



Activated Bentonite Modified-Carbon Paste Electrode for Determination The Level of Copper Ion (Cu^{2+}) in Tomato

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Abstract – Voltammetry is an electroanalytical method measure current as a function of applied potential. The working electrode in the voltammetry method dramatically affects the result of the electrochemical analysis. Modification of the working electrode can improve measurement performance. In this research, the carbon paste electrode (CPE) was modified with Bentonite (CPEB) to determine copper's level using differential pulse voltammetry technique. CPE and CPEB were used as working electrodes, handmade Ag/AgCl as a reference electrode, and Pt wire as the counter electrode. The measurement parameters were optimized, including the composition of bentonite in carbon paste and scan rates. Furthermore, the measurement conditions were validated, involved linear concentration range, detection limit (LoD), the limit of quantization (LoQ), repeatability, and recovery. The results showed that bentonite's optimum composition was 40% of the total weight of graphite and activated bentonite. The scan rate optimum for Cu^{2+} measurement was obtained at 20 mV/s with CPE and became faster to be 25 mV/s with CPEB. The linearity of the standard solution measurement of Cu^{2+} using CPE was in the range of 5 to 100 $\mu\text{g/L}$ and changed to 5 to 500 $\mu\text{g/L}$ using CPEB. LoD and LoQ values of standard solution Cu^{2+} measurement with CPEB were slower than CPE. The Horwitz ratio calculation was smaller than two for both CPE and CPEB. The recovery of Cu^{2+} standard measure in sample solution as the matrix was obtained $93,49 \pm 6,39\%$. According to the Decree of the Ministry of Health Number, the level of Cu^{2+} in the tomato sample was found 6.019 \pm 0.69 mg/kg, which is over than threshold value of Cu^{2+} (5 mg/kg) 03725/B/SK/VII/89.

Keywords: Carbon paste electrode, Bentonite, Differential pulse voltammetry, Copper, Tomato

Introduction

The development of an analytical method for heavy metal analysis in biological samples has been increased recently. Some of the methods commonly used for metals analysis are Atomic Absorption Spectrophotometry (AAS) (Khan et al., 2016), Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES) (Jusufi et al., 2016), and voltammetry (Irdhawati et al., 2019). Most of these techniques give accurate results but have high detection limits, narrow working concentration range, high response time, and poor selectivity. The voltammetry method has many advantages compared with other methods, namely high sensitivity, the working electrode surface can be modified to decrease detection limit, low cost, user friendly and easy sample preparation (Harvey, 2000; Wang, 2001).

The voltammetry method's basic principle is the electrolysis of a solution containing electroactive analytes (Skoog et al., 1996). A three system electrode is used for measurement, including a working electrode (WE), a counter electrode (CE), and a reference electrode (RE). The active electrode is an essential part of the voltammetry method. Some materials can be used as working electrodes, such as platinum, gold, glassy carbon, carbon paste, carbon rod, copper, and mercury. Carbon paste electrode (CPE) is commonly used as the working

electrode to determine organic compounds and inorganic elements because it has good conductivity, nontoxic, and abundant (Al-zahrani *et al.*, 2016). Modification of working electrodes can improve electrode performances (Swamy *et al.*, 2020; Piovesan *et al.*, 2020; Kumar *et al.*, 2020). Some of the modifiers can be mixed with CPE, such as chitosan (Bouabi *et al.*, 2016), zeolite (Mobarakeh *et al.*, 2015), poly (vanillin) (Madhuchandra *et al.*, 2019), and Bentonite (Acar *et al.*, 2016).

Indonesia is one of the countries located on the equator, rich in minerals, including bentonite. Bentonite is a hydrated aluminum silicate mineral with a nano-scale layered structure and many ion exchanger sites. Character and number of ion exchanger sites depend on several factors such as interlayer space, charge, and site location in the layers. The cation exchanger in bentonite is influenced by the character and number of ion exchange sites and the electrolyte solution's chemical composition. Due to its high ion exchange capacity, strong mechanical stability, and large surface area, bentonite is widely used as a modifier in CPE (Azad *et al.*, 2014). Based on previous research, bentonite-carbon paste electrode has high chemical stability, controllable structure, and high adsorption properties, low cost and can be used for determination of organic and inorganic compounds. Bentonite in CPE can also increase oxidation peak currents and sensitivity, improve LoD and LoQ, precision, stability, selectivity, and recovery percentage (Alves *et al.*, 2019; Ourari *et al.*, 2018).

Copper is an essential element required for plant growth in limited quantities; excess copper in plants can cause toxic effects for humans and the environment. The copper element source in plants can come from the soil and uncontrolled use of fungicides containing copper. The farmers added pesticide or fungicide in their plantation land to increase production, but sometimes uncontrollable doses. Some researches have already been done and reported the content of heavy metals in soil or vegetables. The previous research on the analysis of copper element content in soil samples planted with tomatoes obtained 49.64 mg/kg (Siaka *et al.*, 2014). Another study has been conducted, and it was found 1.67 mg/kg of copper in tomato (Siaka *et al.*, 2013). Based on the Decree of the Ministry of Health Number: 03725/B/SK/VII/89, about Threshold Value of Metal Pollutants in Food, the maximum level of Cu in fresh vegetables is 5.0 mg/kg. The research was conducted seven years ago. Therefore, in this study, an analysis of copper content in tomatoes was carried out to monitor the feasibility of consuming vegetables, especially tomatoes grown in Bedugul Bali. Analysis of Cu²⁺ metal ions was carried out using bentonite modified carbon paste electrodes in tomato samples from the Bedugul horticulture center, one of the plantation areas that supplies vegetables for Bali consumption.

Materials and Methods

All the voltammetry measurements were performed using an Ingsens 1030 potentiostat instrument in three electrodes system. The working electrode and the reference electrode were handmade. The reference and counter electrodes were silver/silver chloride and Pt wire electrodes, respectively. Analytical balance (Shimadzu ATY224), magnetic stirrer, agate mortar, metal block digester, and commonly used laboratory equipment. The chemicals were analytical grade reagent include H₂SO₄, HNO₃, HCl, Cu (NO₃)₂ were obtained from Merck, KCl was from Wako, distilled water and double distilled water (IKA) were purchased from chemicals shop. All of the chemicals were used directly without further purification. Natural Bentonite was purchased from an online shop, taken from Padalarang, West Java.

A 100 gram of bentonite was added 750 ml of 1.5 M sulfuric acid solution, then stirred using a magnetic stirrer for 6 hours. Furthermore, the suspension solution was vigorous magnetically stirred for 6 hours to activate bentonite's active sites. After completing the reaction, the mixed suspension solution was precipitated for 24 hours and filtrated to separate activated bentonite and acid solution. The activated bentonite was washed several times with distilled water until the filtrate pH is neutral. Finally, a white-brown precipitate solid bentonite was obtained, dried in the oven at 100°C for 24 hours. Dry activated bentonite was crushed and sifted using 100 mesh sieves and then stored in an air-tight jar.

Determination of Optimum Bentonite Composition

All of the experiments were done with three replicates. Approximately 7 cm of copper wire 1,0 mm inner diameter was inserted into a teflon tube with an inner diameter of 2,0 mm, 6 cm long. On the bottom side, let a small space for carbon paste around 5 mm. The unmodified CPE was prepared as follows: 200 mg reagent-grade graphite powder was mixed with 90 μ L of liquid paraffin, stir gently until

mix well and formed paste in an agate mortar. Both unmodified and modified CPEs were packed into the bottom part of the electrode body manually. The fresh surfaces of the carbon paste electrode were polished on the wax paper until they showed a smooth, flat, and shiny appearance. The graphite powder was mixed with activated bentonite in various composition ratios to modify the CPE, as shown in Table 1.

Table 1. Composition of bentonite carbon paste electrodes

No	Graphite (mg)	Activated bentonite (mg)	Liquid paraffin (μL)	Activated Bentonite composition (%)
1	200	0	90	0
2	140	60	90	30
3	130	70	90	35
4	120	80	90	40
5	110	90	90	45
6	100	100	90	50
7	90	110	90	55

Optimization of Scan Rate

Carbon paste, Pt wire, and Ag/AgCl were used as working, counter, and reference electrodes, respectively. The electrodes were immersed in a voltammetry cell containing 10.0 ml of 500 $\mu\text{g/L}$ copper standard solution. Peak current measurement was conducted by differential pulse voltammetry technique, with scan rates varying from 5, 10, 15, 20, 25, and 30 mV/s. The differential pulse voltammetry has been applied from -200 mV to 200 mV vs. Ag/AgCl.

Determination of Linear Concentration Range

Linear concentration range was observed by measuring the peak current of 10.0 mL copper standard solutions with concentration variations of 5, 10, 20, 50, 100, 200, 500, 1000, 1500, and 2000 $\mu\text{g/L}$, diluted by 0.1 M HNO_3 as supporting electrolyte and solvent. The measurement of current was done using CPE and CPEB at the optimum scan rate.

Determination of Detection and Quantization Limits

Limit of detection (LoD) and limit of quantization (LoQ) were calculated using equations 4 and 5, based on linear concentration range data (Miller and Miller, 2010). The measurement detection limit value is determined by the following equation:

$$\hat{y}_i = a + bx \tag{1}$$

$$S_{y/x} = \sqrt{\frac{\sum(y_i - \hat{y}_i)^2}{n-2}} \tag{2}$$

$$S_b = \frac{S_{y/x}}{\sqrt{\sum(\bar{x} - x)^2}} \tag{3}$$

$$\text{LoD} = y_b + 3 S_b \tag{4}$$

$$\text{LoQ} = y_b + 10 S_b \tag{5}$$

$S_{y/x}$ = standard deviation of the linear line

S_b = standard deviation blank

b = slope

y_b = intercept

LoD = limit of detection

LoQ = limit of quantization

The \hat{y}_i value was obtained by substitution x value in linear regression equation with standard concentration.

Determination of Repeatability

Repeatability measurements were performed by measuring the peak current of 500 µg/L copper standard solution, ten times using CPE and CPEB. The coefficient of variance (CV) was compared with predicted CV Horwitz to determine Horwitz Ratio (HorRat) value. A good repeatability measurement when HorRat value is less than 2 (AOAC, 1998).

Determination % recovery

The percentage of recovery was determined using the standard addition method. The concentration of the standard solution is measured in the presence of the sample solution as a matrix. The measurement result of the standard solution was compared with the theoretical standard concentration. Measurement was conducted in three replicated. The percentage of recovery was calculated using Equation 5 (AOAC, 1998).

$$\% \text{ Recovery} = \frac{[\text{standard+sample}] - [\text{sample}]_{\text{measurement}}}{[\text{standard}]_{\text{theoretical}}} \times 100\% \quad (6)$$

Sample Preparation and Measurement of Cu²⁺ Metal Ion Concentration in Tomatoes

For DPV measurement of copper, fresh tomatoes were used. Tomato sample was taken from an agriculture area of Bedugul Bali with a geographical position of 8°17'37 "S 115°10'14" E. Sample was picked on three points. A sample of tomatoes was washed to remove soil and dust from the surface and then sliced into small parts. Small parts of the sample were weighed and dried in oven (80 °C) for 24 hours to constant weight to measure their water content. The dried sample was crushed in a mortar. The dry sample was weighed 1 gram and moved into a digestion tube, inserted into a metal block digester hole, then added 20 ml of aqua regia (HNO₃:HCl = 1 : 3). The sample was heated at 120°C for 1 hour. The acid extract was filtered through filter paper to remove any solid residue and dissolved until 25.0 mL in a volumetric flask. Afterward, the content of Cu²⁺ ions was determined by differential pulse voltammetry using the standard addition method. A 2 mL sample solution was mixed with the standard solution in varying concentrations of 0, 100, 200, 300, and 500 µg/L, and diluted until 10.0 mL.

Results

Optimization of Measurement Conditions

Determination of The Optimum Bentonite Composition

Figure 1. shows that CPE (0%) produced a lower peak current than CPEB. It is demonstrated that peak current increases with increase modifier percentage up to 40%. The peak current by CPE was at 0.01 µA while CPEB increases to 0.06 µA because the active sites in bentonite for adsorption Cu²⁺ were increased. After a 40% increase in the resistance of activated bentonite, thus the peak current decreased. The addition of bentonite in carbon paste can increase measurement sensitivity.

Determination of Optimum Scan Rate

The optimum scan rate with CPE was obtained 20 mV/s with a peak current of 0.6037 µA and peak potential of 0.04 V. Meanwhile, with CPEB was obtained 25 mV/s and peak current of Cu²⁺ ion was 0.6784 µA at the potential of 0.05 V. Scan rate optimization with CPE and CPEB can be seen at Figures 2 and 3.

Validation

Determination of Linear Concentration Range

The linear concentration range was observed in the range of 5 to 2000 µg/L with CPE and CPEB. The results were shown in Figures 4 and 5 for both CPE and CPEB. Peak current increases proportionally with concentration over the range of 5 to 100 µg/L for CPE, while 5 to 500 µg/L for

CPEB. The coefficient determination for CPE was obtained at 0.9992 and CPEB at 0.9966. The linear range of CPEB is wider than CPE, showed modifier could increase the significant response of peak current toward increasing concentration.

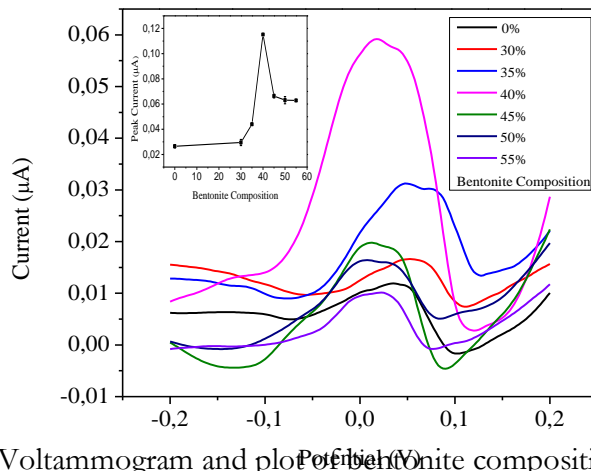


Figure 1. Voltammogram and plot of bentonite composition vs. peak current.

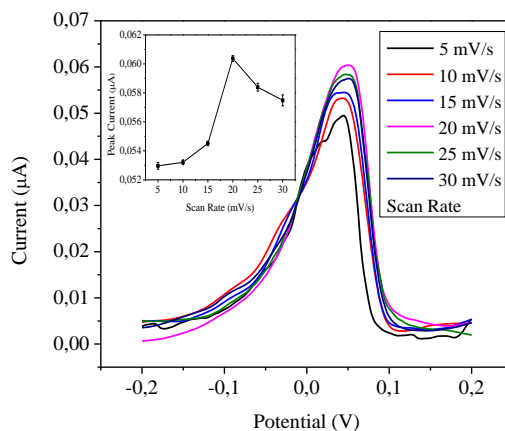


Figure 2. Voltammogram and plotted scan rate with a peak current of Cu^{2+} 500 $\mu\text{g/L}$ using CPE.

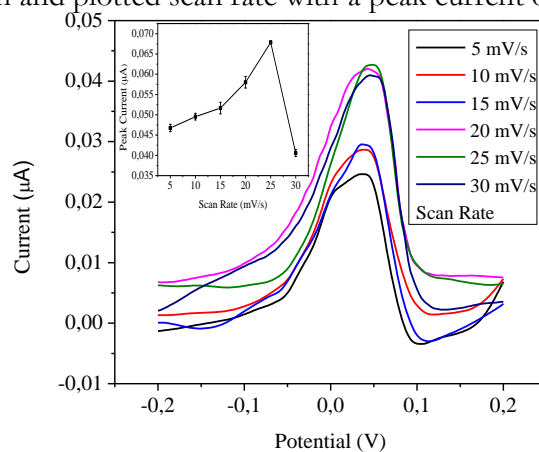


Figure 3. Voltammogram and plotted scan rate with a peak current of Cu^{2+} 500 $\mu\text{g/L}$ using CPEB

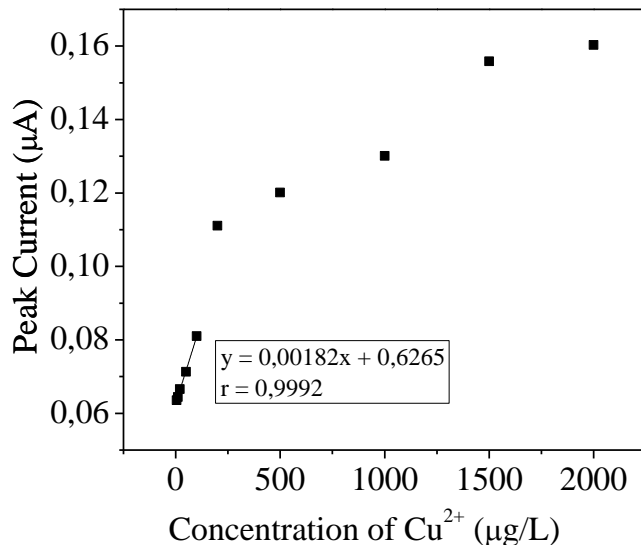


Figure 4. Calibration curve for measurement of Cu²⁺ with CPE

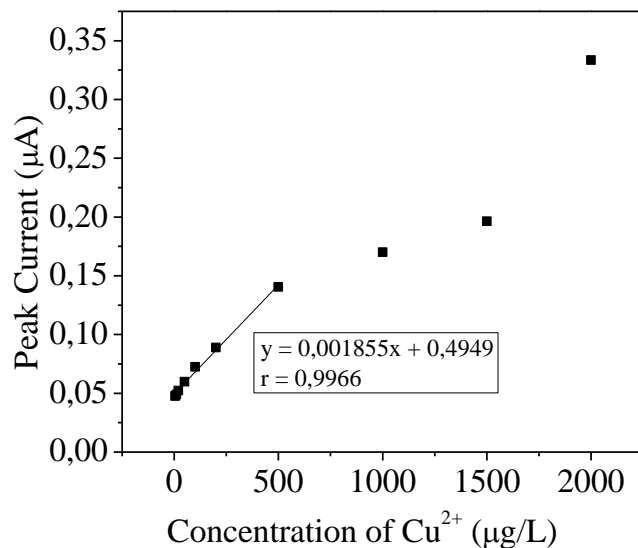


Figure 5. Calibration curve for measurement of Cu²⁺ with CPEB

Determination of Detection Limit and Quantization Limit

The result of LoD and LoQ calculation using CPE was 0.6266 µg/L, and LoQ was 0.6269 µg/L. Meanwhile, the detection limit for CPEB decrease to be 0.4661 µg /L, and LoQ was 0.4665 µg/L.

Repeatability

Repeatability is determined to observe the precision of measurement. The CV value was calculated and compared with the CV Horwitz to find the ratio Horwitz (HorRat) factor. The Horwitz ratios were 0.34 and 0.32 for CPE and CPEB, respectively. The plot between the peak current for each measurement is shown in Figure 6.

Recovery

Determination of the percentage recovery aims to measure the accuracy of instrument measurements. The result of calculating the percentage recovery of Cu²⁺ was 93.49 ± 6.39 %.

Measurement of Cu²⁺ in Tomato Sample

The content water content of the tomato sample was found at $95.47 \pm 0,42 \%$. The results of the calculation showed Cu²⁺ level in tomatoes was 6.02 ± 0.69 mg/kg. The standard addition curve for determining the level of Cu²⁺ in the tomato sample was given in Figure 7.

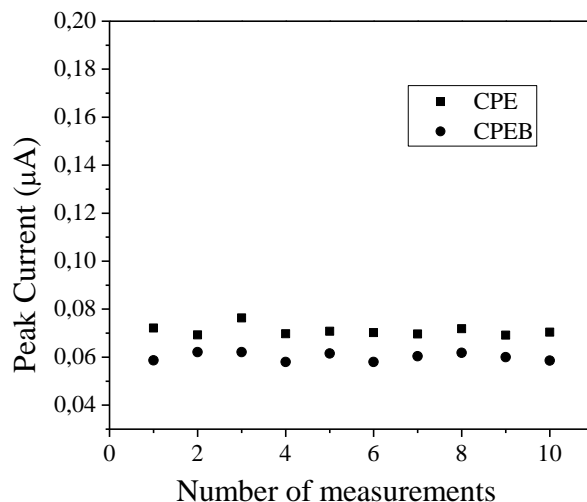


Figure 6. Plots of peak current vs. the number of measurement Cu²⁺ with CPE and CPEB

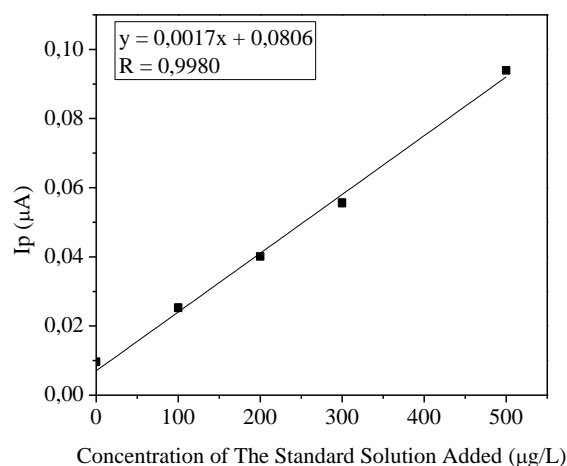


Figure 7. Calibration curve for standard addition of Cu²⁺ metal ion solution in tomato samples with CPEB

Discussions

In this study, bentonite was activated using H₂SO₄ 1.5 M. The purpose of bentonite activation is to release Al, Mg, Fe ions, and other impurities in the structure and exchange with H⁺; besides, the activation also aims to open the pores of bentonite and enlarge the surface area. The excess of H⁺ ion in bentonite was removed by washing it with distilled water until pH neutral. The actives sites of H⁺ ions in the bentonite structure will be exchanged with the metal cations in the sample. Bentonite has an interlayer space between its layers that can be occupied by cations of water molecules and other molecules.

On the determination of optimum bentonite composition, the peak current increased until 40% of Bentonite for Cu²⁺ measurement, but the peak current decreased at the higher compositions. In this study, the optimum design of bentonite obtained was lower than the previous study of 50% (Suliana

and Setiarso, 2014). This is due to the different sources of natural bentonite. The high bentonite composition in carbon paste causes the graphite particles' distance to be further away, causing the conductivity to decrease. Two possible reactions occur on the carbon paste electrode's surface, modified by Bentonite, namely adsorption (Grim, 1953) and cation exchange reactions. Bentonite can act as an adsorbent because it has a large surface area. Also, bentonite can be an ion exchanger due to having many active sites. The active sites in bentonite can be a mediator for electron transfer at the carbon paste electrode surface. Therefore the peak current obtained using CPEB are higher than CPE. The peak potential for both unmodified and modified CPEs was found at a similar potential around 0.02 V, indicating no different energy in a redox reaction. Bentonite has several advantages that make it very useful as a modifier in electrodes, such as its lack of toxicity and chemical reactivity, high surface area, and low cost.

The scan rate is related to the electron transfer rate when there is a redox reaction on the electrode's surface. The optimum scan rate obtained using CPEB is 25 mV/s, faster than CPE, 20 mV/s. The peak current received using CPEB is higher than the CPE. This is due to bentonite in carbon paste that can accelerate the transfer rate of electrons from the bulk solution to the electrode's surface. The presence of bentonite in carbon paste causes the potential peak measurement to shift slightly to the right, from 0.04 V using CPE to 0.05 V using CPEB. The only slight difference in peak potential can be assumed that no significant difference in redox reaction energy occurred. The addition of bentonite as a modifier in determining the scan rate makes the scan rate at the measurement increase and the peak current increases; this is because the addition of bentonite in the carbon paste electrode can accelerate the transfer of electrons to the electrode surface.

The validation parameter was observed, including the linear concentration range. Using CPEB, the linear concentration range is wider than CPE. This shows bentonite as a modifier in carbon paste can increase the significance of the response between the concentration and peak current. The limit of detection and limit of quantization using CPEB is lower than CPE. This means that the bentonite-modified carbon paste electrode can measure a smaller analyte concentration in a sample compared with CPE. Figure 6 shows that the peak current of 10 times the Cu^{2+} ion measurement has a Horwitz Ratio value less than 2 for both CPE and CPEB. It is shown that the measurement has good repeatability (Horwitz and Albert, 2006). At the optimum condition, CPEB is used to determine the percentage of recovery, measuring the standard's concentration in the presence of a sample as a matrix. The result obtained is $93.49 \pm 6.39 \%$. According to AOAC rules, the percentage of recovery acceptable value for analyte measurements should be in the range of 80% to 110% (AOAC, 2011). Thus, the working electrode of CPEB has a good recovery.

The result of Cu^{2+} measurement in the tomato sample was found 6.02 ± 0.69 mg/kg. The result has exceeded the threshold Cu^{2+} value of 5.0 mg/kg according to the Decree of the Ministry of Health Number: 03725/B/SK/VII/89. The high Cu^{2+} level in the tomato sample is probably due to the excessive use of pesticides. In addition, the source of Cu^{2+} can also come from the water used for watering from Beratan Lake, where there are fish ponds that use fungicide containing Cu.

Conclusion

The presence of bentonite on carbon paste can increase electron transfer rate or charged ions toward the electrode surface. The validation investigation for several parameters, including linear concentration range, the limit of detection, the limit of quantization, repeatability measurement, and recovery percentage, indicated that measurement of Cu^{2+} ion using bentonite-carbon paste electrode has a better result, compared with carbon paste electrode without modification. The concentration of Cu^{2+} in the tomato sample was higher than the acceptable value.

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