

## Article

# Sustainable Process to Recover Metals from Waste PCBs Using Physical Pre-Treatment and Hydrometallurgical Techniques

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**Abstract:** Printed Circuit Boards (PCBs) are an essential component of electronic devices. The digitalization and upgrading of gadget generates lots of PCB-containing electronic waste. Conserving resources and protecting the environment requires the recycling of such e-waste. This paper focuses on the recovery of metals from waste PCBs using physical pre-treatment and hydrometallurgical processes. Initially, the waste PCBs were pre-treated and beneficiated to separate the metallic and non-metallic fractions. The metallic concentrate obtained was leached using nitric acid (a strong oxidative agent) to dissolve the metals. The system was fully jacketed with a scrubber and condenser to prevent the emission of toxic gases into the environment. The process parameters, such as the effect of acid concentration, pulp density, temperature, time, etc., were studied, optimized, and scientifically validated. The kinetics of leaching fitted well with the following shrinking core models:  $X_B = k_c \cdot t$  for Cu,  $(1 - (1 - X_B)^{1/2})$  for Ni, and  $1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$  for Pb. The activation energy was 19.42 kJ/mol. The tin left in the residue was treated separately. The developed process is useful for recovering metals from waste PCBs and has the potential to be commercialized after conducting scale-up studies.

**Keywords:** recycling; e-waste; PCBs; leaching

**Citation:** Kumari, S.; Panda, R.; Prasad, R.; Alorro, R.D.; Jha, M.K. Sustainable Process to Recover Metals from Waste PCBs Using Physical Pre-Treatment and Hydrometallurgical Techniques. *Sustainability* **2024**, *16*, 418. <https://doi.org/10.3390/su16010418>

Received: 27 November 2023

Revised: 22 December 2023

Accepted: 30 December 2023

Published: 3 January 2024



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## 1. Introduction

The production and utilization rates of electronic devices are increasing at a concerning pace due to the reduced longevity of most electronic devices. Subsequently, this has led to the generation of electronic waste (e-waste) at a rapid rate. The development of the electronics sector and the disposal of massive amounts of electronic trash have major impacts on the environment. Such trash is growing at a rate of 5–10% annually [1]. E-waste disposal raises a number of health concerns due to the emission of harmful and dangerous substances, which also contaminate water, land, and the atmosphere. E-waste management rules are lacking in many countries, particularly in developing countries. Open burning, dumping, and acid digestion are common methods of extraction in the informal e-waste sector. These poor recycling methods produce large amounts of byproducts and toxins, which harm human health [2].

Electronic devices comprise a heterogeneous collection of materials, and constant improvements in the features and aesthetics of electronic items leads to dynamic shifts in their content. Most electronic equipment relies heavily on PCBs, which are typically highly complex. Therefore, majority of e-waste contains PCBs. However, they only account for about 3–6% of total e-waste. Effective recycling can turn e-waste into a valuable metal resource. Electronics manufacturers employ precious metals in huge amounts due to their chemical stability, corrosion resistance, and electrical conductivity. These metals often act as contacts, electrodes, or connectors. Mining requires a lot of land, energy, and water, and

also releases harmful gases, such as sulfur dioxide and carbon dioxide. It also generates a lot of secondary solid and liquid pollutants. Primary resource production of these metals substantially impacts the environment. Due to a significant increase in the number of electronic products manufactured, the demand for valuable metals used in electrical and electronic equipment has increased dramatically [3]. PCBs contain a number of valuable metals, often in much higher concentrations than those found in ores containing those metals [4,5]. PCBs typically comprise of PVC polymers, heavy metals, brominated flame retardants, soldering materials, and valuable metals of interest. Hence, waste PCBs are a lucrative option for metal extraction. Research shows that PCBs have distinct components, mainly consisting of 20.13% copper (Cu), 3.59% aluminum (Al), 2.78% zinc (Zn), 2.10% lead (Pb), 3.27% tin (Sn), 7.1% iron (Fe), and 0.6% nickel (Ni) [6–8]. Thus, the utilization of waste PCBs for the extraction of metals can be an essential component in meeting the demand for these materials.

Addressing the dual challenge of environmental degradation and resource scarcity has driven the exploration of sustainable methods for recovering valuable metals from waste PCBs. Several routes have been reported in the literature to treat waste PCBs. These employ mechanical processing, pyro-metallurgy, bio-leaching, and hydrometallurgical processes [9–12]. The recycling of PCBs through pyrometallurgical processes results in the emission of hazardous gases at elevated temperatures, which significantly impacts the environment. Additionally, it demands a substantial amount of energy [13]. The majority of research on bio-leaching has been limited to laboratory settings, and scaling it up for commercial operation is difficult due to its slow reaction kinetics [14]. On the other hand, the hydrometallurgical method of recovering metal is less harmful to the environment, has a lower capital cost than the other methods, and is easy to control.

Hydrometallurgy, as a branch of metallurgy, is characterized by its use of aqueous solutions and selective chemical reactions to extract metals from their primary ores or secondary sources [2]. Hydrometallurgical techniques have emerged as a prospective method for metal recovery due to their potential for high metal extraction rates, reduced environmental footprint, and relatively low energy consumption [15,16]. Most prior studies have concentrated on methods for recovering precious metals, such as Au and Ag, and the remaining base metals are precipitated as their hydroxides and disposed in landfill [17]. The economic viability of the recycling process is heavily influenced by the recovery of base metals (Pb, Sn, and Cu), since these elements are predominant constituents of PCBs. The efficiency of recovering precious metals, such as gold and silver, is significantly enhanced with the preliminary removal of base metals. The literature reports numerous hydrometallurgical processes used to recycle waste PCBs for metal recovery, employing a range of chemical reagents in the process [10,18,19]. However, the economic viability of the process is compromised due to the need for numerous supplementary stages involving multiple chemical reagents, including unreacted acid, neutralizing agents, and metal salts. There are few research articles reporting on the nitric acid leaching of waste PCBs, which is a time-consuming and energy-intensive process [20,21]. Table 1 summarizes the hydrometallurgical processes for metal extraction using various chemical reagents, including their pros and cons [22–42].

The present research investigates the use of nitric acid (HNO<sub>3</sub>), which is a strong oxidative agent. Nitric acid is used in a controlled manner to selectively leach and dissolve metals from the waste PCBs. This helps in the efficient recovery of valuable metals and involves implementing recirculation systems where nitric acid is reused in the system. Closed-loop systems can help to contain and reuse chemicals, reducing the overall environmental impact.

**Table 1.** Hydrometallurgical processes using various chemical reagents.

Leaching Details	Targeted Metals	Remarks	References
Sulfuric acid leaching with oxidizing agent H <sub>2</sub> O <sub>2</sub>	Cu	Pros: Higher leaching efficiency, reduced corrosivity, and enables selective leaching. Cons: <ul style="list-style-type: none"> <li>Requirement for additional oxidizing impacts cost-effectiveness;</li> <li>Complexity of process control;</li> <li>Safety concerns due to the nature of the strong oxidizing agent.</li> </ul>	[22–24]
Aqua regia	Au, Ag	Pros: Specificity for metal leaching. Cons: <ul style="list-style-type: none"> <li>Needs to be done in many stages;</li> <li>Difficulty in controlling the reaction due to high corrosivity and oxidizing nature towards the reactor;</li> <li>Applicability limitations (the industrial-scale application of aqua regia remains restricted).</li> </ul>	[21,25,26]
Cyanide leaching	Au, Ag, Pd, Pt	Pros: Highly efficient to recover gold. Cons: Toxicity, regulatory challenges, and limited selectivity.	[27,28]
Thiourea leaching CS(NH <sub>2</sub> ) <sub>2</sub>	Au, Ag	Pros: High selectivity for gold and silver. Cons: <ul style="list-style-type: none"> <li>High cost and high consumption of thiourea;</li> <li>Thiourea is not stable in acidic conditions.</li> </ul>	[22,29,30]
Thiosulphate leaching	Au, Ag	Pros: Less toxicity, lower environmental impact, and non-corrosivity. Cons: <ul style="list-style-type: none"> <li>Sensitivity to pH;</li> <li>Slower reaction rate and complexity of the process;</li> <li>Cost of the reagents makes it less cost-effective.</li> </ul>	[22,28,29,31,32]
Halide leaching	Au	Pros: Higher recovery of base metal, as well as precious metal. Cons: Emission of toxic gases, such as chlorine gas.	[19,33]
Supercritical methanol (SCM) process	Cu	Pros: Ease of implementation and no additional reducing agents required. Cons: <ul style="list-style-type: none"> <li>Energy intensive and time consuming;</li> <li>Scale-up challenges.</li> </ul>	[34–37]
Cuprous Chloride synthesis	Cu	Pros: Applicability of non-corrosive acids during the process. Cons: Limited to copper recovery.	[23,38]
Chelation technology	Cu	Pros: Effective for extracting toxic metals. Cons: Expensive and lacks selectivity.	[39,40]
Iodine leaching	Precious metals	Pros: Iodine/iodide is a superior substitute for chlorine/chloride due to its rapid kinetics, non-toxicity, and high selectivity for precious metals. Cons: Elevated costs and high consumption rates of iodine prevent industrialization.	[41]

Table 1. Cont.

Leaching Details	Targeted Metals	Remarks	References
Nitric acid leaching	Cu, Pb, Sn	<p>Pros: Dissolution percent is higher and versatile in extracting more metals.</p> <p>Cons:</p> <ul style="list-style-type: none"> <li>Leach liquor cannot be used directly for the electrodeposition of Cu;</li> <li>Formation of gaseous by-products: formation of harmful gases, such as NO<sub>x</sub>, during leaching.</li> </ul>	[1,25,42]
HNO <sub>3</sub> leaching (our work)	Cu, Pb, Ni	<p>Fast kinetic reaction due to the powerful oxidizing agent, facilitating the dissolution of various metals, resulting in maximum recovery and less time consumption.</p> <p>Closed-loop system curbs NO<sub>x</sub> formation and helps to reuse chemicals by reducing the overall environmental impact.</p>	Present Research

A systematic basic study involving the characterization of various setups was carried out. The system was fully jacketed with a scrubber and a water-cooled condenser was used to effectively absorb and dissipate the heat generated during the condensation process of NO<sub>x</sub> gases. The high specific heat capacity of water and its wide availability makes it suitable for this application. The closed system was utilized to capture the generated nitrogen oxides (NO<sub>x</sub>) and to prevent their release into the environment. This research work aimed to optimize various experimental parameters for the effective extraction of metals. Kinetic models and Arrhenius plots have also been reported. The plot fits well with established scientific models with satisfactory validation. The reported basic studies were carried out while adhering to all safety measures and considering environmental norms. The developed process has the potential to be employed in the industry after scale-up studies. Additionally, this study aimed to promote more sustainable recycling processes. The recycling of waste PCBs is a step toward a circular economy, where materials are reused and recycled and the environmental impact of e-waste is lessened. Leaching with nitric acid in a closed-loop system helps in the efficient recovery of valuable metals and contributes to overall energy savings and sustainable development.

## 2. Materials and Methodology

### 2.1. Raw Material and Chemical Reagents

The PCBs of discarded computers were employed as a source of raw material for the investigation. The PCBs were collected from a local computer repairing center. The combined weight of eight PCBs was approximately 3.2 kg.

For chemical treatment, laboratory-grade chemicals, such as HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub>, were used. The chemicals used for experimental purposes were supplied by Merck, Mumbai, India. In order to make the diluted solutions, distilled water was utilized. The raw material used for the experiment consisted of 21.19% Cu, 0.068% Ni, 1.90% Pb, and 2.39% Sn.

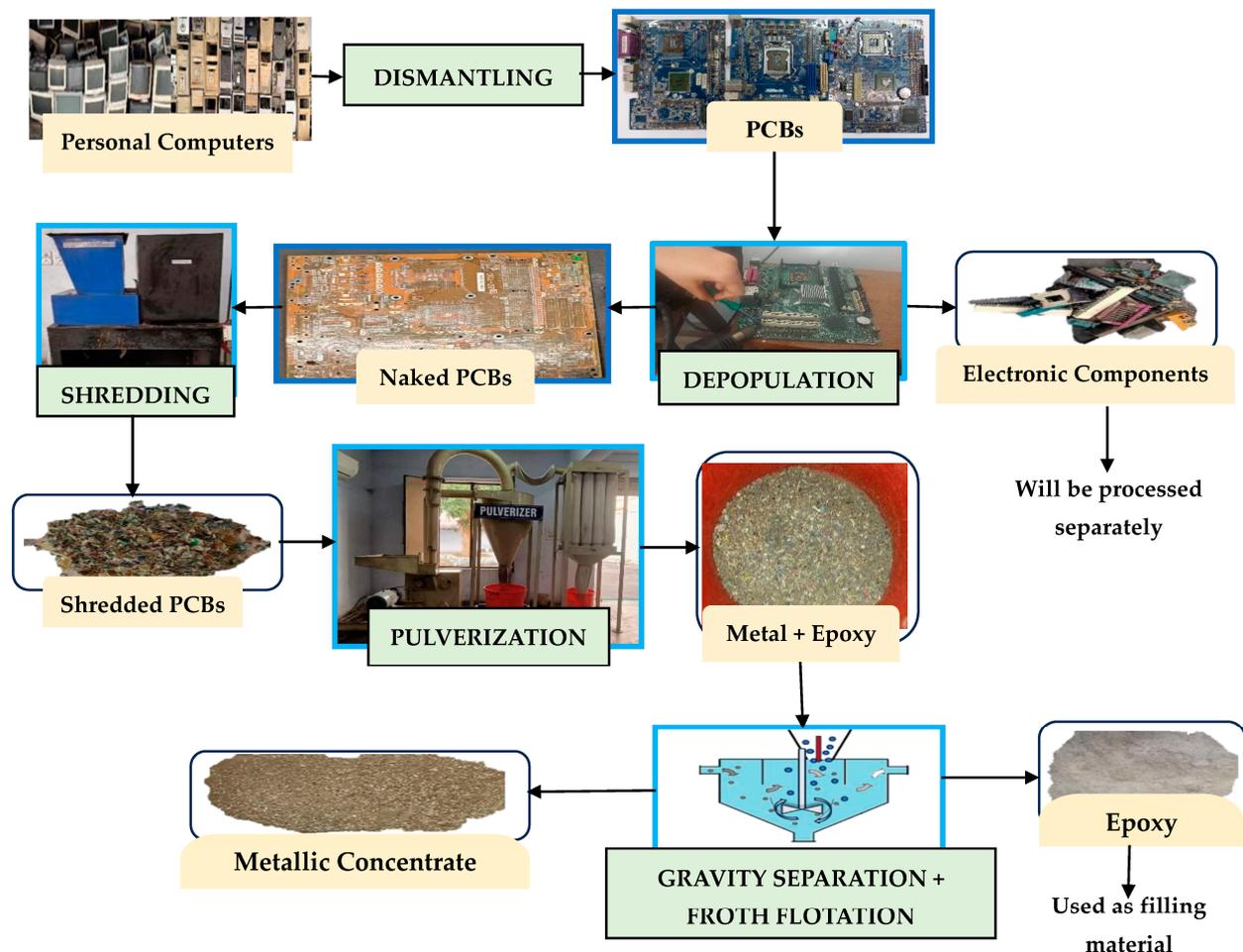
### 2.2. Pre-Treatment Processes

Pre-treatment refers to the step in which a manual, semi-automatic, or automatic method is used to separate the parts of the e-waste that cannot be used for the extraction of any valuable metals because they are typically toxic or contain epoxy. When disassembling a computer or mobile device to extract the PCBs, three different sorts of materials can be found in the PCBs: organic materials, metals, and ceramics. The organic materials in the PCBs are mainly made of plastics with flame retardants [43].

Regardless of the brand, waste PCBs were collected from the local computer shop and collectively weighed about 3.2 kg. The PCBs were subjected to pre-treatment processes, such as mechanical and chemical pre-treatment. Mechanical pre-treatment is commonly

referred to as physical pre-treatment. The populated components were manually separated from the PCBs, including diodes, resistors, capacitors, and plastic components, which were physically disassembled and removed. After this, the shredder was used to shred the PCBs to reduce their size, resulting in a weight of up to 3.04 kg and a thickness of 5 mm. The shredded PCBs were pulverized using pulverizer to produce powdered PCBs containing epoxy and valuable metals. Six distinct portions were identified as follows: +32, −32, +150, −150, +14, and −14  $\mu\text{m}$ . These materials were identified by sieving using a vibratory screen mounted on the sieve shaker. The selection of sieve sizes in the study was a carefully considered decision based on a combination of material characteristics, research objectives, industry standards, and the capabilities of the available equipment. The selected range of sieve sizes enabled the comprehensive analysis of particle size distribution within the context of the present study.

The component mixtures were subjected to froth flotation with varying impeller speeds and a mixing time of 15 min for the separation process. Gravity separation was also used to separate the ground PCBs into light and heavy fractions, which resulted in two separate components: epoxy (wt. 1.65 kg) and metallic concentrate (wt. 1.26 kg), as shown in Figure 1. The enriched metallic concentrate was further utilized as a feed material during the extraction process.



**Figure 1.** Flow diagram of the pre-treatment process of PCBs for sample preparation.

### 2.3. Methodology

The PCBs were treated using hybrid mineral and metallurgical approaches, including physical pre-treatment followed by chemical leaching. A flow diagram of the systematic process was developed for the recovery of metals from waste PCBs. All the experiments

in this study were conducted to efficiently extract the metals present in the PCBs. The pre-treated PCBs were subjected to leaching with varying process parameters, including temperature, pulp density, concentration, and time. The generated leach liquid was further processed using solvent extraction (SX) and electrowinning (EW) processes to obtain purified metals.

#### 2.4. Analytical Procedure

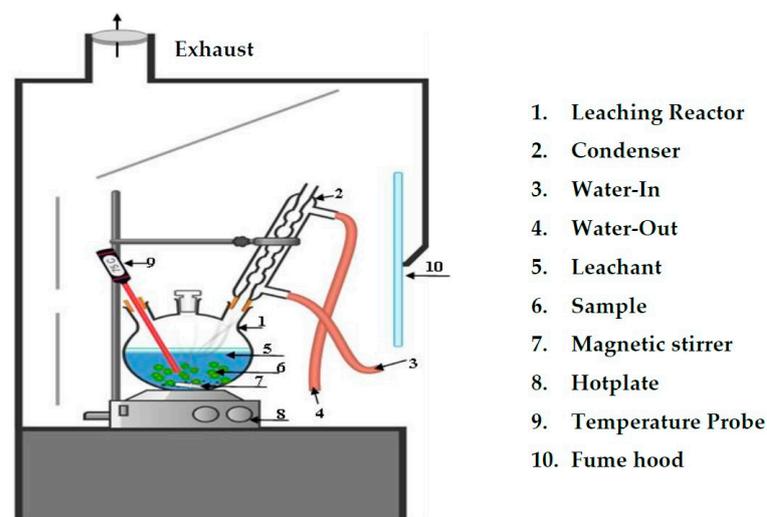
To explore the fresh PCB specimens and leach residue, chemical analyses and characterizations were performed using an Atomic Absorption Spectrophotometer (AAS) (AA240, VARIAN Agilent Technologies, Santa Clara, CA, USA), X-ray Powder Diffraction (XRD) (Rigaku Ultima IV, Tokyo, Japan), and a Scanning Electron Microscope (SEM-EDS) (JXA-8230 Electron Probe micro-Analyzer, JEOL, Tokyo, Japan).

### 3. Results and Discussion

The rapid increase in electronic gadgets and PCBs has led to a significant increase in e-waste generation and environmental risks. To maximize the recovery of metals from waste PCBs, while maintaining the excellent selectivity and low cost of the hydrometallurgical technique, systematic studies were conducted to determine the most efficient operating conditions. Pre-treated waste PCBs were used to explore the hydrometallurgical method. The aim was to strengthen the scientific rigor and depth of discussion, ensuring that the kinetic foundations and leaching processes were thoroughly integrated into the present interpretation of the results.

#### 3.1. Leaching Studies

Studies on leaching were performed in order to recover metals in a three-neck round-bottom flask with a condenser. A temperature-controlled magnetically stirring hot plate was used, and the stirring speed was maintained at 350 rpm. The leaching process was carried out using a variety of different leachants with varying concentrations (1–6 M), time spans (5–60 min), temperatures (35–90 °C), and pulp densities (50–200 g/L) in order to optimize various process parameters for efficient metal recovery. Figure 2 presents a schematic diagram of the experimental leaching setup.



**Figure 2.** Experimental setup for leaching.

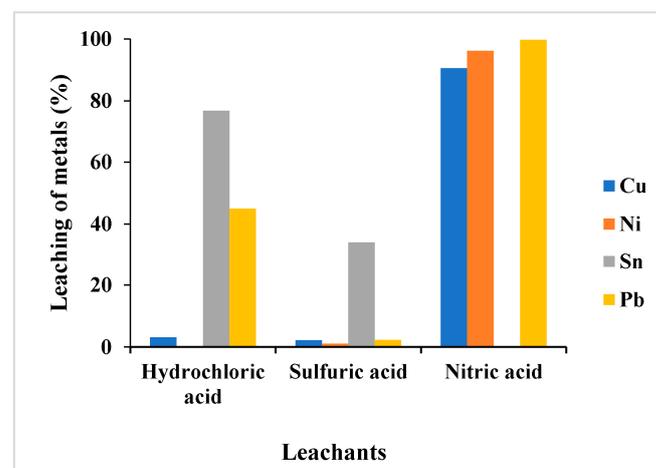
##### 3.1.1. Selection of Leachant

Maximum metal solubilization is highly recommended from an ecological perspective. Therefore, three distinct leachants (HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub>) were used to examine the optimal leachant for maximizing the percentage extraction of metals present in the PCBs. The leaching procedure was conducted using HCl, H<sub>2</sub>SO<sub>4</sub>, and HNO<sub>3</sub> as leachants under

similar experimental conditions. It was discovered that HCl and H<sub>2</sub>SO<sub>4</sub> leached the least amount of metals (HCl: Cu 3.09%, Ni 0.32%, Sn 76.89%, and Pb 44.89%; H<sub>2</sub>SO<sub>4</sub>: Cu 2.18%, Ni 1.07%, Sn 33.74%, and Pb 2.24%) compared to HNO<sub>3</sub>, as presented in Figure 3. Thus, HNO<sub>3</sub> is suitable for the efficient recovery of metals (Cu 90.58%, Ni 96.19%, and Pb 99.72%) from waste PCBs. Since HNO<sub>3</sub> is a strong oxidizing agent, it dissolves most metals, with the general liberation of lower oxides of nitrogen rather than hydrogen. Based on its effectiveness in selectively extracting target metals from the materials under investigation, HNO<sub>3</sub> was selected as a leachant. The leaching efficiency of Cu was calculated using the following equation:

$$\text{The leaching efficiency of metals (\%)} = \frac{M_{\text{solution}}}{(M_{\text{solution}} + M_{\text{residue}})} \times 100 \quad (1)$$

where,  $M_{\text{solution}}$  (g) and  $M_{\text{residue}}$  (g) represent the mass of metal in the leach solution and residue, respectively [44].



**Figure 3.** Selection of the leachant (leachant concentration: 6 M; leaching time: 60 min; temperature: 75 °C; pulp density: 100 g/L; and stirring speed: 350 rpm).

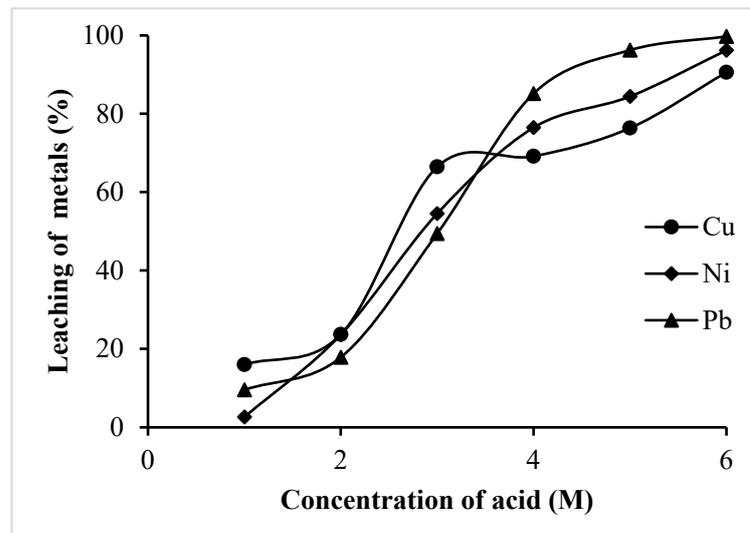
### 3.1.2. Effect of Leachant Concentration

To ensure that the experiments were conducted in a sustainable manner, the emission of poisonous gases and effluent discharge was appropriately managed. Therefore, studies were conducted to determine the effect of acid concentration on the percentage of metals extracted using HNO<sub>3</sub> acid at varying concentrations (ranging from 1–6 M) at 75 °C, 350 rpm, and 100 g/L for 60 min. Increasing the leachant concentration from 1 M to 6 M increased the leaching percentage from 15.99% to 90.58% for Cu, from 2.61% to 96.19% for Ni, and from 9.56% to 99.72% for Pb, as shown in Figure 4. Increasing the leachant concentration enhanced the extraction by providing more reactive species for the dissolution of the target substance [7]. The dissolution of metals in HNO<sub>3</sub> typically involves a redox reaction. HNO<sub>3</sub> is a strong oxidizing agent, and it can oxidize certain metals to form metal nitrates and other products. The specific reaction depends on the metal being dissolved. The general representation of the dissolution of a metal (M) in HNO<sub>3</sub> is as follows:



where  $n$  represents the stoichiometric coefficient for the number of moles of nitric acid reacting with one mole of the metal. One mole of Cu, Ni, and Pb reacts with four moles of HNO<sub>3</sub>. These chemical reactions are as follows:



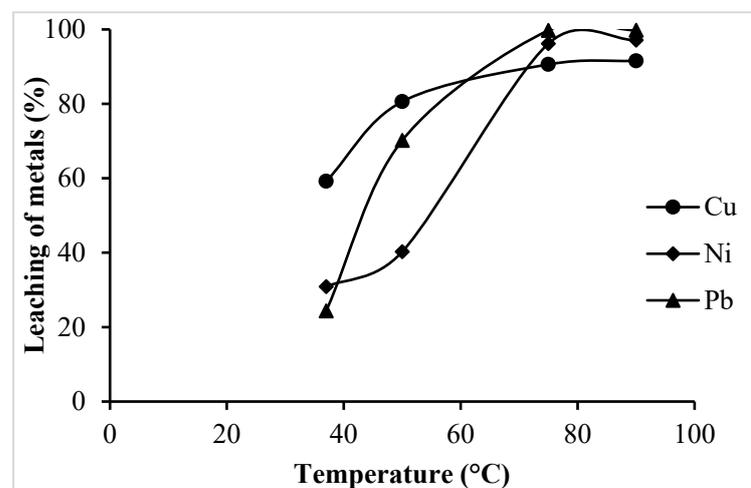


**Figure 4.** Selection of the leachant concentration (leachant:  $\text{HNO}_3$ , leaching time: 60 min, temperature:  $75^\circ\text{C}$ , stirring speed: 350 rpm, and pulp density: 100 g/L).

Hence, a 6 M concentration of  $\text{HNO}_3$  medium is adequate for the efficient recovery of metals from PCBs.

### 3.1.3. Effect of Temperature

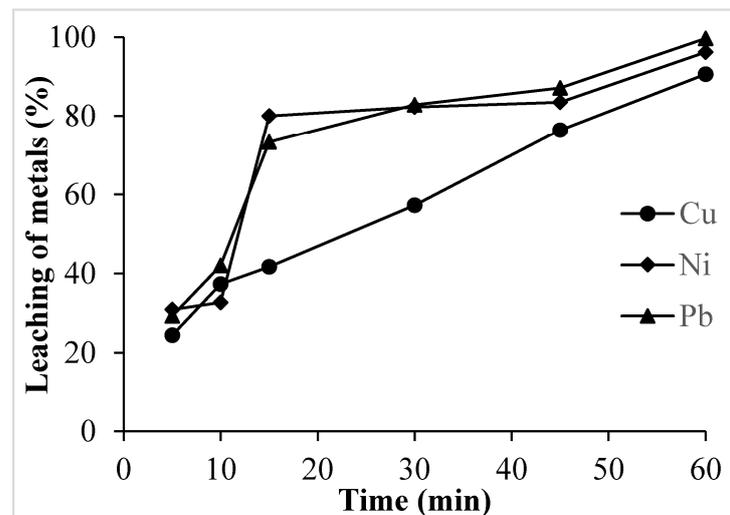
To study the effect of temperature on the percentage extraction of metals, the leaching processes were carried out under varying temperatures, ranging from  $35^\circ\text{C}$  to  $90^\circ\text{C}$ , using an  $\text{HNO}_3$  leachant of 6 M concentration, maintaining a stirring speed of 350 rpm, and using a pulp density of 100 g/L. It was found that the leaching of metals increased from 59.22% to 91.56% for Cu, 30.88% to 97.11% for Ni, and 24.39% to 99.76% for Pb with an increase in temperature from  $35^\circ\text{C}$  to  $90^\circ\text{C}$ . As temperature increases, the enhanced mass transfer between the liquid and solid phases results in increased leaching percentages [45]. It was observed that maximum leaching occurred at  $75^\circ\text{C}$ , and there was a slight increase in leaching at  $90^\circ\text{C}$ , as shown in Figure 5. Hence,  $75^\circ\text{C}$  is considered the optimal temperature for energy conservation.



**Figure 5.** Effect of temperature (leachant:  $\text{HNO}_3$ , leaching time: 60 min, acid concentration: 6 M, stirring speed: 350 rpm, and pulp density: 100 g/L).

### 3.1.4. Effect of Time

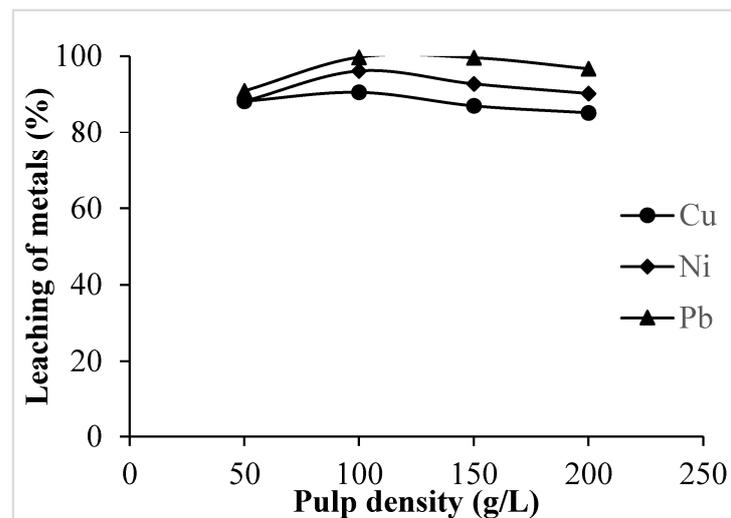
To study the effect of time on the percentage extraction of metals, the experiment was conducted for 60 min using an  $\text{HNO}_3$  leachant with a concentration of 6 M, at 75 °C, a stirring speed of 350 rpm, and a pulp density of 100 g/L. The samples were collected at different intervals (5–60 min) of time throughout the leaching process. The recovery of metals increased from 24.39% to 90.58% for Cu, 30.88% to 96.19% for Ni, and 29.31% to 99.72% for Pb as time increased from 5 to 60 min, as shown in Figure 6. The rates of mass transfer and solute diffusion through solids into the liquid are influenced by time. Longer contact time allows for more extensive diffusion and mass transfer, leading to increased leaching efficiency [1]. The maximum recovery of metals (Cu, 90.58%; Ni, 96.19%; and Pb, 99.89%) occurred at 60 min. Hence, a leaching time of 60 min was considered for further studies.



**Figure 6.** Effect of time (leachant:  $\text{HNO}_3$ , acid concentration: 6 M, temperature: 75 °C, stirring speed: 350 rpm, and pulp density: 100 g/L).

### 3.1.5. Effect of Pulp Density

Pulp density, also known as the solid–liquid ratio, plays an essential role in the leaching process, especially in hydrometallurgical processes in which solid materials are extracted or dissolved in a liquid (leachant). The effect of pulp density on percentage extraction during the leaching process varies depending on the specific system and the minerals or metals being extracted. Here, we present some general observations regarding the effect of pulp density. To study the effect of pulp density on the percentage extraction of metals, leaching processes were carried out with varying pulp densities (from 50–200 g/L), with an  $\text{HNO}_3$  acid concentration of 6 M, a temperature of 75 °C, a stirring speed of 350 rpm, and 60 min of leaching time. We found that the recovery of metals decreased from 90.58% to 85.27% for Cu, 96.19% to 90.30% for Ni, and 99.72% to 96.72% for Pb as pulp density increased from 100 to 200 g/L. However, the extraction percentage decreased when the pulp density was above 100 g/L, as shown in Figure 7. Lower pulp densities are often associated with improved mixing and agitation. Better mixing can lead to more efficient mass transfer and increased contact between the solid material and the leachant. In turn, this can enhance the extraction rate [45]. Therefore, a pulp density of 100 g/L was considered optimal for the efficient recovery process. The selection of 100 g/L of solid density was based on achieving the highest leaching percentages for the three metals under consideration.

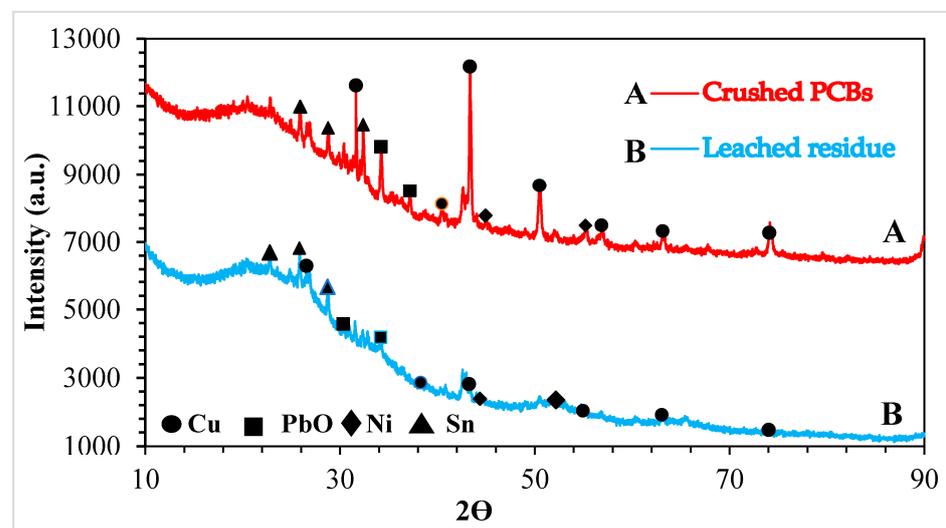


**Figure 7.** Effect of pulp density (leachant: HNO<sub>3</sub>, leaching time: 60 min, acid concentration: 6 M, temperature: 75 °C, and stirring speed: 350 rpm).

### 3.2. Characterization Studies

#### 3.2.1. X-ray Powder Diffraction (XRD)

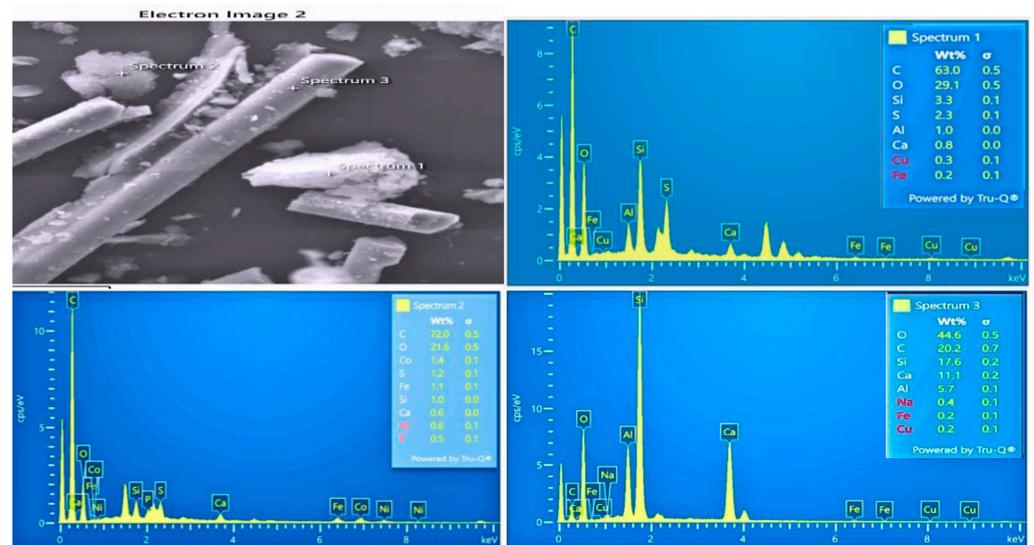
The XRD spectra, acquired through measurements of the powdered samples of the PCBs and leached residue, displayed rapid-phase composition scans from 5 to 90°, 2θ, and Copper Kα radiation, as shown in Figure 8. The XRD pattern indicates that Cu, Ni, Pb, and Sn were present in the powdered PCB samples, and that the concentration or peak of Cu, Ni, and Pb decreased after leaching.



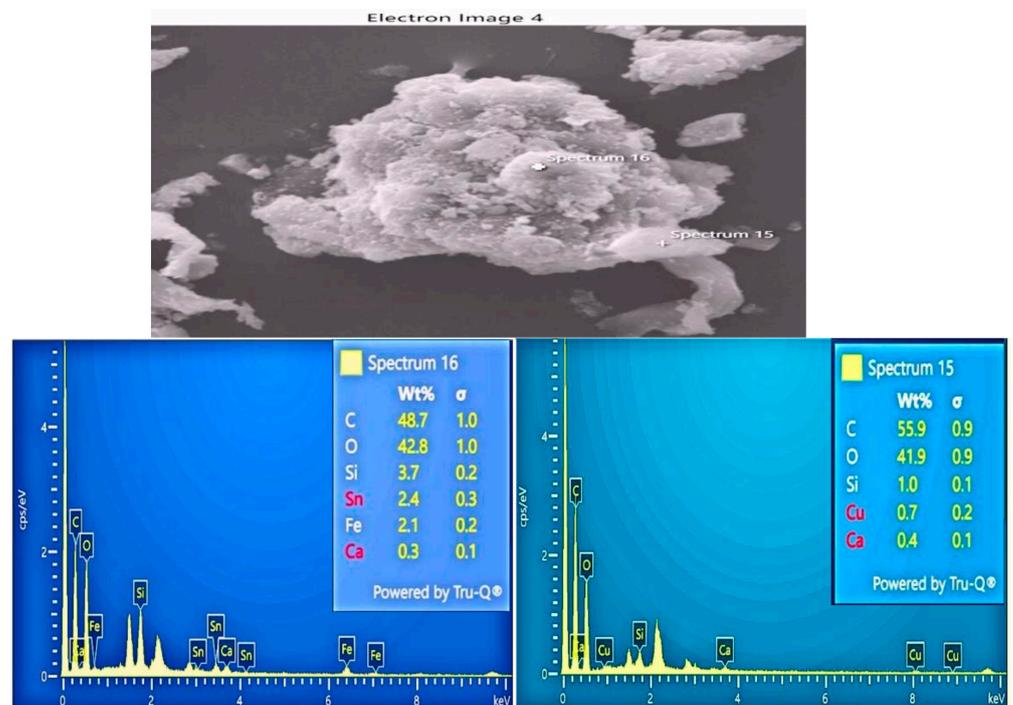
**Figure 8.** XRD analysis of pulverized PCBs and leached residue.

#### 3.2.2. Scanning Electron Microscopy (SEM-EDS)

The powdered PCB and leach residue samples were analyzed using scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM-EDS) to determine the structural and compositional features of the metals present. The spherical shapes representing elements present in the PCBs were identified in spectrum 1, 2, and 3 in the powdered sample. As illustrated in Figure 9a,b, the observations indicate that the structural and compositional features of powdered PCBs changed after leaching.



(a)



(b)

**Figure 9.** (a) Structural and compositional analysis of crushed PCBs (SEM-EDS). (b) Structural and compositional analysis of leach residue (SEM-EDS).

### 3.3. Scientific Validation of Leaching

According to various reports, leaching reactions take place at the interface between the solid–liquid phases, where the lixiviant moves from the bulk solution to the boundary layer, resulting in chemical reactions at this interface [25]. Hence, the leaching mechanism was investigated by studying the kinetics of metal dissolution from the waste PCBs by altering the concentration. The metal leaching data, obtained with variable concentrations and times at a constant pulp density of 100 g/L and a temperature of 75 °C, were fitted with several standard equations of the shrinking core models and were evaluated for reaction kinetics (Figures 10–12).

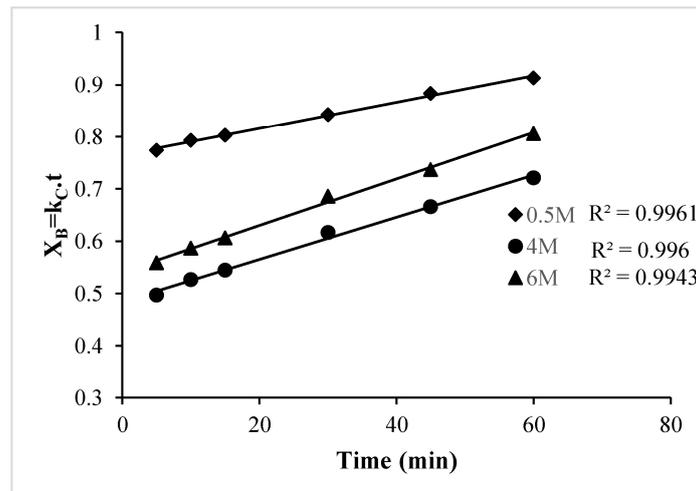


Figure 10. Regression co-efficient ( $R^2$ ) values for Cu in the shrinking core model for the leaching kinetics of waste PCBs.

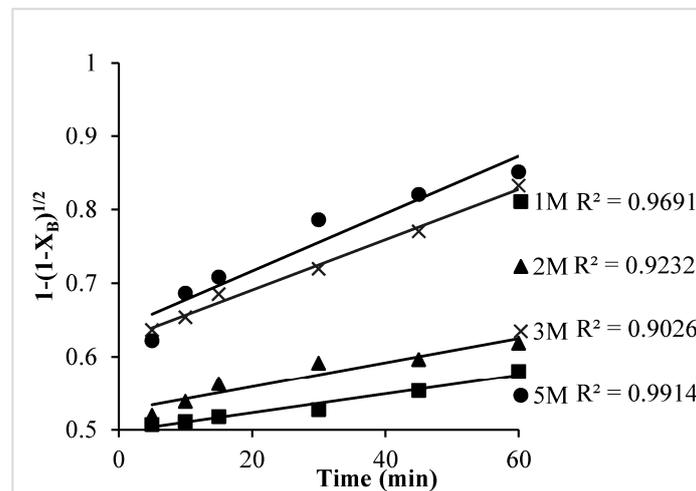


Figure 11. Regression co-efficient ( $R^2$ ) values for Ni in the shrinking core model for the leaching kinetics of waste PCBs.

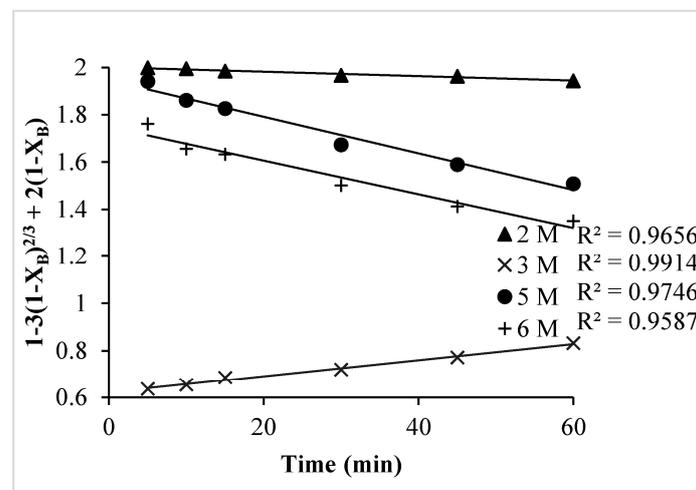


Figure 12. Regression co-efficient ( $R^2$ ) values for Pb in the shrinking core model for the leaching kinetics of waste PCBs.

The standard kinetic equations for the shrinking core models are as follows [19]:  
Film diffusion control of constant size particles

$$X_B = k_c \cdot t \quad (6)$$

Reaction control of constant-size cylindrical particles

$$1 - (1 - X_B)^{1/2} = k_c \cdot t \quad (7)$$

Ash diffusion control of constant-size spherical particles

$$1 - 3(1 - X_B)^{2/3} + 2(1 - X_B) = k_c \cdot t \quad (8)$$

Film diffusion control of small-size shrinking sphere particles

$$1 - (1 - X_B)^{2/3} = k_c \cdot t \quad (9)$$

Reaction control of large-size shrinking sphere particles

$$1 - (1 - X_B)^{1/3} = k_c \cdot t \quad (10)$$

All the equations were tested using the obtained experimental data. We found that the data fit excellently with various models, including the film diffusion control dense constant-size small particle model (all geometries) (i.e.,  $X_B = k_c \cdot t$ ), the chemical reaction control dense constant-size model ( $1 - (1 - X_B)^{1/2}$ ), and the ash diffusion control dense constant-size model ( $1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$ ) for Cu, Ni, and Pb, respectively (where  $X_B$  is the fraction reacted,  $k_c$  is the kinetic parameter for chemical reaction control, and  $t$  is the reaction time).

The regression coefficient ( $R^2$ ) was calculated for each model using the following formula:

$$\frac{\sum_{i=1}^{i=n} (Y_i - \bar{Y})^2 (Y_i^o - \hat{Y})^2}{\sum_{i=1}^{i=n} (Y_i - \bar{Y})^2 \sum_{i=1}^{i=n} (Y_i^o - \hat{Y})^2} \quad (11)$$

where  $\bar{Y}$  represents the experimental value,  $Y_i$  represents the calculated value,  $Y_i^o$  represents the mean experimental value, and  $\hat{Y}$  represents the mean calculated value.

### 3.4. Arrhenius Equation

The kinetics of leaching can be influenced by temperature in multiple ways. Temperature has the potential to increase the diffusion rate, expedite chemical reaction rates, impact the solubility of both reactants and products, and alter the direction of reversible reactions. The relationship between temperature and the rate of leaching can be mathematically described using the Arrhenius equation, as follows [45]:

$$k = k' \exp\left(\frac{-Ea}{RT}\right) \quad (12)$$

where  $k$  represents the leaching rate constant,  $Ea$  represents the activation energy,  $T$  denotes the absolute temperature,  $R$  is the universal gas constant, and  $k'$  represents the pre-exponential factor.

Using Equation (12) and the  $\ln k$  vs.  $1000/T$  graph, the activation energy was determined as 19.42 kJ/mol, as shown in Figure 13.

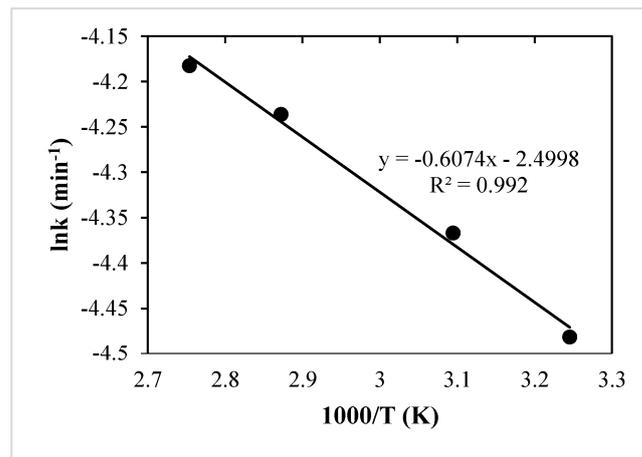


Figure 13. Arrhenius plot (activation energy,  $E_a = 19.42$  kJ/mol).

Based on the experimental studies, a process flow diagram was devised and is depicted in Figure 14.

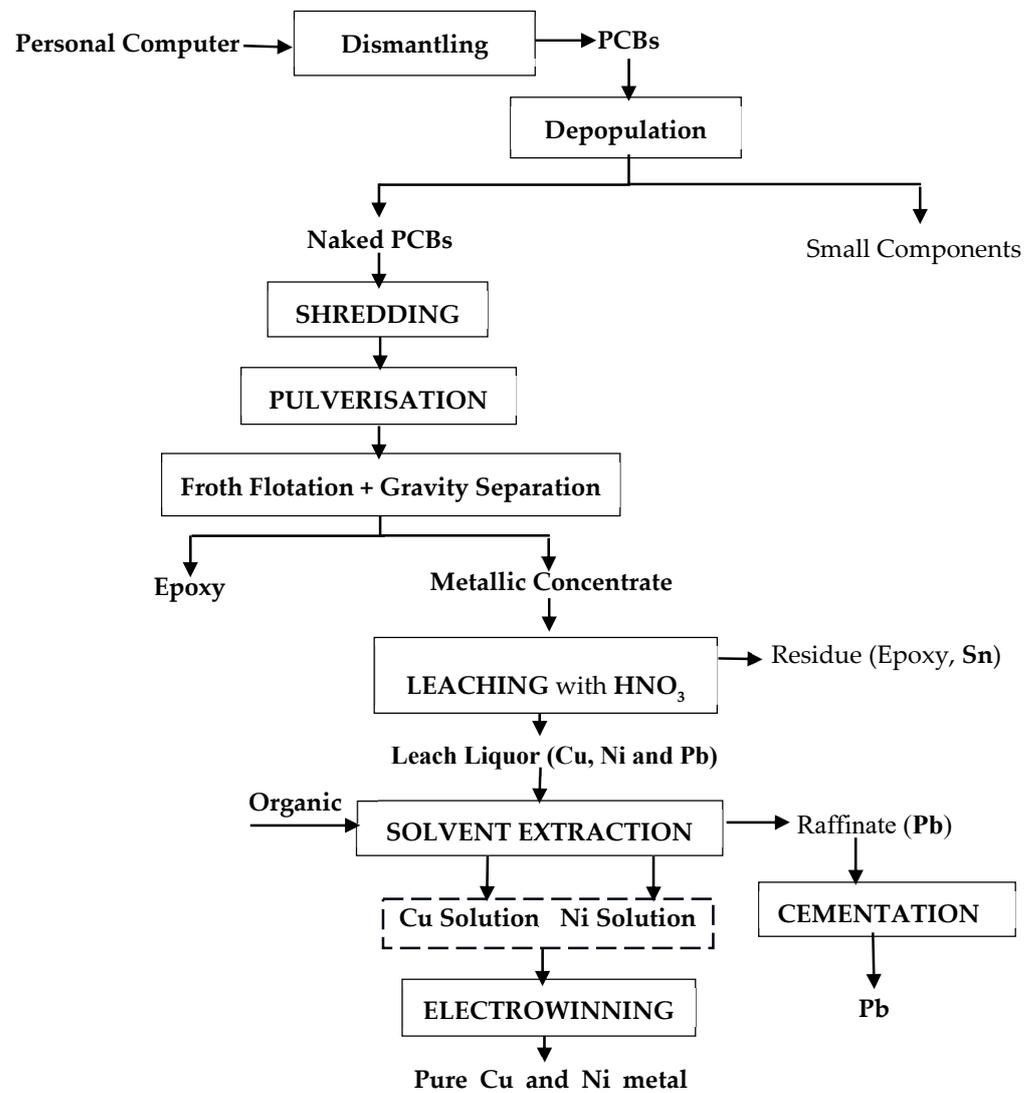


Figure 14. Process flow diagram for metal recovery from printed circuit boards (PCBs).

#### 4. Conclusions

The following findings are based on the systematic investigations that were carried out to extract valuable metals from the waste PCBs obtained from personal computers.

- Metal liberation was found to be ~99.90%; however, with the removal of epoxy resins or plastics, metal liberation reached 99.99%.
- The optimum conditions for the recovery or dissolution of 90.58% Cu, 96.19% Ni, and 99.72% Pb were a nitric acid concentration of 6M, a temperature of 75 °C, a pulp density of 100 g/L, and a time of 60 min. The higher concentration of HNO<sub>3</sub> and elevated temperature were chosen to achieve optimal leaching efficiency within a reasonable timeframe during the present research.
- The film diffusion control dense constant-size small particle (all geometries) model ( $X_B = k_c \cdot t$ ) fit well with the leaching kinetics for Cu.
- The chemical reaction control dense constant-size model ( $1 - (1 - X_B)^{1/2}$ ) fit well with the leaching kinetics for Ni.
- The ash diffusion control dense constant-size model ( $1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$ ) fit well with the leaching kinetics for Pb.
- The activation energy for Cu was 19.42 kJ/mol.
- Nitric leaching in a closed-loop system can result in high metal recovery rates and a larger percentage of the target metal could be leached without emitting noxious gases. As nitric acid is a strong oxidizing agent, it facilitates faster metal dissolution. Efficiency is crucial for economic and environmental reasons, as it reduces waste and increases the overall yield of valuable metals by considering implementation and mitigation measures during the leaching process.
- The generated leach liquid could be further processed using solvent extraction, cementation, and electrowinning processes to obtain purified metal products. The flow diagram of this process is shown in Figure 14.
- The process is viable and eco-friendly at the laboratory scale and has potential for commercial exploitation. The leached residues and effluents produced during the experiment will be properly treated and can be reused using standard procedures before their final disposal into the environment.
- Complete recycling will not only reduce the loss of valuable metals, but will also aid in the establishment of an organized sector for e-waste recycling, taking into account environmental regulations and raising public awareness about the loss of valuable metals caused by the dumping of such waste into the environment.

**Author Contributions:** Methodology, S.K.; validation, R.P. (Rekha Panda) and M.K.J.; investigation, S.K. and R.D.A.; resources, R.P. (Ranjit Prasad); data curation, R.P. (Rekha Panda); writing—original draft preparation, S.K.; writing—review and editing, R.P. (Rekha Panda) and M.K.J.; supervision, M.K.J. All authors have read and agreed to the published version of the manuscript.

**Funding:** This research received no external funding.

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Data is contained within the article.

**Acknowledgments:** We acknowledge the support received from CSIR-NML, Jamshedpur (India). The authors express gratitude to CSIR-NML, Jamshedpur, for granting permission to publish this article. One of the authors, Suruchi Kumari, would like to extend gratitude towards CSIR-NML, Jamshedpur, for providing the research facility to carry out this work.

**Conflicts of Interest:** The authors declare that there are no conflicts of interest.

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