



## Corrosion Inhibition of Mild Steel in Hydrochloric Acid Solution by *Gnetum gnemon*. L Peel Extract as Green Inhibitor

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### ABSTRACT

The inhibition of corrosion of mild steel in hydrochloric acid in the presence of *Gnetum gnemon* L. peel extract (GGPE) has been studied using the weight loss, potentiodynamic polarization, FTIR and scanning electron microscopy (SEM) analysis. It was found that the inhibition efficiency increased with increasing concentration of GGPE and temperature. The inhibition was assumed to occur via adsorption of inhibitor molecules on the metal surface. The adsorption of the extract on the mild steel is found to obey Langmuir adsorption isotherm and acts as a mixed-type inhibitor. Thermodynamic and kinetic parameter data for the adsorption process were calculated and discussed.

**Keywords:** *Gnetum gnemon*. L, Peel extract, Corrosion inhibitor, Isotherm Langmuir.

### INTRODUCTION

Mild steel is one of materials that are widely used in the field of industry and construction due to its excellent mechanical properties and low cost. However, mild steel also has a weakness such as it tends to be susceptible to corrosion, especially in the acid environment [1,2]. As a result, research continues to be undertaken to develop effective ways of corrosion control. There are several ways to slow down the corrosion rate, namely coating, anodic or cathodic protection and with the addition of inhibitors [1-3].

The addition of an inhibitor is one of effective ways to slow down corrosion rate. A number of synthetic compounds and natural compounds have been studied and are known to be applied as good corrosion inhibitors for metals. Although the synthesis compound has shown the effect of high corrosion inhibition, but its toxic nature can damage the environment as well as the cost of more expensive synthesis becomes one of the problems for its use in industry [4].

The use of natural inhibitor or 'Eco friendly Inhibitor' in recent years has been widely studied, because it shows good inhibition efficiency, natural inhibitors are also non-toxic, biodegradable, environmentally friendly and cost less expensive than synthetic compounds, so this is very interesting to investigate [5]. Several studies have been conducted with the use of environmentally friendly materials as corrosion inhibitors such as leaf extract of *Theobromacacao* [3], leaf extract of cassava (*Manihot esculenta*) [6], leaf extract of *Dodonaea viscosa* (L.) [7], leaf extract of *Ziziphus mauritiana* [8], and *Toona sinensis* leaf extract [9].

*Gnetum gnemon* L. is one of the plants that grow in Indonesia. The *Gnetum gnemon* L. peel is proven to contain phenolic compounds, flavonoids,  $\beta$ -carotene, lycopene, carotenoids, vitamin C, and antioxidant activity [10]. Organic compounds which contained in the *Gnetum gnemon* L. peel is expected to be adsorbed on the steel surface, so it can act as a corrosion inhibitor.

### MATERIAL AND METHODS

#### Preparation of materials (mild steel specimen)

**Mild steel strips of size:** 3.0 cm x 2.0 cm x 0.1 cm containing 0.0149% P, 0.0715% Si, 0.001% Ni, 0.141% Mn, 0.189% C, 0.019% Se, 0.0018% Cr and remainder Fe were used for measurement. The surface of the steel is cleaned and smoothed by steel grinder, washed with distilled, rinsed with acetone and dried with an oven temperature of 60°C. After drying, the steel is weighed and the weighing result is expressed as the initial weight ( $W_1$ ).

#### Preparation of *Gnetum gnemon*. L peel extract

Fresh GGP was dried up for 1 month, ground until it become powder and weighed 500 g. The sample was extracted with methanol as much as  $\pm$  1500 ml for 3 days. The extract was filtered and the solvent was evaporated using a rotary evaporator to obtain a concentrated extract. The concentrated GGPE is stored into a glass to make an inhibition solution with different concentration.

**Phytochemical analysis**

Phytochemical analyses of GGPE were screened for several secondary metabolite compounds such as terpenoid, steroid, flavonoid, phenolics, saponins, and alkaloid.

**Weigh loss measurement**

The pretreated steel is immersed in 50 mL of HCl 1 N solution as corrosive medium with various concentration of GGPE for 7 hours using a water bath, then cleaned, washed, and dried in the oven. After drying, the steel is weighed and the weighing result is expressed as the final weight ( $W_2$ ).

The corrosion rate (CR) was determined using the following equation [1]:

$$CR = \frac{W_1 - W_2}{At} \quad (1)$$

Where A is area in  $\text{cm}^2$  and t is time in h. From corrosion rate (CR), the degree of surface coverage ( $\theta$ ) and inhibitor efficiency (IE%) can be determined with equation [2] and [3]:

$$\theta = \frac{CR_0 - CR_1}{CR_1} \quad (2)$$

And

$$IE\% = \frac{CR_0 - CR_1}{CR_1} \times 100\% \quad (3)$$

Where  $CR_0$  and  $CR_1$  are corrosion rate in the absence and presence of extract, respectively.

**Potentiodynamic polarization measurement**

Electrochemical measurements were carried out using eDAQ. A conventional three-electrode system was used for this purpose. Mild steel specimen was used as a working electrode. Pt electrode and Ag/AgCl served as auxiliary and reference electrodes, respectively. The three electrodes were immersed in vessels containing corrosive medium (1 N HCl) in the absence and in the presence of inhibitors of various concentrations. The potentiodynamic current potential curves were obtained by changing the electrode potential from -700 to 400 mV. The percentage inhibition efficiency of inhibitors were determined using equation (4):

$$IE\% = \frac{I_0 - I_1}{I_1} \times 100\% \quad (4)$$

where  $I_0$  and  $I_1$  are current density in the absence and presence of extract, respectively.

**Fourier Transform Infrared measurement (FTIR)**

FT-IR measurements were carried out by taking corrosion products from surface of steel that has been immersed in 1 N HCl in the presence and absence of inhibitor for 7 h at room temperature, then corrosion products were dried and analyzed by FT-IR using KBr pellet. FT-IR measurements were also performed for GGPE.

**Analysis of Scanning Electron Microscopy (SEM)**

Mild steel was immersed in 1 N HCl without and with the addition of GGPE for 7 days and then dried and analyzed by Scanning Microscopy Electron (SEM) for to record surface morphology of mild steel.

**RESULTS AND DISCUSSION****Phytochemical analysis of *Gnetum gnemon* L peel extract**

Phytochemical analysis was to identify the secondary metabolite compound that exists in GGPE. Table 1 shows that GGPE consist of several secondary metabolite compounds such as Triterpenoids, Steroids, Flavonoids, Phenolics and Saponins and Alkaloids did not exist in GGPE. Secondary metabolite compounds that consist in GGPE have potential as corrosion inhibitors and indicate can decrease inhibition efficiency.

**Table 1: The Result of Phytochemical Test from GGPE**

Compounds	Results
Flavonoids	+
Phenolics	+
Steroids	+
Triterpenoids	+
Alkaloids	-
Saponins	+

(+): Present, (-): Absent

Weight loss measurements

Corrosion rate and inhibition efficiency

Figure 1 show that corrosion rate decrease and efficiency inhibition increases with increasing concentration of GGPE. This is due to an increase in the amount of adsorption and coverage of compounds contained GGPE on mild steel surface. It can be also seen that corrosion rate and inhibition efficiency increase with increase in temperature. It is noted that at elevated temperature, reacting molecules collide faster leading to more depletion of the reactant and formation of the product.

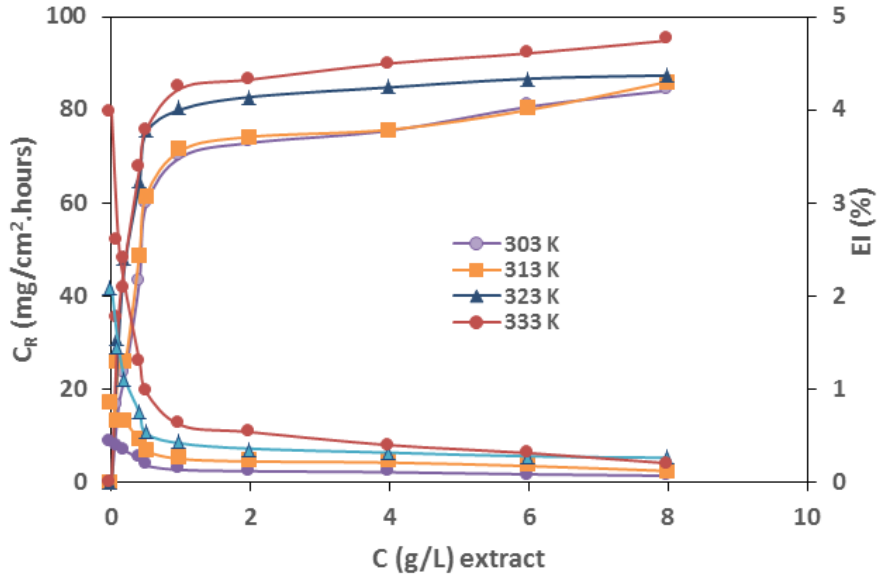


Figure 1: Effect of GGPE concentration on corrosion rate of mild steel and efficiency inhibition in 1 N HCl for 7 h at different temperature

Adsorption isotherm and thermodynamic parameters

The Adsorption isotherm is one of methods used to explain the mechanism of corrosion inhibition using organic compound (extract) where it block the metal surface to prevent the corrosion. The degree of surface coverage ( $\theta$ ) is very useful to discuss about the adsorption isotherm. It was observed that data fitted the Langmuir, Temkin, and Freundlich adsorption isotherm and the correlation coefficients were used to determine the best fitted isotherm. Based on experimental data obtained this study tits with Langmuir isotherm formulated as [11-14]:

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

Where  $\theta$  is the degree of surface coverage, C is the concentration of inhibitor and  $K_{ads}$  is the adsorption equilibrium constant. The plot of  $C/\theta$  versus C as shown in Figure 2 with correlation coefficients ( $R^2$ ) equal to 1, which indicated the experimental data obtained GGPE onto metal surface follows Langmuir isotherm.

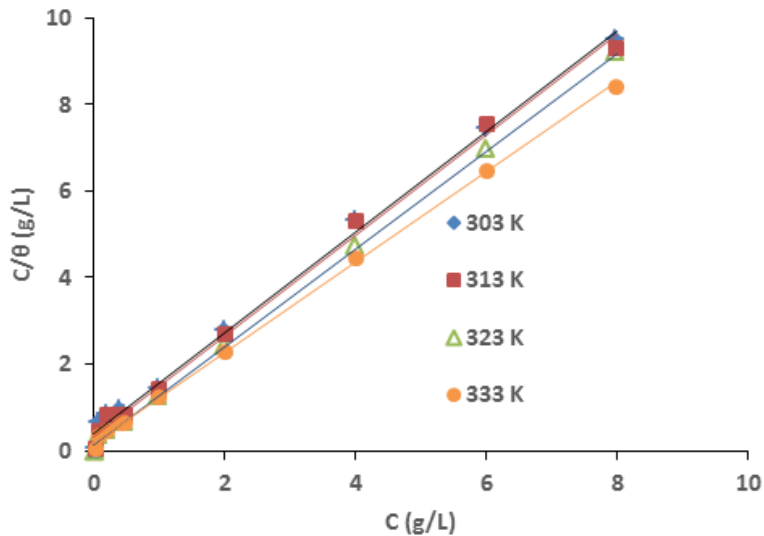


Figure 2: Isotherms Adsorption Langmuir for mild steel in 1 N HCl with different concentration of GGPE

Table 2: Thermodynamic parameters for adsorption of GGPE on mild steels in 1 N HCl at different temperature

Temperature (K)	$K_{ads}$ (kJ / mol)	$\Delta G^0_{ads}$ (kJ / mol)
303	2.62	-16.75
313	3.16	-20.7
323	7.13	-36.44
333	6.36	-35.39

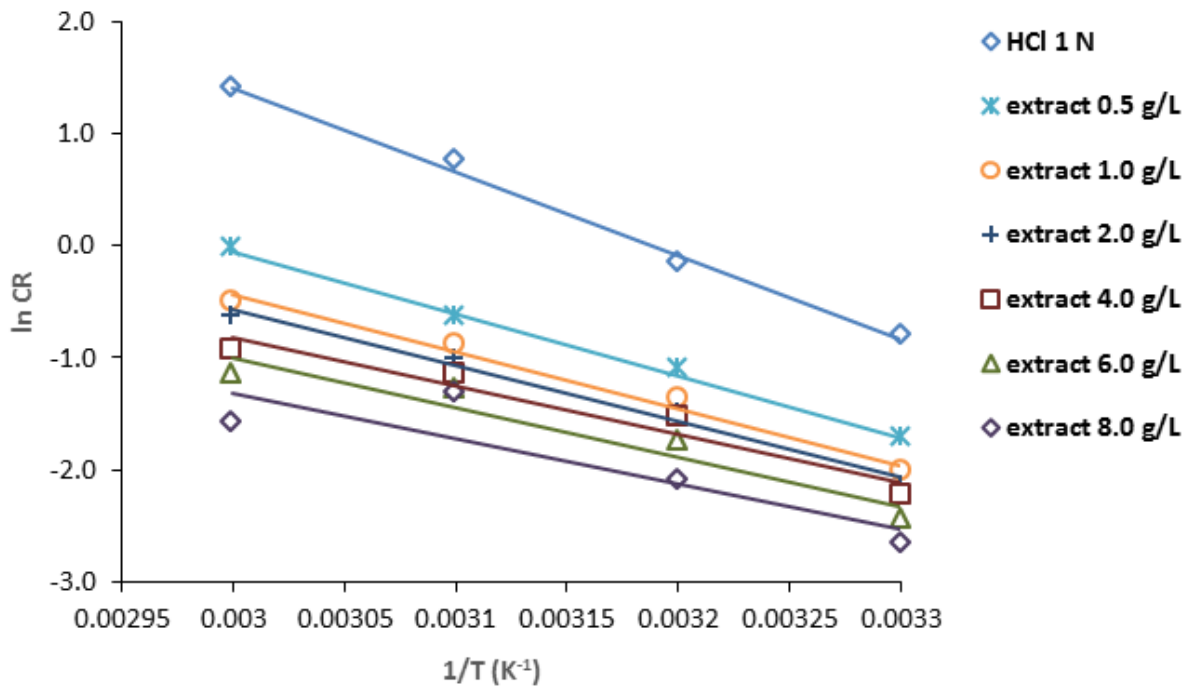
From Table 2, it was found that the value of  $K_{ads}$  increases with increasing of temperature. It shows that the higher the value of  $K_{ads}$ , the adsorption of extracts on the steel surface is more stable, as evidenced by the increasing percentage of corrosion inhibition efficiency with the rising of temperature. The value of free Gibbs ( $\Delta G^0_{ads}$ ) obtained by a negative value indicates a spontaneous and stable adsorption reaction between the extract and the steel surface [11].

#### Kinetic-thermodynamic corrosion parameters

An Arrhenius plot (corrosion rate ( $\ln v$ ) versus temperature ( $1/T$ ) for mild steel in 1 N HCl solution in the absence and presence of different GGPE concentrations shown in Figure 3. The Arrhenius equation can be used to determine activation energies ( $E_a$ ) for mild steel corrosion. The values of activation energy of corrosion of mild steel in 1 N HCl solution were obtained from the slopes of the linear plots (Arrhenius plot) and are given in Table 3. Results shown in the table indicate that  $E_a$  of extract is lower than in their absence. The activation energy  $E_a$  was found to be  $62.46 \text{ kJmol}^{-1}$  for absence of extract and decrease to  $55.53 \text{ kJmol}^{-1}$  with added  $0.1 \text{ g l}^{-1}$  of extract. It suggested that the more GGPE were added, the smaller corrosion reactions energy were required. It will reduce the corrosion reaction of the steel in HCl solution and the more difficult the corrosion reaction occurs.

$$\ln CR = \ln A - \frac{E_a}{RT} \quad (6)$$

Where  $C_R$  is corrosion rate,  $E_a$  is apparent activation energy,  $R$  is molar gas constant,  $T$  is absolute temperature and  $A$  is the frequency factor.

Figure 3: Arrhenius plot  $1/T$  ( $K^{-1}$ ) vs.  $\ln CR$  for mild steel in HCl 1 N for blank and different concentration of GGPETable 3: The value of activation energy ( $E_a$ ), enthalpy ( $\Delta H^0$ ) and entropy ( $\Delta S^0$ )

Medium HCl 1 N + Extract (g/l)	Activation Energy (kJ / mol)	$\Delta H^0$ (kJ / mol)	$\Delta S^0$ (J / mol)
(Blank)	62.46	59.83	142.15
0.5	46.05	43.43	80.79
1	42.55	39.94	67.15
2	41.69	39.08	63.42
4	36.26	33.64	45.07
6	36.55	33.93	44.33
8	33.35	30.73	32.08

An alternative formulation of Arrhenius Equation is [12-14]:

$$\ln\left(\frac{CR}{T}\right) = \left[ \ln\left(\frac{R}{hN}\right) + \left(\frac{\Delta S^0}{R}\right) \right] - \frac{\Delta H^0}{RT} \quad (7)$$

Where  $h$  is the Plank's constant,  $N$  is the Avogadro's number,  $T$  is the absolute temperature,  $R$  is the universal gas constant,  $\Delta S^0$  is the entropy of activation, and  $\Delta H^0$  is the enthalpy of activation. The values  $\Delta S^0$  and  $\Delta H^0$  (Table 4) can determined from plot of  $\ln CR/T$  versus  $1/T$ . Straight line were obtained with a slope of  $-\Delta H^0/R$  and intercept of  $\ln R/Nh + \Delta S^0/R$ , from which the values of  $\Delta H^0$  and  $\Delta S^0$  were calculated.

The positive value of  $\Delta H^0$  (Table 3) reflects the endothermic nature of the mild steel dissolution process.  $\Delta S^0$  can be interpreted positive values of  $\Delta H^0$  indicated that the immersion of GGPE produced an endothermic reaction and the value of  $\Delta H^0$  of blank was higher than  $\Delta H^0$  by adding GGPE shown that energy which is needed to require the corrosion was higher. As well as the value of  $\Delta S^0$  with the addition of GGPE was smaller than  $\Delta S^0$  of blank described the ability of GGPE to slow down corrosion rate [14].

#### Potential polarization measurement

The effect of GGPE concentration on the corrosion behavior of mild steel in 1 N HCl solution has been studied by polarization measurements and Tafel plots are shown in Figure 4. From polarization curves, the electrochemical parameters obtained are presented in Table 4. It can be seen that current densities decrease considerable and inhibition efficiency increase in the present of GGPE. This phenomenon indicates that the inhibitor could reduce anodic reaction of the mild steel dissolution as well as cathodic hydrogen evolution. These results are comparable with weight loss measurement.

In the presence of inhibitor, the  $E_{corr}$  of mild steel shifted toward cathodic region compared to without inhibitor in solution. However, a compound is usually classified as anodic or cathodic type inhibitor when the change in  $E_{corr}$  value is larger than 85 mV [15]. Since the largest displacement of the corrosion potential was about 70 mV (Table 4) in the present of GGPE, suggesting that inhibitor acted as mixed-type inhibitor.

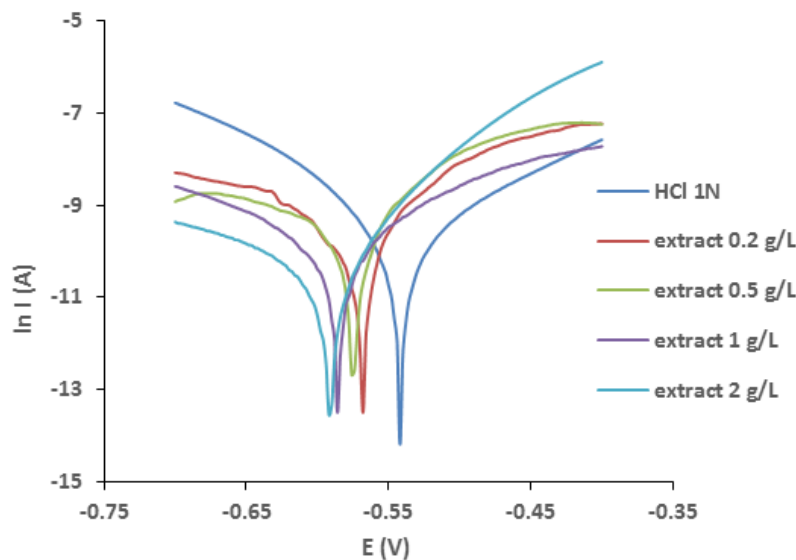


Figure 4: Potentiodynamic polarization curves without and in the presence of GGPE in 1 N HCl solution

Table 4: The potential value of corrosion, corrosion current and efficiency of corrosion inhibition of steel without and with the addition of GGPE

The concentration of extract (g/l)	$E_{corr}$ (V)	$I_{corr} \times 10^{-3}$ ( $\mu$ A)	EI (%)
0	-0.53	7.41	0
0.2	-0.56	6.01	18.93
0.5	-0.57	4.11	44.53
1	-0.59	3.08	58.43
2	-0.6	2.39	67.74

#### FT-IR analysis

The analysis by using FT-IR was done to identify functional groups of organic compounds, which contained in GGPE that play a role as corrosion inhibitors of secondary metabolite compounds in GGPE and determine the type of bonding that occurred from inorganic adsorbents that adsorbed on the steel surface.

The FT-IR spectrum of Figures 5a, 5b shows no significant difference as some dominant peaks are in the range of wavelengths despite the shift of wave numbers. The shift of wave numbers indicates the occurrence of bonds between compounds contained in GGPE with steel surfaces. Figures 5a and 5b there are hydroxy groups (-OH) ( $3500-3000 \text{ cm}^{-1}$ ), CH-stretching groups ( $3000-2500 \text{ cm}^{-1}$ ), -C = C- stretching ( $1650-1450 \text{ cm}^{-1}$ ). From the above data it can be concluded that these two spectra have a shift of wave numbers and GGPE has a role as a corrosion inhibitor on steel. However, there is little difference in the strength or weakness of the resulting absorption peaks, as well as the missing absorption peaks and the newly emerging absorption peaks.

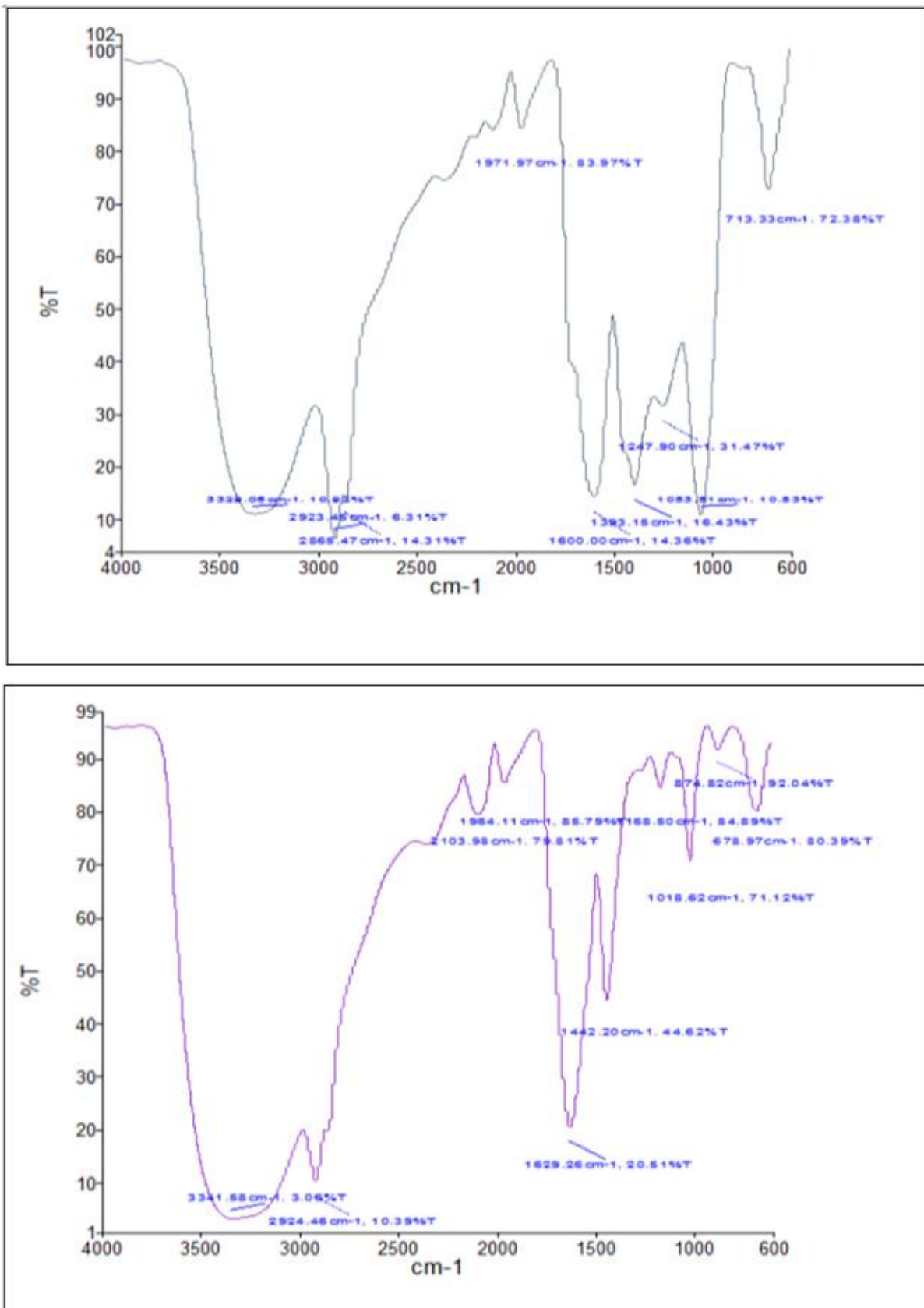
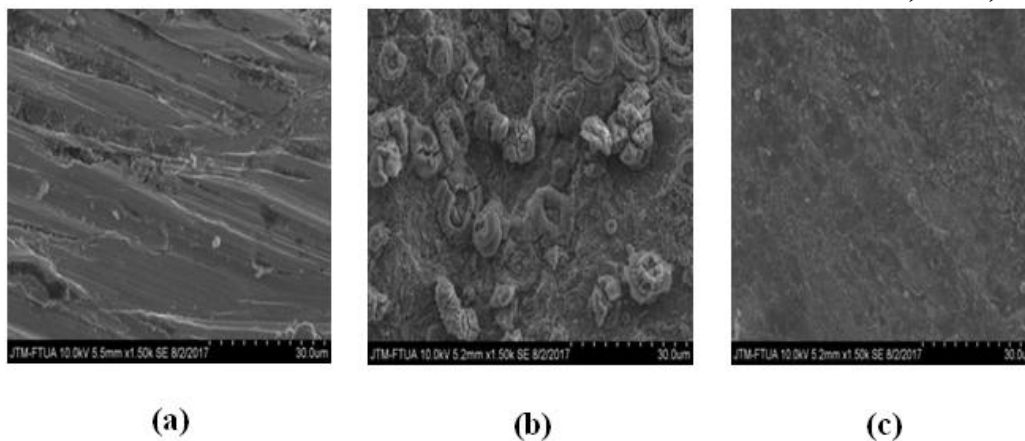


Figure 5: (a) FT-IR spectra of GGPE, (b) FT-IR spectra of the products of corrosion of steel in 1 N HCl with the addition of 1 g/l GGPE by immersion for 7 days

#### SEM analysis

Figure 6a is a steel surface without treated. The steel still looked good, flat and non-corroded because there was no interaction of steel with corrosive medium. Figure 6b shows the steel which has been immersed for 7 days in corrosive medium of 1 N HCl for 7 days which shown its surface. There are holes and rust in the surface. This hole and rust occurs due to the interaction between the steel with corrosive medium 1 N HCl. While in Figure 6c shown the surface of the steel has been soaked for 7 days in 1 N HCl solution and GGPE of 1 g/l smoother and more flat than immersion with 1 N HCl. This due to the presence of a protective layer of GGPE adsorbed on a steel surface which can protect the steel from 1 N HCl [16].



**Figure 6:** SEM results for steel surfaces with 1500X magnification (a) steel before it soaked (without treatment) (b) steel after being soaked with 1 N HCl (c) steel after being soaked with 1 N HCl + extract 1 g/l

### CONCLUSION

In the research that has been done, it can be concluded that GGPE can be used as corrosion inhibitor. It acts as a mixed-type inhibitor by inhibiting both anodic and cathodic reaction. The inhibition efficiency increases with the increases the concentration of GGPE and rise in temperature. The Adsorption of GGPE follows the Langmuir adsorption isotherm model and the adsorption is spontaneous. The kinetic and thermodynamic parameters of corrosion.

### REFERENCES

- [1] R.T. Loto, C.A. Loto., A.P.I. Popoola. *J. Mater. Environ. Sci.*, **2013**, 3(5), 885-894.
- [2] A.A.H. Kadhum, A.B Mohamad, L.A Hammed, A.A. Al-Amiery, Ng H. San, A.Y. Moses, *Materials*, **2014**, 7, 4335-4348.
- [3] Y. Yetri, Emriadi, N. Jamarun and Gunawarman, *Environment Asia*, **2016**, 9 (1), 45-59.
- [4] M.S. Al-Otaibi, A.M. Al-Mayouf, M. Khan., A.A. Mousa, S.A. Al-Mazroa, H.Z Alkathlan, *Arabian J. Chem.* **2014**, 7, 340-346.
- [5] E.E. Oguzie, *Corr. Sci.*, **2008**, 43, 168-178.
- [6] D.R. Gusti, Emriadi, A. Alif, M. Efdi, *Int. J. Chem. Tech. Res.*, **2017**, 10(2), 163-171.
- [7] S. Leelavathi, R. Rajalakshmi, *J. Mater. Environ. Sci.*, **2013**, 4(5), 625-638.
- [8] S.S. Shivakumar, K.N.S. Mohanna. *Eur. J. Chem.*, **2012**, 3(4), 426-432.
- [9] Emriadi, A. Santoni., Y. Stiadi. *Der Pharma Chemica*, **2016**, 8(18), 266-273.
- [10] T.M. Siregar, M. Cornelia, Ermiziar, *Assoc. Indonesian Food Technol. Experts (PATPI)*, **2010**.
- [11] V.G. Vasudha and P.K. Shanmuga, *Res. J. Chem. Sci.*, **2013**, 3(1), 21-26.
- [12] A.I. Ali and Y. Sh. Mahrous, *Royal Soc. Chem.*, **2017**, 7, 23687-23698.
- [13] L. Xianghong, D. Shuduan, X. Xiaoguang, *Corr. Sci.*, **2014**, 81, 162-175.
- [14] E.I. Ating, S.A. Umoren, I.I. Udousoro, E.E. Ebenso, A.P. Udoh, *Green Chem. Lett. Rev.*, **2010**, 3(2), 61-68.
- [15] N. Soltani, N. Tavakkoli, M. Khayakashani, M.R Jalali, A. Mosavizade, *Corros. Sci.*, **2012**, 62, 122-135.
- [16] B.E.R. Amitha, B.J.B. Barathi, *Int. J. Corr.*, **2012**, 12, 1-15.