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# Dynamic Contact Angle and Corrosion Test Measurements on Cu and CuO-Stearic Acid Modifications on Steel Surfaces

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## ABSTRACT

In this study, a copper (Cu) coated steel surface's dynamic contact angle and corrosion rate was compared to the bare steel and stearic acid modified surfaces. Various steps of surface treatment have been performed including electrodeposition of Cu, CuO formation from $H_2O_2$ immersion with stearic acid modification to obtain dynamic contact angle and the corrosion rate data. The Cu-coated steel's dynamic contact angle was increased as it implied the surface after Cu treatment was more hydrophilic than the bare steel, with sliding angle and contact angle hysteresis of 54.9° ± 2.39° and 39.5° ± 1.91°, respectively. However, corrosion test measurements by using a mass loss method to quantify the corrosion rate showed that Cu-coated steel and stearic acid-modified Cu-O coated steel had no remarkable difference in corrosion rate. It was found that the Cu-coated steel and stearic acid-modified Cu-O coated steel had a corrosion rate eight times slower than the bare surface.

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## 1. INTRODUCTION

The study on surface modification has attracted wide interest among researchers due to its potential for many industrial applications such as in infrastructure, transportation, and telecommunication (Usher *et al.*, 2014; Du *et al.*, 2019; Li & Yu, 2016). Various treatments such as lipid bilayer, polymer, and other organic and inorganic materials deposition have been performed on solid substrates to produce the desired surface characteristic depend upon its application (Spinke *et al.*, 1992; Tien & Salamon, 1989; Majewski *et al.*, 1998). This study focuses on steel surface modification because of the importance of steel as the main material for many industries worldwide. Steel has been used extensively due to its strength, durability as well as affordability properties. Industries such as construction, automotive, transportation, energy, and even household application heavily rely on steel as the main materials for production. Therefore, there have been many efforts and studies performed to either preserve or increase the strength and durability of the steel. Despite the advantages, steel still suffers material degradation if it is placed in certain extreme environmental conditions such as in high humidity, temperature, and acidity. These conditions typically caused corrosion and erosion to the steel structure and therefore damaging the steel structure and decreasing the strength and durability of the steel.

In order to prevent surface corrosion on the steel, many studies were focusing on the modification of the steel surface with certain materials. One of the methods was by developing a hydrophobic surface. The idea of creating a hydrophobic surface was motivated by the hydrophobic behavior of the lotus leaf. It is well-known that the surface of the lotus leaf is very hydrophobic as water droplets will roll over the surface without much inhibition (Ensikat *et al.*, 2011). Besides, anti-corrosion hydrophobic surface also has potential as anti-fouling, anti-icing, and self-cleaning properties (Ensikat *et al.*, 2011; Motlagh *et al.*, 2013; Zhang *et al.*, 2014). These properties may prevent the degradation of the metal surface and preserve the strength of the metal structures further.

A hydrophobic surface has been fabricated on a metal substrate by employing various methods. A superhydrophobic surface fabricated by sulfur-induced morphological development has been reported (Han *et al.*, 2005). Wang *et al.* (2015) reported developing a corrosion resistance by spraying highly amphiphobic polymer materials coating surfaces. Other techniques in developing superhydrophobic surface such as sol-gel, chemical vapor deposition, spraying, spinning, etching, and plasma treatment also have been reported in the literature (Wu *et al.*, 2012; Zhang *et al.*, 2014; Brassard *et al.*, 2014; Gurav *et al.*, 2015; Cho *et al.*, 2016; Vilaró *et al.*, 2017; Li & Yu, 2016). Among all these techniques of fabrication, electrodeposition is widely used because it allows full control of the metal deposition to the surface (Shi *et al.*, 2005).

Surface hydrophobicity usually determines by measuring the static contact angle and the dynamic contact angle of the water droplet on the surface. The values of the contact angles indicate the degree of hydrophobicity or hydrophilicity of the surface. It is reported in the literature that, the high value of static contact angle indicates that water will be repelled easily on the surface while a low value < 90 degree shows that water will be retained on the surface. As for dynamics contact angle, it is indicated by sliding angle value, where the low value of sliding angle shows water will slide easily on the surface as opposed to high value. It is also reported that if the value of static contact angle is > 1500 while the sliding angle below 100, the surface can be labeled as a superhydrophobic surface (Motlagh *et al.*, 2013; Law, 2014; Brassard *et al.*, 2014; Jagdheesh *et al.*, 2017).

Therefore, the goal of this study was to obtain the dynamics contact angle and corrosion rate information for copper (Cu) coating steel surface and compared the effect of Cu coating treatment to the bare steel and CuO-stearic acid-modified steel surface. The deposition of Cu was performed by electrodeposition. It is expected the deposition Cu will give effects on the steel surface in terms of hydrophobicity as well as the corrosion rate.

## 2. RESEARCH METHODOLOGY

### 2.1. Materials

The specimen preparation method followed the method published in the literature (Brassard *et al.*, 2014; Liu *et al.*, 2015; Li *et al.*, 2016; Trisnanto *et al.*, 2019; Wen *et al.*, 2018). The steel metal was obtained from PT Santo Jaya Teknik. It was composed of 99.27% Fe, 0.11% C, 0.24% Si, 0.35% Mn, 0.018% P and 0.014% S (Liu *et al.*, 2001). The steel substrate was cut to the size of 50 mm x 20 mm x 2 mm. A copper plate with a purity of > 97.5% was used as an anode. All chemicals used such as NaOH, $Na_2CO_3$, $Na_2SiO_3$, $CuSO_4$, anhydrous ethanol, $H_2O_2$, and stearic acid are analytical grade and used as it is without further purification.

### 2.2. Sample Preparation

Initially, the steel substrate was polished with silicon carbide (SiC) abrasive paper ranging from 180 to 1200 grit before further treatment. This procedure is meant to clean the surface from contaminants. The steel substrate was rinsed with distilled water and anhydrous ethanol to remove surface contaminants and then the specimen was dried. After the substrate was dried, the steel substrate was treated with an alkali cleaning process to remove grease from the substrate surface. A solution containing 30 g/L NaOH, 20 g/L $Na_2CO_3$, and 10 g/L $Na_2SiO_3$ at 60°C (Trisnanto *et al.*,2018; Hao *et al.*, 2016; Li *et al.*,2016; Li *et al.*, 2017) was used for the alkali cleaning process. The steel substrate was then removed after 15 minutes in the solution and rinsed with distilled water.

The substrate modification followed the method published in the literature (Trisnanto *et al.*, 2018). The layer by layer deposition started with the electrodeposition of Cu on the steel substrate on step 1, CuO formation by immersion into $H_2O_2$ solution, and Stearic Acid Modification as shown in **Figure 1**.

1. ***Cu layer formation on the steel***. The cathode in this process was the steel substrate and the anode is a copper plate. The condition for the Cu electrodeposition followed the most optimum parameters condition determined from static contact angle measurement.

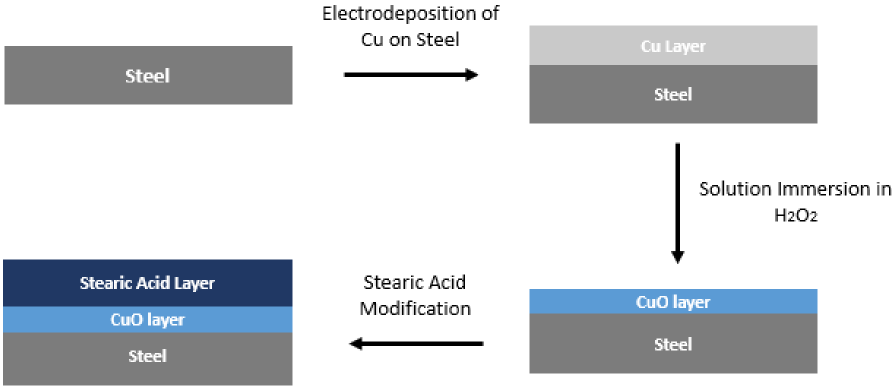

**Figure 1. Schematic diagram of the fabrication of Cu and CuO-Stearic Acid coating**

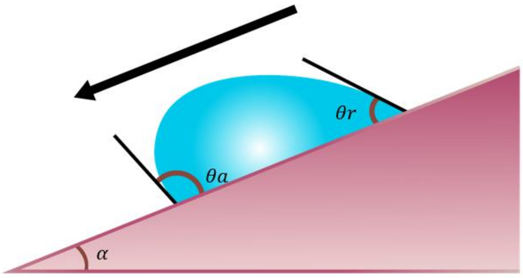

**Figure 2. Dynamics contact angle schematic**

2. ***Fabrication of CuO layer***. The Cu modified substrate was immersed into a mixture of 2.5 mol/L NaOH and 0.1 mol/L $H_2O_2$ solutions at 60°C for 30 minutes to grow a CuO crystal layer on the steel substrate.
3. ***Deposition of Stearic Acid layer***. The CuO coated steel substrate was immersed into a stearic acid solution with various concentrations for 24 hours at room temperature. The stearic acid solution was prepared by dissolving the stearic acid in ethanol solution. The stearic acid concentrations were prepared for 0.01 M, 0.05 M, 0.10 M, 0.15 M to 0.20 M.

### 2.3. Dynamics Contact Angle Measurement

The dynamics contact angle measurement was performed following the method published in the literature (Trisnanto *et al.*, 2019). This measurement was used to obtain the sliding angle and contact angle hysteresis information.

The sliding angle was measured by the inclination angle of the water droplet on the surface starts to roll off the surface. The contact angle hysteresis was calculated by ImageJ Drop-snake software analysis (Stalder *et al.*, 2006).

Theoretically, the contact angle hysteresis was measured by subtracting the receding angle ($\theta_r$) from the advancing contact angle ($\theta_a$) when the substrate is tilted as shown in **Figure 2**. Dynamics contact angle measurement consists of a light source for illumination, translucent screen, specimen, and digital camera with 10x optical zoom as shown in **Figure 3**.

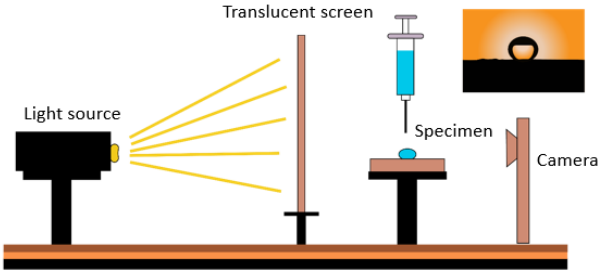

**Figure 3. Set up for dynamics contact angle measurement**

### 2.4. Corrosion Test Measurement

The CuO-stearic acid substrate was prepared by immersing into 5 wt% NaCl solution for several days to test its anti-corrosion properties (Antunes *et al.*, 2013). As a comparison, bare steel and Cu-coated steel samples were also subjected to the same testing condition.

Corrosion test resistance was performed using ASTM G1 standard where the corrosion rate was obtained using mass loss method where the substrate's mass was measured repeatedly after several days of immersion in the NaCl solution (Afolabi *et al.*, 2014; Desiati *et al.*, 2018). The corrosion rate was obtained using the following equation:

$$C_r = \frac{K \, x \, W}{A \, x \, T \, x \, D} \quad (1)$$

where,

$K$ = a constant (depends on the desired unit)

$T$ = time of exposure in hours to the nearest 0.01

$A$ = contact surface area in $cm^2$ to the nearest 0.01

$W$ = mass loss in gram

$D$ = density of sample in $g/cm^3$

## 3. RESULTS AND DISCUSSION

### 3.1. Dynamics Contact Angle Results

The dynamic contact angles including sliding angle and contact angle hysteresis were observed in samples after various sequential treatments. The dynamic contact angle data is shown in **Table 1**. It was found that contact angle hysteresis – the difference between advancing and receding contact angle, decreased after series of treatments. Bare steel or untreated steel, Cu and CuO coated steels had high contact angle hysteresis.

On the other hand, oxidized Cu-electrodeposited / Cu-coated steel modified with stearic acid had the smallest contact angle hysteresis. Untreated steel had contact angle hysteresis of $27.7^o \pm 2.7^o$. After electrodeposition of Cu onto the steel surface, the contact angle hysteresis was slightly raised to $39.5^o \pm 1.91^o$. The increasing contact angle hysteresis of Cu treated surface indicating a slight increase of hydrophilicity of the surface. It is suggested that there was a slight change in wettability from untreated steel to Cu-electrodeposited steel according to contact angle hysteresis value.

As for the sliding angle, the untreated steel had a sliding angle of $42.6^o \pm 1.50^o$. After electrodeposition treatment, the sliding angle notably increased to $54.9^o \pm 2.39^o$ standard error. It was inferred that surface was more wetted in the Cu-electrodeposited steel sample than in the untreated steel sample. Furthermore, there was a remarkable reduction in both sliding angle and contact angle hysteresis after sequential treatments from the oxidation of Cu-electrodeposited steel to stearic acid modification.

The oxidized Cu-coated steel had a sliding angle and contact angle hysteresis of $56.8^o \pm 3.49^o$ and $29.6^o \pm 2.41^o$ respectively. It was suggested that oxidized Cu-coated steel was also very hydrophilic. This result was consistent and corroborated with the data of static contact angle in the literature (Trisnanto *et al.*, 2019). The stearic acid treatments steel, the sliding angle, and contact angle hysteresis were extremely reduced to $7.2^o \pm 0.43^o$ and $15.1^o \pm 3.43^o$ respectively. This result indicated that the non-wettability of the surface was enhanced from hydrophilic to superhydrophobic (Trisnanto *et al.*, 2019).

**Table 1. Dynamic Contact Angle Measurement for Various Processing Condition**

| **Treatment** | **Sliding Angle** | **Receding Contact Angle ($\theta_{rec}$)** | **Advancing Contact Angle ($\theta_{adv}$)** | **Contact Angle Hysteresis ($\theta_h = \theta_{rec} - \theta_{rec}$)** |
|---|---|---|---|---|
| Bare Steel (untreated) | 42.6° ± 1.50° | 60.1° ± 2.39° | 87.7° ± 3.35° | 27.7° ± 2.70° |
| Cu-electrodeposited Steel | 54.9° ± 2.39° | 62.9° ± 3.72° | 102° ± 3.65° | 39.5° ± 1.91° |
| Oxidized Cu-electrodeposited Steel | 56.8° ± 3.49° | 21.3° ± 3.29° | 50.9° ± 2.77° | 29.6° ± 2.41° |
| Oxidized Cu-electrodeposited Steel Modified with Stearic Acid | 7.2° ± 0.43° | 138° ± 2.16° | 153° ± 3.39° | 15.1° ± 3.43° |

### 3.2. Corrosion Test Results

The results of the corrosion test were shown in the **Figure 4**. It was obtained by measuring the corrosion rate of bare steel, Cu-electrodeposited steel and CuO coated with Stearic Acid modification. The red, green and blue lines represent corrosion rate of bare steel and Cu-coated steel and stearic acid modified steel after placed in 5 wt% NaCl solution for several days respectively. The data for bare steel and stearic acid modified has been published by (Trisnanto *et al.*, 2019). In this study, we compared the Cu-coated steel with bare steel and stearic acid modified steel. From the results, it was found that bare steel had the fastest corrosion rate than the other two substrates. The Cu-coated steel and stearic acid modified CuO-coated steel had almost indistinguishable corrosion rate as published elsewhere.

There was a significant reduction of the bare steel substrate's corrosion rate 0.91 mm/year to 0.22 mm/year on the first four days. On the other hand, the Cu-coated steel and stearic acid modified CuO-coated steel did not show sharp drop of corrosion rate reduction. The results of Cu-coated, and stearic acid modify steels were quite stable after immersion to NaCl for more than twelve days. It was from 0.1723 mm/year to 0.0862 mm/year for Cu-coated steel and from 0.1848 mm/year to 0.0616 mm/year for stearic acid modified CuO-coated steel. As it was indicated by significant reduction of the corrosion rate, therefore, the corrosion of bare steel was occurred much faster than those of Cu-coated steel and stearic acid modified CuO-coated steel substrates. From the results shown in the **Figure 4**, the corrosion rate of the bare steel was approximately eight times faster than Cu-coated and stearic acid modified CuO-coated steel substrate.

The reduction of corrosion rate showed how fast the corrosion forms on the surface. The experimental results show that there was a more rapid electron transfer process from surface of the bare steel to the salt solution in compare to the surface coated with Cu and Stearic Acid. There was a layer of black-coloured ferrous oxide accumulation on the surface of the bare steel when the corrosion was starting to form on the surface rapidly. Overtime, this ferrous oxide layer will block the salt solution to interact with the steel surface. The formation of ferrous oxide showed that the corrosion rate was decreasing as a function of time.

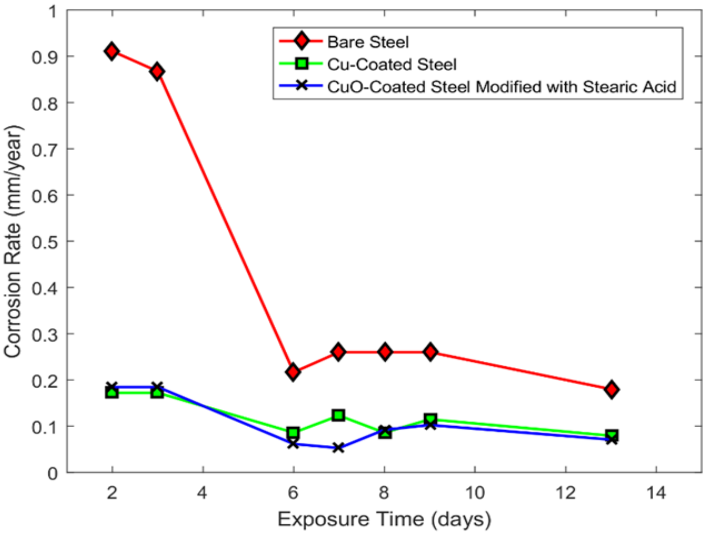

**Figure 4. Rate of Corrosion for Bare Steel, Cu-Coated and Cu-Coated with Stearic Acid Steels Deposition**

## 4. CONCLUSION

This study has shown that, a Cu and Stearic acid modified steel surface was successfully fabricated. Various measurements were performed on different steel substrates to compare bare steel, Cu coated steel with Cu-Stearic acid modified surface. The dynamic contact angle data for Cu coated steel such as the sliding angle (54.9° ± 2.39°) and contact angle hysteresis (39.5° ± 1.91°) indicated there is not much change in compare with the untreated steel surface. However, the corrosion test results showed a rapid reduction rate of bare steel surface in compare to the Cu coated surface which show no significant difference the corrosion rate after several days of NaCl immersion. This corrosion result indicated that the Cu coated surface has slower corrosion formation than the bare steel.

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