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Synthesis of Copper Carbonate from Copper Waste Using the Hydrometallurgical Method

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ABSTRACT: ABSTRACT. Electronic waste in Indonesia continues to increase, electronic waste is categorized as B3 waste which can threaten the environment. Electronic waste contains metals that can berecovery namely 20% copper (Cu), 8% iron (Fe), 4% tin (Sn), 2% nickel (Ni), 2% lead (Pb), 1% zinc (Zn), 0.2% silver (Ag), 0.1% gold (Au) and 0.005% palladium (Pa). Copper can be used as a raw material for making pigments mountain blue. Pigment extraction from copper metal can be done using the hydrometallurgical method which is considered more environmentally friendly and economical. The hydrometallurgical method uses solvents in the liquid phase to dissolve copper metal from waste and convert it into the desired compound. The materials used to make mountain blue pigment are copper waste, sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), hydrogen peroxide (H_2O_2), and distilled water. Meanwhile, the materials used for pigment application are Carboxymethyl Cellulose (CMC) and titanium dioxide (TiO_2). In this process, washing or leaching will be carried out(leaching) namely a chemical concentration process to release ore impurities from a mineral by dissolving it using certain reagents. Factors that influence the metal leaching process are temperature and acid concentration. In this experiment, the hydrometallurgical method succeeded in processing electronic waste into a blue pigment (mountain blue). The average pigment yield mountain blue in this experiment it was 1.25 grams of montain blue/gram of copper. Furthermore, the average conversion of pigment mountain blue was 89.3%.

Keywords: Copper, hydrometallurgy, mountain blue, pigments

1. Introduction

As technology develops, Indonesia experiences an increase in the use of electronic goods. Electronic goods are considered a mandatory necessity by most Indonesians to support their daily lives. Almost every individual has one to two cell phones and laptops which is due to the high tendency towards changing models so that the level of public consumption of electronics is increasing. With this condition, the rate of electronic waste generation in Indonesia has increased drastically in the last 2 years, namely from 2014 to 2016 [1].

Electronic waste contains various components that have economic value and threats to the environment[2], [3]. Electronic waste can be categorized as B3 waste because it contains dangerous and toxic materials in the form of heavy metals. In electronic waste there are 20% copper (Cu), 8% iron (Fe), 4% tin (Sn), 2% nickel (Ni), 2% lead (Pb), 1% zinc (Zn), 0.2 % silver (Ag), 0.1% gold (Au) and 0.005% palladium (Pa). Apart from that, the plastic components contain polypropylene, polyethylene, polyester and polycarbonate. If electronic waste is not processed properly, it will pose a danger to the environment and human health. One way that can be done to reduce this waste is to use it as raw material for making pigments and other materials[4].

Pigment is a chemical substance which, when associated or bound to a certain material, will give the material its color [5]. Pigments can be obtained from several transition metals such as copper, iron, nickel, zinc, cobalt, manganese, chromium, and so on. Transition metals come from various types of materials such as ores, salts, living creatures, and even waste. The copper content in electronic waste dominates, creating opportunities to process it into pigments with special methods such as hydrometallurgy.

In this research, the hydrometallurgical method is used, namely the processing of metal from rocks and ores with the help of an aqueous solvent (aqueous solution). Hydrometallurgy is a process that uses a liquid chemical substance to dissolve particles. The solvent used is an acid or base so that the metal can be dissolved and purified again to extract the metal content. The chemical reaction chosen is usually very selective, meaning that only the desired metal will react (dissolve) and then be separated from the undesired material. In this process, washing or leaching will be carried out(leaching) to remove ore impurities from a mineral by using certain reagents [6].

The hydrometallurgical method was chosen in the synthesis of copper carbonate from electronic waste because it is more environmentally friendly and economical when compared to the pyrometallurgical method which involves high temperature processing. The hydrometallurgical method uses a solvent in the liquid phase to dissolve copper metal from e-waste and convert it into a copper carbonate compound that can be used in various applications such as making pigments. With this method, it is hoped that we can create products in the form of pigments that can increase the use value of electronic waste which has not been utilized so far.

Pigments have high use value because they are used as substances that provide color to various products such as paint, ink, plastic, cosmetics, food, and so on. Several industries use pigments in their production, namely the paint, ink, cosmetics, plastics, food, beverage, paper and other industries. Considering that pigments have high economic value, it is very important to carry out research to process copper from electronic waste into

more valuable products in the form of pigments Mountain blue.

2. Experimental Method

2.1 Material

The tools used in making pigments from copper waste are as follows: analytical scales, thermometers, electric stoves, glass stirrers, flasks, beakers, measuring flasks, volume pipettes, dropper pipettes, pipette pumps, glass funnels, statives, clamps, ovens, desiccators, and porcelain cups and tools for dispersing dyes, including spatulas, brushes, watch glasses, and filter paper.

The materials used to make mountain blue pigment are copper waste, sulfuric acid (H_2SO_4), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), hydrogen peroxide (H_2O_2), and distilled water. Meanwhile, the materials used for pigment application are Carboxymethyl Cellulose (CMC) and titanium dioxide (TiO_2).

2.2 Methodology

2.2.1 Pigment Manufacturing

Level of Leaching

Fig 1. Level of Leaching

Solution H_2SO_4 20% and Na_2CO_3 2.5 M is prepared as much as 200 mL. 2.5 grams of copper waste was dried in the oven for 30 minutes. The dried copper waste was put into the H_2SO_4 a temperature 80°C. Solution H_2O_2 is added drop by drop into the mixed solution until the copper waste is completely dissolved. The mixed solution was filtered with filter paper and the residue was washed using 100 mL water.

Level Precipitation and Synthesis

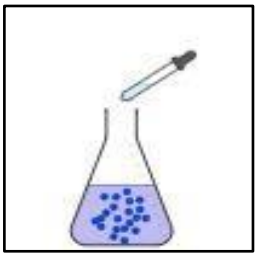


Fig 2. Precipitation and Synthesis Stages

NaOH is added to the filtrate until the pH reaches 4-5. Na solution$_2CO_3$ added to the filtrate solution until a blue precipitate forms. The precipitate was filtered and washed with 100 mL of water then dried in the oven until powder was obtained.

2.2.2 Pigment Application

The pigment formed was weighed at 2 grams and mixed with 3% w/w CMC solvent then dispersed using a spatula. The pigment is spread on filter paper and dried in the oven. Repeat the same steps with variations of pigment + TiO2 with a pigment ratio: TiO2 1:1 and 3:1. Compare pigment coloring results.

3. Results and Discussion

Leaching process in pigment manufacture *mountain blue* using solvent H_2SO_4 20% (v/v). Then add H_2O_2 dropwise to help the copper dissolve completely[7]. The reaction that occurs is as follows:

$$2Cu_{(s)} + 2H_2SO_{4\ (Aq)} + H_2O_2 \rightarrow 2CuSO_{4\ (aq)} + 2H_2O_{(g)}$$

Once the copper is completely dissolved, filter the mixture with filter paper and wash the precipitate with 100 mL of water. Add NaOH until pH 4-5 then add Na_2CO_3 into the filtrate until a blue precipitate forms. Filter the precipitate that forms and wash with 100 mL of water then dry the precipitate in the oven until powder is obtained. The reaction that occurs is as follows:

$2Na_2CO_{3\,(aq)} + 4H_2O_{(I)} \rightarrow 4Na^{+}{}_{(aq)} + 2H_2CO_{3(aq)} + 4OH^{-}$

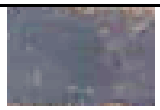
$4Na^{+}{}_{(aq)} + 2H_2CO_{3(aq)} + 4OH^{-}{}_{(aq)} + 2CuSO_{4(aq)} \rightarrow Cu_2(OH)_2CO_{3(s)} + 2Na_2SO_{4(aq)} + 3H_2O_{(I)} + CO_{2(I)}$

Table 1. Pigment Experiment Results Data Mountain Blue

Sample	Pigment Weight (grams)	Yield (gram montain blue/gram copper)	Conversion (%)
Experiment 1	4.2	1.68	96
Experiment 2	0.94	0.73	80
Experiment 3	3.34	1.34	92
Average	2.8	1.25	89.3

Next, the pigment powder that has been obtained will be applied by dispersing the pigment powder with 3% w/w CMC solvent. The pigment is applied to filter paper and then oven until dry. Repeat the same steps with various pigments and TiO2 and compare the resulting colors[8].

Table 2. Data from Pigment Application Experiment Results Mountain Blue

No	Pigment Mix	Results		
		Experiment 1	Experiment 2	Experiment 3
1	Pigment + solvent			
2	Pigmen + TiO_2 (3:1) + solvent			
3	Pigmen + TiO_2 (1:1) + solvent			

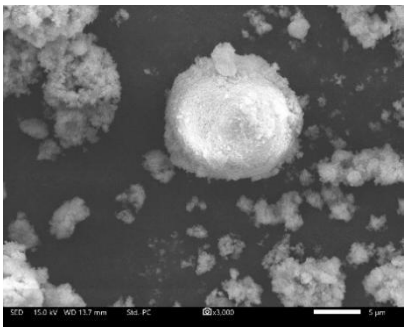
Based on Table 2, experiment 3 obtained a darker pigment color compared to other experiments. This occurs due to the influence of high temperatures during the oven, causing the mountain blue pigment to oxidize with the following reaction.

$Cu_2(OH)_2CO_3(s) \rightarrow 2CuO(s) + H_2O(I) + CO_2(I)$

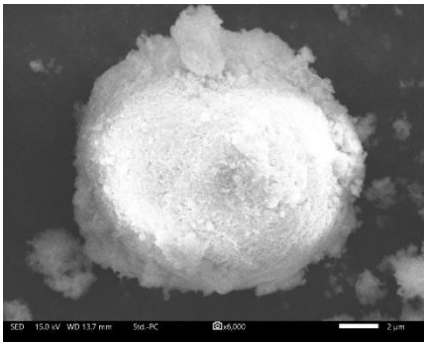
The factors that influence this practicum process include:

1. Temperature
   The higher the temperature, the faster the collisions between molecules. Because temperature provides energy for the ions in the sample and solvent to move.
3. Acid Concentration
   The addition of acid has the effect of accelerating the reaction process which increases.
4. Time
   The longer the contact between the sample and the solvent media, the more precipitate will be produced[1], [9].

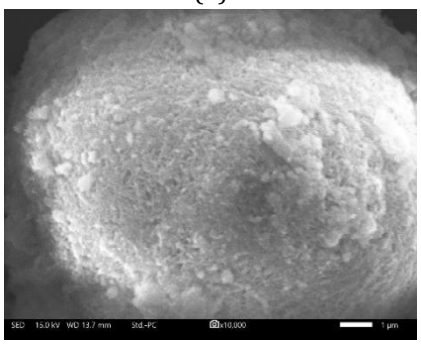
SEM Analysis



(a)



(b)



(c)

Fig 3. SEM Analysis (a) 3.000x (b) 6.000x (c) 10.000x

Figure 3 shows the results of analysis of calcium carbonate samples at various magnifications such as (a) 3,000x (b) 6,000x, and (c) 10,000x. Calcium carbonate samples have a round shape with a size of 1-15 microns. If observed, the sample has two types of particles, namely primary particles which agglomerate into secondary particles.

4. Conclusion

It can be concluded that the hydrometallurgical method successfully processes electronic waste into blue pigment (mountain blue). The average pigment yield of mountain blue in this experiment was 1.25 grams of mountain blue/gram of copper. The average value of pigment conversion mountain blue the result in this experiment was 89.3%. The greater the ratio of TiO2 when dispersing pigment powder, then it can influence the brightness of the pigment produced.

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Author Contributions

Luthfia Ummul Fadhilah, Putri Khyrul Afifah, Ragil Sumantri carried out the experiment. Luthfia Ummul Fadhilah, Putri Khyrul Afifah, Ragil Sumantri and Meidiana Arinawati wrote the manuscript with support Tika Paramitha and Windhu Griyasti Suci. The final report was committed by all contributors.

References

[1] F. Lambert *et al.*, "Copper leaching from wastes electrical and electronic equipment (WEEE) using alkaline monosodium glutamate: Thermodynamics and dissolution tests," *Miner. Eng.*, vol. 5, pp. 38–46, 2021, doi: 10.1016/j.clet.2021.100312.

[2] D. J. Garole, R. Hossain, V. J. Garole, V. Sahajwalla, J. Nerkar, and D. P. Dubal, "Recycle, Recover and Repurpose Strategy of Spent Li-ion Batteries and Catalysts: Current Status and Future Opportunities," *ChemSusChem*, vol. 13, no. 12, pp. 3079–3100, 2020, doi: 10.1002/cssc.201903213.

[3] N. Nagarajan and P. Panchatcharam, "Cost-effective and eco-friendly

copper recovery from waste printed circuit boards using organic chemical leaching," *Heliyon*, vol. 9, no. 3, p. e13806, 2023, doi: 10.1016/j.heliyon.2023.e13806.

[4] X. Zheng *et al.*, "Spent lithium-ion battery recycling - Reductive ammonia leaching of metals from cathode scrap by sodium sulphite.," *Waste Manag.*, vol. 60, pp. 680–688, Feb. 2017, doi: 10.1016/j.wasman.2016.12.007.

[5] A. G. Abel, *Pigments for paint*, Second Edi. Woodhead Publishing Ltd, 1999.

[6] T. Or, S. W. D. Gourley, K. Kaliyappan, A. Yu, and Z. Chen, "Recycling of mixed cathode lithium-ion batteries for electric vehicles: Current status and future outlook," *Carbon Energy*, vol. 2, no. 1, pp. 6–43, 2020, doi: 10.1002/cey2.29.

[7] N. Habbache, N. Alane, S. Djerad, and L. Tifouti, "Leaching of copper oxide with different acid solutions," *Chem. Eng. J.*, vol. 152, no. 2–3, pp. 503–508, 2009, doi: 10.1016/j.cej.2009.05.020.

[8] M. T. Islam, M. S. Farhan, F. Faiza, A. F. M. F. Halim, and A. Al Sharmin, "Pigment Coloration Research Published in the Science Citation Index Expanded from 1990 to 2020: A Systematic Review and Bibliometric Analysis," *Colorants*, vol. 1, no. 1, pp. 38–57, 2022, doi: 10.3390/colorants1010005.

[9] I. Meer and R. Nazir, "Removal techniques for heavy metals from fly ash," *J. Mater. Cycles Waste Manag.*, vol. 20, no. 2, pp. 703–722, 2018, doi: 10.1007/s10163-017-0651-z.