



## Water extracts of cassava leaf as corrosion inhibitor for mild steel in sulfuric acid solution

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### ABSTRACT

Water extracts of cassava leaves (*Manihot esculenta*) has been studied as a corrosion inhibitor for steel in sulfuric acid solution. Cassava Leaf Extracts are Soluble in Water (CLESW) is obtained by evaporation. Cassava leaves so that the hot steam flows wither. Cassava leaves are withered squeezed resulting in a water solution. Aqueous solution left for 3 days and then separated between deposition and solution. The solution obtained was concentrated to vaporize. The concentrated extract at a concentration of 0.1% for; 0.5%; 1%; 5%, and 10% and tested on steel as a corrosion inhibitor in sulfuric acid solution. Measurement of steel corrosion rate and corrosion inhibition efficiency with methods of losing weight, electrochemical instrument and the steel surface seen from SEM measurements. Results showed that the cassava leaf extract from soluble in water in sulfuric acid solution can be used as a corrosion inhibitor of steel. Corrosion rate without the use of a cassava leaf extracts corrosion inhibitor are soluble in water is greater than the use of the corrosion inhibitor. The surface of the steel without corrosion inhibitor is more porous than the presence of inhibitor corrosion it. The adsorption mechanism of the CLESW on mild steel in 0,5 M H<sub>2</sub>SO<sub>4</sub> solution was typical of physisorption.

**Keywords:** inhibitor, corrosion, physisorption, cassava

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### INTRODUCTION

Corrosion is known as rusting which is an event of damage or loss of quality of a metal caused by the reaction with the environment. In the industrial world, the steel is widely used because it is easy to get, easy to make and very interesting. One of the shortage of materials made of steel is that it is susceptible to corrosion and are very susceptible to corrosive attack[1] Metals such as mild steel corrosion is an electrochemical reaction that can cause degradation and damage to physical and chemical properties of metals under attack. In addition to natural factors such as air humidity and wet time, the use of acid was found to be the main factor driving to corrosion problems .Impact that can be caused due to damage by corrosion would have a great effect on people's lives, such as from an economic point of impact on the environment. The process of corrosion prevention one of them is to use inhibitors. There are two corrosion inhibitors corrosion , synthesis inhibitors and inhibitors based of natural products. Corrosion inhibitors from natural materials began to be developed as eco-friendly.

Corrosion process is a natural process that can not be avoided because there will be changes in the composition of the steel surface reactions with its surroundings [2]. There are several ways to slow the corrotion rate, namely coating, anodic or cathodic protection and the addition of inhibitor [2-3]. Inorganic inhibitor is common widely used inhibitor substance up to know. However, the use of the conventional inorganic inhibitors has a negative impact because of its toxicity and non-biodegradable like chromates, phosphates, molybdates, etc(2,4,5). Reports in the literature on the use of plant extracts as corrosion inhibitors are focused on plant part of leaves, stems, bark, roots,

seed, fruits etc. Certain plant extracts which are organic compound containing heteroatom like nitrogen, sulphur, and oxygen was being investigated as corrosion inhibitor. It may be advisable for using organic inhibitors from natural product because of non toxic and biodegradable [2,4]. The examples are numerous such as *Theobroma cacao* peels [2], citrus peels [6], gummara of the Phoenix *Dactylifera* [7], *Manihot esculentum* root peels [8], *Garcinia mangostea* fruit [1], *Carica papaya* leaves [9]. *Artemisia Halodendron* leaves [10]

Cassava (*Manihot esculenta*) is one of the most important food crop in tropical regions of the world, become the principal source of carbohydrate energy for human consumption. Isolation of cassava starch are functional ingredients used in the food industry, paper, textile and pharmaceutical and economic value for the countries exporting flour. The amount of utilization of cassava creates an enormous waste of cassava leaves. Currently, cassava leaves are still underused and only used as a vegetable. Desirable to look for higher-value products from cassava leaves that can be economically valuable for commercial.

Bokanisereme [11] reported that cassava leaves with phytochemical test contains carotenoids, flavonoids, tannins, and terpenoids. Cassava (*Manihot esculenta* Crantz) is also rich in antioxidant compounds [12]. Cassava leaves which have a complex mixture of organic chemicals such as flavonoids and tannins allows it can be used as a corrosion inhibitor. The use of cassava leaf extract as a corrosion inhibitor has been reported by Adejo et al [13] that extracts the ethanol from cassava leaves can inhibit corrosion of the aluminum in a sulfuric acid solution with cassava leaf extract obtained by maceration method of ethanol in dry cassava leaves. In this study reported the use of cassava leaf extract dissolved in water (CLESW) which was obtained by the evaporation method and tested the corrosion inhibition efficiency on steel in a sulfuric acid solution with several methods of weight loss and electrochemical measurements

## EXPERIMENTAL SECTION

### Materials Preparation

The steel used is mild steel specimens (ST 37) are commonly used in construction materials with the following composition 3.38% C, 1.36% of O, 0.57% Si, 0.53% Mn and the remainder Fe. Mild steel plate round shape with a diameter of  $\pm 2.5$  cm in thickness from 0.3 to 0.5 cm. Specimen polished using emery paper, washed with water, degreased with acetone

### Cassava Leaves Extract Soluble in Water (CLESW) Preparation

50 kg of cassava leaves withered with steaming hot water for 3 hours. Cassava leaves that have been withered compressed and result be filtered water from the felts and left overnight and then filtered with gauze pads. The filtrate was evaporated water by using a water bath at 50°C. Concentrated extract is used as a corrosion inhibitor.

### Solution Preparation

The corrosive medium was 0.5 M H<sub>2</sub>SO<sub>4</sub> (Merck) was prepared from 95% analytical grade by dilute of water. The corrosive solution is diluted with 0.01%, 0.05%, 0.1%, 0.5% and 1% by CLESW

### Weight Loss Method

Each specimen weighed prior to treatment. After it was soaked in a solution of sulfuric acid without CLESW and with additional CLESW with a concentration of 0.1%, 0.5%, 1%, 5% and 10% for 6 hours at each temperature 30°C, 40°C, 50°C and 60 °C. After soaking for 6 hours specimen removed and then washed with water, acetone and dried and then weighed back. Experiments performed in triplicate. Weight loss data is used to calculate the corrosion rate (CR) in mg cm<sup>-2</sup>h<sup>-1</sup> and inhibition efficiency ( $\eta$ ) in%.

### Electrochemical Measurement

Potentiodynamic polarization study was done using computer controlled EDAQ Potentiostat 466-Advance Electrochemical System [2]. The mild steel samples was put on holder footage of the equipment, and dipped in a corrosion cell containing a solution of 10 mL corrosive media. The mild steel sample was put as the working electrode. While, platinum and AgCl was put as auxiliary electrode and counter electrode, respectively. The three electrodes were then connected to the potentiostat instrument. The results of measurements include the corrosion current density ( $I_{corr}$ ) and corrosion potential ( $E_{corr}$ ) [1,2]

## RESULTS AND DISCUSSION

## Weight Loss Measurements

## Effect of Inhibitor Concentration on Corrosion Rate

Mild steel which is corroded in a solution of sulfuric acid with and without Cassava Leaves Extract Soluble in Water (CLESW) loss severity was measured by the following equation[6] :

$$C_R = \frac{W_b - W_a}{S \cdot t} \quad (1)$$

Where  $W_b$  dan  $W_a$  are the sample weight measured before and after soaking in a solution of corrosive.  $S$  is exposed area and  $t$  is time in hour.

Inhibitor Efficiency ( $\eta$  in %) is calculated by following equation :

$$\eta (\%) = \frac{CR(\text{blank}) - CR(\text{inh})}{CR(\text{blank})} \times 100 \% \quad (2)$$

$C_{R(\text{blank})}$  and  $C_{R(\text{inh})}$  indicate corrosion rate the absence and presence of the inhibitor in the sulfuric acid.

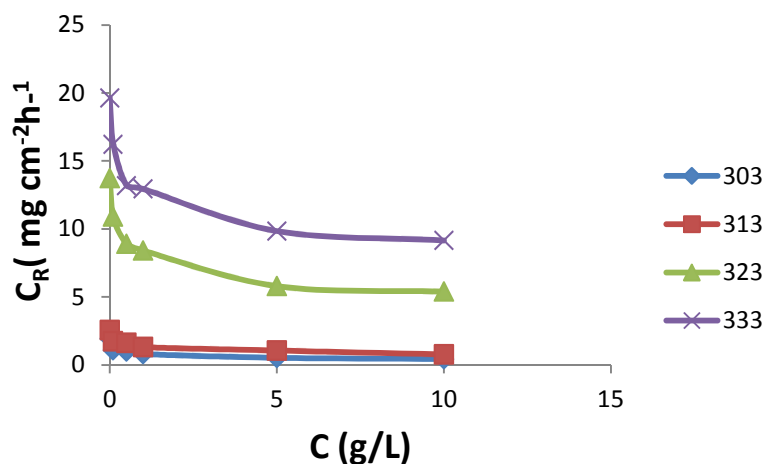


Figure 1. The Effect of concentration of extract on corrosion rate at different temperature

Figure 1 shows the relationship of the concentration of the extract CLESW with the corrosion rate of the temperature difference. Increasing of CLESW extract concentration resulted in the corrosion rate decreases. The existence of the CLESW extract has been to protect the mild steel from corrosion [14]. The greater the corrosion rate with increasing temperature.

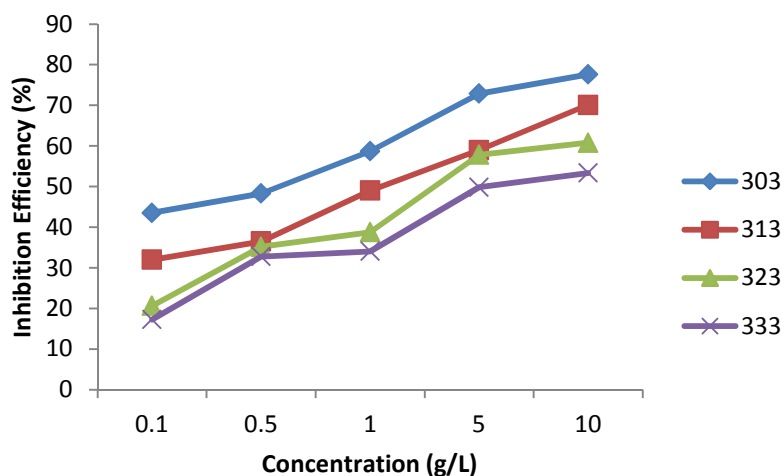


Figure 2. The effect of concentration of extract on inhibition efficiency at different temperature On figure 2, the optimum of inhibition efficiency is 77.6% at a concentration of 1% CLESW at a temperature of 303 K . Lower the inhibition efficiency with increasing temperature

**Effect of Temperature**

Calculation of activation energy for the corrosion reaction using the Arrhenius equation [6]:

$$C_R = A \exp \left[ - E_a / RT \right] \quad (3)$$

Where  $C_R$  is the corrosion rate,  $R$  the gas constant,  $T$  the absolute temperature,  $A$  the pre-exponential factor,  $E_a$  is activation energy.

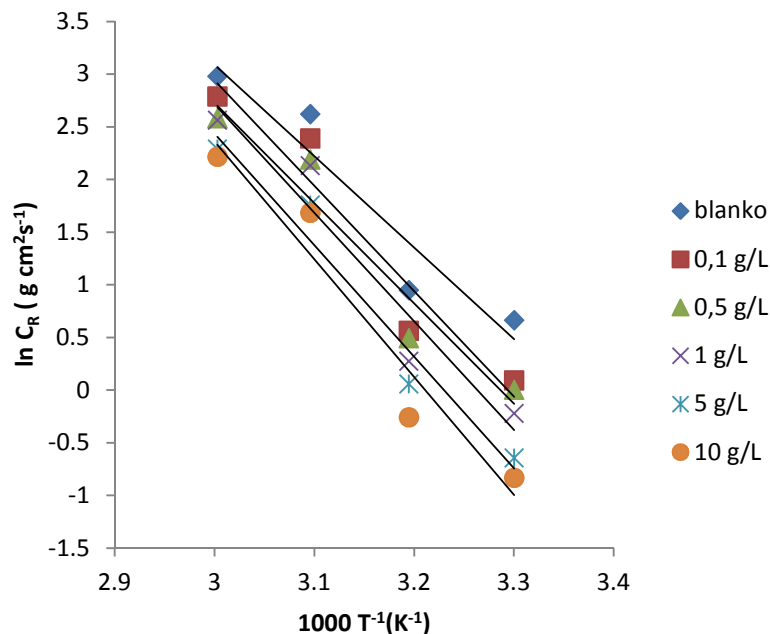


Figure 3. Arrhenius plots for the corrosion rate of steel in 0,5 M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of CLESW at different concentration

Figure 3 shows the relationship between  $\ln CR$  with  $1/T$  gives a straight line with presence and absence of CLESW. The value of activation energy can be obtained from the slope value  $E_a/R$ .

Table 1. Activation energy  $E_a$  value for mild steel corrosion rate in 0,5 M H<sub>2</sub>SO<sub>4</sub> in the absence and in the presence of different concentrations of CLESW

Konsentrasi CLEDW	$E_a$ (kJmol <sup>-1</sup> )
0,0 (blanko)	72,20709
0,1 g/L	83,18988
0,5 g/L	79,08443
1 g/L	85,59263
5 g/L	88,02863
10 g/L	92,99209

In figure 3 shows that the greater the temperature is resulting the greater the corrosion rate means that CLESW effective at low temperatures. Figure 3 and Table 1 show that the activation energy with presence the CLESW as a corrosion inhibitor is greater than the absence for CLESW that means the interaction between the surface of the iron with inhibitors [6]. The higher values of  $E_a$  in the presence of inhibitor compared to its absence are generally consistent with a physisorption, while unchanged or lower values of  $E_a$  in inhibited solution suggest charge sharing or transfer from the organic inhibitor to the metal surface to form coordinate covalent bonds [16, 17].

**Isotherm Adsorption**

CLESW adsorption layer has covered the steel surface. The value of surface coverage ( $\theta$ ) corresponding to different concentration of CLEDW have been used to determine the adsorption isotherm at constant temperature according to equation[6]:

$$\theta = C_R(\text{Blank}) - C_R(\text{Inh}) / C_R(\text{Blank}) \quad (4)$$

By assuming, CLEDW in sulfuric acid solution is caused by the adsorption of inhibitor on the mild steel surface and allows Langmuir Isotherm that can be expressed [2,6] as

$$\frac{c}{\theta} = \frac{1}{K_{ads}} + C \quad (5)$$

Where C is the concentration of inhibitor,  $K_{ads}$  is adsorptive equilibrium constant and  $\theta$  is the surface coverage. In addition, the free energy of adsorption process  $\Delta G_{ads}$  can be expressed[10]

$$K = \frac{1}{55,5} \exp(-\Delta G_{ads}^0 / RT) \quad (6)$$

Where 55,5 is the concentration of water in the solution in mol dm<sup>-3</sup>, K = equilibrium adsorption constant, R = the universal gas constant, and T = the thermodynamic temperature.

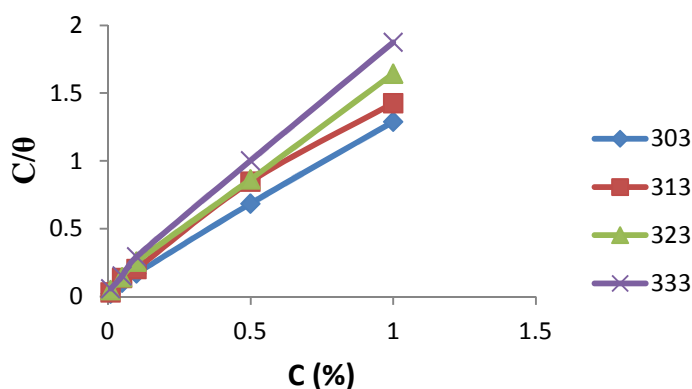


Figure 4. Langmuir adsorption isotherm plots of CLEDW extract on the mild steel surface at different temperature

Table 2. Adsorption parameters derived from Langmuir adsorption isotherms for mild steel corrosion 0,5 M H<sub>2</sub>SO<sub>4</sub> at different temperature

T (K)	$K_{ads} (gL^{-1})^{-1}$	$\Delta G (kJmol^{-1})$
303	0,790514	-10,1535
313	0,711896	-10,4849
323	0,630477	-10,816
333	0,551177	-11,147

From Table 2 shows that the value  $K_{ads}$  decreases with increasing temperature. The value of  $\Delta G_{ads}^0$  around -20 kJ mol<sup>-1</sup> or lower are consistent with the electrostatic interaction between the charged and molecules and the charged metal (physisorption) [8,10, 18]. The value around -40 kJmol<sup>-1</sup> or higher involve charge sharing or charge transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [10,18]. The adsorption mechanism of the CLESW on mild steel in 0,5 M H<sub>2</sub>SO<sub>4</sub> solution was typical of physisorption. Inhibitor of CLESW effective at a lower temperature. negative value of  $\Delta G_{ads}$  means that adsorption of inhibitor molecules to the surface of the steel is spontaneous [18].

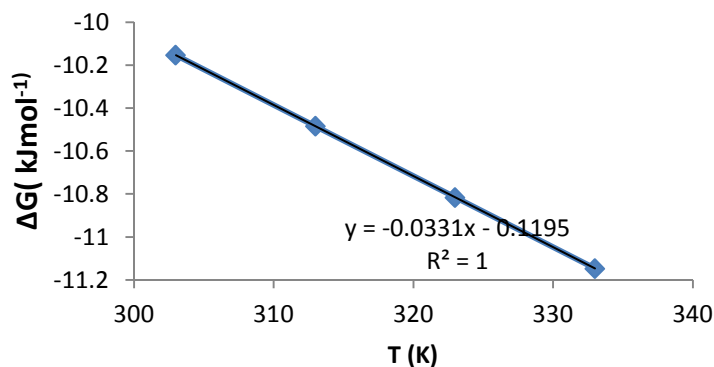


Figure 5. Expression for straight regression line of the standard free energy of adsorption vs T

From the resulting regression straight line is the standard adsorption enthalpy and entropy adsorption standard. Intercept in figure 6 yield  $\Delta H_{ads} = -0,1195 \text{ kJmol}^{-1}$  and slope yield  $\Delta S_{ads} = 0,0331 \text{ kJ mol}^{-1}\text{K}^{-1}$ . The negative value of  $\Delta H_{ads}$  shows that adsorption process is exothermic. An exothermic adsorption process shows chemisorption or

physisorption or mixture of both], whereas endothermic process indicates to chemisorption [18]. In exothermic adsorption process, the difference of physisorption and chemisorption may be on the basis of values of  $\Delta H_{ads}$  [18].  $\Delta H_{ads}$  is around -40 kJ/mol or less negative for physisorption, and the value -100 kJ/mol or more negative for chemisorption. The values of  $\Delta H_{ads}$  from extract CLESW as corrosion inhibitors absorb on the surface of mild steel through physisorption process.

### Electrochemical Measurement Results

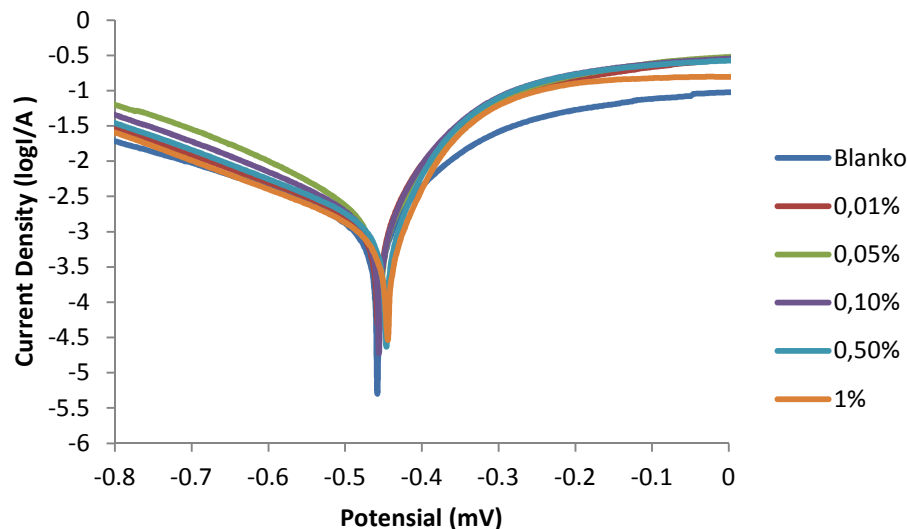


Figure 6. Potentiodynamic polarization curves of mild steel in the absence and presence CLEDW in 0.5 M sulfuric acid

Potentiodynamic polarization curves of mild steel in the absence and presence CLEDW in 0.5 M sulfuric acid shown in Figure 6. The measurement of potentiodynamic polarization with the electrodynamic parameter where Tafel slope of polarization curves extrapolated to determine the corrosion current density ( $I_{corr}$ ), corrosion potential ( $E_{corr}$ ) and inhibition efficiency (% EI).

Table 3. Potentiodynamic polarization value of mild steel in the absence and presence CLEDW in 0.5 M sulfuric acid

Konsentarsi	$E_{corr}$ (V)	$\log I/A$	$I/A$	$i_{corr}$ (mA/cm <sup>2</sup> )	EI (%)
[H <sub>2</sub> SO <sub>4</sub> ]	-0,48	-2,85	0,001413	7,03E-05	
[0.1 g/L]	-0,46	-3	0,001	4,97E-05	29,20542
[0.5 g/L]	-0,46	-3,05	0,000891	4,43E-05	36,90427
[1 g/L]	-0,448	-3,12	0,000759	3,77E-05	46,29682
[5 g/L]	-0,444	-3,35	0,000447	2,22E-05	68,37722
[10 g/L]	-0,442	-3,7	0,0002	9,92E-06	85,87462

Table 3 shows that the addition of s CLESW cause of decreasing in current and increase inhibition efficiency. CLESW can inhibits the H<sup>+</sup> ions attack to mild steel. It means, the CLESW is a good inhibitor.  $E_{corr}$  shifts to positive value, it can be classified as anodic inhibitor that sulfuric acid solution reduces the anodic dissolution of metal [10,19].

### Surface Morphology

Surface morphology of the mild steel with absence and presence of CLESW are shown in figure 7.

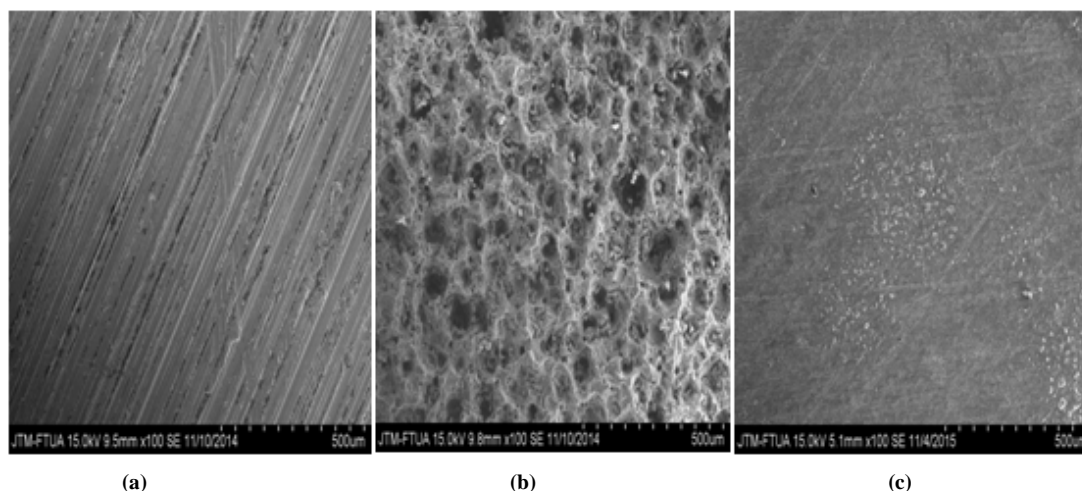


Fig 7. Mild Steel Surface a. Mild Steel Surface Before Treatment . b. Mild Steel Surface After Treatment in Sulfuric Acid . c. Mild Steel Surface After Treatment in Sulfuric Acid + CLESW Extract as Inhibitor Corrosion

Figure 7a is shown the mild steel surfaces before treatment. Initial steel surface flat, clean and non-porous and no hole. It means there is no corrosion caused by environmental influences such as water or acid [2]. The mild steel surface after immersion in sulfuric acid in figure 7b had porous and hole that there had occurred corrosion. While in figure 7c, mild steel surface after immersion in sulfuric acid CLESW extract had a little hole and porous. That means had occurred a decrease rate of corrosion because of absorption steel mild against CLESW extract.

### CONCLUSION

The Cassava (*Manihot esculenta*) leaf extracts of soluble in water (CLESW) can be used as a corrosion inhibitor and acts as an anodic type inhibitor. Increased concentrations of CLESW causes increased inhibition efficiency and reduction in the rate of corrosion. The greater the corrosion rate with increasing temperature. The activation energy with presence the CLESW as a corrosion inhibitor is greater than the absence for CLESW. The higher values of  $E_a$  in the presence of inhibitor compared to its absence are generally consistent with physisorption.  $\Delta H_{ads} = -0,1195 \text{ kJmol}^{-1}$  shows that adsorption process is exothermic. The values of  $\Delta H_{ads}$  from extract CLESW as corrosion inhibitors absorb on the surface of mild steel through physisorption process.

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