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Research Article

Box-Behnken Optimization and Theoretical Study for Copper Leaching from Scrap Laptop Computer Printed Circuit Board by Malonic Acid and Hydrogen Peroxide

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Abstract: The hydrometallurgical method of copper leaching from scrap electronics is commonly undertaken using pulverized printed circuit boards. Though studies on the use of organic acids like citric and oxalic acids for copper removal are well documented, those on the use of malonic acid are rare. Herein, we report on the investigation of the efficiencies of mixtures of malonic acid and hydrogen peroxide for copper leaching from unpulverized scrap PCB by the Box-Behnken design and the theoretical determination of the most stable copper-malonic acid complex. The average copper content in each unpulverized printed circuit board was found to be (0.84 ± 0.13) mg/g following aqua-regia digestion and atomic absorption spectrophotometry measurement. The conditions at which the highest leaching efficiency of 51.3% was obtained were a malonic acid concentration of 0.5 M, a hydrogen peroxide concentration of 1.0 M, and a contact time of 75 min. The contact time was the most significant individual parameter that influenced the efficiency of copper leached with a p-value of 0.001. Theoretical calculations show that malonic acid prefers to coordinate with copper in a 2:1 malonic acid: copper ratio. This study shows that appreciable amounts of copper can be leached from the minimally processed unpulverized printed circuit board.

***Keywords*:** printed circuit boards, copper, leaching efficiency, malonic acid, hydrogen peroxide, optimization, Box-Behnken

1. Introduction

Copper (Cu) is used in building materials, jewelry, and nutritional supplements.[1] Although Cu is sourced mainly from primary mining of ore deposits, secondary mining from sources like Printed Circuit Boards (PCB) is gaining attention as it is a more environmentally friendly option.[2] Popular methods employed for secondary Cu recovery include pyrometallurgy,[3] hydrometallurgy,[4] biohydrometallurgy,[5] and electrochemical.[6] Hydrometallurgy is the most favoured because it is relatively cheaper, easier to undertake, and requires lower energy input.

Hydrometallurgical processes fundamentally consist of three major stages. The first stage, known as leaching, is undertaken to transfer Cu from the PCB into the leach solution. The second stage, known as concentration, is aimed at the reduction of the amount of leach solution thereby increasing the concentration of Cu. The third stage, known as recovery is carried out to separate the Cu from the leach solution.[7] Since the success of the leaching stage depends on

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the choice of the leach solution and leach conditions, investigations to develop new leach solutions and optimization of leach parameters is being undertaken. Agents employed for Cu leaching include acids, bases, salts, and ionic liquids. Typical acids used for base metal extraction are sulfuric acid,[8] nitric acid,[9] hydrochloric acid,[10] trifluoromethanesulfonic acid,[9] and mixtures of acids.[11] These acids have often been used in combination with oxidants such as oxygen, H_2O_2, ferric salts, and chlorine gas[12,13] to achieve higher leaching efficiencies.

Despite the attractive features of hydrometallurgy, it is intrinsically hazardous as the commonly used leaching agents-acids and bases are generally corrosive, difficult to work with, and environmentally unfriendly.[14] To make hydrometallurgy more environmentally friendly, organic leaching agents like citric and oxalic acid have been investigated for metal leaching.[15] However, studies reporting on Cu leaching using malonic acid (Figure 1) are rare. Yet, malonic acid has properties that can facilitate Cu removal including the presence of four oxygen donors, which can coordinate with Cu and high solubility in water. Also, hydrometallurgical leaching of Cu is commonly undertaken using pulverized or powdered PCB. The use of unpulverized PCB is an attractive option as not only can be Cu leaching process be cheaper and simpler but also the residual PCB piece can be conveniently recycled.[16] To the best of our knowledge, no study has reported on the leaching of Cu from unpulverized PCB using malonic acid.

Herein, we report the investigation of the efficiency of the mixtures of malonic acid and hydrogen peroxide (H_2O_2) (Figure 1) for Cu recovery from the unpulverized printed circuit board by the Box-Behnken design. The Box-Behnken design is an experimental design that allows for the investigation of the effect of more than one experimental parameter per time allowing for the quick optimization of a process. Moreso, it requires less data than the traditional experimental designs where only one experimental parameter can be varied per time. The leaching parameters investigated in this study include malonic acid concentration, hydrogen peroxide concentration, and contact time. The addition of H_2O_2 was informed by studies where the use of mixtures of an organic acid and H_2O_2 was shown to improve the Cu leaching efficiencies compared to only the organic acid.[17]

Malonic acid *Hydrogen peroxide*

Figure 1. Structures of malonic acid and hydrogen peroxide (H_2O_2)

2. Experimental details

2.1 *Materials and reagents*

Printed Circuit Boards (PCBs) were removed from scrap laptop computers. Aqua-regia (volume ratio of HCl to HNO_3 = 3:1) was used to completely digest the PCB to analyze their Cu contents. All chemical reagents used in this study were of analytical grade, and all solutions were prepared and diluted using distilled water to the desired concentration. Unless otherwise stated, all leaching experiments were undertaken in duplicates and at room temperature (28 °C).

2.2 *NaOH treatment and aqua-regia digestion*

The large PCBs were cut into small pieces (2 cm × 2 cm) and 80 g of the PCB pieces were immersed in NaOH (10 M, 800 mL) for 24 h. The PCB pieces were subsequently washed thoroughly with distilled water until a neutral pH of the wash water was obtained.[16] One randomly selected piece of the NaOH- treated PCB was completely digested in aqua-regia (volume ratio of HCl to HNO_3 = 3:1) for 24 h. This was carried out in duplicates. The aqua-regia solution was filtered and the filtrate was prepared for the determination of Cu concentration.

2.3 *Malonic acid leaching*

All leaching experiments were undertaken in 50 mL beakers placed in a fume cupboard. Malonic acid and H_2O_2 of known concentration were added to a single piece of the PCB (2 cm × 2 cm) and left for the pre-determined contact time. The malonic acid leaching was undertaken following the Box-Behnken experimental design. In the Box-Behnken experimental design, malonic acid concentration, H_2O_2 concentration, and contact time of leaching were selected as independent variables. Cu leaching efficiency was chosen as the dependent variable. The real values of the independent variables coded as -1, 0, and +1 were set at the low, center, and high levels, respectively (Table 1).

Table 1. Experimental ranges and levels of the malonic acid concentration (X_1), H_2O_2 concentration (X_2), and contact time (X_3)

Independent variable	Range and level		
	Low (-1)	Centre (0)	High (+1)
Malonic acid concentration MA, M (X_1)	0.1	0.3	0.5
H_2O_2 concentration HP, M (X_2)	0.2	0.6	1.0
Contact time CT, min (X_3)	30	75	120

Table 2. Box-Behnken design matrix with three independent variables for the experimental and predicted copper leaching efficiencies

	Independent variable						Dependent variable	
	Coded values			Real values			Leaching efficiencies (%)	
Run	X_1	X_2	X_3	MA	HP	CT	LE_{exp}	LE_{pred}
1	-1	-1	0	0.1	0.2	75	22.2	27.2
2	1	-1	0	0.5	0.2	75	3.5	5.1
3	-1	1	0	0.1	1	75	7.9	6.3
4	1	1	0	0.5	1	75	51.3	46.4
5	-1	0	-1	0.1	0.6	30	1.9	4.3
6	1	0	-1	0.5	0.6	30	3.0	8.8
7	-1	0	1	0.1	0.6	120	38.0	32.3
8	1	0	1	0.5	0.6	120	48.1	45.8
9	0	-1	-1	0.3	0.2	30	0.5	-6.8
10	0	1	-1	0.3	1	30	3.1	2.3
11	0	-1	1	0.3	0.2	120	23.8	24.6
12	0	1	1	0.3	1	120	28.5	35.8
13-15	0	0	0	0.3	0.6	75	47.3	40.9

Consequently, the input factors were malonic acid concentration (X_1), H_2O_2 concentration (X_2), and contact time (X_3)

values. The three-factorial Box-Behnken design was performed with 15 runs with 3 center points (Table 2).

After the PCB pieces had been contacted with the leach solution for the required duration, the leaching solution was filtered, and the filtrate was prepared for the determination of Cu concentration. Leaching efficiency was determined by

$$\text{Leaching efficiency LE (\%)} = \frac{C_e}{C_o} \times 100,$$

where C_e is the Cu concentration in the malonic acid/hydrogen peroxide leach solution filtrates and C_o is the Cu content as determined by aqua-regia digestion.

2.4 *Software and instrumentation*

The Box-Behnken experimental design was undertaken utilizing Minitab statistical software (v21.2). Cu concentrations were determined from the filtrates of the aqua-regia and malonic acid solutions by employing atomic absorption spectrophotometry (Buck Scientific 210 VGP).

2.5 *Computational details*

Density Functional Theory (DFT) calculations were performed utilizing Maestro (Schrödinger 2021-4). Geometry optimizations and energetics were computed using Jaguar[18] in implicit water solvent and at pH 7 from processed structures, designed on ChemDraw (v20.1, PerkinElmer Informatics Inc.), using the hybrid B3LYP functional[19-21] with the LANL2ZD basis set for Cu[22] but the 6-31 G basis set for other atoms - C, H, and O.[23] For the heavy atom Cu, Effective Core Potential (ECP) was used. Binding energies of the complexes were determined from calculated free energies using the formula:[24]

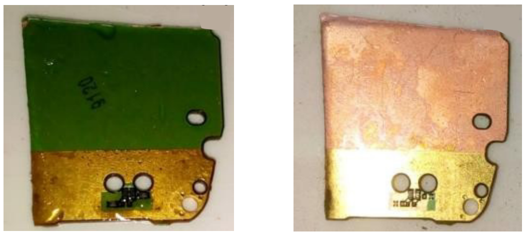
$$\text{Binding Energy (BE)} = E_{complex} - E_{metal} - E_{ligand}$$

Where $E_{complex}$, E_{metal}, and E_{ligand} are the calculated free energies of the malonic acid-Cu complexes, Cu, and free malonic acid respectively.

3. Result and discussion

3.1 *Epoxy coating removal using NaOH solution*

Unpulverized PCB pieces as opposed to the pulverized PCB were used in this study to simplify the Cu leaching process and to reduce the cost of PCB grinding.[25] PCB materials are coated with epoxy resins to achieve flame retardant purposes.[26] However, in hydrometallurgical processes, these resins can prevent the efficient leaching of metals. Presently, mechanical and thermal methods are widely employed to treat waste PCB and separate the metal and non-metal components.[27] One important disadvantage of mechanical separation processes is the notable loss of valuable metals. The reasons for these losses include the insufficient liberation of metals due to their intimate association with plastics and the inefficiency of separation processes for metal leaching from fine fractions. Therefore, it is necessary to find a better process for removing the chemical coatings from PCB without the loss of metals. NaOH solutions have often been employed for the efficient removal of epoxy resins from the surfaces of PCB.[25] In this study, the PCB pieces were treated with NaOH solution. Following the NaOH treatment, most of the epoxy coatings were noticeably detached from the PCB pieces. This was observed by the disappearance of the green-colored coating on the PCB surface (Figure 2). Accounts from other studies report that this change of color is indicative of the removal of the epoxy coating.[16] The reaction was highly exothermic due to the heat produced.



(a) (b)

Figure 2. PCB piece (a) before and (b) after NaOH solution treatment for 24 hours at ambient temperature (28 °C)

The epoxy coating removal could be described by Figure 3.[28,29]

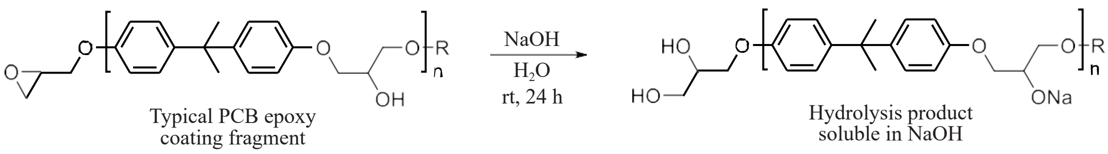


Figure 3. Removal of PCB epoxy coating using NaOH solution

In addition to removing the epoxy coating, it has been reported that the NaOH leaches some Cu, making the determination of the Cu content of the NaOH solution important. However, results from other studies indicate that the Cu leached by NaOH is usually negligible.[17] For example, Jadav and Hocheng reported that (0.43 ± 0.001) μg/g Cu was leached.[16] Therefore, in this work, the determination of the Cu content of the spent NaOH solution was not undertaken.

3.2 *The average copper content of the PCB pieces*

Following the removal of the epoxy coating, the PCB pieces were digested completely in aqua-regia to determine the Cu content. While significant work has been reported on the hydrometallurgical leaching of metals from PCB using HNO_3, HCl, H_2SO_4, and aqua-regia, aqua-regia, is popular for the determination of the initial Cu content of PCB samples and has been observed to demonstrate excellent efficiency in Cu leaching than other leach solutions.[30-32] It was important to determine the initial Cu content of the PCB to have a reference to which the efficiency of the test leach solution (mixture of malonic acid and H_2O_2) can be compared. Though PCB contains many metals including Cu, Ag, Au, Sn, and Ni to state a few, Cu is the focus of this study because it has the single highest composition of all metals in most PCB samples including that of scrap laptop computers.[13,16] The average Cu concentration in the PCB pieces was determined to be (0.84 ± 0.13) mg/g, which is lower than that reported by other studies,[33,34] and this was attributed to the fact that the Cu content in the PCB of laptop computers are generally lower than that in other products like desktop computers and television sets.[35] The relatively large error (standard deviation) in the Cu content value was attributed to a large variation in the Cu content in different parts of the large PCB from which the samples were cut.[36]

3.3 *Box-Behnken statistical analysis*

The Box-Behnken design is an example of a response surface methodology employed to optimize a process in this case, the leaching of Cu from PCB pieces.[37] The choice of malonic acid and H_2O_2 for this study stems from the fact that with regards to the product of their degradation, these reagents are greener and biodegradable alternatives to the popular mineral acid leaching agents including HCl, HNO_3, and aqua regia.[38]

The linear model represents the leaching system. Results from the Box-Behnken designed experiment are displayed in Table 2. A p-value lower than 0.05 shows that a model fits the experimental data.[39]

Analysis of variance data presented in Table 3 indicated that the model is most suitable for fitting the experimental results as the linear model terms had *p*-values less than 0.05 (0.005).[40]

Table 3. Analysis Of Variance (ANOVA) table for the linear model of the leaching of copper using malonic acid and H_2O_2[a]

Source	Degree of freedom	Adjusted sum of squares	Adjusted mean squares	F-value	*P*-value
Model	9	4,757.76	528.64	10.99	0.008
Linear	3	2,478.43	826.14	17.17	**0.005**
X_1 - malonic acid concentration	1	161.10	161.10	3.35	0.127
X_2 - hydrogen peroxide concentration	1	208.08	208.08	4.32	0.092
X_3 - contact time	1	2,109.25	2,109.25	43.83	**0.001**
Square	3	1,293.87	431.29	8.96	0.019
$X_1 * X_1$	1	109.67	109.67	2.28	0.192
$X_2 * X_2$	1	747.14	747.14	15.53	**0.011**
$X_3 * X_3$	1	595.53	595.53	12.38	**0.017**
2-Way interaction	3	985.46	328.49	6.83	0.032
$X_1 * X_2$	1	964.10	964.10	20.03	**0.007**
$X_1 * X_3$	1	20.25	20.25	0.42	0.545
$X_2 * X_3$	1	1.10	1.10	0.02	0.886
Error	5	240.62	48.12		
Lack-of-Fit	3	240.62	80.21		
Pure Error	2	0.00	0.00		
Total	14	4,998.37			

[a]R^2 = 0.9591, predicted R^2 = 0.2298, adjusted R^2 = 0.8652

The final equations in terms of the actual factors (malonic acid concentration, MA; H_2O_2 concentration, HP; and contact time, CT) and coded factors (X_1, X_2, and X_3) can be represented by:

$$\text{Leaching efficiency (\%)} = -38.2 - 31\text{MA} + 59\text{HP} + 1.209\text{CT} - 136.2\text{MA}^2 - 88.9\text{HP}^2 - 0.00627\text{CT}^2 + 194.1\text{MA} \cdot \text{HP} + 0.250\text{MA} \cdot \text{CT} + 0.029\text{HP} \cdot \text{CT} \quad (1)$$

$$Y = 40.9 + 4.49X_1 + 5.1X_2 + 16.24X_3 - 5.45X_1^2 - 14.22X_2^2 - 12.7X_2^3 + 15.53X_1X_2 + 2.25X_1X_3 + 0.52X_2X_3 \quad (2)$$

The R^2 and R^2 (adjusted) values of the model are 0.9519 and 0.8652 (Table 3) which shows that equations 1 and 2 represent the system under the experimental ranges investigated.[41] Moreover, the experimental and predicted Cu leaching efficiencies are presented in Table 2 and Figure 4. The actual leaching efficiencies (LE_{exp}) represent the experimental data collected under specified conditions while the predicted efficiencies (LE_{pred}) are estimated using equation 1. However, the R^2 (predicted) value of 0.2298 indicates that the predictive power of the model is low, which is not observed in the difference in the experimental and predicted leaching efficiencies (Table 3). This is because the Cu content in the PCB sheets varies widely.[36]

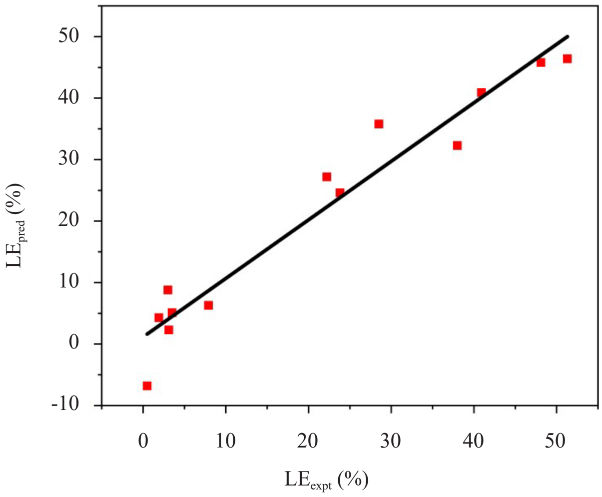


Figure 4. Correlation of actual (LE_{expt}) and predicted (LE_{pred}) leaching efficiencies

3.3.1 *Contact time significantly influences leaching efficiency*

The degree of influence of each of the independent variables including malonic acid concentration, H_2O_2 concentration, and contact time on the dependent variable which is the efficiency of Cu leaching was investigated by the Box-Behnken design. The *p*-value of the input factors indicates the degree of influence of the independent variable(s).[40] A *p*-value less than 0.05 at a 95% confidence interval generally indicates the high significance of the independent variable in influencing the dependent variable or outcome.[37] The *p*-value of the model terms X_3, X_2^2, X_3^2, and X_1X_2 representing contact time, the square of H_2O_2 concentration, the square of contact time, and the product of malonic and H_2O_2 concentrations respectively was lower than 0.05 (Table 3) which means that these terms are significant in influencing the efficiency of Cu leaching. However, the *p*-value of the model terms X_1, X_2, X_1^2, X_1X_3, and X_2X_3 are greater than 0.05 indicating that these model terms are not significant in the determination of Cu leaching efficiency. Therefore, amongst the independent variables, the contact time has the single highest influence on the leaching efficiency of Cu.

3.3.2 *Effect of interaction of pairs of independent variables on the leaching efficiency*

Three-dimensional response surface plots were constructed to understand how interactions of pairs of the independent variables influence leaching efficiency (Figure 5).

(a) Malonic acid and H_2O_2 concentrations: The response surface relationship between the concentrations of malonic acid and H_2O_2 presented in Figure 5a reveals that the interaction of high malonic acid concentration with high H_2O_2 concentration had a positive effect on leaching efficiency. In other words, increases in both malonic acid and H_2O_2 concentrations increase leaching efficiency, and a maximum leaching efficiency of about 50% was attained. However, the interaction of high malonic acid concentration and low H_2O_2 concentration influenced the leaching efficiency negatively. Similarly, a negative effect on leaching efficiency was observed for the synergy between low malonic acid concentration and high H_2O_2 concentration. The reason for the positive effect on leaching efficiency at high malonic acid and H_2O_2 concentrations can be understood by the mechanism of Cu leaching from sources like PCB sheets. The mechanism is as follows (a) H_2O_2 oxidizes malonic acid to peroxymalonic acid (Equation 3),[42] (b) the peroxymalonic acid oxidizes Cu(0) on the PCB surface to Cu(II), and malonic acid (Equation 4),[17] and (c) the malonic acid can lose a proton to water to give a malonate (Equations 5)[43] which coordinates to Cu(II) (Equations 6)[44] or the malonic acid coordinates to Cu(II) to give a Cu hydrogen malonate in the presence of H_2O_2 (Equation 7).[17] The solubility of Cu(II) in water is enhanced by its complexation.[45]

$$CH_2(COOH)_2 + 2H_2O_2 \rightarrow CH_2(COOOH)_2 + 2H_2O \quad (3)$$

$$CH_2(COOOH)_2 + Cu + 2H^+ \rightarrow CH_2(COOH)_2 + H_2O + Cu^{2+} \quad (4)$$

$$HOOCCH_2COOH + H_2O \rightarrow HOOCCH_2COO^- + H_3O^+ \quad (5)$$

$$2(HOOC)CH_2COO^- + Cu^{2+} \rightarrow (OOCCH_2COO)_2Cu \quad (6)$$

$$2HOOCCH_2COOH + Cu + H_2O_2 \rightarrow (OOCCH_2COO)_2Cu + 2H_2O \quad (7)$$

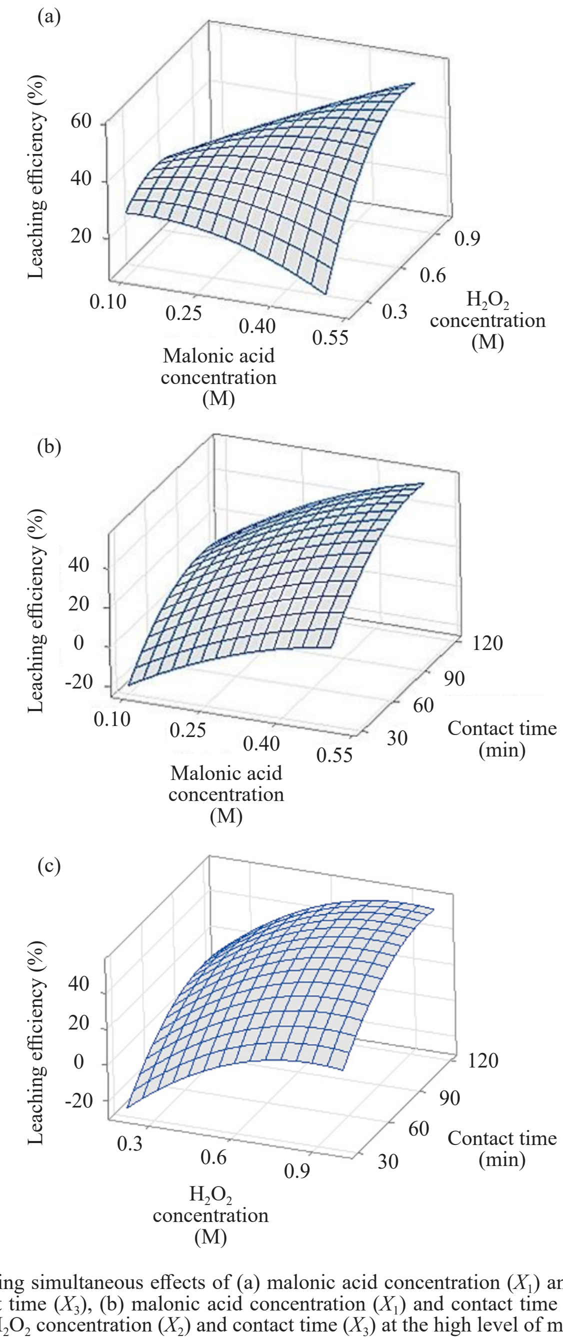


Figure 5. Response surface graphs showing simultaneous effects of (a) malonic acid concentration (X_1) and H_2O_2 concentration (X_2) on Cu leaching efficiency at the high level of the contact time (X_3), (b) malonic acid concentration (X_1) and contact time (X_3) on Cu leaching efficiency at the high level of the H_2O_2 concentration (X_2), (c) H_2O_2 concentration (X_2) and contact time (X_3) at the high level of malonic acid concentration (X_1)

Based on Equation 3, the mole ratio of malonic acid to H_2O_2 must be at least 1:2 for efficient generation of peroxymalonic acid which will lead to effective oxidative leaching of Cu(0) to Cu(II). However, at lower ratios, for example at a high concentration of malonic acid, but a lower concentration of H_2O_2, the generation of peroxymalonic acid will be low leading to poor leaching of Cu.

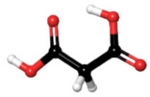
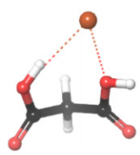
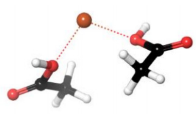
(b) Malonic acid concentration and contact time: The interaction between high malonic acid concentration and prolonged contact time yielded a positive influence on leaching efficiency (Figure 5b). The leaching efficiency increased at low malonic acid concentration and short contact time and the increase continued until a maximum of about 50% was attained at a malonic acid concentration of 0.5 M and a contact time of 120 min. At high malonic acid concentration and short contact time, a negative influence on leaching efficiency was observed. Similarly, low malonic acid concentration and prolonged contact time had a negative influence on leaching efficiency. The observation of high leaching efficiency at high malonic acid concentration and prolonged contact time could be because there is a corresponding generation of high amounts of peroxyacetic acid by the excess amount of H_2O_2 (Equation 3) for the leaching of Cu and sufficient contact time for the leaching processes described in Equations 3-7 to occur respectively. However, at low malonic acid concentration and short contact time low amount of peroxymalonic acid is generated and there is insufficient time for the leaching process leading to low leaching efficiency.

(c) H_2O_2 concentration and contact time: A positive influence on leaching efficiency was achieved at high H_2O_2 concentration and prolonged contact time (Figure 5c). A negative effect on leaching efficiency was obtained both at high H_2O_2 concentration and short contact times and at low H_2O_2 concentration and lengthy contact times. The highest leaching efficiency of 50% was obtained at an H_2O_2 concentration of about 0.8 M and a contact time of 120 min. The rationale for the observation is the same as that described for the interaction between malonic acid concentration and contact time.

3.4 *Computational study*

Density Functional Theory (DFT) calculations were performed using Maestro (Schrödinger Release 2021-4: Maestro, Schrödinger, LLC, New York, NY, USA) to gain insight into the interaction between malonic acid and Cu. The optimized structure of malonic acid was obtained, and the corresponding free energy was recorded (Table 4, entry 1). Thereafter, the structures of possible Cu-malonic acid complexes with different binding stoichiometries (Table 4, entries 2 and 3) were modeled and the associated free energies were recorded. The binding energies of all modeled complexes were determined and the Cu-malonic acid complex with the 2:1 malonic acid-Cu binding stoichiometry (Table 4, entry 3) was found to be the most favorable as it had the lowest binding energy of the complexes modeled.

Table 4. Optimized structures, free energies, and binding energies of malonic acid and some Cu complexes of malonic acids at B3LYP/6-31G for carbon, oxygen, and hydrogen, and LANL2DZ for Cu

Entry	Optimized structure	Free energy (eV)	Binding energy (eV)
1	 $CH_2(COOH)_2$	-11,361	-
2	 $CH_2(COO)_2Cu$	-16,700	-3
3	 $(OOCCH_2COO)_2Cu$	-28,065	-11,367

4. Conclusion

We investigated the efficiency of mixtures of malonic acid and hydrogen peroxide for copper leaching from unpulverized printed circuit boards sourced from scrap laptop computers by the Box-Behnken experimental design. In addition, we determined the structure of the most stable copper-malonic complex by density functional theory calculations. The average copper content in the unpulverized PCB pieces was quite low compared to that reported in other studies. The highest efficiency leaching of 51% was attained at the malonic acid concentration of 0.5 M, the hydrogen peroxide concentration of 1.0 M, and a contact time of 75 min. Density functional theory calculations show that the 1:2 copper-malonic acid complex is the most stable type of copper-malonic acid complex. Though the highest leaching efficiency observed in this study is lower than that reported in related studies, we show that malonic acid is a promising candidate for copper recovery from minimally processed unpulverized PCB.

Conflicts of interest

The authors declare no conflict of interest.

References

[1] Doebrich, J. Copper - A Metal for the Ages. USGS Science for a Changing World, Fact Sheet. **2009,** 1-4. https://pubs.usgs.gov/fs/2009/3031/FS2009-3031.pdf (accessed Oct 17, 2022).

[2] Chen, J.; Wang, Z.; Wu, Y.; Li, L.; Li, B.; Pan, D.; Zuo, T. Environmental benefits of secondary copper from primary copper based on life cycle assessment in China. *Resour. Conserv. Recycl*. **2019,** *146*, 35-44.

[3] Moskalyk, R. R.; Alfantazi, A. M. Review of copper pyrometallurgical practice: Today and tomorrow. *Miner. Eng*. **2003,** *16*, 893-919.

[4] Álvarez, M. L.; Fidalgo, J. M.; Gascó, G.; Méndez, A. Hydrometalurgical recovery of cu and zn from a complex sulfide mineral by Fe^{3+}/H_2SO_4 leaching in the presence of carbon-based materials. *Metals (Basel).* **2021,** *11*, 1-10.

[5] Habibi, A.; Shamshiri Kourdestani, S.; Hadadi, M. Biohydrometallurgy as an environmentally friendly approach in metals recovery from electrical waste: A review. *Waste Manage. Res*. **2020,** *38*, 232-244.

[6] Rajahalme, J.; Perämäki, S.; Budhathoki, R.; Väisänen, A. Effective Recovery Process of Copper from Waste Printed Circuit Boards Utilizing Recycling of Leachate. *Jom*. **2021,** *73*, 980-987.

[7] Gunarathne, V.; Rajapaksha, A. U.; Vithanage, M.; Alessi, D. S.; Selvasembian, R.; Naushad, M.; You, S.; Oleszczuk, P.; Ok, Y. S. Hydrometallurgical processes for heavy metals recovery from industrial sludges. *Crit. Rev. Environ. Sci. Technol*. **2022,** *52*, 1022-1062.

[8] Brožová, S.; Lisińska, M.; Saternus, M.; Gajda, B.; Simha Martynková, G.; Slíva, A. Hydrometallurgical recycling process for mobile phone printed circuit boards using ozone. *Metals (Basel)*. **2021,** *11*, 820.

[9] Ajiboye, A. E.; Olasehinde, F. E.; Adebayo, O. A.; Ajayi, O. J.; Ghosh, M. K.; Basu, S. Extraction of copper and zinc from waste printed circuit boards. *Recycling*. **2019,** *4*, 1-13.

[10] Havlik, T.; Orac, D.; Petranikova, M.; Miskufova, A.; Kukurugya, F.; Takacova, Z. Leaching of copper and tin from used printed circuit boards after thermal treatment. *J. Hazard Mater*. **2010,** *183*, 866-873.

[11] Vijayaram, R. N. D.; Chandramohan, K. Copper extraction from the discarded printed circuit board by leaching. *Res. J. Engineering Sci*. **2013,** *2*, 2278-9472.

[12] Cui, H.; Anderson, C. G. Literature review of hydrometallurgical recycling of Printed Circuit Boards (PCBs). *J. Adv. Chem. Eng*. **2016,** *6*, 1-11.

[13] da Silva, C. S. M.; Zeba, G. T. C.; da Rocha, C. M. R.; Gismonti, P. R.; Afonso, J. C.; da Silva, R. S.; Vianna, C. A.; Mantovano, J. L. Processing of a metal concentrate from ground waste printed circuit boards in acidic media using hydrogen peroxide as oxidant. *Quim. Nova*. **2020,** *43*, 914-922.

[14] Huang, Y. F.; Chou, S. L.; Lo, S. L. Gold recovery from waste printed circuit boards of mobile phones by using microwave pyrolysis and hydrometallurgical methods. *Sus. Environ. Res*. **2022,** *32*, 1-11.

[15] Verma, A.; Kore, R.; Corbin, D. R.; Shiflett, M. B. Metal recovery using oxalate chemistry: A technical review. *Ind. Eng. Chem. Res*. **2019,** *58*, 15381-15393.

[16] Jadhav, U.; Hocheng, H. Hydrometallurgical recovery of metals from large printed circuit board pieces. *Sci. Rep*.

2015, *5*, 1-10.
[17] Jadhav, U.; Su, C.; Hocheng, H. Leaching of metals from large pieces of printed circuit boards using citric acid and hydrogen peroxide. *Environ. Sci. Pollution Res*. **2016,** *23*, 24384-24392.
[18] Bochevarov, A. D.; Harder, E.; Hughes, T. F.; Greenwood, J. R.; Braden, D. A.; Philipp, D. M.; Rinaldo, D.; Halls, M.; D., Zhang, J.; Friesner, R. A. Jaguar: A high-performance quantum chemistry software program with strengths in life and materials sciences. *Int. J. Quantum. Chem*. **2013,** *113*, 2110-2142.
[19] Becke, A. D. Density-functional thermochemistry. IV. A new dynamical correlation functional and implications for exact-exchange mixing. *J. Chem. Phys*. **1996,** *104*, 1040-1046.
[20] Lee, C.; Yang, W.; Parr, R. G. Development of the Colic-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B*. **1988,** *37*, 785-789.
[21] Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*. Oxford University Press: Oxford, 1989.
[22] Ghaffar, A.; Nawaz, S.; Munawar, A.; Zierkiewicz, W.; Michalczyk, M.; Helios, K.; Hussain, S. Z.; Rashid, A.; Ahmad, S. DFT calculations and SEM-EDX analysis of Copper(II)-Azide complexes; $[Cu(en)_2(N3)_2]$ and $[Cu(Tmen)(N_3)_2]_2$ (Tmen = N,N,N,N'-Tetramethylethylenediamine). *Russ. J. Phys. Chem. B*. **2021,** *15*, 42-51.
[23] Abdalla, E. M.; Hassan, S. S.; Elganzory, H. H.; Aly, S. A.; Alshater, H. Molecular docking, DFT calculations, effect of high energetic ionizing radiation, and biological evaluation of some novel metal (II) heteroleptic complexes bearing the thiosemicarbazone ligand. *Molecules*. **2021,** *26*, 1-24.
[24] Fan, E.; Yang, J.; Huang, Y.; Lin, J.; Arshad, F.; Wu, F.; Li, L.; Chen, R. Leaching mechanisms of recycling valuable metals from spent lithium-ion batteries by a malonic acid-based leaching system. *ACS Appl. Energy Mater*. **2020,** *3*, 8532-8542.
[25] Adhapure, N. N.; Dhakephalkar, P. K.; Dhakephalkar, A. P.; Tembhurkar, V. R.; Rajgure, A. V.; Deshmukh, A. M. Use of large pieces of printed circuit boards for bioleaching to avoid 'precipitate contamination problem' and to simplify overall metal recovery. *MethodsX*. **2014,** *1*, e181-e186.
[26] Liu, K.; Zhang, Z.; Zhang, F. S. Advanced degradation of brominated epoxy resin and simultaneous transformation of glass fiber from waste printed circuit boards by improved supercritical water oxidation processes. *Waste Manage*. **2016,** *56*, 423-430.
[27] He, X.; Wu, X.; Cai, X.; Lin, S.; Xie, M.; Zhu, X.; Yan, D. Functionalization of magnetic nanoparticles with dendritic-linear-brush-like triblock copolymers and their drug release properties. *Langmuir*. **2012,** *28*, 11929-11938.
[28] Balaji, R.; Prabhakaran, D.; Thirumarimurugan, M. A novel approach to epoxy coating removal from Waste Printed Circuit Boards by solvent stripping using NaOH under autoclaving condition. *Cleaner Mater*. **2021,** *1*, 1-7.
[29] Tsuji, Y.; Kitamura, Y.; Someya, M.; Takano, T.; Yaginuma, M.; Nakanishi, K.; Yoshizawa, K. Adhesion of epoxy resin with hexagonal boron nitride and graphite. *ACS Omega.* **2019,** *4*, 4491-4504.
[30] Palanisamy, M. M.; Myneni, V. R.; Palaniyappan, A.; Kandasamy, K.; Veerappan, P. Effect of clay minerals on copper reclamation from leached solution. *Indian J. Chem. Technol*. **2022,** *29*, 157-165.
[31] Pinho, S. C.; Ribeiro, C.; Ferraz, C. A.; Almeida, M. F. Copper, zinc, and nickel recovery from printed circuit boards using an ammonia-ammonium sulphate system. *J. Mater. Cycles Waste Manag.* **2021,** *23*, 1456-1465.
[32] Park, Y.; Eom, Y.; Yoo, K. Leaching of copper from waste-Printed Circuit Boards (PCBs) in sulfate medium using cupric ion and oxygen. *Metals*. **2021,** *11*, 1-11.
[33] Kaliyaraj, D.; Rajendran, M.; Angamuthu, V.; Antony, A. R.; Kaari, M.; Thangavel, S.; Venugopal, G.; Joseph, J.; Manikkam, R. Bioleaching of heavy metals from Printed Circuit Board (PCB) by Streptomyces albidoflavus TN10 isolated from insect nest. *Bioresour. Bioprocess*. **2019,** *6*, 1-11.
[34] Isildar, A.; Rene, E. R.; Hullebusch, E. D. van; Lens, P. N. L. Two-step leaching of valuable metals from discarded printed circuit boards, and process optimization using response surface methodology. *Adv. Recyc. Waste Manage*. **2017,** *2*, 1-10.
[35] Cucchiella, F.; Adamo, I. D.; Koh, S. C. L.; Rosa, P. Recycling of WEEEs: An economic assessment of present and future e-waste streams. *Renew. Sus. Energ. Rev*. **2015,** *51*, 263-272.
[36] Charles, R. G.; Douglas, P.; Hallin, I. L.; Matthews, I.; Liversage, G. An investigation of trends in precious metal and copper content of RAM modules in WEEE: Implications for long term recycling potential. *Waste Manage*. **2017,** *60*, 505-520.
[37] Lin, S.; Wei, W.; Lin, X.; Bediako, J. K.; Kumar Reddy, D. H.; Song, M. H.; Yun, Y. S. Pd(II)-imprinted chitosan adsorbent for selective adsorption of Pd(II): Optimizing the imprinting process through Box-Behnken experimental design. *ACS Omega*. **2021,** *6*, 13057-13065.
[38] Alder, C. M.; Hayler, J. D.; Henderson, R. K.; Redman, A. M.; Shukla, L.; Shuster, E.; Sneddon, H. F. Updating

and further expanding GSK's solvent sustainability guide. *Green Chem*. **2016,** *16*, 3879-3890.
[39] Azeez, S. O.; Jimoh, A. A; Saheed, I. O.; Otun, K. O.; Mustapha, A. O.; Adekola, F. A. Optimization by Box Behnken design for eosin yellow dye removal from aqueous medium using date palm seeds-porous carbon@TiO_2 blend. *J. Niger. Soc. Phys. Sci*. **2022,** *4*, 183-192.
[40] Bas, A. D.; Deveci, H.; Yazici, E. Y. Treatment of manufacturing scrap TV boards by nitric acid leaching. *Sep. Purif. Technol*. **2014,** *130*, 151-159.
[41] Aliemeke, B. N. G.; Oladehinde, M. Box-Behnken design optimization of sand casting process parameters. *Int. J. Eng. Technol*. **2020,** *6*, 25-36.
[42] Kumar, M.; Lee, J. C.; Kim, M. S.; Jeong, J.; Yoo, K. Leaching of metals from Waste Printed Circuit Boards (WPCBs) using sulfuric and nitric acids. *Environ. Eng. Manag. J*. **2014,** *13*, 2601-2607.
[43] Steer, J. M.; Griffiths, A. J. Investigation of carboxylic acids and non-aqueous solvents for the selective leaching of zinc from blast furnace dust slurry. *Hydrometallurgy.* **2013,** *140*, 34-41.
[44] Saidan, M.; Brown, B.; Valix, M. Leaching of electronic waste using biometabolised acids. *Chin. J. Chem. Eng*. **2012,** *20*, 530-534.
[45] Goyne, K. W.; Brantley, S. L.; Chorover, J. Rare earth element release from phosphate minerals in the presence of organic acids. *Chem. Geol*. **2010,** *278*, 1-14.