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Study of Alternative Oxidants in Sulphuric Acid Leaching of Copper from PCBs

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Abstract: *The growing volume of electronic waste (e-waste) necessitates sustainable metal recovery methods. Printed circuit boards (PCBs), rich in valuable metals like copper are a key target however, improper disposal causes environmental harm, and conventional sulphuric acid leaching achieves low recovery due to limited oxidation capability. This study investigates and compares the effectiveness of selected alternative oxidants hydrogen peroxide (H_2O_2), calcium hypochlorite ($Ca(ClO)_2$), and ferric sulphate ($Fe_2(SO_4)_3$) in enhancing copper dissolution from waste PCBs during sulphuric acid leaching. Experiments were conducted under controlled conditions, and the oxidant efficiency was evaluated by varying oxidants concentrations and temperatures. Results showed that oxidants significantly improve copper dissolution, with H_2O_2 yielding the highest efficiency of 94.11% at 55°C. Additionally, the study identified diffusion through the product layer as the rate-limiting step. And activation energy of 11.559 kj/mol indicated that the process is diffusion controlled.*

Keywords: *Printed Circuit Boards, Copper, Leaching, Sulphuric Acid, Oxidants*

I. Introduction

Electronic waste (e-waste) is one of the largest and fastest-growing waste streams worldwide. The total global amount of e-waste was approximately 41 million tonnes in 2014 (Kumar et al., 2017), rising to around 44.7 million tonnes in 2016, and reaching about 52.2 million tonnes in 2021. It is estimated to be growing at a rate of at least 17% per year (Yaashikaa *et al.*, 2022), with projections suggesting that annual generation may exceed 70 million tonnes in the near future. According to Babu et al. (2007)(Babu, Parande and Basha, 2007), the European Parliament and Council's Directive separate e-waste into several categories, including large household appliances, medical systems, and communication equipment. Photovoltaic panels, laptops, gaming consoles, televisions, LED lights, drills, refrigerators, and washing machines are a few examples. The worldwide demand for electronic devices and, by extension, base and precious metals is closely linked to the sharp increase in e-waste.

PCBs, which make up 4–7% of e-waste, are particularly valuable due to their high concentration of copper, aluminium, rare earth elements, and precious metals (Au, Ag, and Pt) (Barrueto *et al.*, 2021). Studies show that over 80% of PCB mass is composed of the metal foil layer alone (Duan and Zhu, 2022). Because they contaminate soil, air, and water systems, improper disposal techniques like burial or incineration present major environmental risks (Twagirayezu *et al.*, 2022).

In hydrometallurgy, acid leaching is a well- established method for dissolving metal values into solution for further separation and recovery. In the case of copper, sulphuric acid ($H_2 SO_4$) is commonly used because it forms soluble copper(II) sulphate complexes. However, when negligible copper leaching from PCBs unless an oxidant (such as $H_2 O_2$, O_3 or Fe^{3+}) was used (Cui and

Anderson, 2016; Lisińska *et al.*, 2024). From an extraction metallurgy viewpoint, while much of the research on copper leaching has been directed at primary oxide or sulphide ores, the adaptation of these methods to secondary sources like PCBs raises additional challenges: heterogeneous feed composition (resins, fibres, solder alloys, laminate matrix, copper foil), the presence of tin/lead in solder, potential passivation effects on copper surfaces, and varying physical–chemical accessibility of copper foil within the board microstructure (Kim, M.S., Jeong, J., 2012).

Hence, a systematic investigation into leaching copper from PCBs using sulphuric acid combined with alternative oxidants (not just H_2O_2) is timely. By comparing oxidants like ferric sulfate ($Fe_2(SO_4)_3$ providing Fe^{3+}) and hydrogen peroxide (and potentially a third alternative oxidant) under controlled conditions, the study can clarify which oxidant gives superior performance for PCB copper recovery

The aim of this study is to evaluate and compare the performance of selected alternative oxidants in sulphuric acid leaching of copper from waste printed circuit boards (PCBs), in order to identify optimal operating conditions and to assess practical feasibility for recovery of copper from secondary resources.

2. Methodology

2.1. Material and equipment

Equipment that were used are, Atomic Absorption Spectrometry (AAS), X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Scanning Electron Microscopy (SEM), PH Meter, Analytical balance, Hot plate, Conical flasks, Beakers, Rod mill, chipping material and Analytical balance

Chemicals that were used are Sulphuric acid (HCl), Hydrogen peroxide (H2O2), Ferrous Sulphate ($FeSO_4$), Ferric Chlorite ($FeCl_3$), NaOH (pH control), and deionized water.

2.2. Sample preparation

The circuit boards of the discarded personal computers were first reduced in size to about 2 × 2 cm by utilizing a chipping machine. then to get the required particle size, the material was then ground in a rod mill. After that, a basic density-based technique with potable water was used to separate the plastic components. After that, magnetic materials were manually removed using a magnet. The remaining valuable material was then carefully combined and separated using a rotary splitter into samples weighing around 30 grams each.

2.3.Sample characterization

The PC PCB sample was used as a dissolution feed with particle size range of +45µm–106µm. Using X-ray fluorescence (XRF), the samples were analysed for mineral composition. XRF was used to determine elemental composition. X-ray diffraction (XRD) was used to determine the phase composition. SEM was used to identify minerals and their crystalline structures.

2.4. Leaching test

The leaching experiments were conducted by mixing 150 mL of 2M H2SO4 solution with different oxidants (H_2O_2, $FeSO_4$, and $Fe_2(SO_4)_3$) in an Erlenmeyer flask. The experiments varied oxidants concentration, Temperature, and Time. The stirring speed was kept constant at 250rpm. The concentrations of the oxidants were varied at 0 M, 0.1 M, 0.3 M, and 0.5 M. The temperature of the leaching solution was adjusted to one of the predetermined levels: 25°C, 40°C, or 55°C. The system was allowed to equilibrate for a few minutes prior to initiating the leaching process. The leaching proceeded for varying durations: 30, 60, 120, 210 minutes. At each specified time interval, a sample of the leachate (approximately 15 mL) was withdrawn and filtered to remove solid particles, and the filtered solution was stored in a labelled container for subsequent analysis. Once the test is completed, an aliquot of 10 to 15 mL was extracted for analysis. After the completion of the leaching experiments, the concentrations of dissolved Cu in the leaching solutions were analysed using Atomic Absorption Spectrophotometer (AAS).

3. Results and Discussion

3.1. Characterisation

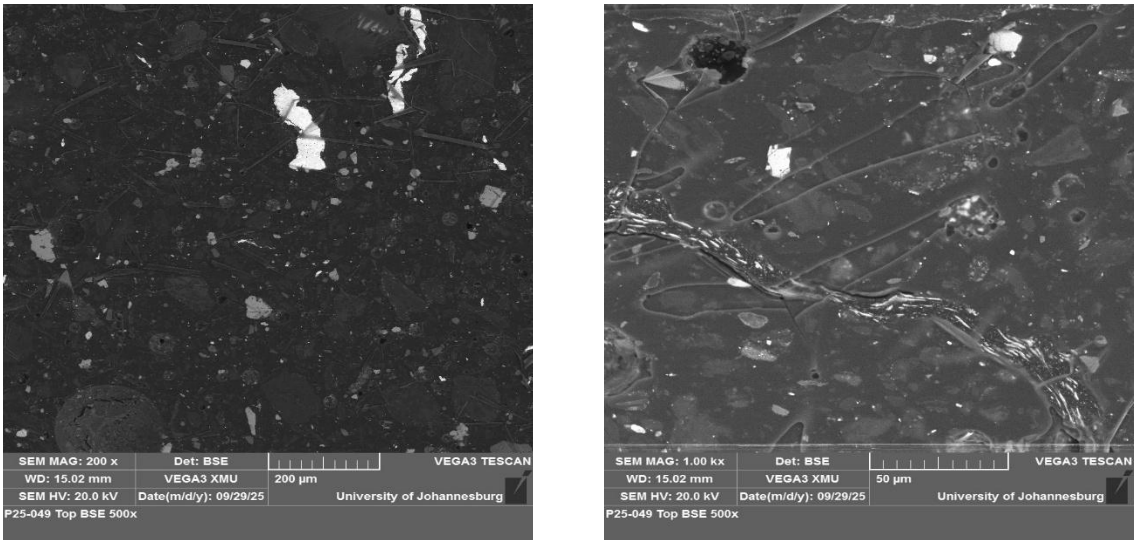
X-ray fluorescence (XRF) analysis was carried out to determine the elemental composition of the waste printed circuit board (PCB) sample prior to leaching. The XRF spectrum (Table 1) revealed that iron (Fe) was the most abundant metallic element at 22.11%, followed by copper (Cu) at 7.43 %, tin (Sn) at 6.54 %, and bromine (Br) at 6.54 %. Significant amounts of silicon (Si, 6.08 %) and zinc (Zn, 3.46 %) were also detected, while lead (Pb, 3.15 %) and aluminium (Al, 2.39 %) were present in moderate concentrations. Minor constituents included calcium (Ca, 2.03 %), magnesium (Mg, 0.89 %), and nickel (Ni, 0.94 %).

TABLE 1: METALS CONTENT OF PRINTED CIRCUIT BOARDS (PCBS) FROM XRF

Components	Content (%)
Cu	7,43
Fe	22,11
Al	2,39
Si	6,08
Sn	6,54
Pb	3,15
Zn	3,46
Br	6,54
Ca	2,03
Mg	0,89
Mn	5,16
Ni	0,94

The surface morphology of the untreated PCB sample was examined using Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy (SEM–EDS), as shown in figure 1.

The EDS spectrum confirmed that the major elements present in the head sample were oxygen (71.48 wt%) and silicon (20.88 wt%), followed by smaller amounts of calcium (3.86 wt%), aluminium (1.38 wt%), and tin (1.12 wt%). Trace quantities of magnesium (0.52 wt%), chlorine (0.46 wt%), iron (0.22 wt%), and copper (0.10 wt%) were also detected. The high oxygen and silicon contents indicate that the sample surface is dominated by silicate glass fibers and epoxy resin, consistent with the non-metallic substrate of PCBs (Sethurajan and van Hullebusch, 2019). The presence of aluminium, calcium, and magnesium further supports the occurrence of filler and laminate materials used in board manufacturing.



Element	Weight%	Atomic%
O K	71.48	82.62
Mg K	0.52	0.39
Al K	1.38	0.94
Si K	20.88	13.75
Cl K	0.46	0.24
Ca K	3.86	1.78
Fe K	0.22	0.07
Cu K	0.10	0.03
Sn L	1.12	0.17
Totals	100.00	

Fig. 1: Scanning electron microscope–Energy dispersive X-ray spectroscopy (SEM-EDS) spectra of PC PCBs

3.2. Leaching with H_2SO_4 alone

Figure 2 presents the leaching behaviour of copper from waste printed circuit boards (PCBs) using sulphuric acid (H_2SO_4) as the sole leaching agent. The purpose of this graph is to establish a reference baseline for subsequent comparison with oxidant-assisted systems. This baseline curve provides a benchmark for evaluating how the introduction of oxidants such as hydrogen peroxide or ferric ions can enhance copper dissolution by improving oxidative conditions and overcoming passivation effects.

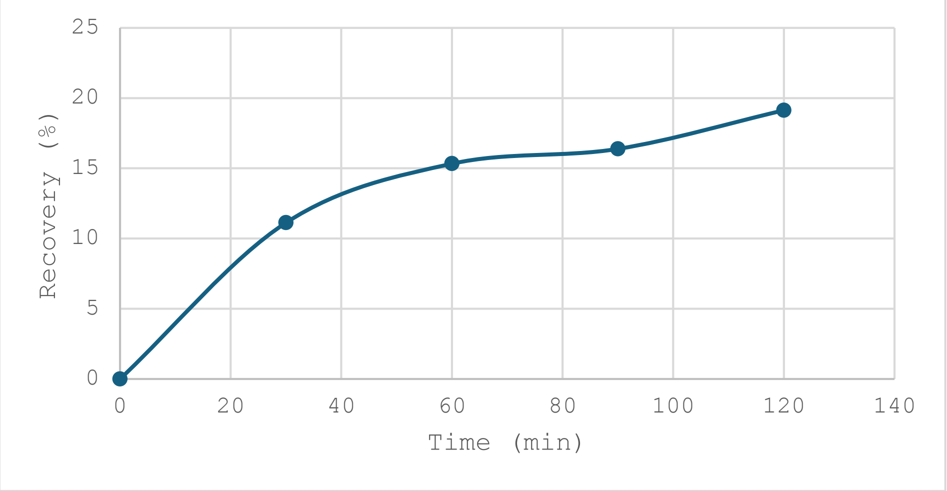


Figure 2: Copper dissolution from PCBs in H_2 SO_4 solution

The results for copper recovery are very low as the highest recovery at 120 min was 19.13%, which shows that leaching copper without oxidants is insufficient. Lisinska et al., 2019 (Lisińska *et al.*, 2024) stated that sulfuric acid is not sufficient enough to flush all copper in PCBs, they need a strong oxidizing agent.

3.3. Leaching with a mixture of H_2SO_4 and H_2O_2

Figure 3 illustrates the effect of oxidant concentration on the leaching efficiency of copper from waste printed circuit boards (PCBs) in a sulphuric acid (H_2 SO_4) medium. In this experiment, H_2O_2 concentration was varied at 0.1 M, 0.3 M, and 0.5 M at different durations while maintaining constant leaching parameters such as 2M of H_2 SO_4 , Temperature of 50°C, and 300 rpm agitation speed.

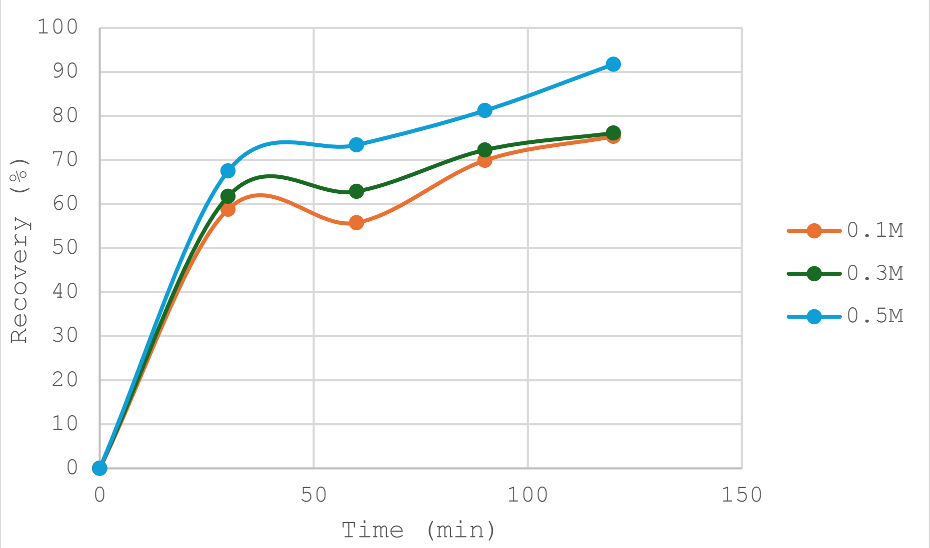


Figure 3: Effect of H_2O_2 on copper leaching

The analysis of the dissolution of copper from PCBs shows significant patterns impacted by addition of Hydrogen peroxide. The graph shows that recovery of copper increased rapidly after addition of H_2O_2. At 120 min it was recorded that at 0.1 M, 0.3 M, and 0.5 M copper recovery were 75.3%, 76,1% and 91,7% respectively which indicated that as concentration of H_2O_2 increased the recovery of copper also increased.

Figure 4 presents the effect of temperature on the leaching efficiency of copper from waste printed circuit boards (PCBs) using a sulphuric acid (H_2 SO_4) solution in the presence of an Fe_2 $(SO_4)_3$.

The experiments were conducted at varying temperatures (25°C, 40 °C and 55 °C) under identical acid of 3M $H_2 SO_4$ and 0,1M H_2O_2 concentrations, and agitation speed of 300 rpm.

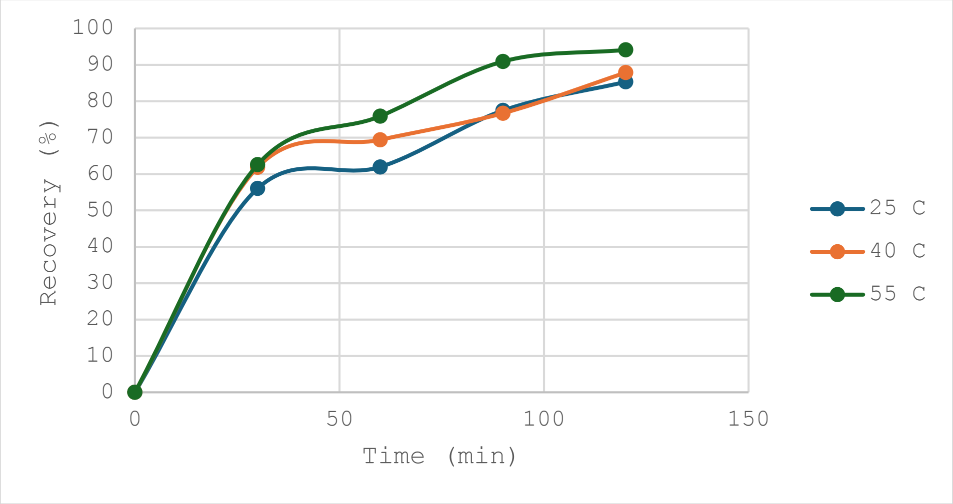


Fig. 4: Copper Dissolution from PCBs in 3M $H_2 SO_4$ and 0,1M H_2O_2 Solution at Various Temperatures

Figure 4 shows that as the temperature increases from 25°C to 55°C, there is a noticeable enhancement in the amount of copper dissolved over the specified time intervals. At 25°C, the maximum dissolution after 120 minutes is approximately 66.48%, while at 55°C, the maximum reaches an impressive 94.11%. This significant increase highlights the critical role of temperature in enhancing reaction kinetics and overall dissolution efficiency. The graphs reveal a progressive increase in copper dissolution at all temperatures, with more pronounced increases observed at higher temperatures. For instance: At 25°C, the dissolution rises from about 50.63% at 30 minutes to 66.48% at 120 minutes, indicating steady extraction but slower kinetics. 11 In contrast, at 55°C, the extraction increases from 62.57% at 30 minutes to 94.11% at 120 minutes, demonstrating a much more rapid and efficient dissolution process.

3.4. Leaching with a mixture of H_2SO_4 and Ca(ClO)2

Figure 5 illustrates the effect of oxidant concentration on the leaching efficiency of copper from waste printed circuit boards (PCBs) in a sulphuric acid ($H_2 SO_4$) medium. In this experiment, $Ca(ClO)_2$ concentration was varied at 0.1 M, 0.3 M, and 0.5 M at different durations while maintaining constant leaching parameters such as 2M of $H_2 SO_4$, Temperature of 50°C, and 300 rpm agitation speed.

Addition of $Ca(ClO)_2$ also increases the copper recovery. At 120 min it was recorded that at 0.1 M, 0.3 M, and 0.5 M copper recovery were 61,18%, 64,29% and 76,18% respectively which indicated that as concentration of oxidant increased the recovery of copper also increased. The recovery from $Ca(ClO)_2$ is not higher than of H_2O_2 addition. This shows that peroxide is a stronger oxidizing agent for copper in comparison to Hypochlorite. The recovery started increasing slowly after 60 minutes, at 0.5M the recovery increased only by 7% and 0.1M and 0.3M increased by 1% and 2% respectively. This is due to reagent depletion since hypochlorite decompose faster at high temperatures or low alkalinity (Adam and Gordon, 1999).

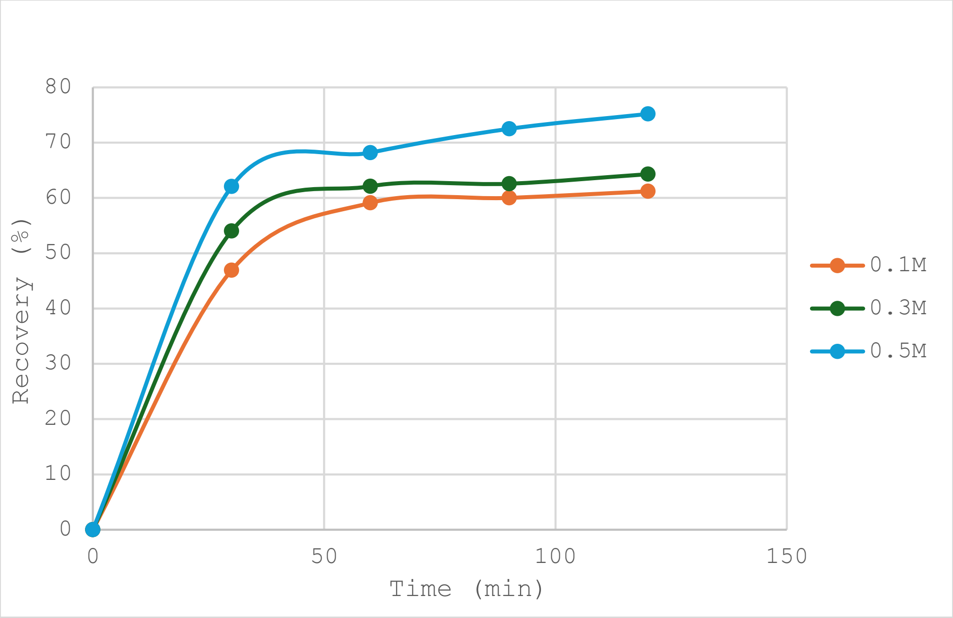


Figure 5: Effect of $Ca(ClO)_2$ on copper leaching

Figure 6 presents the effect of temperature on the leaching efficiency of copper from waste printed circuit boards (PCBs) using a sulphuric acid (H_2SO_4) solution in the presence of an $Ca(ClO)_2$. The experiments were conducted at varying temperatures (25°C, 40 °C and 55 °C) under identical acid of 3M H_2SO_4 and 0,1M $Ca(ClO)_2$ concentrations, and agitation speed of 300 rpm.

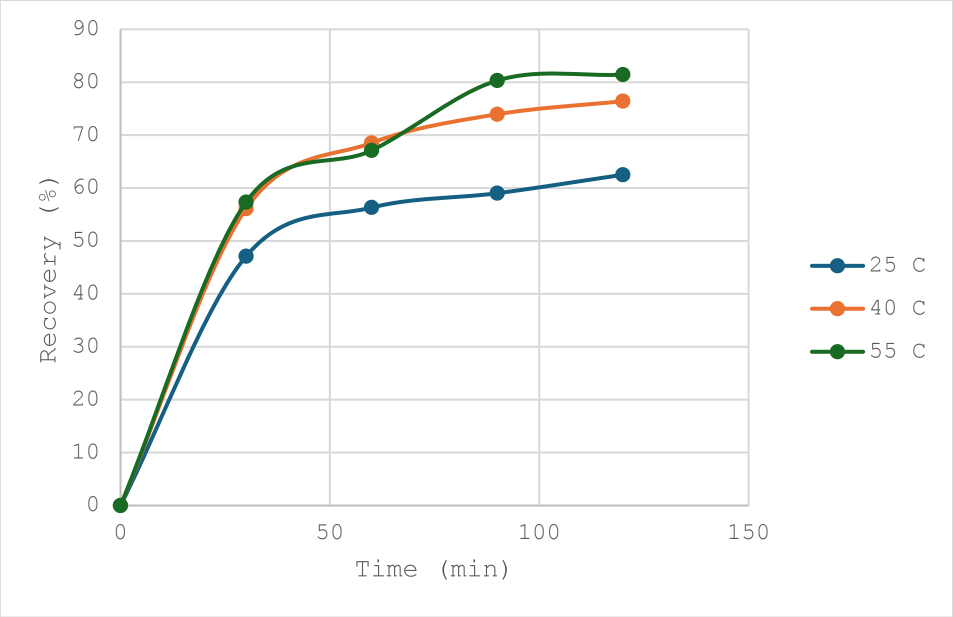


Figure 6: Copper Dissolution from PCBs in 3M H□SO□ and 0,1M $Ca(ClO)_2$ Solution at Various Temperatures

Figure 6 illustrates that increasing the temperature from 25 °C to 55 °C leads to a marked enhancement in copper dissolution over the 120-minute period. At 25 °C, the maximum dissolution after 120 minutes is approximately 62.52%, whereas at 55 °C it reaches about 81.44%. This notable improvement emphasizes the significant influence of temperature on reaction kinetics and overall dissolution efficiency.

Across all tested temperatures, copper recovery shows a steady upward trend with time, though the rate of increase becomes more pronounced at higher temperatures. For example, at 25 °C, dissolution rises from roughly 47.11% at 30 minutes to 62.52% at 120 minutes an increase of about 15%, indicating moderate but consistent leaching kinetics. In contrast, at 55 °C, extraction increases from 57.33% at 30 minutes to 81.44% at 120 minutes an improvement of approximately 24%, reflecting a much faster and more efficient dissolution process

3.5. Leaching with a mixture of H_2SO_4 and $Fe_2(SO_4)_3$

Figure 7 illustrates the effect of oxidant concentration on the leaching efficiency of copper from waste printed circuit boards (PCBs) in a sulphuric acid (H_2SO_4) medium. In this experiment, H2O2 concentration was varied at 0.1 M, 0.3 M, and 0.5 M at different durations while maintaining constant leaching parameters such as 2M of H_2SO_4, Temperature of 50°C, and 300 rpm agitation speed.

Addition of $Fe_2(SO_4)_3$ also increases the copper recovery. At 120 min it was recorded that at 0.1 M, 0.3 M, and 0.5 M copper recovery were 75,1%, 80,37% and 84.28% respectively which indicated that as concentration of oxidant increased the recovery of copper also increased. The recovery from $Fe_2(SO_4)_3$ is not higher than of H_2O_2 addition. This shows that peroxide is a stronger oxidizing agent for copper in comparison to $Fe_2(SO_4)_3$. However ferric sulphate is a stronger oxidizing agent than hypochlorite which recovered 76,18% at 0.5M $Ca(ClO)_2$.

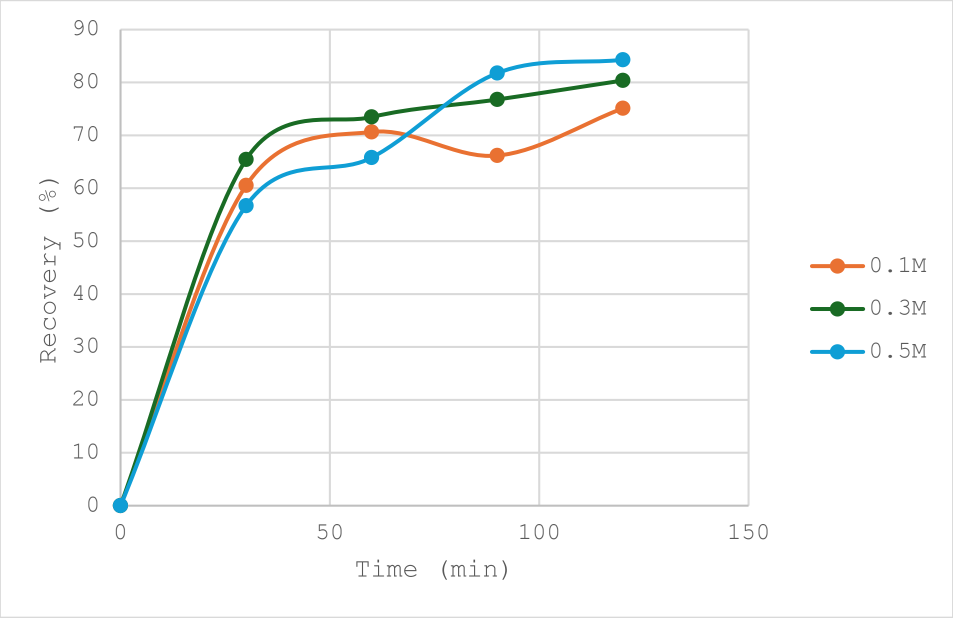


Figure 7: Effect of $Fe_2(SO_4)_3$ on copper leaching

Figure 8 presents the effect of temperature on the leaching efficiency of copper from waste printed circuit boards (PCBs) using a sulphuric acid (H_2SO_4) solution in the presence of an $Fe_2(SO_4)_3$. The experiments were conducted at varying temperatures (25°C, 40 °C and 55 °C) under identical acid of 3M H_2SO_4 and 0,1M $Fe_2(SO_4)_3$ concentrations, and agitation speed of 300 rpm.

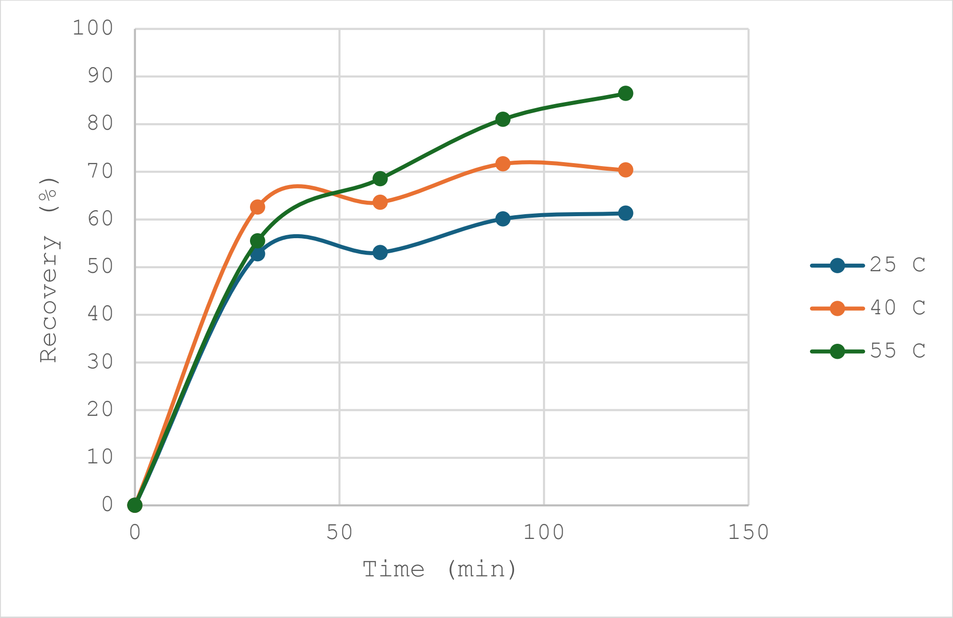


Figure 8: Copper Dissolution from PCBs in 3M H_2SO_4 and 0,1M $Fe_2(SO_4)_3$ Solution at Various Temperatures

Figure 8 indicates that increasing the temperature from 25 °C to 55 °C significantly enhances copper dissolution over the 120-minute leaching period. At 25 °C, the maximum dissolution achieved after 120 minutes is approximately 61.29%, whereas at 55 °C it increases to about 86.44%. This substantial improvement underscores the strong influence of temperature on accelerating reaction kinetics and improving overall dissolution efficiency.

The data further show a consistent increase in copper dissolution across all temperatures, with the rate of extraction becoming more pronounced at elevated temperatures. For example, at 25 °C, dissolution rises from around 52.76% at 30 minutes to 61.29% at 120 minutes an increase of roughly 8%, indicating gradual but relatively slow kinetics. In contrast, at 55 °C, extraction increases from 55.48% at 30 minutes to 86.44% at 120 minutes an improvement of approximately 31%, reflecting a much faster and more efficient dissolution process.

3.6. Leaching Kinetics

Experimental data were used to investigate the mechanism of copper leaching using Hydrogen Peroxide. Various shrinking core models, including the surface chemical reaction model and the product layer diffusion model, were used for this analysis.

The shrinking core model is widely utilized to describe the kinetics of leaching processes. This model encompasses both the diffusion of the leaching agent through the solid product layer and the reaction occurring at the surface of the unreacted core. When one of these steps is significantly slower than the other, it becomes the rate-controlling step, resulting in the leaching rate becoming the same as the rate of that step (Faraji *et al.*, 2022).

The study aimed to understand the kinetic behaviour of the leaching process and identify the dominant factors affecting the rate of dissolution Table 2 shows the rate constant values along with their correlation coefficients for the models analysed. A comprehensive analysis of the data indicated that diffusion through the product layer is the rate limiting step in the dissolution reaction. As a result, the values from the temperature-related experiments were linearized using the model equation 1-(3/2)*X-(1-X)2/3=kt. The plot for temperature is illustrated in Figure 9.

TABLE II: THE APPARENT RATE CONSTANTS AND CORRELATION COEFFICIENTS FOR SHRINKING CORE MODEL

	surface chemical reaction 1-(1-X)^(1/3)=KT		diffusion through product layer 1–(2/3)* X–(1 –X)^(2/3)	
	kIt	R2	kIt	R2
Temperature (K)				
273	0,0037	0,9296	0,0037	0,9791
313	0,0037	0,8926	0,0039	0,9659
328	0,005	0,9461	0,0057	0,9837
		0,92276667		0,976233333

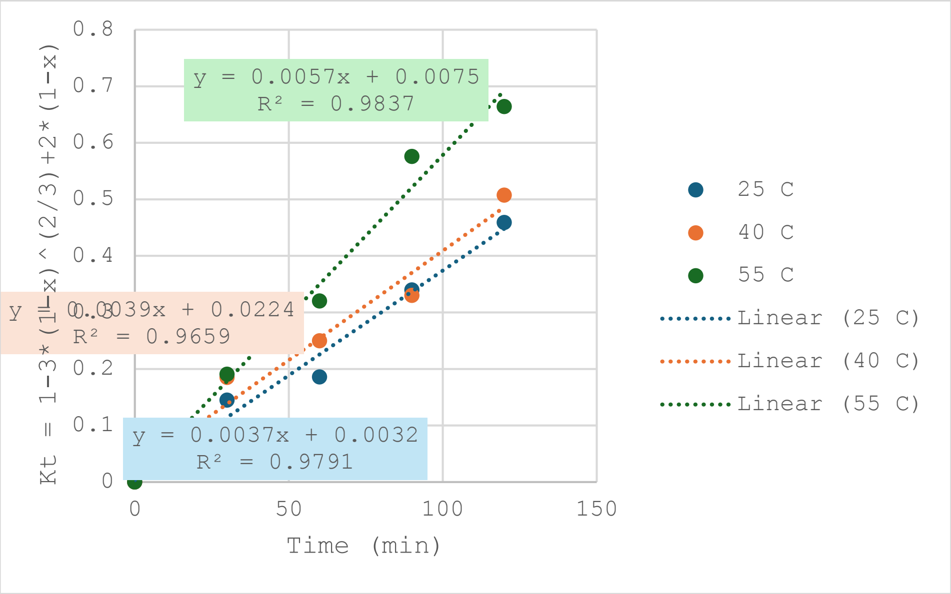


Figure 9: Graph illustrating the shrinking core model showing the influence of temperature on the reaction rate

Figure 10 displays a plot of lnK against 1000/T, where the slope of the graph is equal to −Ea/R (Kim *et al.*, 2011). The activation energy (Ea) for this reaction was determined to be 11,556 kJ/mol over the temperature range of 25 to 55º. In this respect, activation energy values above 40 kJ/mol usually indicate chemical reaction-controlled process. In contrast, values below 20 kJ/mol usually identify diffusion-controlled process (Dávila-Pulido *et al.*, 2021). This indicate that copper leaching from PCBs is diffusion controlled.

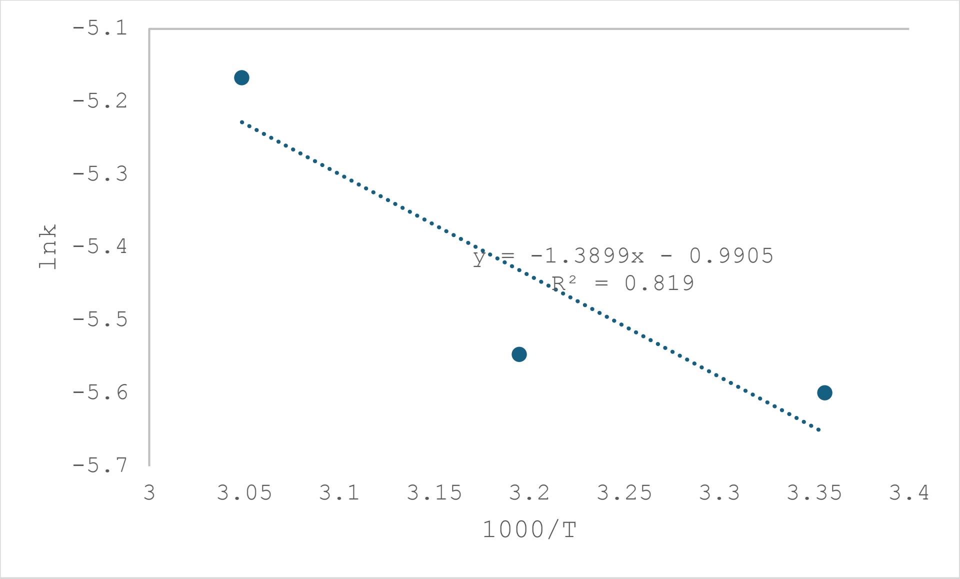


Figure 10: Graph of lnK against the inverse of temperature (Arrhenius plot)

4. Conclusion

This study demonstrates that addition of oxidants significantly influences the leaching behaviour of copper, enhancing its dissolution rates. The presence of Hydrogen peroxide increased copper leaching from 19.13% without oxident to 91.7%, highlighting its role as a most effective oxidizing agent for copper dissolution. Temperature further amplified this effect at 55°C, copper dissolution rates soared to 94.11% when was present $H_2 O_2$. Other oxidants also increased the copper dissolution, as Ferric sulphate achieved recovery of 84.28% at 0.5M and 86.44% at 55 °C and calcium hypochlorite achieved 75.18% at 0.5 M and 81.44% at 55 °C and it was the lowest among the oxidant systems.

The analysis of rate-limiting factors indicates that diffusion through the product layer is the primary constraint in the dissolution reaction. This conclusion is supported by the R^2 value of 0.9801 obtained from the shrinking core model, which confirms that this mechanism governs the leaching process. Additionally, the activation energy (Ea) for this reaction was determined to be 11. 556 kJ/mol, confirming that this process is diffusion controlled.

5. Acknowledgement

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