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SCIENTIFIC PAPER

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TWO-PHASE LEACHING FOR METAL RECOVERY FROM WASTE PRINTED CIRCUIT BOARDS: STATISTICAL OPTIMIZATION

Article Highlights

- Two-stage leaching was employed for the efficient recovery of heavy metals from PCBs
- Optimization by RSM results in a leaching efficiency of 97.06% Cu, 94.66% Sn, 96.64% Zn, and 96.89% Pb
- Simultaneous extraction has proved to be successful in separating and recovering heavy metals

Abstract

The rapid growth of technology is inevitable in humankind's life and has a significant stint in electronic waste (e-waste) generation. Electronic waste possesses tremendous environmental and health effects, and one such major contributor to it is printed circuit boards (PCBs). The present work deals with the recovery of heavy metals from PCBs by using aqua regia as a leaching reagent in two stages (first stage HCl and HNO_3 and second stage HCl and H_2SO_4). The response surface methodology was used to determine the optimal recovery conditions for the heavy metal ions: the recovery time of 5 h, the pulp density of 25 g/L, and the temperature of 90.1 °C with desirability 0.761. These optimized values provide a maximum recovery rate of Cu (97.06%), Sn (94.66%), Zn (96.64%), and Pb (96.89%), respectively. EDXs are used to analyze the metal concentrations of the sample before and after treatment.

Keywords: aqua regia, e-Waste, printed circuit board, response surface methodology, two-step leaching.

Electronic waste (e-waste) means electrical or electronic waste. Technological advancement, business expansion, economic growth, and shorter electrical and electronic equipment (EEE) have contributed to a significant rise in e-waste. PCBs are the main components of this e-waste, which typically includes 40% metals, 30% ceramics, and 30% plastics [1,2]. The metallic composition consists primarily of 10-30 % of cu and other metals such as Sn Zn, Pb Ni, Fe, Ag, Cd, Au, etc., in different proportions based on PCB sources [3]. The recovery of metals from PCBs is very difficult due to the heterogeneous distribution of materials in PCBs. An analysis of PCBs by atomic adsorption spectroscopy shows that 2 kg of PCBs contains 5.94% of Sn, 21.3% of Cu, 3.2% of Pb, and 2.24% of Fe [4]. Informal processing of e-waste in developing countries can lead to adverse effects on human health and environmental pollution. In 2016, 44.7 million metric tons of e-waste were produced worldwide [1,2]. An estimated 3.8 tons of e-waste were produced annually in India, of which only 19,000 tons were recycled. India faces a considerable challenge to dispose of an estimated 4.5 tons of e-waste per year produced domestically and imports from abroad [5]. If the e-waste was directly disposed of by filling the soil without removing metal ions from PCBs, the pollution of land and water supplies would result.

E-waste recycling has been accomplished through formal and informal techniques in several countries [6]. While formal recycling techniques ensure protection and efficient separation but are costly to install and

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operate. Therefore, cheaper informal processes are highly admirable and oriented [7]. These metals can be found in dust, air, water, and soil, affecting human health and the environment. Exposure to metals such as Pb and Cd affects reproductive health, development, mental instability, and damage to human DNA [8-11]. Also, low levels of Pb exposure in children and pregnant women indicate major growth problems [12]. It also reported that the lung dysfunction of workers, such as diggers and scrap disposers, is due to the inhalation of nickel-contaminated air [9,13,14]. Health symptoms, like headache, dizziness, irritation in the eye, nose, mouth, etc., are due to exposure to Cu, which is present in the landfills [15-17].

The methods used to recover metals from PCBs are essentially physical/mechanical and chemical separation. As far as chemical separation is concerned, electro-winning, hydrometallurgy, and pyrometallurgy have been widely used [18]. The pyrometallurgy process involves heating e-waste at high temperatures to recover precious metals. This procedure develops dangerous gases, which must be extracted from the air using a flue gas cleaning device [19]. Several studies on the feasibility of metal recovery from PCBs have been published in the last decade. Hydrometallurgical procedures, such as leaching, are very crucial in these studies. Several leaching reagents demonstrate major improvements in metal recovery. When treated with different acidic media HNO_3, HCl, and H_2SO_4, PCBs were cut to extract Cu^{2+} ions, the recovery % of Cu^{2+} was 97.5%, 65%, and 76.5%, respectively [18]. Just traces of other metals can be extracted through this copper targeted extraction. While using HCl as leaching reagent under the stated conditions, the PCBs sample of size 4x4 cm results in separation of Cu, Zn, Sn, and Pb with composition 117.33 mg g^{-1}, 28.97 mg $^{g-1}$, 10.41 mg g^{-1}, and 9.34 mg g^{-1}, respectively [19]. The Zn and Pb leached amounts were very small compared to the typical PCB metal content. By leaching crushed PCBs (size between 0.43–3.33 mm) using sodium cyanide solution, the grades are 16%, 2.0%, 1%, and 1% of Cu, Pb, Zn, and Sn, respectively [20]. It has the most negligible compositional value compared to the average weight of the total metals. PCB waste leaching with H_2SO_4 and H_2O_2 yielded 76% Zn, 85% Cu, 82% Fe, 77% Al, and 70% Ni after 480 min of leaching [21]. Other valuable metals remain as traces in the leaching solution. The deposition of extracted metals possesses different dendritic growth concerning the leaching reagent used. The copper obtained by leaching of PCBs with H_2SO_4 solution presented a fine dendritic structure with branches of about 80–100 µm [22,23]. Besides that, the significant recovery rate of copper through bioleaching was reported in our previous research [24,25].

Several studies showed that heavy metals were successfully extracted from printed circuit boards by hydrometallurgical techniques. There were limitations such as the sluggishness of the process; higher processing times, which had resulted in less efficient recovery and had an impact on the recycling economy. Few researchers proposed methods of hydrometallurgical leaching followed by selective extraction of metals, which is more costly. The proposed recovery process utilizes two stages of leaching, which gave a more efficient recovery of heavy metals. This study deals with extracting metal ions such as Zn^{2+}, Sn^{2+}, Cu^{2+}, Pb^{2+}, etc., from PCBs by two-stage leaching technology. Furthermore, the experimental results are optimized through RSM at various parameters, like shaking speed, size, contact time, pulp density, and temperature.

MATERIALS AND METHODS

Sample collection and preparation

The waste PCBs were obtained from the e-waste disposal units in India. For the experiments, 500 g of PCB scraps were broken into 15–20 cm particles and shredded using pliers and four-blade cutting shredder into small pieces around 50x50–30x30 mm [22,23,26-28]. Metals and non-metals need to be separated [22,23]. This separation is not simple due to the difference in the physical characteristics of metals and non-metals, so different separation methods, such as pneumatic separation, magnetic separation, filtering, eddy current separation, electrostatic separation, etc., can be used to enrich metals and non-metals [20]. The electronic components, such as a capacitor, diode, resistor, transistors, etc. [29], are disassembled. These shredded PCBs were then heated at 700-900 °C in a muffle furnace to enhance the PCBs' flexibility and crushing properties [19,27]. Therefore, samples are comminuted using a jaw crusher to reduce the particle size. The crushed PCBs obtained from the crusher were then pulverized and milled using a ball mill to reduce the particles further. Particles of different mesh sizes were analyzed. The step-wise procedure employed is explained in Fig.S1 (available from the author, upon request).

The crushed PCBs fraction from the lower screens of jaw crushers of an 80 kg hr^{-1} capacity with a clearance of 10 mm was not feasible for a better ions recovery. Thus, it was further subjected to the 5 mm clearance jaw crusher, resulting in the samples of 65, 53, 48, or 36 g from the sieves with a mesh size of 0.3, 0.18, 0.05 mm, and pan, respectively, when screened using a rotary sieve shaker (0.25 HP. 80 V) at a speed of 60 rpm. As the reduction in size increased the recovery rate of metal ions [8], the resulting crushed samples were processed into the powder form using a pulverizer with a disk diameter of 175 mm operated by a three-phase motor (225-445 V) at 1400 rpm. The resulting powder samples were screened through sieves of different mesh sizes, and the weight fraction of the bottom product (sieves from 52 B.S.S. to pan) increased but was not adequate for the anticipated recovery. The pulverized PCB powder was milled in a ball mill having 5000 g balls at a speed of 60-120 rpm with a mill diameter of 200 mm driven by a 0.25 HP three-phase motor, which resulted in a much size reduction; the highest weight fraction was obtained at the lowest sieve. The weight fractions obtained at each sieve were separately collected and used for leaching (Table 1).

Mixture compositions

The metal recovery from PCB was carried out in two leaching stages using HCl and HNO_3 in the first stage and HCl and H_2SO_4 in the second stage. The leaching agent was prepared by mixing HCl and HNO_3 in a 3:1 ratio under the specified conditions. In previous studies with aqua regia as a leaching reagent, heavy metals, such as Cu, Sn, Pb, and Zn, were extracted from PCBs with a high recovery rate (Table 2).

The aqua regia preparation mixing concentrated strong acids, namely HCl (35%) and HNO_3 (65%), in a 3:1 ratio. The solutions were kept away from the organic contaminants to avoid vigorous or violent reactions at a low temperature.

Experimentation with various parameters on metal recovery

All the experiments were conducted in conical flasks fixed at a temperature-controlled shaker. The primary analysis was performed by applying the specific conditions to obtain a standard recovery rate. Namely, 20 g of PCB samples were treated with 0.5 L of the leaching agent in the conical flask at 80 °C and shaken by the shaker at a shaking speed of 120 rpm for 3 h. At the end of this effective contact time, the shaker was stopped, and the solution in the conical flask was filtered using filter paper. After filtration, the metal composition of the retained filtrate was determined. The leaching rate depends on various parameters, such as shaking intensity, particle size, contact time, pulp density, and temperature. Different values for the recovery rate and the composition of heavy metals were obtained by varying these parameters.

Pulp density

The 0.05 mm PCBs samples (5, 10, 15, 20, and 25 g) were taken in separate conical flasks, and 0.5 L of aqua regia was inserted in each flask. The conical flasks were securely closed using a lid, fixed on the shaker, and shaken (80 rpm) at 80 °C for 3 h. After 2 h, the solutions in the conical flasks were filtered separately using filter paper. The metal components deposited on the filter paper were dried and analyzed.

Temperature

Some acids improve the recovery rate with increased temperature, while others exhibit a decreased recovery rate at higher temperatures [31].

Table 1. Analysis of PCBs size reduction

Mesh size		Weight fraction (grams)			
		Jaw crusher		Pulveriser	Ball mill
B.S.S	(mm)	Clearance (10 mm)	Clearance (5 mm)	Feed size (6 mm)	Ball weight (500g)
4	4	155	118	45	27
7	2.3	125	92	57	35
25	0.6	95	76	69	58
52	0.3	52	65	87	64
85	0.18	30	53	60	78
300	0.05	22	48	85	82
Pan	-	15	36	79	120

Table 2. Recovery data of metals with different leaching agents

Leaching media used	Heavy metals recovery %									References
	Cu	Sn	Zn	Pb	Cr	Ni	Ag	Au	Fe	
$H_2SO_4 + H_2O_2$	96.72	-	98		53.03	97.7	-	-	0.44	[22]
HNO_3 and HCl+ HNO_3	86.9	92.7	-	-	-	-	-	-	-	[23]
HCl + HNO_3	92.7	93.3	-	-	-	-	-	-	-	[26]
NaCN	77.7	-	-	-	-	-	51.6	47.9	-	[27]
$(NH_4)_2S_2O_3$ and $CuSO_4$	78.8	-	56.7	-	-	-	-	-	-	[28]
$H_2SO_4 + NH_3$	88.6	-	99.2	-	98.2	98	-	-	-	[30]

However, the dissolved oxygen concentration of the aqueous phase is reduced as the temperature increases. The 0.3 mm particles (20 g) were mixed with 0.5 L of aqua regia in a conical flask and shaken for 3 h in a shaker at 120 rpm at 20, 40, 60, 80, and 100 °C. After shaking, the solutions were filtered and analyzed.

Time

Duration is another primary parameter influencing the recovery rate. The leaching rate rises with time, but there is no appreciable recovery after a certain period. The time range with the maximum recovery rate is known as the efficacy of the leaching cycle [22,23]. The samples were combined 0.5 L of the leaching agent with 20 g of 0.3 mm particles in conical flasks and shaken separately at 80 rpm for 1, 2, 3, 4, and 5 h at 80 °C. The solutions were filtered, dried, and analyzed.

Shaking Speed

The collision between the leaching agent and the PCB particles increases with increasing the shaking speed, leading to an increased ion exchange rate. The effect of shaking speed was tested at 40, 80, 120, 160, and 200 rpm. In these experiments, 5 g of 0.3 mm PCB particles were shaken with 0.5 L of aqua regia at 80 °C. The solution collected at each speed was filtered and analyzed.

Size

The sample size has an essential role in metal leaching. The leaching rate can increase or decrease with a change in the particle size. The PCB samples (20 g) containing 4, 2.3, 0.6, 0.3 mm, or <0.05 mm particles were combined with 0.5 L of the leachate agent in different conical flasks. The mixtures in conical flasks were shaken for 2 h at 80 rpm at 80 °C. The resulting solutions were filtered, and the filtrates were analyzed.

Response surface methodology (RSM)

The study was conducted to obtain the optimum values of various parameters for recovering metal ions from PCBs by the response surface methodology [31]. The influence of various process factors (shaking speed, size, contact time, pulp density, and temperature) are studied for metal ions recovery. In the present study, the input process factors were temperature, pulp density, and time. The levels of the selected process factors in coded and uncoded forms correspond to the Box-Behnken design (Table 3). The response (output variable) is the metal recovery (in %).

Table 3. Levels of different process variables in coded and uncoded form chemical leaching % of heavy metals (Box-Benhken Method)

Variable	Name of the Process Variable	Range and levels		
		-1	0	1
A	Time, h	3	4	5
B	Temperature, °C	60	80	100
C	Pulp density, g L^{-1}	15	20	25

RESULTS AND DISCUSSION

Sample analysis of PCBs (Sizes and metal elements)

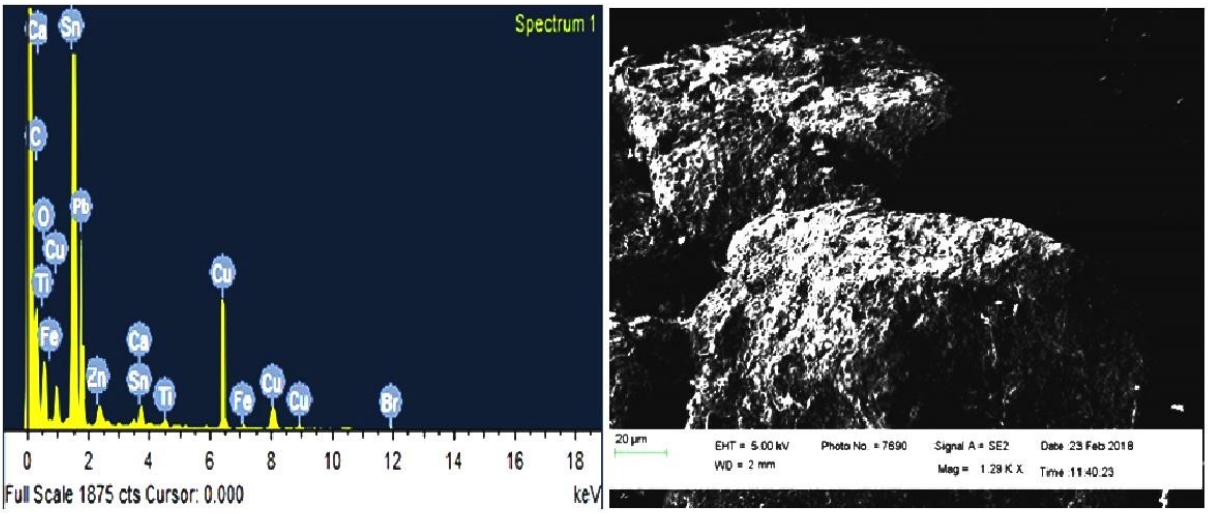
The graphical representation of the size analysis reveals that subject to the size decrease sequence, the fraction of sample generated on the screens with larger mesh sizes has decreased. However, the total weight collected in the sieves was maintained roughly with marginal loss. The sample collected at the ball mill was much less than 0.05 mm from the analytical data of each procedure. Numerous experiments were used a shredded sample dimension less than 0.5 mm, contributing to an elevated heavy metal recovery rate [32-35]. The graphical representation of the PCB sample size analysis showed that the fraction of the sample obtained in the sieves with larger mesh size decreased when it was subjected to a sequence of size reduction operations. Various studies used a shredded sample size of less than 0.5 mm, which resulted in a high recovery rate of heavy metals [32]. The present work used the 0.05 mm particles, while the same analyses were performed. Fig. S2 (available from the author upon request) shows the results obtained with the 0.05 mm sample.

EDXs and SEM were used to analyze the metal concentrations of the preliminary samples. To ensure uniformity and to obtain metal composition by SEM with EDXs, the samples were randomly mixed, and the final contents of the metals were as follows: 3.15% Cu, 42.4% Sn, 1.16% Zn, 27.81% Pb, and 25.48% the other metals (Fig.1).

Experimental results

Effect of pulp density

The recovery rate increases with an increase in the pulp density of the sample over time [34]. After reaching the state of equilibrium, the recovery becomes constant. The graph (Fig. 2) shows an improvement in



(a) (b)

Figure 1. Presence of metals from PCBs sample by a) EDXS & b) SEM images

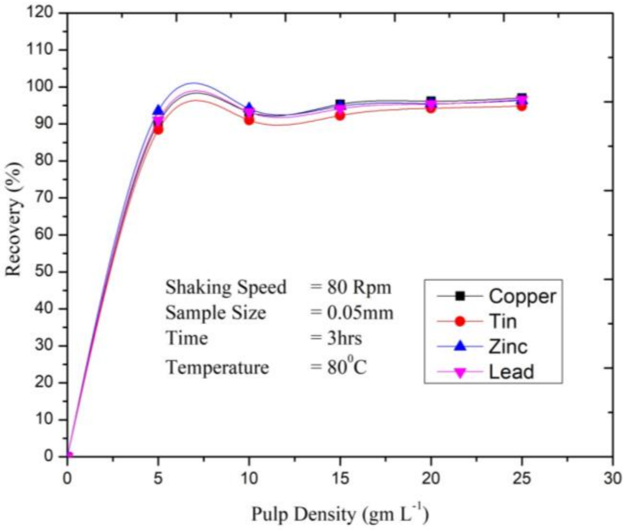


Figure 2. Graphical representation of % recovery of metals with a pulp density.

the PCB pulp density. The metals recovered in the deteriorating order of Cu, Sn, Zn, and Pb. The pulp densities were improved by 5 g L^{-1}, and all metals displayed a marginal improvement in recovery rates of 97.06% Cu, 94.87% Sn, 96.39% Zn, and 96.60% Pb.

Effect of temperature

Fig. 3a shows an appreciable rise in the recovery with increased temperature. The previous results show no noticeable improvement in recovery at temperatures above 80 °C [36]. Thus, the leaching depends on temperature only up to a certain limit above which it is independent of the temperature. At 80 °C, the following recoveries were achieved: 97.46% of Cu, 93.59% of Sn, 92.56% of Zn, and 97.84% of Pb.

Effect of Time

Fig. 3b shows that the metal recovery increases with an increase in the time over some time, and after that, it becomes almost constant. After 3 h leaching, the metal recovery values were 97.46% Cu, 93.56% Sn, 92.56% Zn, and 96.91% Pb.

Effect of Speed

Fig. 3c indicates the relationship between the metal recovery and shaking intensity. At first, the recovery increases by increasing the shaking speed while decreasing at higher speeds [37]. The ionic metal dissociation depends on how long the acid holds on the sample's surface. As the speed increases, there is insufficient time to detach ions from the metal surface because of a shorter interaction time between the metal surfaces and the leaching agent. The result shows a complete metal regeneration at a speed of 80 rpm. It gives a recovery of 95.35% of Cu, 97.76% of Sn, 96.39% of Zn, and 98.76% of Pb.

Effect of Size

In the study of leaching the particles of different sizes using aqua regia, the highest recovery rate was obtained with the PCB sample with the smallest particle size (0.05 mm). The recovery values were as follows: 95.79% of Cu, 93.59% of Sn, 92.56% of Zn, and 97.84% of Pb (Fig. 3d).

Optimization parameters by Design of Experiments (DOE)

The present study used the central composite design (CCD) with three factors. The experimental design had 17 runs, including 8 (23) factorial points, 6 (2×3) axial points, and 5 center points were conducted. All experiments were done using 250 ml Erlenmeyer flasks containing 50 ml solution while the shaking speed and the sample size were adjusted at 80 rpm and 0.05 mm, respectively. The CCD for Cu, Sn, Zn, and Pb leaching was combined with the RSM to optimize the

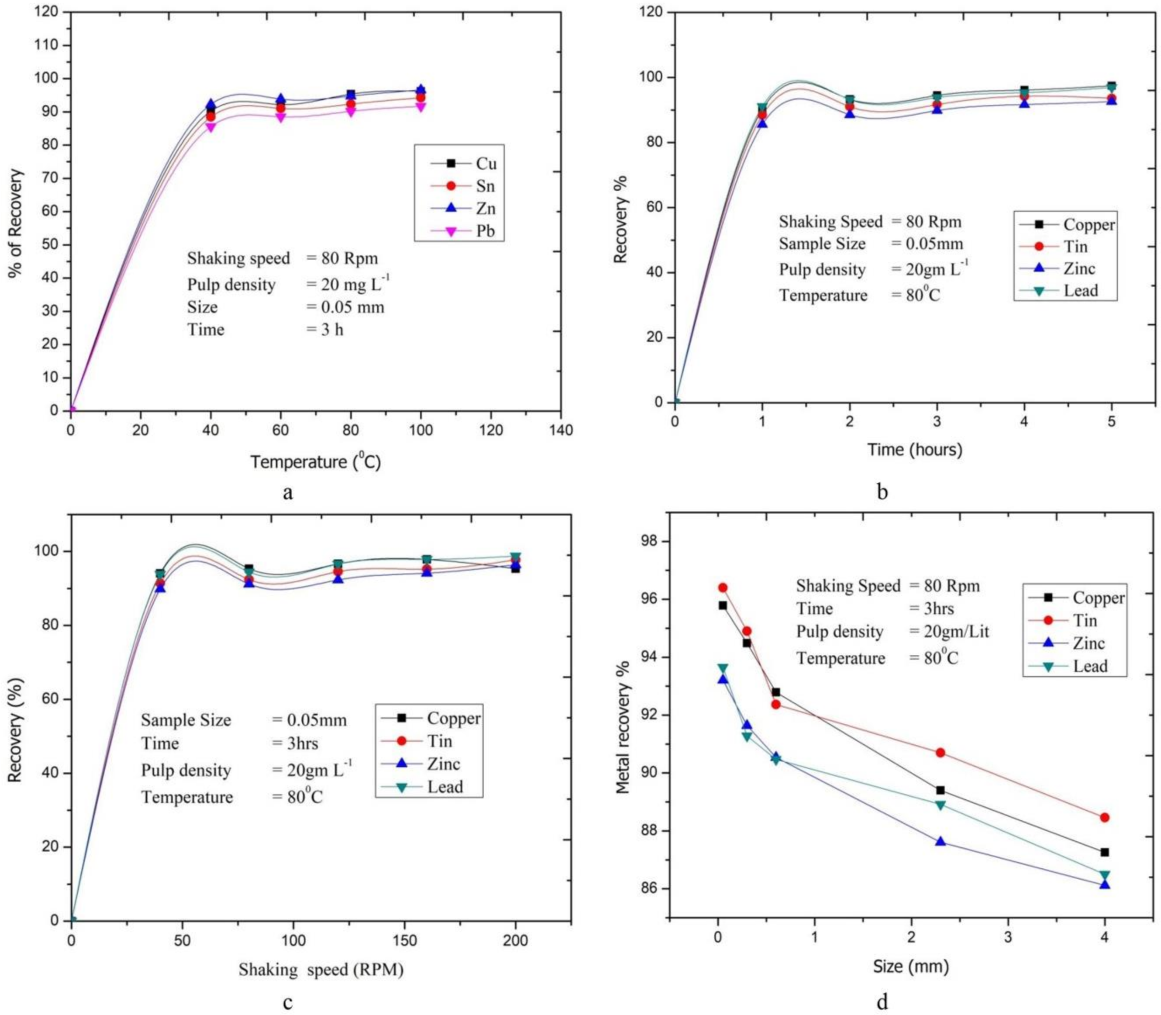


Figure 3. Graphical representation of % recovery of: a) metals with temperature; b) metals with time; c) metals with shaking speed; d) metals with size.

operating parameters and the maximum metal recovery Table 4.

RSM for heavy metals (Cu, Sn, Zn, and Pb) from PCBs

The multiple nonlinear regression was used to determine the multivariable equation connecting the Cu, Sn, Zn, and Pb recoveries with the coded leaching variables (Table 4):

$$\%\ of\ C = +94.61 + 0.1 \cdot A + 2.01 \cdot B + 1.21 \cdot C + 0.21 \cdot A \cdot B - 0.14 \cdot A \cdot C - 0.57 \cdot B \cdot C - 0.54 \cdot A^2 - 1.42 \cdot B^2 - 0.45 \cdot C^2 \quad (1)$$

$$\%\ of\ Sn = +91.62 + 0.014 \cdot A + 1.62 \cdot B + 1.35 \cdot C + 0.41 \cdot A \cdot B + 0.37 \cdot A \cdot C - 0.57 \cdot B \cdot C - 0.27 \cdot A^2 - 1.14 \cdot B^2 - 0.58 \cdot C^2 \quad (2)$$

$$\%\ of\ Zn = +89.49 - 0.20 \cdot A + 1.96 \cdot B + 1.63 \cdot C + 0.40 \cdot A \cdot B + 0.89 \cdot A \cdot C - 0.68 \cdot B \cdot C - 0.77 \cdot A^2 - 1.49 \cdot B^2 - 0.50 \cdot C^2 \quad (3)$$

$$\%\ of\ Pb = +93.71 - 0.030 \cdot A + 1.78 \cdot B + 1.31 \cdot C - 0.075 \cdot A \cdot B + 0.38 \cdot A \cdot C - 0.72 \cdot B \cdot C - 0.62 \cdot A^2 - 1.19 \cdot B^2 - 0.84 \cdot C^2 \quad (4)$$

where *A* represents the contact time (h), *B* is the temperature (°C), and *C* is the pulp density (g L^{-1}). The response of each parameter was predicted within the limits through the model in function of coded factor. Here, the maximum and minimum coded factor levels are +1 and -1. The response surface was visualized in three-dimensional plots that exhibit the two factors' functions while keeping the third factor constant. The interaction between the pulp density and the temperature was observed when the time was kept constant at the optimal value (4 hours). The effect of these parameters on the Cu separation was significant, up to their optimal values. However, the effect was insignificant or negative when exceeding the optimal concentrations. Furthermore, the pulp density positively affected the recovery when the concentration of the leaching agent increased at a constant contact time. Similarly, the recovery rate increased initially in the first two hours and then slightly decreased due to the reduction of the Sn concentration. Figures 4(c) and 4(d) show the surface plots indicating the simultaneous effect of the two factors on the Zn and Pb extraction, while the third factor was at the center level. The predicted design plots (Fig.4a–d) show the red zones above 95.38% of Cu, 92.49% of Sn, 90.96% of Zn, and 94.7% of Pb and the yellow zones above 93% of Cu, 91% of Sn, 89% of Zn, and 93% of Pb, and the blue zones above 88.95% of Cu, 86.36% of Sn, 83.65% of Zn, and 88.51% of Pb.

Table 4. Experimental and predicted results from CCD with optimal parameters for leaching

Run no.	A	B	C	Leaching of heavy metals (%)							
				Experimental				Predicted			
				Cu	Sn	Zn	Pb	Cu	Sn	Zn	Pb
1.	-1	-1	0	90.68	88.99	85.51	90.07	90.6875	88.9875	85.49625	90.07125
2.	1	-1	0	90.6	88.2	85.9	90.16	90.5925	88.19	85.89625	90.16125
3.	-1	1	0	94.27	91.4	90.2	93.79	94.2775	91.41	90.20375	93.78875
4.	1	1	0	95.05	92.26	89	93.58	95.0425	92.2625	89.01375	93.57875
5.	-1	0	-1	92.1	89.78	88.1	91.34	92.1	89.77625	88.10125	91.34125
6.	1	0	-1	92.7	89.06	85.94	90.53	92.715	89.06375	85.93125	90.53125
7.	-1	0	1	94.82	91.73	89.57	93.22	94.805	91.72625	89.57875	93.21875
8.	1	0	1	94.86	92.49	90.96	93.91	94.86	92.49375	90.95875	93.90875
9.	0	-1	-1	88.95	86.36	83.65	88.51	88.9425	86.36625	83.6625	88.5075
10.	0	1	-1	94.11	90.75	88.94	92.22	94.1025	90.74375	88.935	92.22
11.	0	-1	1	92.5	90.18	88.27	91.28	92.5075	90.18625	88.275	91.28
12.	0	1	1	95.38	92.31	90.84	94.7	95.3875	92.30375	90.8275	94.7025
13.	0	0	0	94.8	91.77	90.25	93.8	94.612	91.62	89.92	93.712
14.	0	0	0	94.62	91.6	90	93.44	94.612	91.62	89.92	93.712
15.	0	0	0	94.5	91.6	89.8	93.8	94.612	91.62	89.92	93.712
16.	0	0	0	94.56	91.68	89.67	93.75	94.612	91.62	89.92	93.712
17.	0	0	0	94.58	91.45	89.88	93.77	94.612	91.62	89.92	93.712

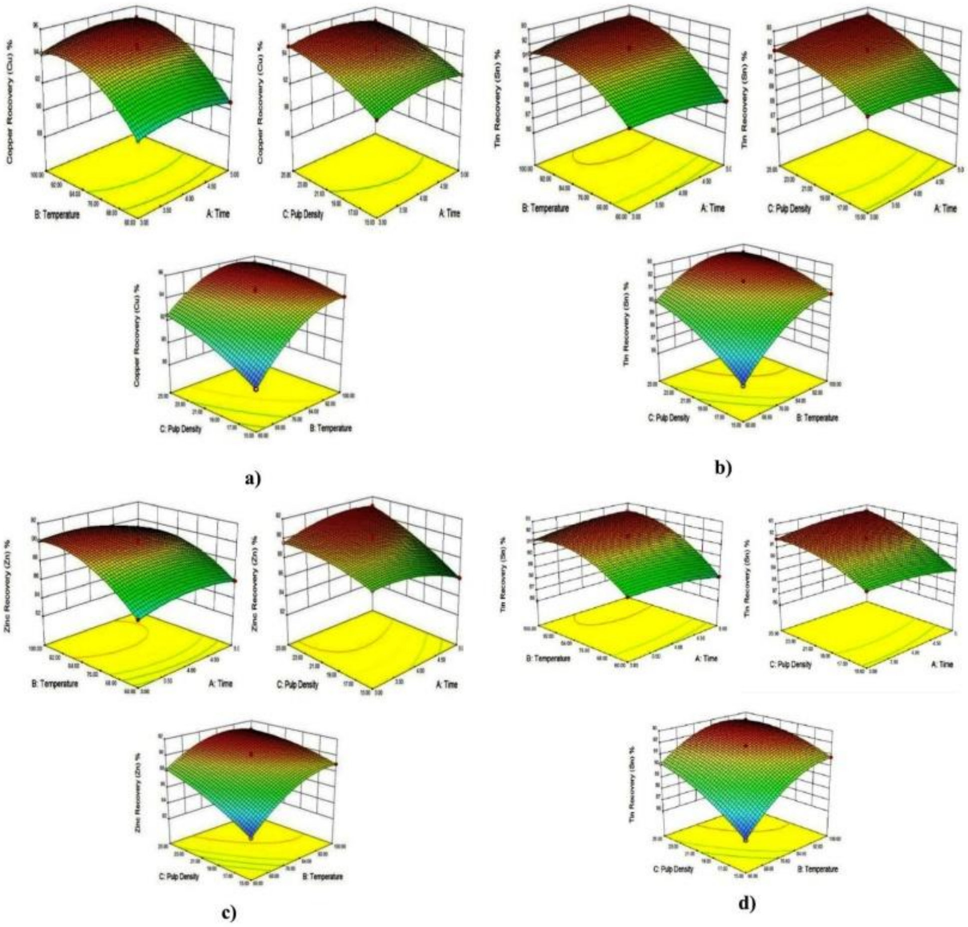

a)
b)
c)
d)

Figure 4. RSM plots and Interactions between the pulp density, temperature, and time by a) Cu; b) Sn; c) Zn; d) Pb recovery rate.

Evaluation of the model

The stability models were validated using the analysis of variance (ANOVA) (Table 5). The low probability (<0.05) with F-values of 848.04, 633.92, 286.97, and 425.51 for Cu, Sn, Zn, and PB, respectively, implied that the model was accurate. Also, the acceptable and reasonable values of the lack of fit with F-value of 0.023 0.010, 0.006, and 0,0004 for Cu, Sn, Zn, and PB, respectively, with the probability values higher than 0.05 indicated the suitability of the developed equations on an excellent presentation of the experimental data.

As presented in Table 6, the model has high R^2 values of 0.999, 0.999, 0.997, and 0.998 for Cu, Sn, Zn, and PB, respectively, indicating a good agreement between the experimental and predicted values. Also, the predicted R^2 values of 0.998, 0.998, 0.996, and 0.997 for Cu, Sn, Zn, and PB, respectively, are in reasonable agreement with the adjusted R^2 values of 0.998, 0.997, 0.994, and 0.996 for Cu, Sn, Zn, and PB, respectively. The model's adequate precision (signal to noise ratio) was found to be 96.96, 89.14, 57.04, and 69.590 for Cu, Sn, Zn, and PB, respectively, which indicated an adequate signal and demonstrated that this model could be used to navigate the design space. The predicted values of the responses were in agreement with the observed values over the selected range of the independent variables with the reasonably higher values of the coefficient of determination (R^2), as can be seen in Fig. 5a.

Desirability plot for recovery of heavy metals from PCBs

The desirability profile for the heavy metals removal versus the variables is shown in Fig. 5b. The desirability varies from 0.0 to 1.0, corresponding to approaching the undesirable to the very desirable condition. The optimum removal of 95.33% of Cu, 92.95% of Sn, 90.99% of Zn, and 94.44% of Pb was obtained under the following operating conditions: the leaching time of 5 h, the temperature of 90.01 °C, and the pulp density of 25 g L^{-1} with the desirability of 0.761.

Maximum recovery by optimization study

Under the optimum conditions, i.e., the time of 5 h, the temperature of 90.01 °C, and the pulp density of 25 g L^{-1} (20 g of the sample treated with 0.5 L of aqua regia, 80 rpm of shaking speed, and 0.05 mm of particle size, the recovery of heavy metals were 97.06% of Cu, 94.66% of Sn, 96.64% of Zn, and 96.89% of Pb.

The metal contents present in the PCB after leaching were 0.09% of Cu, 2.28% of Sn, 0.04% of Pb, 0.91% of Zn, and 1.72% of the others (Fig. 6)

Table 5. ANOVA table for the model to predict % of leaching of copper, tin, zinc, and lead

Source	Model to predict % of leaching of Cu					Model to predict % of leaching of Sn				
	Sum of Squares	df	Mean Square	F-value	p-value Prob> F	Sum of Squares	df	Mean Square	F-value	p-value Prob> F
Model	57.33024	9	6.370027	848.0447	< 0.0001	45.82593	9	5.09177	633.9242	< 0.0001
A-Time	0.22445	1	0.22445	29.88113	0.0009	0.001513	1	0.001513	0.188306	0.4774
B-Temp	32.3208	1	32.3208	4302.883	< 0.0001	21.09251	1	21.09251	2626.013	< 0.0001
C-P den	11.76125	1	11.76125	1565.781	< 0.0001	14.4722	1	14.4722	1801.786	< 0.0001
AB	0.1849	1	0.1849	24.61582	0.0016	0.680625	1	0.680625	84.73766	< 0.0001
AC	0.0784	1	0.0784	10.43743	0.0144	0.5476	1	0.5476	68.17608	< 0.0001
BC	1.2996	1	1.2996	173.0164	< 0.0001	1.2769	1	1.2769	158.9738	< 0.0001
A^2	1.220978	1	1.220978	162.5494	< 0.0001	0.309796	1	0.309796	38.56954	0.0004
B^2	8.532009	1	8.532009	1135.87	< 0.0001	5.436059	1	5.436059	676.7882	< 0.0001
C^2	0.865946	1	0.865946	115.2838	< 0.0001	1.434796	1	1.434796	178.6318	< 0.0001
Residual	0.05258	7	0.007511	-	-	0.056225	7	0.008032	-	-
Lack of Fit	0.0009	3	0.0003	0.02322	0.9945	0.000425	3	0.000142	0.010	0.4984
Pure Error	0.05168	4	0.01292	-	-	0.0558	4	0.01395	-	-
Cor Total	57.38282	16	-	-	-	45.88215	16	-	-	-

Table 5. ANOVA table for the model to predict % of leaching of copper, tin, zinc, and lead (Continued)

Source	Model to predict % of leaching of Zn					Model to predict % of leaching of Pb				
	Sum of Squares	df	Mean Square	F-value	p-value Prob> F	Sum of Squares	df	Mean Square	F-value	p-value Prob> F
Model	71.84526	9	7.982807	286.967	< 0.0001	51.59225	9	5.732472	425.5056	< 0.0001
A-Time	0.31205	1	0.31205	11.21761	0.0123	0.0072	1	0.0072	0.534436	0.4885
B-Temp	30.61531	1	30.61531	1100.563	< 0.0001	25.45411	1	25.45411	1889.389	< 0.0001
C-P den	21.15751	1	21.15751	760.5731	< 0.0001	13.80751	1	13.80751	1024.894	< 0.0001
AB	0.632025	1	0.632025	22.72012	0.0020	0.0225	1	0.0225	1.670113	0.2373
AC	3.150625	1	3.150625	113.2591	< 0.0001	0.5625	1	0.5625	41.75282	0.0003
BC	1.8496	1	1.8496	66.48966	< 0.0001	0.021025	1	0.021025	1.560628	0.2517
A^2	2.528947	1	2.528947	90.91093	< 0.0001	1.617221	1	1.617221	120.0419	< 0.0001
B^2	9.379184	1	9.379184	337.1642	< 0.0001	5.985095	1	5.985095	444.2571	< 0.0001
C^2	1.063184	1	1.063184	38.21949	0.0005	2.986884	1	2.986884	221.7082	< 0.0001
Residual	0.194725	7	0.027818	-	-	0.094305	7	0.013472	-	-
Lack of Fit	0.000925	3	0.000308	0.006364	0.9992	2.5E-05	3	8.33E-06	0.000354	1.0000
Pure Error	0.1938	4	0.04845	-	-	0.09428	4	0.02357	-	-
Cor Total	72.03999	16	-	-	-	51.68655	16	-	-	-

Table 6. Quality of the quadratic model for the leaching of heavy metals

Parameters	Cu	Sn	Zn	Pb
Standard deviation (SD)	0.087	0.090	0.170	0.120
Mean	93.48	90.68	88.62	92.46
Coefficient of variation (CV %)	0.092	0.099	0.190	0.130
Predicted residual error sum of squares (PRESS)	0.095	0.094	0.320	0.150
R-Squared(R^2)	0.999	0.999	0.997	0.998
Adj R-Squared (R^2_{adj})	0.998	0.997	0.994	0.996
Pred R-Squared (R^2_{pred})	0.998	0.998	0.996	0.997
Adequate precision (AP)	96.96	89.14	57.04	69.59

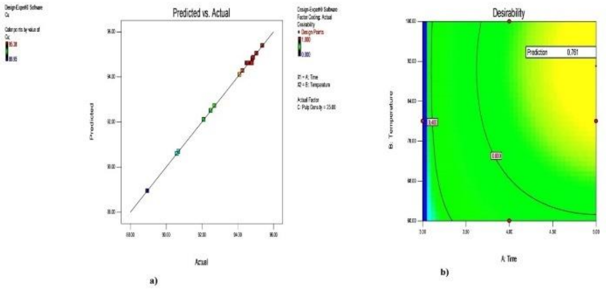


Figure 5. a) Comparison plot between the experimental and predicted data b) Desirability plot for recovery of heavy metals from PCBs.

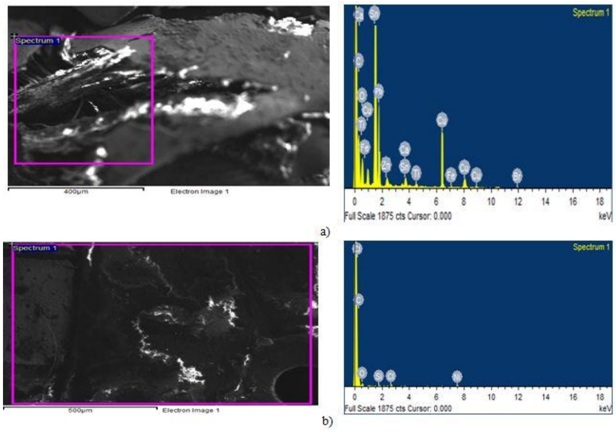


Figure 6. EDXs spectrum analysis for metal ions obtained before (a) Metals composition in before treatment of (PCBs) and after (b) Metals composition in after-treatment of (PCBs) PCBs.

CONCLUSION

The two-phase leaching was used to recover the heavy metals from PCBs under various operating conditions. Temperature, time, and pulp density were the most crucial process factors, while the particle size and the shaking speed showed a marginal effect on the metal recovery. The optimum removal of 95.33% of Cu, 92.95% of Sn, 90.99% of Zn, and 94.44% of Pb with the desirability of 0.761 was achieved in 5 h, the temperature of 90.01 °C, and the pulp density of 25 g L^{-1}. Hence, this metal leaching process was proposed to reduce the environmental impacts of e-wastes caused by the leaching of heavy metals.

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Nomenclature

CCD	-	Central Composite Design
Cu	-	Copper
e-waste	-	Electronic Waste
EDS	-	Scanning Electron Microscopy
EDXs	-	Energy-Dispersive X-Ray Spectroscopy
EEE	-	Electrical and Electronic Equipment
H_2SO_4	-	Sulphuric acid
HCl	-	Hydrochloric acid
HNO_3	-	Nitric acid
P den	-	Pulp density
Pb	-	Lead
PCBs	-	Printed Circuit Boards
RSM	-	Response Surface Methodology
Sn	-	Tin
WEEE	-	Waste of Electrical and Electronic Equipment
Zn	-	Zinc

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NAUČNI RAD

IZDVAJANJE METALA IZ OTPADNIH ŠTAMPANIH PLOČA DVOSTEPENIM LUŽENJEM: STATISTIČKA OPTIMIZACIJA

Brzi razvoj tehnologije je neizbežan i ima značajan udeo u generisanju elektronskog otpada (e-otpada). Elektronski otpad ima ogromne efekte na životnu sredinu i zdravlje ljudi, a veliki doprinos tome daju štampane ploče. Ovaj rad se bavi dobijanjem teških metala iz otpadnih štampanih ploča carskom vodom (aqua regia). kao reagensa za luženje u dve faze (prva faza HCl i HNO_3 *i druga faza HCl i* H_2SO4*). Metodologija površine odziva je korišćena za određivanje optimalnih uslova izdvajanja jona teških metala: vreme luženja od 5 h, gustina suspenzije od 25 g/l i temperatura od 90,1 oC sa vrednošću funkcije poželjnosti 0,761. Ovi optimalni procesni uslovi obezbeđuju maksimalnu stepen izdvajanja metala: Cu (97,06%), Sn (94,66%), Zn (96,64%) i Pb (96,89%). Energijska disperziona spektrofotometrijska (EDX) analiza je korišćena za analizu koncentracije metala u uzorku pre i posle tretmana.*

Ključne reči: carska voda, e-otpad, štampana ploča, metodologija površine odziva, dvostepeno luženje.