper to avoid splinters being lost, and thus all generated dust was counted and used for the characterization steps. This size was necessary for the sample to fit the mill opening of vibrating dishes for comminution.

For the comminution, the vibratory disk mill was used by adding the previously guillotined PCBs maintaining in vibration until the sample was totally comminuted. The comminution of the PCBs increases the contact surface area of the samples allowing the attack of the leaching agent, which increases the extraction of the metals, as reported by Sun et al. [26].

After comminution, the samples were solubilized under acid attack to determine the concentration of metals, especially copper. For this purpose, a solution of aqua regia in the proportion (%v/v) of 1 HNO_3:3 HCl that had the original purities of 37.5% and 69%, respectively [27] was used, and the experiment was performed in triplicate. In this stage, the S/L ratio of 1g of sample to 20 mL of aqua regia was used, according to studies by Yamane et al. [11], Park and Fray [28] and Petter, Veit, & Bernades [29].

In order to avoid foaming and possible overflow of suspension, the procedure employed in this step involved slowly adding the sample to the aqua regia contained in 500mL beaker, subjecting the suspension to constant manual shaking. After addition of the entire sample, the beaker was covered with a watch glass to minimize evaporation of the acids, and the whole suspension was kept under occasional stirring with a glass rod for 24 hours at room temperature. After this period, the suspension was then filtered using a filter (7µm porosity) mounted in a simple filtration system, and the soluble fraction was diluted to a final volume of 500mL in a volumetric flask.

For quantitative determination of the metals present in tablets PCBs, aliquots were analyzed in PerkinElmer's Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES) model OPTIMA 800.

2.2. Stage 2 – Nitric acid leaching for copper recovery

In Sage 2, the optimum copper extraction conditions of the tablets PCBs were evaluated by leaching with nitric acid by varying the acid concentration and the solid liquid ratio (S/L). The purpose of this step was to apply a method of copper leaching already studied for other types of PCBs in order to verify the similarity of the behavior of the PCBs of tablets and also to generate data for the comparative statistical analysis of the FFD and CCRD methods. Previous research has involved the selective extraction of metals, such as copper, tin, aluminum, lead, zinc, nickel, and iron from e-waste commonly using nitric and sulfuric acid [16-19, 20, 25, 30, 31]. Sulfuric acid is often more used as demonstrated by Silvas et al. [30] in a compiled table with results for PCB contents recycled with leaching processes. Due to the oxidizing characteristic of HNO_3, its use as a leaching agent does not require an auxiliary oxidizing agent such as H_2O_2. This is not true of H_2SO_4, which requires an auxiliary oxidant in order for the process to work efficiently with respect to the reaction rate [14]. Thus, nitric acid was chosen as the leaching agent in this study.

The acid leaching tests with HNO_3 were conducted at the following concentrations: 1.0, 2.0, 3.5, 5.0, and 6.0M. The experiments were performed in triplicate and lasted 6 hours. The S/L ratios (g/L) used included: 10.0, 19.3, 33.0, 46.7, and 56.0. A control was conducted in parallel in all experiments under the same conditions but without the addition of comminuted PCBs.

PCBs samples were used for each experiment, and the HNO_3 solution was added to Erlenmeyer flasks of 250mL nominal capacity, according to the desired S/L ratio, in a thermostatic bath at a temperature of 60°C without stirring. Condensation equipment was coupled to each flask to avoid losing reagents by evaporation. At the end of the experiment, the leached suspensions were diluted to a final volume of 500mL and, then, filtered on a filter (pore size 7μm). The suspension was filtered a second time using a filter (2μm pores). The aliquots of the leached solution were analyzed by atomic absorption spectrometry (FAAS), model Zeenit 700 from Analytik Jena, at the Laboratory of Atomic Spectrometry (LEA) of UFES, Brazil.

The results of the percentage of copper extracted were calculated using the initial concentration of copper determined in Stage 1, namely 25.77%, according to Equation 1.

$$P_{Cu}E = 100 - [(M_i * P_{Cu} - C_{Cu} * V_a)/M_i * P_{Cu})] * 100 \quad \text{(Eq. 1)}$$

Were:

$P_{Cu}E$= percentage of copper extracted (%);

C_{Cu}= concentration of copper in the sample (g/L);

M_i= sample Initial Mass (g);

P_{Cu}= percentage of copper in the characterization (%);

V_a= Volume of the volumetric flask (L).

2.3. Stage 3 - Analysis of interfering factors in copper leaching using FFD and CCRD methods

The evaluation of the factors that most influenced the extraction of copper through acid leaching, as well as the identification of the maximum extraction values, were analyzed statistically through the FFD and CCRD methods. The FFD method evaluates all possible interactions between variables one by one. In this sense, an overview of the process and its variables are presented as results in the form of response surfaces and graphs of interactions between them. However, since this method uses a creation rule for the exponential tests, the number of tests can become too large if one works with several variables [32].

By using the CCRD method, it is possible to reduce the number of experiments and, in the same way as the FFD, to generate response surfaces in order to quantify the effects of the independent factors and their interactions. These can be statistically significant depending on the result and also used to optimize the process of copper extraction according to the variables tested [33, 34].

The experimental design according to the FFD and CCRD methods suggests that the studied variables (HNO_3 concentration and S/L ratio) were tested according to concentration values presented in the Table 1.

Table 1 – Level values used in the CCRD and FFD for two factors (HNO_3 molar concentrations and S/L ratio) in the nitric acid leaching

Variables	CCRD Levels					FFD Levels				
Independent	-1.41	-1	0	1	1.41	-2	-1	0	1	2
HNO_3 concentration (M)	1.0	2.0	3.5	5.0	6.0	1.0	2.0	3.5	5.0	6.0
S/L ratio (g/L)	10.0	19.3	33	46.7	56.0	10.0	19.3	33.0	46.7	56.0

Thus, following the number of experiments determined by the FFD and CCRD methods, both with 2 factors, there are Table 2 and 3, respectively.

Table 2 - Experiments of the Full Factorial Design (FFD) using values coded and applied in the leaching with nitric acid

Experiments	Coded values		Applied values	
	HNO_3 concentration (M)	S/L ratio (g/L)	HNO_3 concentration (M)	S/L ratio (g/L)
1	-2	-2	1.0	10.0
2	-1	-2	1.0	19.3
3	0	-2	1.0	33.0
4	1	-2	1.0	46.7
5	2	-2	1.0	56.0
6	-2	-1	2.0	10.0
7	-1	-1	2.0	19.3
8	0	-1	2.0	33.0
9	1	-1	2.0	46.7
10	2	-1	2.0	56.0
11	-2	0	3.5	10.0
12	-1	0	3.5	19.3
13	0	0	3.5	33.0
14	1	0	3.5	46.7
15	2	0	3.5	56.0
16	-2	1	5.0	10.0
17	-1	1	5.0	19.3
18	0	1	5.0	33.0
19	1	1	5.0	46.7
20	2	1	5.0	56.0
21	-2	2	6.0	10.0
22	-1	2	6.0	19.3
23	0	2	6.0	33.0
24	1	2	6.0	46.7
25	2	2	6.0	56.0

Table 3 - Experiments of the CCRD using coded values and applied in the nitric acid leaching

Experiments	Coded values		Applied values	
	HNO_3 concnetration (M)	S/L ratio (g/L)	HNO_3 Concentration (M)	S/L ratio (g/L)
1	-1	-1	2.0	19.3
2	1	-1	5.0	19.3
3	-1	1	2.0	46.7
4	1	1	5.0	46.7
5	-1.41	0	1.0	33.0
6	1.41	0	6.0	33.0
7	0	-1.41	3.5	10.0
8	0	1.41	3.5	56.0
9	0	0	3.5	33.0
10	0	0	3.5	33.0
11	0	0	3.5	33.0

From Tables 2 and 3, an estimate was generated for the regression coefficients through the Action Stat software, which generated a mathematical model describing the influence of acid concentration and S/L ratio on the extraction with nitric acid for each method used. This influence can be represented by the Pareto graph that is used to visualize the influence of the variables as a function of the response variable

[34]. Another graphical tool is the boxplot, which can measure the variability of a factor, as well as the distribution of the data sets [35].

To determine if the mathematical model is statistically significant, the ANOVA ($p \leq 0.05$) was used.

From the statistical analysis, the concentration of HNO_3 and S/L ratio was determined by the CCRD method, which resulted in a higher rate of copper extraction. Twenty tests were performed under the optimal conditions defined by the CCRD method and the same experimental procedures already described in Stage 2 in order to validate the mathematical models.

3. Results and Discussion

3.1. Stage 1 - Characterization of obsolete tablets PCB

The first stage was to determine the initial concentration of copper used as reference in Stage 2 and other metals present, being presented in Table 4. This also allowed for comparison of the recycling potential of tablet PCBs with those of other e-waste.

Table 4 - Concentration (wt.%) of the metals from printed circuit boards of tablets

Metals	**Metals concentration (wt.%)**
Cu	25.76
Sn	3.58
Ba	2.16
Fe	1.62
Ni	1.36
Al	0.69
Zn	0.63
Pb	0.40
Sr	0.04
Au	0.01

The percentage distribution of metals to the group of new e-waste (smartphones, tablets, and notebooks) is presented in different studies [36-38]. According to Tesfaye et al. [8], tablets have a higher content of valuable metals for recycling than notebooks (for a given weight), which exist both in the screen and in PCBs. While smartphones are more similar to notebooks due to manufacturing, the concentration of copper is greater in tablets than in smartphones [36]

The concentration of copper in tablet PCBs represents up to 25% of the mass of the PCB, but the quantity of gold (0.01%) has the greater recycling potential in tablets. A study by Cucchiella et al. [36] showed that copper is the second material in a top ten material list with 13.9% profit potential, behind only gold that represented 50.4% profit potential.

Additionally, copper represents a viable alternative for secondary source of metals and also prevents intensive exploitation of the natural reserves of metals [39].

Tesfaye et al. [8] suggested that, despite being a relatively new group of products, e-waste from TIC equipment is likely to be the most profitable source of recycling, noting that the same processes for recovering components with market value can also be applied to smartphones, notebooks, and tablets.

3.3. Stage 2 – Nitric acid leaching for copper recovery

In the nitric acid leaching experiments, 90% copper extraction was obtained from tablet PCBs at the experimentally determined optimum condition, namely 56 g/L (solid/liquid ratio) and 1M nitric acid concentration as shown in Table 5.

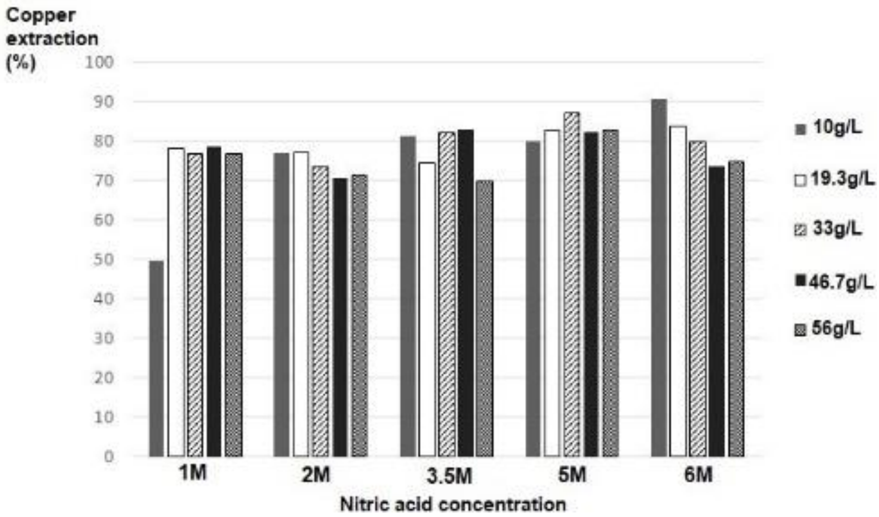
Table 5 - Copper extracted (%) by nitric acid leaching under different HNO_3 molar concentrations (1, 2, 3.5, 5 and 6M) and S/L ratio (10, 19.3, 33, 46.7 and 56g/L)

Experiments	HNO_3 concentration (M)	S/L ratio (g/L)	Cu concentration (g/L)	Copper extracted (%)
1	1.0	10.0	0.53	49.43
2	1.0	19.3	0.88	76.69
3	1.0	33.0	0.89	81.08
4	1.0	46.7	0.94	79.98
5	1.0	56.0	0.92	90.46
6	2.0	10.0	0.77	77.85
7	2.0	19.3	0.80	77.14
8	2.0	33.0	0.69	74.42
9	2.0	46.7	0.81	82.60
10	2.0	56.0	0.88	83.59
11	3.5	10.0	0.73	76.72
12	3.5	19.3	0.67	73.43
13	3.5	33.0	0.47	70.00
14	3.5	46.7	0.83	87.04
15	3.5	56.0	0.67	79.68
16	5.0	10.0	0.79	78.37
17	5.0	19.3	0.55	70.66
18	5.0	33.0	0.93	82.76
19	5.0	46.7	0.82	82.18
20	5.0	56.0	0.79	73.42
21	6.0	10.0	0.70	76.78
22	6.0	19.3	0.76	71.31
23	6.0	33.0	0.58	69.66
24	6.0	46.7	0.87	82.59
25	6.0	56.0	0.75	74.81
μ	-	-	0.76	76.91
σ (g)	-	-	0.12	7.78
C_v	-	-	0.16	0.10

Legend: μ = Arithmetic mean, σ = standard deviation, C_v= Coefficient of variation.

Figure 1 shows the average copper extraction percentages obtained by varying the S/L ratios at each of the 5 concentrations of nitric acid studied.

Fig. 1 - Copper extraction (%) varying the solid/liquid ratio and the molar concentration of nitric acid



As observed in Figure 1, the highest percentages of extraction were obtained in the S/L ratio of 56 g/L, however, above 3.5M of HNO_3, the S/L ratio was in 46.7 g/L. The results do not follow a linear tendency, presenting a deviation for extraction increase.

Additionally, at concentrations above 1 M, the S/L ratio of 10 g/L maintained a percentage of copper extraction between 75 and 80%.

Table 6 summarizes results from other studies that were performed with nitric acid also aiming at copper extraction from e-waste.

Table 6 - Results compilation for copper extraction from e-waste by nitric acid leaching

Reference	E-waste	Optimal conditions	Copper extraction (wt.%)
Mecucci & Scott (2002)	PCB	80°C; 6 h; 6M HNO_3	Above 95
Kinoshita et al. (2003)	PCB	90°C; 6 h; 1M HNO_3; S/L 20g/L	Above 90
Torre & Lapidus (2016)	PCB	25°C; S/L 20g/L; 6h; 0.5M HNO_3 + 0.1 M H_2O_2 per hour	Above 50
Javed et al. (2018)	AMD Athlon processors	48.89°C; 1h; ultrasound power of 5.52 W; 20% HNO_3	Above 70
Present study	PCB	60°C; 6h; 1M HNO_3; S/L 56g/L	Above 90

Legend: PCB: printed circuit boards; AMD: advanced micro devices

The copper recovery behavior from tablets PCBs by nitric acid leaching was similar with other studies performed by Kinoshita et al. [19] and Mecucci & Scott [20]. Nitric acid is considered a good lixiviant for the copper extraction according to Javed et al. [25], due to its powerful oxidizing effect when compared to hydrochloric acid and sulfuric acid.

Despite that, Torres & Lapidus [31] concluded that the addition of hydrogen peroxide increases the copper removal rate by nitric acid by approximately 20% to 50%.

Mecussi & Scott [20] used different PCBs, and they were ground to a size of less than 2.5mm. Then, they were leached with a solution of 1-6 M HNO_3 over a period of 6 hours, and the temperatures used were 23 and 80°C. At the end, values above 95% of copper and lead were extracted in 6 hours, as also observed in this study.

The use of nitric acid was also studied by Kinoshita et al. [19] when using various PCBs cut into pieces of approximately 10 x 20 x 2 mm, which were then leached with a solution of 1 M HNO_3 and an S/L ratio ranging from 20, 50, and 100. The test period was 6 and 24 hours, and the temperatures studied were 23, 50, 80, and 90°C. At the end, values above 90% of copper and nickel were extracted in 6 hours. The authors described that in order to obtain a copper and nickel extraction above 95%, the ideal reaction time was 24h.

Regarding the research performed by Kinoshita et al. [19] and Mecussi & Scott [20], it was observed that the concentration of HNO_3 and the size of the particle influenced the percentage of extraction, but in general, there is no direct link that relates the variables, using the same parameters in the experiments.

In relation to other variables, study performed by Javed et al. [25] demonstrated that ultrasound power shows no significant impact on the copper extraction, but the temperature and, then, nitric acid concentration were the most significant process variables to the copper leaching.

Considering the studied literature, the variables that stand out among those cited as interfering in the copper recovery process of PCB include: nitric acid concentration, S/L ratio, temperature, reaction time, and particle size. This is because they can directly influence efficiency and treatment costs [40]. It is noteworthy that all the cited studies used the Full Factorial Design method for the experimental planning.

The optimization process uses the improvement of the system performance as a reference and is used in the experimental planning, emphasizing the laboratory experiments. These experimental objectives reveal conditions in which the application of a process produces the best possible response [41].

In view of the above, the concentration parameters of HNO_3 and S/L ratio were defined as independent variables to be investigated by the CCRD method.

3.4. Stage 3 - Analysis of interfering factors in copper leaching using FFD and CCRD methods

In this study, the main goal was to apply the CCRD method to build a mathematical model for copper leaching from tablets PCBs. This design allows for obtaining response surfaces and quantification of independent factors and their interactions. The surfaces describe how the desired response varies according to two variables for evaluation and prediction of what happens within the entire experimental domain [41]. In this sense, the multivariate planning used, besides estimating the main effects of the parameters and the respective interactions, inform the degree of curvature and generate a quadratic response surface [42]. The mathematical model generated by multivariate planning must present good estimates for the coefficients of the model, providing a good regression and reduced lack of adjustment [43].

By the CCRD method, two factors (independent variables) were analyzed: concentration of nitric acid and S/L ratio totaling 11 experiments (Table 7). For the FFD method, 25 experiments were performed (Table 5).

Table 7 - Results used in Central Composite Rotatable Design (CCRD) for two factors

Experiments	**HNO_3 concentration (M)**	**S/L ratio (g/L)**	**Extracted copper (%)**
1	2	19.3	77.14
2	5	19.3	70.66
3	2	46.7	82.60
4	5	46.7	82.18
5	1	33	81.08
6	6	33	69.66
7	3.5	10	74.45
8	3.5	56	79.68
9	3.5	33	85.09
10	3.5	33	80.33
11	3.5	33	82.71
μ (g)	-	-	78.69
σ (g)	-	-	5.10
C_v (g)	-	-	0.06

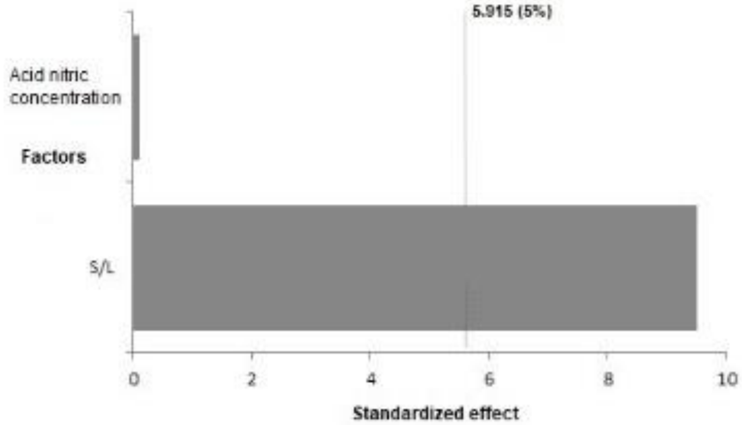
Legend: μ = Arithmetic mean, σ = standard deviation, C_v= Coefficient of variation.

From the results obtained (see Table 5), Table 7 presents the CCRD experiments where the means of extraction were used for the tests 1-8, as well as the values of each triplicate at the central point (3.5; 33.0).

The arithmetic mean of extractions presented in Table 7 was 78.7%, a value close to the FFD method that was determined to be 77% (Table 5). It can be noticed that the standard deviation was also lower at 5.1 for CCRD and was 7.8 for FFD, and the highest CCRD extraction was 85%. Thus, the CCRD method used 44% of the number of tests and leaching inputs of the FFD method, obtaining a similar result.

Regarding the influence of the studied variables, the Pareto Diagram (Figure 2) represents the standardized effects that each variable exerts on the evaluated response (copper extraction). The vertical line indicates the confidence level, which is the rejection limit of the null hypothesis ($\alpha = 0.05$). Only the effects located to the right of the response should be considered for the evaluation of the response.

Fig. 2 - Pareto graphic of the S/L ratio and molar concentration of HNO_3



Legend: S/L = solid/liquid ratio

The analysis of the Pareto Diagram (Figure 2) indicates that the variable S/L ratio was more significant for copper leaching of tablets PCBs, since it was the only one that was present on the right of the 5% line.

In order to confirm the statistical significance of the effects of the variables on copper leaching from tablets PCBs by the CCRD method, a variance analysis (ANOVA) was performed as shown in Table 8 and Table 9.

Table 8 - Anova to Central Composite Rotatable Design (CCRD)

Factors	DF	Sum of Squares	Medium Square	F_{calc}	P-value
$[HNO_3]$ x $[HNO_3]$	1	38.6652	38.6652	4.6943	0.0824
S/L x S/L	1	30.7072	30.7072	3.7281	0.1113
$[HNO_3]$	1	66.3253	66.3253	8.0526	0.0363
S/L	1	74.3432	74.3432	9.0260	0.0299
$[HNO_3]$:SL	1	9.2168	9.2168	1.1190	0.3385
Waste	5	41.1825	8.2365	-	-

Legend: DF: degrees of freedom; $[HNO_3]$: nitric acid concentration (M); S/L: solid liquid ratio (g/L)

Table 9 - Anova to Full Factorial Design (FFD)

Factors	DF	Sum of Squares	Medium Square	F_{calc}	P-value
$[HNO_3]$ x $[HNO_3]$	1	80.9925	80.9925	2.2479	0.15022
S/L x S/L	1	24.4349	24.4349	0.6782	0.4204
$[HNO_3]$	1	3.4911	3.4911	0.0968	0.7589
S/L	1	342.0799	342.0799	9.4946	0.0061
$[HNO_3]$:SL	1	293.5413	293.5413	8.1474	0.0101
Waste	19	684.5462	36.0287	-	-

Legend: DF: degrees of freedom; $[HNO_3]$: nitric acid concentration (M); S/L: solid liquid ratio (g/L)

In this sense, it was possible to analyze the significant influence (P-value <0.05) in the extraction of copper for each variable studied (solid / liquid ratio and molar concentration of HNO_3).

Given the values of the percentage of extracted copper, it was possible to generate Tables 10 and Table 11, which present an estimate for the values of the regression coefficients for each variable.

In order to obtain a table with the significant factors, it is necessary to eliminate the factors that were not statistically significant (P-value> 0.05). These values are in the FFD table: $[HNO_3]$ quadratic, ratio S/L quadratic and $[HNO_3]$; and for the CCRD, these were: S/L ratio and quadratic interaction between variables.

From the values that were statistically significant, Tables 10 and 11 were obtained, where the coefficients of the mathematical model are found.

Table 101 - Statistically significant factors for Full Factorial Design (FFD)

Preditor	Estimative	Standard deviation	Estat.t	P-value
Intercept	77.39422815	1.201109292	64.43562518	1.47054E-26
S/L	2.615645145	0.849312526	3.079720441	0.005478575
$[HNO_3]$:SL	-1.713304976	0.600554646	-2.852871071	0.009251745

Legend: $[HNO_3]$: nitric acid concentration (M); S/L: solid liquid ratio (g/L)

Table 11 - Statistically significant factors for Central Composite Rotatable Design (CCRD)

Preditor	**Estimative**	**Standard deviation**	**Estat.t**	**P-value**
Intercept	80.51786442	1.431269348	56.25626269	1.47094E-10
$[HNO_3]$ x $[HNO_3]$	-2.513231042	1.375787931	-1.826757588	0.110469149
$[HNO_3]$	-2.883645227	1.205261469	-2.392547428	0.047988807
S/L	3.052970854	1.205261469	2.533036137	0.039059301

Legend: $[HNO_3]$: nitric acid concentration (M); S/L: solid liquid ratio (g/L)

With the values of the coefficients statistically significant, it was possible to obtain the mathematical models (Equations 2 and 3) that describe the percentage of copper extraction as a function of the two variables: $[HNO_3]$ and S/L ratio.

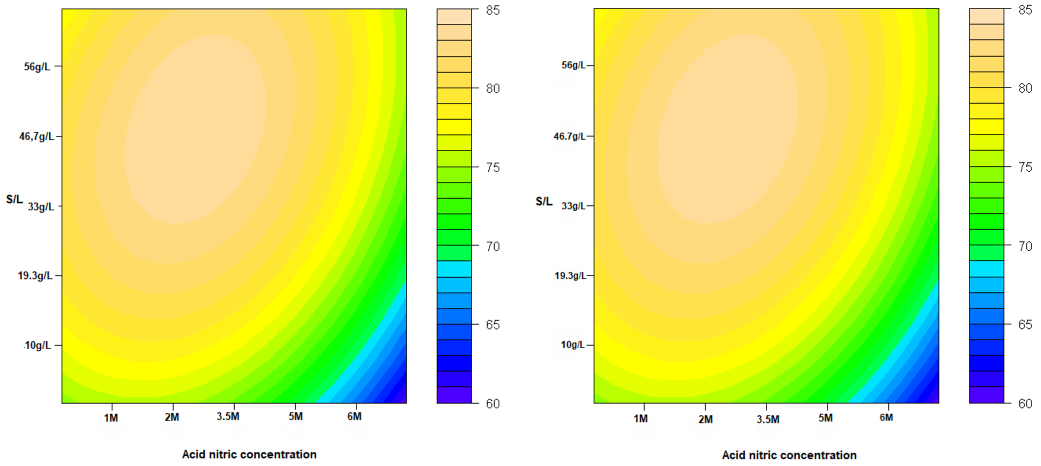
$$\%\text{Copper Extraction} = 77.3942 + 2.6156 * (S/L) - 1.7133 * (S/L) * [HNO_3] \quad \text{(Eq. 2)}$$

$$\%\text{Copper Extraction} = 80.5178 - 2.5132 * [HNO_3]^2 - 2.8836 * [HNO_3] + 3.0529 * (S/L) \quad \text{(Eq. 3)}$$

The mathematical model for the complete factorial analysis presented an R^2 value of 52.09%, whereas the mathematical model of the CCRD presented an R^2 of 68.85%, which are written in terms of the coded variables. Thus, by analyzing only R^2, the CCRD model best fits the results of the experiment performed and can be used as a predictive model [33, 44].

In order to determine if the mathematical models are statistically significant by the ANOVA, the values found in this experimental design for the Full Factorial method were F_{calc} and $F_{experimental}$, respectively, 8.81 and 3.44. For the CCRD, the values were 5.16 and 4.34, which makes the mathematical model statistically significant. From the mathematical model, it was also possible to plot the contour curve for the percentage of copper extraction (Figure 3) and the response surface (Figures 4 and 5).

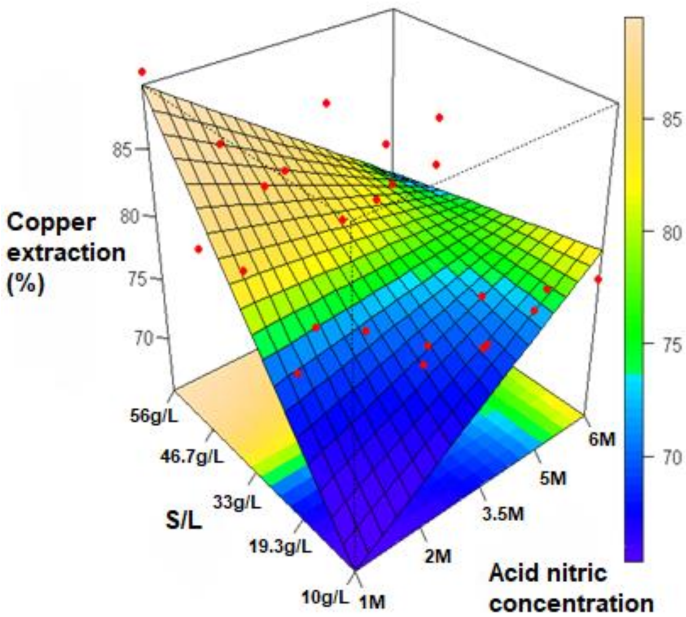
Fig. 31 - Interaction curve between variables for FFD (a) and CCRD (b)



(a) (b)

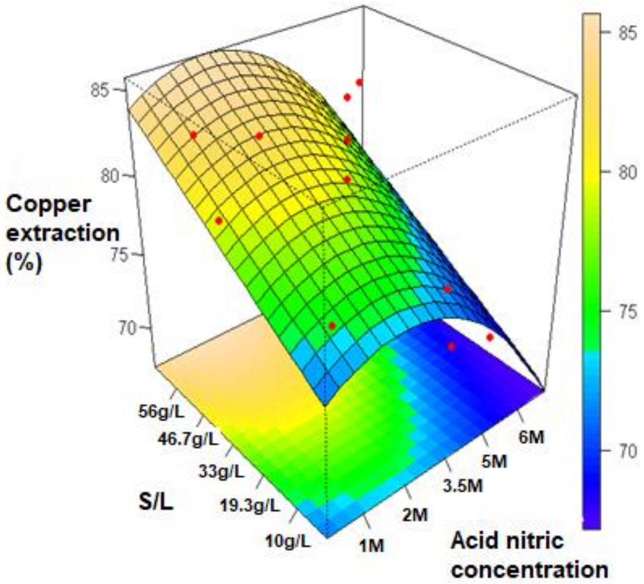
Legend: S/L: solid/liquid ratio.

Fig. 4 - Contour curve for the FFD



Legend: S/L: solid/liquid ratio

Fig. 5 - Contour curve for the CCRD

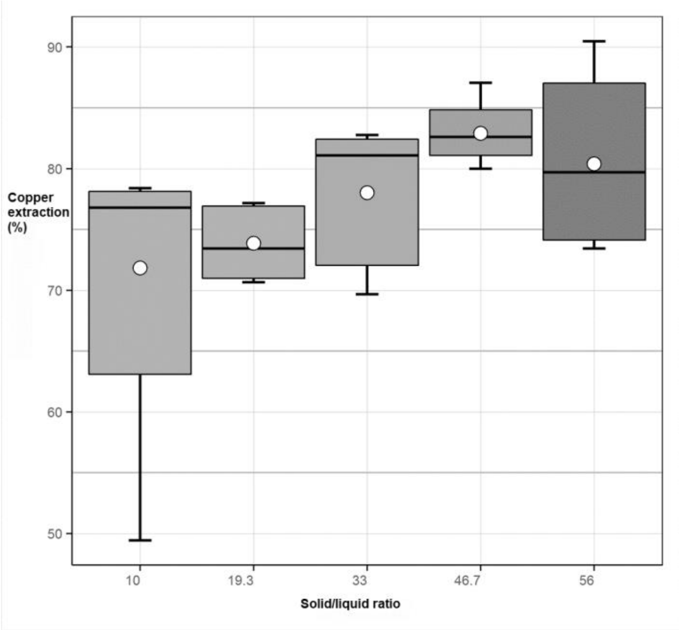


Legend: S/L: solid/liquid ratio

Graphical analysis, together with the values of the Anova Table and the Pareto graph, showed that the S/L ratio is more influential in copper extraction than the increase in HNO_3 concentration in the studied ranges. Another factor that can be observed is that the CCRD method presented a behavior close to the FFD method, but this method uses a smaller number of tests and can be noted for future tests. As there were a smaller number of tests, the reagents and time of preparation for the analyses were reduced.

To confirm the graphical analysis, the boxplot was also used for the S/L ratios studied. Thus, a boxplot (Figure 6) was plotted with different S/L ratios.

Fig. 62 - Boxplot according to solid/liquid ratio



In Figure 6, it can be seen that the lowest S/L ratio (46.7) was obtained with the highest average extraction rate, when comparing to other S/L ratios.

Thus, it is recommended to use the S/L ratio of 46.7 to obtain extraction rates above 80%.

By means of the statistical analysis of the results obtained in Step 2, the concentration of HNO_3 and S/L ratio that results in a higher rate of copper extraction was defined, being a concentration of 2M for nitric acid and an S/L ratio of 46.7 g/L. The results obtained in the 20 experiments are presented in Table 12.

Table 12 - Results of leaching with 2 M concentration for nitric acid and an S/L ratio of 46.7 g/L

Experiments	**Copper concentration (g/L)**	**Extracted copper (%)**
1	4.103	99.37
2	4.117	99.76
3	4.084	99.07
4	3.827	92.27
5	3.935	95.20
6	3.735	89.51
7	3.853	93.02
8	3.706	88.56
9	3.585	84.96
10	4.181	101.33
11	3.642	86.68
12	4.066	98.50
13	3.802	91.54
14	3.052	64.95
15	3.977	96.20
16	4.053	98.16
17	3.847	92.81
18	3.899	94.25
19	3.770	90.47
20	3.548	83.78
μ	3.839	92.02
σ	0.261	8.15
C_v	0.068	0.08

Legend: μ = Arithmetic mean, σ = standard deviation, C_v= Coefficient of variation**.**

According to Equations 2 and 3, the copper extraction value would be 81.72 and 83.94% using the values coded for the concentration and S/L ratio, while the value found with the arithmetic mean of the 20 experiments was 92.02%. Considering the standard deviation (8.15), the result found is within the range predicted by Eq. 3, confirming the validity of the equation. However, Eq. 2 of the Full Factorial method, even with a standard deviation (8.15), presents results 2.15% away from the value determined as the arithmetic mean of the 20 trials.

4. Conclusions

The concentration of copper in the printed circuit boards of tablets studied (25% wt.) is economically viable from the point of view of recycling, and the presence of gold increases the economic potential, as the tablets are part of the group of new WEEE that create greater interest in recycling, along with smartphones.

The optimal condition for 90% copper extraction, as experimentally determined by the FFD method, was 56 g/L (solid/liquid ratio) and 1M nitric acid concentration. However, statistical analysis showed that using the CCRD method at 2M concentration of nitric acid and S/L ratio of 46.7 g/L resulted in optimal copper extraction condition reacing 85% with a much smaller number of tests, which generates input savings and operational time.

Graphical analysis from Pareto and boxplot showed that the S/L ratio is more influential in copper extraction.

Mathematical models were statistically significant. The validation of the mathematical models showed that for the CCRD method, the result is within the expected considering the standard deviation.

With only 44% of all FFD method tests, the experimental design of the CCRD method obtained a comparable result, making it potentially applicable to other studies involving the extraction of metals from WEEE printed circuit boards.

The experimental design of the CCRD method obtained a result comparable to that achieved with only 44% of the total FFD method tests, making it being potentially applicable to other studies involving the extraction of metals from WEEE printed circuit boards.

Acknowledgments

This research was supported by the Fundação de Amparo à Pesquisa e Inovação do Espírito Santo (FAPES), Espírito Santo, Brazil (Process nº 68781369/2014 and Process nº 83757392/2018).

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