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Synthesis of Cuprum (Cu) Layer by Electrodeposition Method with Theobroma cacao Peels as Corrosion Protector of Steel

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Abstract— **Corrosion is a natural phenomenon that can not be prevented the process of occurrence, but the timing may be delayed. Various efforts have been made in reducing the impact of losses caused by corrosion. One such effort is to coat the metal surface with a thin layer. As well as other efforts is to use an inhibitor. Efforts have been made to reduce the impact of corrosion loss by synergizing surface coating and using of inhibitors. Deposition of a thin layer of Cu using electrodeposition method with 0.05 M CuSO4.5H2O electrolyte solution and addition of inhibitor of *Theobroma cacao* peels extract. In this research has been done some variation that is variation of electrodeposition time and variation of concentration of inhibitor of *Theobroma cacao* peels extract. Scanning Electron Microscope (SEM) characterization shows electrodeposition of a thin layer of Cu for three minutes, a voltage of three volts, and with the addition of an inhibitor of *Theobroma cacao* peels extract 1% producing a smooth, homogeneous and more uniform surface morphology. Based on the result of characterization with X-Ray Diffraction (XRD) obtained steel surface at electrodeposition with the addition of an inhibitor of *Theobroma cacao* peels extract, there are sharper peaks of Cu. Based on the corrosion test obtained value of Inhibition Efficiency inhibitor of Theobroma cacao peels extract amounted to 69.4% with the addition of 1%, and 81.9% with the addition of inhibitor 1.5%. Based on this, inhibitor of *Theobroma cacao* peels extract can reduce the attack rate of corrosion on the steel surface in corrosive media HCl 1N.**

Keywords— **electrodeposition; theobroma cacao peels; corrosion; inhibition efficiency.**

I. INTRODUCTION

Steel is a metal material that is widely used as industrial materials. The progress of steel material use has increased, along with the development of infrastructure development, cars, ships, trains, weapons, and tools. Steel is selected because steel material is easy to obtain, easy to fabricate and has strong tensile strength [1]. Along with these advances also cause some problems, such as steel material easily corrodes.

Corrosion results in enormous economic losses [2] and it is an important industrial problem [3]. Some efforts are made to reduce the impact of corrosion, such as by coating the surface. The advantage of this surface coating method is that it can separate the steel surface from the environment, controlling the microenvironment on steel surfaces, as well as for beauty and appearance or decorative purposes.

In addition to the surface coating method, use of corrosion inhibitors to date is still the best solution to protect the metal from corrosion; the non-toxicity and biodegradability are the major advantages for these inhibitors [4]. A corrosion inhibitor is a substance that is added in small amounts to the environment in order to minimize or prevent corrosion [5].

Common corrosion inhibitors exist that are inorganic and organic in nature [6]. Using of inorganic inhibitors to slow the rate of corrosion has several disadvantages, because they contain hazardous chemicals to living things, they are relatively expensive, and they are not environmentally friendly [1], [7], [8], [9], then inhibitors made from natural ingredients are the answer to this problem, such as coriander leaves [10], *Aloe vera* leaves [11], [12], *Theobroma cacao* peels without combine with electrodeposition method [13]. *Theobroma cacao* is an abundant natural resource in Indonesia. Of the 1.5 million tons of production proclaimed by the government in 2017, then 70-75% of the production is cacao peels waste [1]. Until now *Theobroma cacao* waste has not been utilized to the fullest, whereas tannin compounds contained in the *Theobroma cacao* peels quite a lot [14]. To reduce its impact on the environment one of the benefits can be used for inhibitors.

In this research, *Theobroma cacao* peels extract inhibitor will be made as a mixture of electrolyte solution in the electrodeposition process. Electrodeposition is one of the most important techniques for producing coating materials with excellent mechanical and chemical properties [15], versatile and low cost, low processing temperature, simple control of deposition thickness, high purity of deposits, convenience, and low instrumentation cost [16], [17]. Expected that, the addition of *Theobroma cacao* peels extract inhibitors in this electrodeposition process can minimize the occurrence of corrosion in steel and beautify the appearance.

II. MATERIALS AND METHOD

A. Specimens of Steel Preparation

The steel plate is cut to 2x1cm, and given a hole for the hanger. The specimens were polished using emery paper to the size of fineness 600, 1000, 1500 and 2000. Then they washed with detergent and distilled water, and rinsed with alcohol to remove any contaminants. The specimens were subsequently dried with a hot dryer at a temperature of 30°C for 10 minutes, and finally stored in desiccators [9].

B. Electrolyte Solution and Corrosive Media Preparation

$CuSO_4.5H_2O$ weighed as much as 2.495 grams and 3 grams of boric acid. Then both of these substances were dissolved in a 200 mL measuring flask to obtain a solution of electrolytes with a concentration of 0.05 M.

The corrosive medium was prepared from a HCl 5 N solution by means of a pipette of 103.6 mL HCl 37% and fed into a 250 mL glass of water diluted to a boundary mark with aquades. Furthermore, the parent HCl 5 N solution was used to prepare corrosive medium of HCl 1 N by means of 10 mL HCl 5 N parent solution and then diluted with aquades up to 50 mL volume.

HCl 1 N corrosive media was prepared by mixing a *Theobroma cacao* peels extract inhibitor with a concentration of 0%; 0.5%; 1.0%; 1.5%; 2.0% and 2.5%.

C. Theobroma cacao Peels Extracts Preparation

Cacao peels were collected in Lubuk Minturun, Padang City, West Sumatera, Indonesia. This preparation has been done by [1].

D. Electrodeposition Process

The electrodeposition process is carried out by placing the steel substrate as the cathode at the negative pole and graphite as anode at the positive pole. Then the inhibitor solution according to each concentration is mixed with the electrolyte solution into the electrodeposition device of 5 mL each. Further, stirred and flowed DC voltage of 3 volts with variation of electrodeposition time [1]. The electrodeposition voltage of 3 Volts is the optimum voltage obtained in the premilinary research.

E. Weight Loss Method

Each specimen was weighed to determine the initial weight, and then immersed into HCl 1 N medium for 6, 12, 18 and 24 hours. The inhibitor concentration variation was selected as much as 0.0, 0.5, 1.0, 1.5, 2.0, and 2.5% V/V. After exposuring for each predetermined time, corrosion products were then removed from the media, brushed them using a soft brush, washed with distilled water and finally rinsed with acetone. The specimens were dried at room temperature, and then weighed again to obtain final weight [18]. The rate of corrosion is determined by using the following equation (1):

$$v = \frac{\Delta m}{A \;\; t} \tag{1}$$

Where v is the rate of corrosion, Δm loss of mass, A surface area of steel and t is time.

F. Potentiodynamic Polarization Method

Potentiodynamic polarization test using Potensiostat e-Corder 416. Cylindrical steel cut with 2 mm diameter to be used as working electrode. The bottom is coated with resin. Pt as auxiliary electrodes, and Ag/AgCl as comparative electrode. Potentiodynamic polarization measurements were performed in 1N HCl medium and variation in inhibitor concentration of *Theobroma cacao* peels extract; 0.0%, 1.0% and 1.5%. The three electrodes are immersed in each concentration.

Then it is connected with potentiometer and measured potential to obtain the potential interconnection curve (mV) with log current (mA/cm^2). The potential used is from -1000 mV to 1000 mV.

The Inhibition Efficiency value is determined by using (2) the following equation:

$$IE\ (\%) = \frac{I_{unh} - I_{inh}}{I_{unh}}\ 100\ \% \tag{2}$$

Where I_{unh} current without inhibitor and I_{inh} current with the addition of inhibitor.

G. Characterization of Morphology

After the electrodeposition process, an initial morphological observation was performed using optical microscope and the best electrodeposition of steel was characterized using SEM Hitachi S-3400N and PANalytical XRD.

III. RESULTS AND DISCUSSION

A. Results of Optical Microscope Characterization

In Fig. 1 is a selected steel of some electrodeposition steel with electrodeposition time for 3 minutes. This selection is based on the most uniform and non-accumulating steel surface morphology that is considered to represent all electrodeposition steel.

In Fig. 1a visible fine lines influence the sanding on steel surfaces before electrodeposition, Fig. 1b resulting in uneven layers, stacked particles, and coarse grains. The grains are particles of Cu that begin to form. While Fig. 1c obtained a much smoother and more uniform deposition result, no material accumulation in some parts of the deposition result, and the formation of another layer covering Cu particles. Other coatings are suspected inhibitors that participate reacted with electrolyte solution.

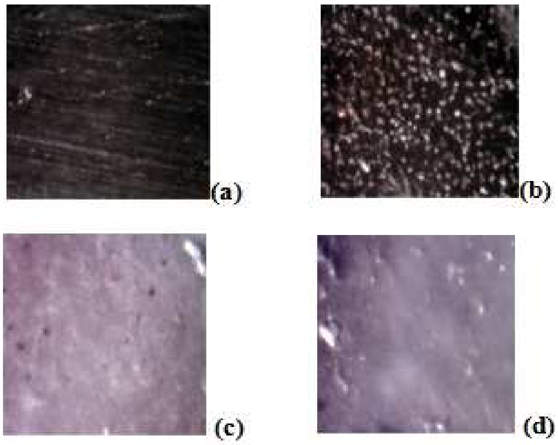

Fig. 1 Results of Steel Characterization with Optical Microscope (a) Before electrodeposition (b) After electrodeposition without inhibitor (c) with 1% inhibitor and (d) with inhibitor 1.5%

While in Fig. 1d is an electrodeposition of steel with the addition of a 1.5% *Theobroma cacao* peels extract inhibitor and the same electrodeposition time, ie 3 minutes. The results of the deposition look quite good when compared to steel without the addition of inhibitors in Fig. 1a. The results of the deposition smooth and evenly, but other layers began to appear accumulate in some parts.

B. Analysis of SEM Characterization Results

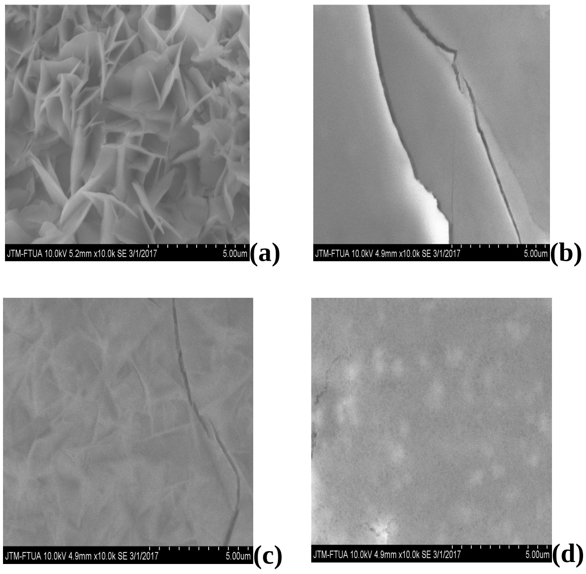

Fig.2 SEM Photo with Surface 10000x Magnification (a) Steel before electrodeposition, (b) after electrodeposition with addition of 1.0% inhibitor (c) 1.5% inhibitor and (d) 1.0% inhibitor and heated at 60^{0}C

Fig. 2a shows the surface of the steel layer before electrodeposition. Visible surface of the steel layer is less evenly distributed, there is a build up of particles that cause the size of the particle is not uniform. After adding the inhibitor to Fig. 2b visible results of finer and homogeneous deposition although there is a thin gap of the resulting layer, but the coating is uniformly distributed and there is no particle accumulation in some parts. The gap formed like this fine line is the effect of grinding and sanding on steel surfaces.

Furthermore, in addition to the inhibitor solution of *Theobroma cacao* peels extract 1.5% of the characterization results are shown in Fig. 2c where the visible result of the deposition is still uniform and visible the passive layer on the surface of the steel sample. This layer serves as a barrier to the attack of corrosive ions on the surface of the steel [1], [19].

Meanwhile, when heated at 60^{0}C at electrodeposition process with the addition of 1.0% *Theobroma cacao* peels extract inhibitor the result of characterization shown in Fig. 2d. Where the heating effect shows the electrodeposition result of aggregate accumulation in some parts, and the barrier layer becomes stacked on a certain part. This proves that heat can damage the surface of the formed layer [1].

C. Analysis of XRD Characterization Results

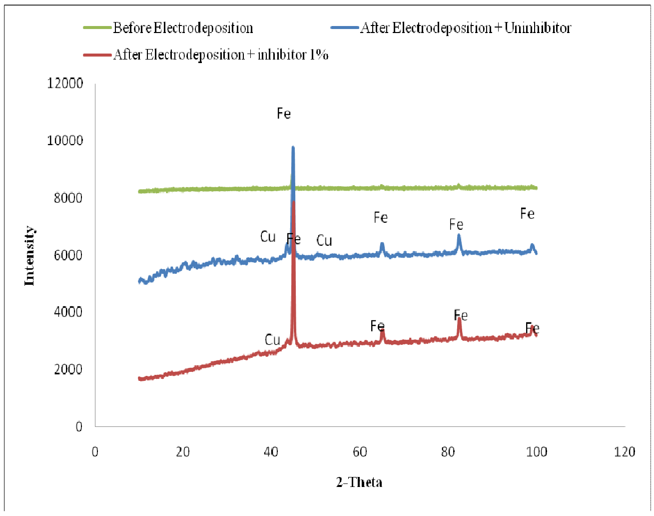

Fig. 3 XRD Steel Diffraction Pattern (a) Before Electrodeposition, (b) After Electrodeposition without *Theobroma cacao* Peels Extract and (c) with Addition 1% *Theobroma cacao* Peels Extract

XRD characterization results in the form of diffraction patterns which are the tops of characteristic crystalline structures formed in Cu layers. The diffraction patterns of the layers are identified at 2-Theta angles. The XRD characterization results for all three samples showed three X-ray diffraction peaks. In the difractrogram the phase margin produced in steel before electrodeposition not yet many peaks formed and none of the Cu peaks are formed (Fig.3a).

Then on Fig. 3b is steel after electrodeposition without the addition of a *Theobroma cacao* peels extract inhibitor, where Cu begins to form and there are Cu peaks on the difractogram and many small peaks are formed.

And at Fig. 3c is electrodeposition of steel with the addition of *Theobroma cacao* peels extract inhibitor, where the peaks that are formed have started more flat and produced peak Cu is sharper than Fig. 3b. This peak difference is formed due to a shift of peaks which reveals that there is a reduction of the interplanar distance of the crystal lattice on the substitution of Cu atoms [20].

The addition of *Theobroma cacao* peels extract inhibitors in the electrodeposition process can minimize contact between the steel surface and the environment. Because the protective layer (barrier) formed on the steel surface is a layer of organic compounds that reside in the *Theobroma cacao* peels extract forming a bond with the atoms on the steel surface [21].

D. Corrosion Rate Analysis of Weight Loss Method

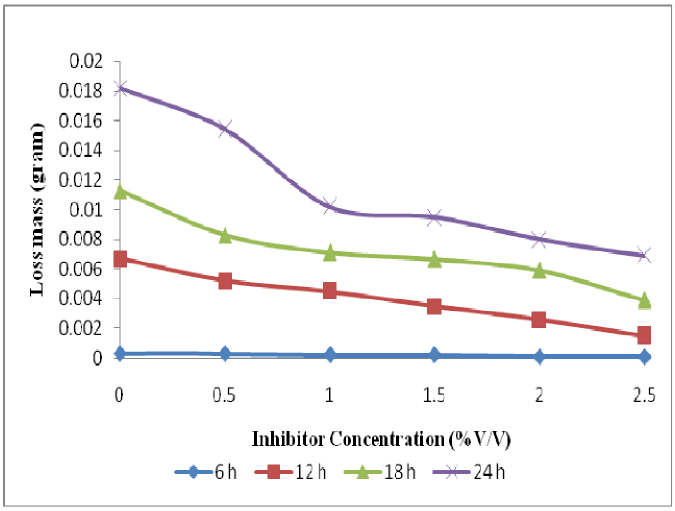

Fig. 4 Relationship of Inhibitor Concentration with Mass Lost

From Fig. 4 shows a decrease in mass lost due to increased concentration of *Theobroma cacao* peels extract inhibitor added. The longer the immersion time, the more mass lost occurs, and otherwise.

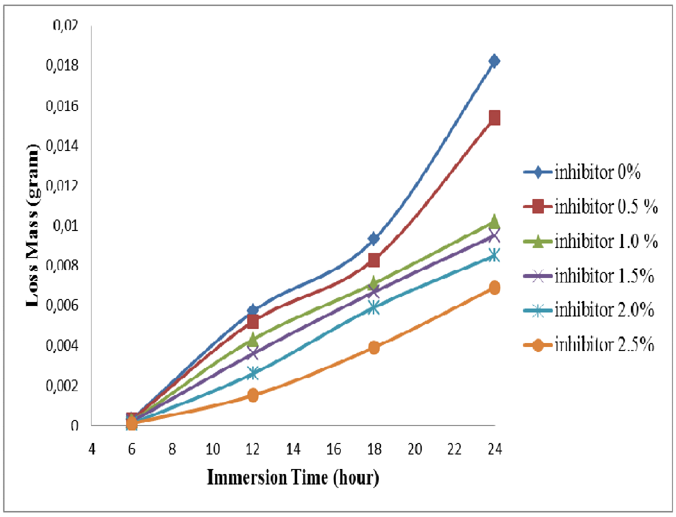

Fig. 5 Relationship of Loss Mass with Immersion Time

Based on Fig. 5, sample without the addition of inhibitors experienced a sharp increase in mass lost compared to other samples. This is because there is no inhibitor that will inhibit the occurrence of corrosion, so that the loss of mass more and more along with the length of time immersion [11], [22].

Relationship between Inhibition Efficiency (IE) of steel with corrosion rate can be seen in Fig. 6, where Efficiency Inhibition of steel has increased with increasing inhibitor concentration, while the corrosion rate has decreased. The increase in inhibition efficiency may be attributed to the increase in number of adsorption of nutrients on the surface of steel which makes a barrier for mass and charge transfer and prevent further corrosion [22].

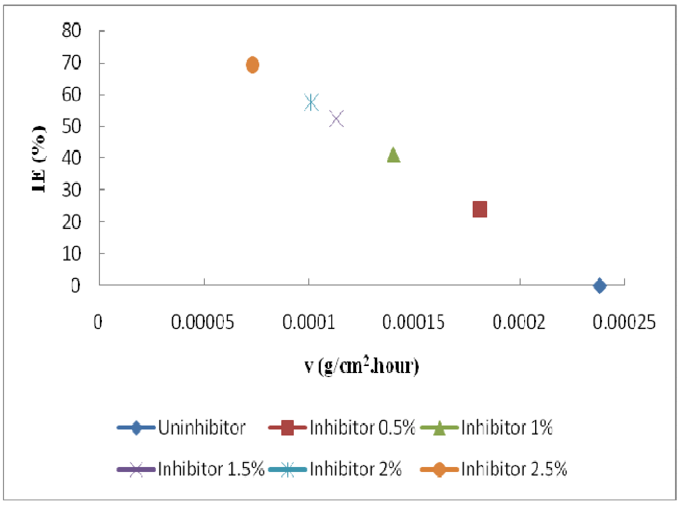

Fig. 6 Connection Inhibition Efficiency with Corrosion Rate

TABLE I
PARAMETER OF CORROSION RATE ANALYSIS

Inhibitor Concentration (%V/V)	Immersion Time (hour)	Corrosion Rate (g/cm^2.hour)
0	6	0.0000025
	12	0.000187
	18	0.000246
	24	0.000361
0.5	6	0.000020
	12	0.000179
	18	0.00022
	24	0.000306
1.0	6	0.0000159
	12	0.000148
	18	0.000163
	24	0.000176
1.5	6	0.0000138
	12	0.000124
	18	0.000153
	24	0.000164
2.0	6	0.00000794
	12	0.000103
	18	0.000135
	24	0.000149
2.5	6	0.00000689
	12	0.0000595
	18	0.000103
	24	0.000119

Table 1 shows the rate of corrosion decreases with increasing concentration of *cacao* peel extract inhibitors added. This is because the more inhibitors of *Theobroma cacao* peel extracts are added, the more *Theobroma cacao* peels extract is adsorbed on the steel surface and form a thin layer. The surface-formed layer is able to inhibit the corrosive rate attack on the steel surface, so that the corrosion rate of the steel can be inhibited [13]. This means that the compounds contained in *Theobroma cacao* peels extract, especially the tannin compound can be used as inhibitors to reduce the corrosion rate value in steel [1].

E. Corrosion Rate and Inhibition Efficiency Analysis of Potentiodynamic Polarization Method

The steel Tafel diagram in corrosive media can be seen in Fig. 7.

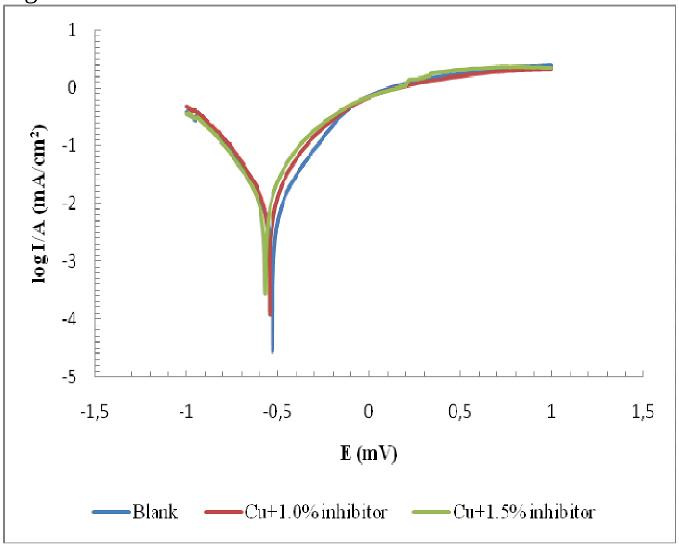

Fig. 7 Polarization Curve of Steel in HCl 1N in the Absence and Presence of *Theobroma cacao* Peels Extract

Based on Fig. 7 can be seen there is a shift potential corrosion value. This shift in corrosion potential values to a more positive and negative direction indicates the added extract is anodic and cathodic [1]. The following will show the values of corrosion parameters in HCl 1N corrosive media.

TABLE II
PARAMETERS OF STEEL CORROSION IN CORROSIVE MEDIA HCL 1 N

Inhibitor Concentration (%V/V)	Icorr (mA/cm^2)	Ecorr (mV)	IE (%)
0	0.0131	0.51	-
1.0	0.0122	0.59	69.4
1.5	0.0072	0.58	81.9

Based on Table 2, Inhibition Efficiency of steel has increased with increasing inhibitor concentration. In this case, not all samples were tested for corrosion analysis, only three samples tested were considered representative of the best samples.

In general, the advantage of the electrodeposition method using *Theobroma cacao* peels extract as inhibitor is to combine the two attempts to prevent corrosion. Electrodeposition method produces Cu-coated on the steel, and then the *Theobroma cacao* peels extract inhibitor can inhibit corrosion.

IV. CONCLUSIONS

Cu layer can be produced using electrodeposition method. With electrodeposition voltage of 3 Volts, the optimum electrodeposition obtained by morphology is at 3 minutes and the concentration of 1% *Theobroma cacao* peels extract inhibitor. Then, the best sample for corrosion rate analysis is the concentration of 2.5% *Theobroma cacao* peels extract.

Based on the characterization of the surface of the electrodeposition of steel, the morphology of the surface is more smooth and evenly distributed in the addition of the *Theobroma cacao* peels extract inhibitor concentration of 1%.

The result of corrosion test showed that Inhibition Efficiency of *Theobroma cacao* peels extract inhibition increased with increasing concentration, while corrosion rate decreased with increasing concentration of *Theobroma cacao* peels extract inhibitors. Meanwhile, based on potentiodynamic polarization method known inhibitor *Theobroma cacao* peels extract is anodic and cathodic.

NOMENCLATURE

v	corrosion rate	g/cm^2hour
Δm	loss mass	g
A	surface area	cm^2
t	time	hour
IE	Efficiency of inhibition	%
I_{unh}	Current without inhibitor	mA
I_{inh}	Current with inhibitor	mA

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