

Corrosion Inhibition of Carbon Steel in Sulfuric Acid Using *Cymbopogon citratus* as a Green Corrosion Inhibitor

Gadang Priyotomo^{1,†}, Tamara Emylia Suci Nurarista², Yanyan Dwiyaniti²,
Bening Nurul Hidayah Kambuna², Arini Nikitasari¹, Siska Prifiharni¹, and Sundjono¹

¹Research Center for Metallurgy, National Research and Innovation Agency, Gedung Manajemen 720,

Kawasan Sains dan Teknologi B.J. Habibie, Setu, Tangerang Selatan, Banten, Indonesia

²Metallurgical Engineering Department, Sultan Ageng Tirtayasa University, Jalan Jendral Sudirman KM.3, Cilegon 42435, Banten, Indonesia

(Received April 20, 2022; Revised August 16, 2022; Accepted August 17, 2022)

The objective of this study was to determine whether *Cymbopogon citratus* extract as a corrosion inhibitor from natural tropical resources could prevent corrosion of carbon steel in sulfuric acid solution. Inhibitory action of this extract was investigated using electrochemical methods such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Those methods revealed corrosion rate, efficiency of inhibition, and adsorption isotherm values when the extract was added to the sulfuric acid solution at concentration up to 500 ppm with various immersion time at ambient temperature. Results revealed that higher concentration of the extract and longer immersion time decreased the corrosion rate of carbon steel whereas the inhibition efficiency of the extract was increased up to 97.25%. The value of charge transfer resistance was increased significantly by adding the extract at concentration up to 500 ppm with an immersion time of 60 minutes. The type of the extract was a mixed inhibitor. It could inhibit the corrosion process in both anodic and cathodic sides electrochemically. Results of this study suggest that the mechanism of adsorption on the surface of carbon steel is related to Langmuir adsorption isotherm.

Keywords: Corrosion, Carbon steel, Green corrosion inhibitor, Acid solution, *Cymbopogon citratus*

1. Introduction

Generally mild Steel is one common of metal that is applied in various industries both as parts or components in, oil tanks, water tanks chemical tanks, oil pipes gas pipes and so on. The remarkable properties of this metal such as strength, durability, toughness, easy heat treatment, easy alloying and manufacturing process is main reason of its usage [1]. Acidic media are used in most all industries such as manufacturing acid cleaning and pickling of steel, petroleum processes, and so on [2]. However, because of the corrosiveness of sulfuric acid, steel tanks applied in various industrial processes are commonly prone to corrosion attack [3]. Generally, an immediate acid attack take places on carbon steel in concentrated sulfuric acid through the formation of hydrogen gas and ferrous ions where it forms a protective layer of FeSO_4 on the steel surface [4], but not in diluted sulfuric acid [1]. Therefore, Corrosion inhibitors have

been commonly used to mitigate metal surfaces against corrosion especially synthetic one [5].

However, there are many synthetic inhibitor are toxic and environmental issues during application. There are many researches that had investigated new environmental friendly active agent of corrosion inhibitor from natural products [6,7]. Natural resources such as plant extracts has a potency for the corrosion inhibition of metals due to their unique chemical structures such as aromatic bonds containing heteroatoms (oxygen, nitrogen, and sulfur) [6-11]. Mostly green corrosion Inhibitors derived from natural extracts usually have antioxidant compounds in the form of polyphenols, alkaloids, flavonoids, and other components.

Furthermore, Lemongrass (*cymbopogon citratus*) extract is a candidate of green corrosion inhibitor containing an active agent of antioxidant compounds where it has the capability to reduce corrosion rate of carbon steel in acidic media and in produced oilfield water [12,13]. The antioxidant compounds as corrosion active agents of lemongrass comprise of alkaloids, polyphenols, saponins, tannins and flavonoids [14]. Miean and co-works reported

[†]Corresponding author: gada001@brin.go.id

that Lemongrass extract also has the highest concentration of flavonoid compounds compared to other active compounds [15]. The presence of those various phenol compounds attribute as active agents in which reduce the corrosion rate of metal and alloys in various corrosive media [6-9]. However, there is no or little study comprehensively for investigating the role of lemongrass (*cymbopogon citratus*) extract as a candidate of green corrosion inhibitor. Therefore, the objective of this work is to elucidate the performance of *cymbopogon citratus* extract as a candidate of green corrosion inhibitor to reduce the aggressiveness of corrosion attack on carbon steel in sulfuric acid solution.

2. Experimental Methods

2.1. Preparation of Material

In this work, a plate of as-received carbon steel was cut into 10 mm × 10 mm × 2 mm for a corrosion test specimen. The specimens were connected by isolated copper wire, mounted with an epoxy resin. After curing

Table 1. Composition of the material investigated

Element	Weight Percentage (wt%)
Fe	98.7819
C	0.1639
Mn	0.3949
Si	0.2507
P	0.0114
S	0.0101
Al	0.0157
Cr	0.2897
Nb	0.0004
Ni	0.0255
Cu	0.0203
Pb	0.0032
Mo	0.0148
Sn	0.0023
Ti	0.0017
V	0.0017
W	0.0012
Zn	0.0183
Zr	0.0012

epoxy mounted resin at least 24 hours, the specimen abraded up to 1200 of grit with silicon carbide paper, washed with distilled water and acetone solution. After this process, it is ready to conduct the electrochemical test as soon as possible due to the common rapid oxidation on surface of steel in open air. The chemical compositions of that prepared material are given in Table 1.

In Table 1, the chemical composition of that material is attributed ASTM A572 steel where that steel is a common grade of high-strength low-alloy (HSLA) steel for structural applications [16].

2.2. Cymbopogon Citratus extract and test solutions

The fresh *cymbopogon citratus* was cleaned with tap water and dried under sunlight and ground into fine powder. A maceration process of that powder was carried out in 70% ethanol solvent where a ratio between weight of dried powder and solvent is 1:5 for 3 days. Then the solutions were filtered and dried in vacuum oven for gaining fine pure extract at temperature of 100 °C.

Corrosive acid medium that applied in this experiment was 0.1 M H₂SO₄. The extract in various concentrations of 0,100, 200, 300, 400, and 500 ppm was added into acid medium at ambient temperature in the open air. All metal specimens were immersed in the corrosion test solutions in different residence time or period of time before electrochemical test in 0, 30 min and 60 min. In addition, residence time of specimen is attributed with the adsorption time of inhibitor molecules on metal surface during immersion [17].

2.3. Chemical characterization of Cymbopogon Citratus extract

The FT-IR analysis was obtained using a Bruker-Tensor II coupled to a work station equipped with the software Opus version 7.5, which is able to carry out the Fourier Transforms (FT) and then convert to a FT-IR spectrogram. The sample of extract was directly examined and measured in a wave number range of 4000 to 400 cm⁻¹.

2.4. Total phenolic content of Cymbopogon Citratus extract

Preparation of reagent for gallic acid solution was conducted with weighing 1 mg of gallic acid then dissolving 1 mL of MeOH (1000 g/mL). This solution

was made in certain series of concentration for 5, 10, 20, 30 and 40 g/mL. For the measurement of the total phenol content, 4 mg of CC extract was dissolved in 4 mL of methanol to obtain a stock solution of sample for concentration of 1000 g/mL. The measurement of the total phenol content for extract used Follin-Ciocalteu method. The content of total phenolic compounds in the extract was determined by the method Follin-Ciocalteu where use a gallic acid as standard. Total phenol content of extract expressed as gallic acid equivalent (mg/g extract) based on the regression equation of the calibration curve ($y = 0.1032x + 0.0708$ $R^2 = 0.9996$). 500 μ L of sample solution (500 L) and standard solutions of gallic acids (25, 50, 100, 150, and 200 μ L) was pipetted into a test tube, and then added to 4 mL of distilled water. That mixed solution was added with 250 μ L of Folin-Ciocalteu solution. After 8 minutes, 750 μ L of 20% Na_2CO_3 was added and shaken homogeneously. A final mixed solution is left for 2 hour. Absorption is measured at a wavelength of 765 nm. The Measurements were carried out 2 times so that the phenol content obtained was as gallic acid equivalent (μ g/mL sample). In addition, the other qualitative characterization of extract is phytochemical screening of cymbopogon Citratus extract.

2.5. Electrochemical test

In present work, this test was carried out in a three electrode glass cell assembly using a potentiostat apparatus (Reference 600, Gamry Instrument), connected to a desktop computer. The assembly consisted of a cell glass with three opening one each for a counter electrode of platinum, a working electrode, and saturated calomel electrode (SCE) as reference electrode. The surface of the working electrode was covered in one side of mounted resin at the surface area of 1 cm^2 . Electrochemical methods comprise a potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) in the same preparation of metal specimen.

In potentiodynamic polarization, the applied potential range was between -250 mV and +250 mV which refer to open circuit potential (OCP) in controlled applied potential scan rate of 1 mV/s. The parameters which comprise corrosion rate, corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic slope (β_a) and cathodic cathodic (β_c) were calculated with a Tafel

formula [6]. The Tafel equation which showed by following equation:

$$I = I_o.e^{2.308(E_o - E)/\beta} \quad (1)$$

where, values of I and I_o are the resulted current density from the reaction and the exchange current density, respectively. Values of E and E_o are the electrode potential and the equilibrium potential during electrochemical test, respectively. The parameter of β is attributed as reaction's Tafel constant. In equation 1, it only elucidates one side of electrochemical reaction. A corrosion process describes two opposing reaction such as anodic and cathodic reactions. Thus, the Butler-Volmer formula generates Tafel equation in both reactions, which later is applied to be a Tafel plot [18]. Finally, Tafel plot is defined as a graph function of $\log I$ versus E. The value of corrosion rate can be calculated in units of distance per year if corrosion process takes places uniformly on the surface of metal.

$$CR = I_{\text{corr}} \frac{KWE}{dA} \quad (2)$$

where, CR and i_{corr} are corrosion rate and corrosion current density, respectively. K is a constant that defines the units for the corrosion rate where EW is the equivalent weight. d and A are metal density and sample area, respectively. On the other hand, from value of corrosion rate (CR), efficiency of corrosion inhibition (η) and the surface coverage of inhibitor molecule layer on metal (θ) were calculated by following equation:

$$\eta(\%) = \frac{C(R_o) - CRi}{C(R_o)} \times 100 \quad (3)$$

$$\theta = \frac{CR_o - CRi}{CR_o} \quad (4)$$

where, CRi and CRo are the corrosion rate values with or without of inhibitor, respectively. For the electrochemical impedance spectroscopy (EIS), the tests were made using a frequency interval between 300 MHz to 1 Hz using alternative current (AC) signal at OCP. One of the results of EIS test is Nyquist plot which comprise the real part (Z') and imaginary part (Z'') of the cell impedances at various applied frequencies. In addition, the behavior of metal surface with and without the addition of corrosion

inhibitor is represented a solution resistance (R_u), a double layer capacitor (C_f) and a charge transfer or polarization resistance (R_p). Both potentiodynamic polarization and electrochemical impedance spectroscopy tests were repeated in three times to make ensure the reliability of the results.

3. Results

3.1. Potentiodynamic Polarization Curves

Fig.1 shows potentiodynamic polarization curves (PPC) of carbon steel in 0.1 M H_2SO_4 without or with various concentrations of cymbopogon citrates (CC) extract in no immersion time prior to electrochemical test. On the basis of results, overall the addition of all different concentrations of CC extract minimize the magnitude of both anodic and cathodic reactions up compared to blank solution with no addition of the extract.

Fig. 2 shows PPC of carbon steel in 0.1 M H_2SO_4 without or with various concentrations of CC extract in immersion time of 30 minutes prior to electrochemical test. Fig. 3 also shows PPC of carbon steel in 0.1 M H_2SO_4 without or with various concentrations of CC extract in immersion time of 60 minutes prior to electrochemical test. The same behavior of reduction anodic and cathodic process also take places up to 60 minutes of immersion time as well as no immersion time. The reduction of current density also minimizes the corrosion attack of metals up to 60 minutes of immersion time in both anodic and cathodic reaction.

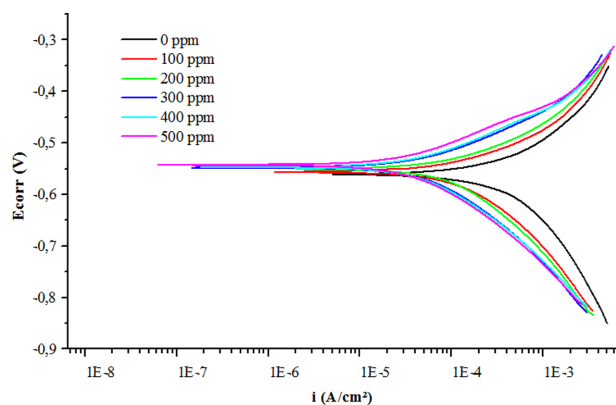


Fig. 1. Potentiodynamic Polarization Curves of carbon steel in 0.1 M H_2SO_4 without or with various concentrations of Cymbopogon Citratus extract in no immersion time at ambient temperature prior to electrochemical test

Furthermore, Fig. 2 shows PPC of carbon steel in 0.1 M H_2SO_4 without or with various concentrations of CC extract in immersion time of 30 minutes prior to electrochemical test. Fig. 3 also shows PPC of carbon steel in 0.1 M H_2SO_4 without or with various concentrations of CC extract in immersion time of 60 minutes prior to electrochemical test. The same behavior of reduction anodic and cathodic process also take places up to 60 minutes of immersion time as well as no immersion time. The reduction of current density also minimizes the corrosion attack of metals up to 60 minutes of immersion time in both anodic and cathodic reaction. In present work, it is found that the magnitude of corrosion rate (CR) decrease with increasing CC extract concentration and immersion time prior electrochemical test, respectively as well as corrosion current density (I_{corr}) as shown in Table 2.

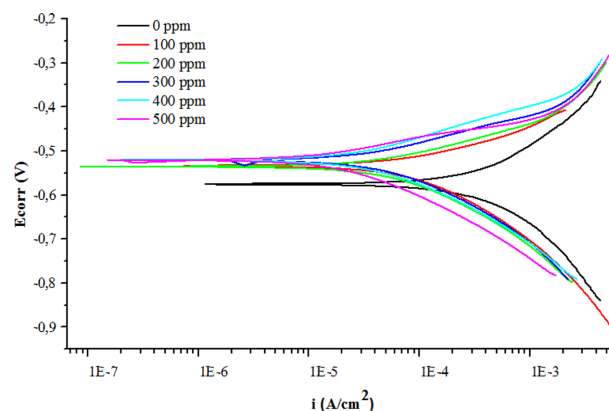


Fig. 2. Potentiodynamic Polarization Curves of carbon steel in 0.1 M H_2SO_4 without or with various concentrations of Cymbopogon Citratus extract in immersion time of 30 min at ambient temperature prior to electrochemical test

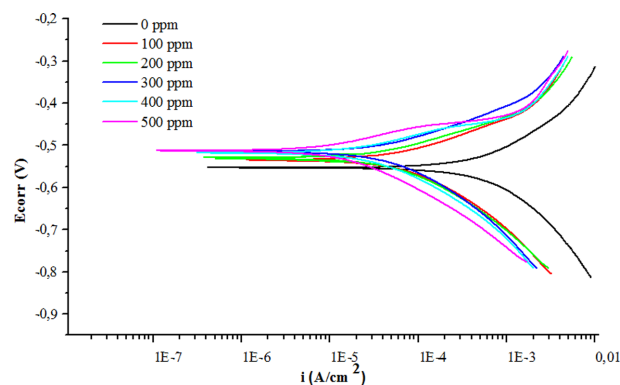


Fig. 3. Potentiodynamic Polarization Curves of carbon steel in 0.1 M H_2SO_4 without or with various concentrations of Cymbopogon Citratus extract in immersion time of 60 min at ambient temperature prior to electrochemical test

Table 2. Parameters obtained from Potentiodynamic Polarization test

t (min)	Cinh (ppm)	Ecorr (mV)	Icorr (mA/cm ²)	CR (mpy)	E (%)	(θ)
0	0	-560	4.81E-01	220.2	0	0
	100	-556.2	1.81E-01	83.05	62.28	0.62
	200	-551.2	1.33E-01	60.88	72.35	0.72
	300	-547.7	8.00E-02	36.22	83.55	0.84
	400	-547.7	7.05E-02	32.29	85.34	0.85
	500	-542.5	5.65E-02	25.88	88.25	0.88
30	0	-575.5	5.01E-01	229.3	0	0
	100	-535.2	1.19E-01	54.52	76.22	0.76
	200	-534.0	8.33E-02	38.17	83.35	0.83
	300	-520.7	7.78E-02	35.63	84.46	0.84
	400	-519.9	5.85E-02	26.81	88.31	0.88
	500	-520.4	2.90E-02	13.29	94.20	0.94
60	0	-552.5	8.10E-01	371.3	0	0
	100	-535.6	1.13E-01	51.84	86.04	0.86
	200	-528.4	8.00E-02	36.63	90.13	0.90
	300	-514.3	7.25E-02	33.22	91.05	0.91
	400	-518.4	5.63E-02	25.79	93.05	0.93
	500	-512.1	2.23E-02	10.21	97.25	0.97

3.2. Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is usual quantitative method for elucidating the performances of protective layer on metal substrate comprehensively, where the ability of that layer to impede the electrical current is easy to be modeled and quantified. The open-circuit potential was employed in different immersion time (0 min, 30 min and 60 min) before electrochemical impedance study (EIS) tests. This method elucidates the behavior of current flow and impedance in present and absents of the CC extract.

All measurements of electrochemical impedance were fitted against an equivalent Randle CPE circuit model that was shown in Fig. 4. Solution resistance (Rs) defines the

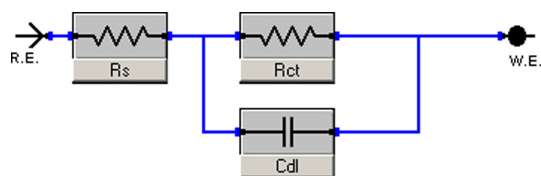


Fig. 4. The electrical equivalent circuit (EEC) applied to fit the impedance plots data for model

ohmic resistance while the charge transfer resistance (Rct) represents the behavior of CC inhibitor's resistance towards oxidation process of the mild steel surface. In addition, Rct is reciprocal to the corrosion rate. On the basis of results in Table 3, the value of charge transfer

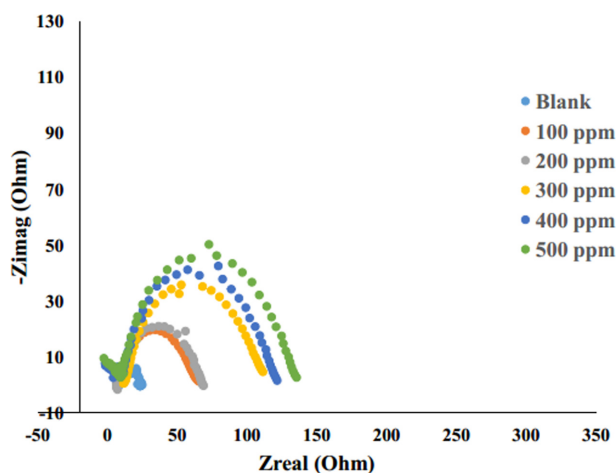


Fig. 5. Nyquist plots in 0.1 M H₂SO₄ solution, fitted by equivalent circuit model for all concentrations of cymbopogon citratus extract without immersion of specimen before EIS experiment

Table 3. Impedance parameters for cymbopogon citratus extract on mild steel in 0.1 M H₂SO₄ solution by fitting the equivalent randle circuit model

T (min)	Conc.(ppm)	Rct (Ω)	Rs(Ω)	Cdl(F/cm ²)	%EI
0	0	13.22	9.058	1.896E-05	0
	100	48.44	7.926	2.714E-05	72.71
	200	52.69	7.492	1.870E-05	74.91
	300	84.53	13.03	2.897E-05	84.36
	400	96.88	4.610	1.532E-05	86.35
	500	108.9	6.171	2.008E-05	87.86
30	0	21.85	8.316	9.468E-05	0
	100	118.5	10.21	2.781E-05	81.56
	200	138.7	4.158	4.767E-05	84.25
	300	155.3	7.012	3.073E-05	85.93
	400	169.9	5.926	2.153E-05	87.14
	500	182.0	2.098	1.447E-05	87.99
60	0	23.00	4.651	8.115E-05	0.0
	100	129.2	6.826	2.611E-05	82.20
	200	162.9	6.350	2.508E-05	85.88
	300	186.9	9.218	2.406E-05	87.69
	400	230.9	9.622	2.757E-05	90.04
	500	243.6	17.21	2.112E-05	90.56

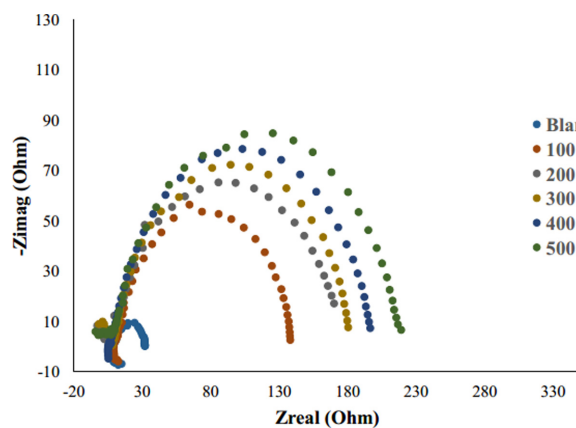


Fig. 6. Nyquist plots in 0.1 M H₂SO₄ solution, fitted by equivalent circuit model for all concentrations of cymbopogon citratus extract with immersion of 30 min

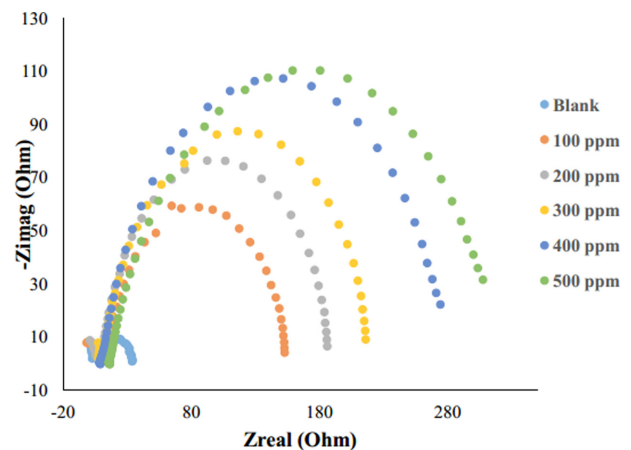


Fig. 7. Nyquist plots in 0.1 M H₂SO₄ solution, fitted by equivalent circuit model for all concentrations of cymbopogon citratus extract with immersion of 60 min

resistance (Rct) increases with increasing concentration of inhibitor and time of immersion. The increase in Rct values is attributed to the formation of an insulating protective film at the metal/solution interface, which means the blocking process of the active sites by the film, formed by the inhibitor at surface of metal [6]. The slight decrease of double layer capacitance (Cdl) is yielded from

a decrease in local dielectric constant and/or an increase in the thickness of the electric double layer. It suggests that these compounds molecules function by adsorption at the metal/solution interface

Nyquist curves in Fig. 5, Fig. 6 and Fig. 7 form a semicircle caused by the transfer of charge between the

inhibitor molecule and the metal layer, where the diameter of semicircle curve elucidates the value of the charge transfer resistance of the system. In the present work, it is found that the increase of concentration for inhibitor extract and time of immersion increase the diameter of that curve. The larger diameter of semicircle curve tends to the high magnitude of charge transfer resistance in the system.

3.3. Phytochemical screening of cymbopogon citratus extract

Phytochemical results obtained for the aqueous extract of cymbopogon citratus extract is shown in Table 4. Tannin, terpenoid/steroid and alkaloid are observed qualitatively but no saponin and flavonoid. Tannins are phenolic compounds with a large molecular weight consisting of a hydroxyl group (OH⁻) and other groups such as carboxyls to form strong complexes. That compounds has ability to chelate with iron and other metal cations. Terpenoids known as isoprenoids are one of the largest and varied group of phytochemicals [19]. The structure of the alkaloids has a free nitrogen (N) heteroatom. Nitrogen serves to donate a pair of electrons to the steel surface where it is adsorbed by blocking the active surface and reducing the corrosion rate [20].

3.4. Chemical characterization of cymbopogon citratus extract

The extract of cymbopogon citratus was chemically characterized by Fourier transform infrared spectroscopy (FT-IR), was probable to observe the vibrations of the main functional chemical groups contained in the sample of CC extract. Fig. 8 shows IR absorption spectra of CC extract by using FTIR spectrometer. A significant vibration at 3347.60 cm⁻¹ is observed a wide and intense band characteristic of O-H bond of hydroxyl groups where

Table 4. Qualitative phytochemical screening results for aqueous extract of *Gongronema latifolium* leaves

Phytochemicals	Inference
Tannins	+
Saponins	-
Flavonoids	-
Terpenoids/Steroids	+
Alkaloids	+

primary amine group NH is at 3191.36 cm⁻¹. At 2933.85 cm⁻¹ is observed a coupled band of signals that evidences C-H bonds like -CH₃ and -CH₂-. The other functional groups comprise carbonyl group C=O at 1582.66 cm⁻¹, absorption alkane at 1385.91 cm⁻¹, carbonyl functional group C-O at 1269.22 cm⁻¹, thiocarbonyl functional group C=S and amine C-N at 1215.21 cm⁻¹. Therefore, the result of FTIR analysis proved evidence of the presence of Tannin, Terpenoids and Alkaloid in cymbopogon citratus eco-friendly corrosion inhibitor where the presence of the presence of polar functions with N and O atoms.

Furthermore, total phenolic content analysis was carried out to determine quantitatively phenolic compounds in cymbopogon citratus extract. Analysis of total phenol in that extracts using gallic acid as the standard of measurement. The result of the phenol content in the extract was expressed in mg gallic acid equivalent/g extract. The measurement of the total phenolic absorption of CC extract with a wavelength of 765 nm was obtained. On the basis of results, the average total phenolic content is 11.329 mg GA/g extract.

3.5. Adsorption isotherm

The adsorption of the green corrosion inhibitor molecules on the metallic surfaces is an essential process that is related to their inhibition efficiency. The value of surface

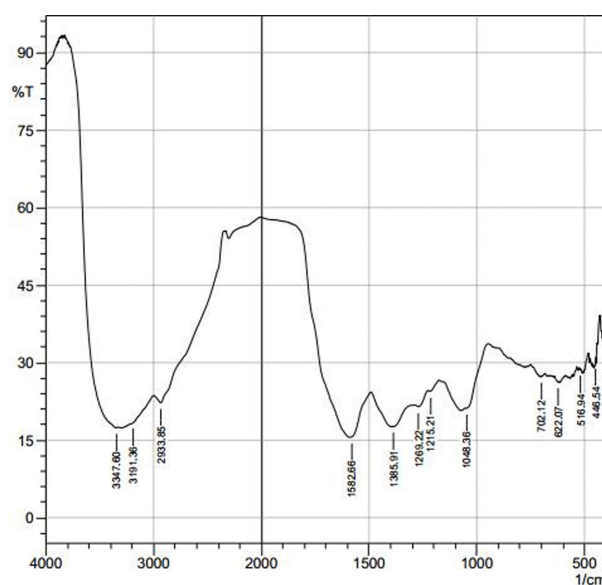


Fig. 8. FT-IR spectrum of the extract of cymbopogon citratus

coverage (θ) of cymbopogon citratus extract can be calculated from the following equation for electrochemical method

$$\theta = \frac{CR_o - CR_i}{CR_o} \quad (5)$$

There are different isotherm models available to explain the process of adsorption characteristic of green corrosion inhibitor which comprises Tempkin, Langmuir and Frumkin [17]. One of isotherm models that commonly used is Langmuir adsorption. The Langmuir adsorption isotherm can elucidate physisorption or chemisorption phenomenon. Data were tested by fitting to isotherm and found to fit with Langmuir adsorption isotherm with the following equation.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (6)$$

where, C is the concentration of corrosion inhibitor, and K is the equilibrium constant describing the adsorption/desorption for each reactant in contact with a metal surface. The values of C/ θ were plotted against C for different concentrations of inhibitors.

The isotherm and thermodynamics law is enough to elucidate the mechanism and the potency of inhibition for CC molecules at interface between corrosion electrolyte and steel surface. On the basis of results, the straight line obtained in Fig. 9 and linear regression coefficients (R^2) each various immersion period that are almost equal to 1 denotes that the adsorption of natural inhibitor on the steel surface follows Langmuir adsorption isotherm as well as the other green corrosion inhibitor [6,7]. In present work, the increase of immersion period prior to electrochemical test tends to increase K_{ads} as shown in Table 5. It implies that inhibitor molecules are easily adsorbed on the mild steel surface at prolonged time. Furthermore, the calculation of the adsorption free energy (ΔG_{ads}^o) is used to classify the category of adsorption (physical and chemical adsorption). ΔG_{ads}^o should be estimated using Equation 7.

$$\Delta G_{ads}^o = -RT \ln (A \cdot K_{ads}) \quad (7)$$

Where, the parameters R, A, and T are universal gas constant, the concentration of pure water in the solution, and solution temperature (K), respectively ($R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ and $A = 10^3$).

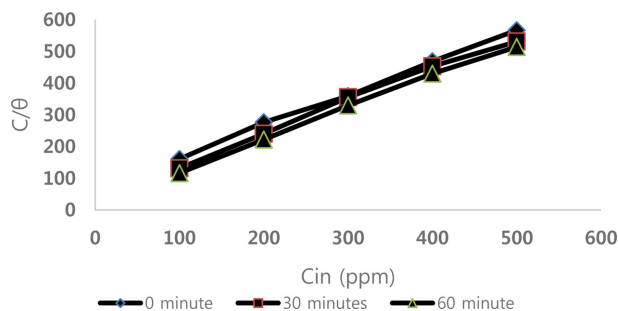


Fig. 9. Langmuir adsorption isotherm plots for the adsorption of cymbopogon citratus extract on steel surface in 0.1 M H_2SO_4 at ambient temperature for various immersion time

Table 5. Langmuir adsorption isotherms fitted for cymbopogon citratus extracts

t (minute)	Y-intercept $1/K_{ads}$ (g/L)	K_{ads} (L/g)	ΔG_{ads}^o (Kj/mol)
0	0.0193	51.6	-19.721
30	0.0064	156.25	-22.4666
60	0.008	125	-21.913

4. Discussion

The reduction of anodic reaction magnitude means the low dissolution of metal ions from metal bulk to electrolyte where that of cathodic side defines the low cathodic hydrogen discharge reaction. Both the reduction of anodic and cathodic process is identified by current density [6] where the magnitude of that density for carbon steel decrease significantly by adding CC extract. The reduction of current density also tends to minimize the corrosion attack of metals [7]. There is no or slightly shift of corrosion potential (E_{corr}) values after addition of the CC extract in different immersion periods. Type of corrosion inhibitors which comprises anodic, cathodic and mixed type is specified by the shift in the value of E_{corr} from potentiodynamic polarization curve. If the shift in the value of E_{corr} for inhibited metals is more than $\pm 85 \text{ mV}$ as compared to that for uninhibited metals, the inhibitor can be classified as anodic or cathodic type [21]. However, if the shift in the E_{corr} value is less than $\pm 85 \text{ mV}$ then the inhibitor can be categorized as mixed type [6,22] as well as recent work. The mixed corrosion inhibitor has ability simultaneously to retard both anodic and cathodic reaction in electrochemical process. It implies that the addition of extract to H_2SO_4 solution

reduces the anodic dissolution of metal and impedes the cathodic hydrogen evolution reaction at the same time.

The adsorption mechanism may be physical or chemical types depending upon the nature of adsorbate and adsorbent. In addition, the adsorption isotherms also elucidate the degree of interaction of molecules of green corrosion inhibitors with the metal surface [23]. Isotherm equations were applied to verify that the inhibition mechanism is a real adsorption. This results implies that monolayer coverage and homogenous distribution of the CC molecules on the steel surface as suggested by Langmuir equation. In addition, the K_{ads} value is related to the magnitude of affinity for a corrosion inhibitor to the adsorption site where a high value of that shows the higher protection of the metal surface [24].

The negative value of ΔG_{ads}^o determines the adsorption process and stability of the absorbed molecule layer on the metal surface. Mostly, the values of ΔG_{ads}^o up to -20 KJ/mol are constant with the electrostatic reaction between the charged inhibitor molecules and charged metal which defines as physisorption interaction. That negative value higher than -40 KJ/mol represents sharing of electrons from the inhibitor molecules to the metal surface to form co-ordinate type of bond which defines as chemisorption interaction. On the basis of results, the calculated value of ΔG_{ads}^o was found to be negative less than 40 KJ/mol in all immersion period up to 60 minutes as shown in Table 5. The values of ΔG_{ads}^o for cymbopogon citratus extract are in the range -19.721 KJ/mol to -22.4 KJ/mol that inhibitor molecules are adsorbed on the metal surface by a strong physical adsorption process. The high and negative ΔG_{ads}^o exhibit spontaneous adsorption of cymbopogon citratus extract on steel surface, which is elucidated with high IE. Therefore, the possible mechanism of inhibition can be proposed for the CC extract which tends to physical adsorption.

5. Conclusions

The capability of cymbopogon citratus extract as an eco-friendly corrosion inhibitor has been investigated comprehensively by using electrochemical and thermodynamic analysis. The presence of tannin and alkaloid groups contributes to inhibit corrosion attack of steel containing hetero-atoms in acid solution. The inhibition

efficiency improved with increasing inhibitor concentrations and immersion periods where the inhibition efficiency of CC extracts increases up to 97.25%. Polarization analysis have elucidated that the inhibitor behaves as a mixed inhibitor. The value of charge transfer resistance increase by adding extract up to 500 ppm with 60 minutes immersion time. The adsorption of inhibitor molecules layer on steel surface was found to follow Langmuir isotherm. The value of Gibbs free energy from the isotherm model suggested that the adsorption mechanism of cymbopogon citratus extract on the steel is physisorption.

Acknowledgments

This work was completed thanks to all researchers, lecturers and student at laboratory of corrosion in both Research Center for Metallurgy, National Research and Innovation Agency and Sultan Ageng Tirtayasa University. The authors also acknowledge the full support of Indonesian government for research, manuscript preparation and publication.

References

1. M. Meryanalinda, D.R. Ardian, M. Shocib, and A. Yasin, Analysis of Corrosion Rate of ASTM A 287 Grade 12 and A 283 Grade for Sulfuric Acid Tank Material, *Journal of Applied Sciences, Management and Engineering Technology*, **1**, 50 (2020). Doi: <https://doi.org/10.31284/j.jasmet.2020.v1i2.1194>
2. A. Fawzy and A. Toghan, Inhibition Evaluation of Chromotrope Dyes for the Corrosion of Mild Steel in an Acidic Environment: Thermodynamic and Kinetic Aspects, *ACS Omega*, **6**, 4051 (2021). Doi: <https://doi.org/10.1021/acsomega.0c06121>
3. O. A. Hazazi, A. Fawzy, M. R. Shaaban, and M. I. Awad, Enhanced 4-amino-5-methyl-4H-1,2,4-triazole-3-thiol inhibition of corrosion of mild steel in 0.5 M H₂SO₄ by Cu(II), *International Journal of Electrochemical Science*, **9**, 1378 (2014).
4. Z. Panossian, N. L. de Almeida, R. M. F. de Sousa, G. de S. Pimenta, and L. B. S. Marques, Corrosion of carbon steel pipes and tanks by concentrated sulfuric acid: A review, *Corrosion Science*, **58**, 1 (2012). Doi: <https://doi.org/10.1016/j.corsci.2012.01.025>

5. G. A. Zhang, Y. Zeng, X. P. Guo, F. Jiang, D. Y. Shi, and Z. Y. Chen, Electrochemical corrosion behavior of carbon steel under dynamic high pressure H₂/CO₂ environment, *Corrosion Science*, **65**, 37 (2012). Doi: <https://doi.org/10.1016/j.corsci.2012.08.007>
6. G. Priyotomo, O. M. Prayoga, Y. Dwiyanti, and S. Oediyani, The Potency of The Potency of Grass Extract as Corrosion Inhibitor on Steel in Hydrochloric Acid Solution, *Walailak Journal of Science and Technology*, **28**, 1 (2021).
7. A. Nikitasari, Sundjono, G. Priyotomo, and A. Royani, Sargassum seaweed extract as a novel green corrosion inhibitor for API-5L carbon steel, *International Journal of Corrosion and Scale Inhibition*, **10**, 1689 (2021).
8. J.R Vimala, L. A Rose, and A. Raja, A study on the phytochemical analysis and corrosion inhibition on mild steel by *Annona muricata* leaves extract in 1N hydrochloric acid, *Der Chemica Sinica*, **3**, 582 (2012).
9. A. A. Rahim, E. Rocca, J. Steinmetz, M. J. Kassim, R. Adnan, and M. Sani Ibrahim, Mangrove tannins and their flavanoid monomers as alternative steel corrosion inhibitors in acidic medium, *Corrosion Science*, **49**, 402 (2007). Doi: <https://doi.org/10.1016/j.corsci.2006.04.013>
10. M. Lebrini, F. Robert, and C. Roos, Alkaloids extract from *Palicourea guianensis* plant as corrosion inhibitor for C38 steel in 1 M hydrochloric acid medium, *International Journal of Electrochemical Science*, **6**, 847 (2011).
11. Ahamad, R. Prasad, and M. A. Quraishi, Adsorption and inhibitive properties of some new Mannich bases of Isatin derivatives on corrosion of mild steel in acidic media, *Corrosion Science*, **52**, 1472, (2010). Doi : <https://doi.org/10.1016/j.corsci.2010.01.015>
12. K. Alaoui Ismaili, S. El Arouji, A. Abdellaoui, F. El Kamani, Z. Rais, M. Filali Baba, M. Taleb, K.M. Emran, A. Zarrouk, A. Aouniti, and B. Hammouti, Electrochemical and gravimetric studies of the corrosion inhibition of mild steel in HCl medium by *Cymbopogon nardus* essential oil, *Der Pharma Chemica*, **7**, 34 (2015).
13. M. A. Deyab, M. M. Osman, A. E. Elkholy, and F. El-Taib Heakal, Green approach towards corrosion inhibition of carbon steel in produced oilfield water using lemongrass extract, *RSC Advances*, **7**, 45241 (2017). Doi: <https://doi.org/10.1039/c7ra07979f>
14. A.S. Udobre, S.B. Alabi, and O.A.S. Uko, The Phytochemistry and Antioxidant Activity of the Ethanol Extract of *Cymbopogon citratus* (POACEAE), *International Journal of Science and Research*, **92**, 2319 (2018).
15. K. H. Miean and S. Mohamed, Flavonoid (myricetin, quercetin, kaempferol, luteolin, and apigenin) content of edible tropical plants, *Journal of Agricultural and Food Chemistry*, **49**, 3106 (2001). Doi: <https://doi.org/10.1021/jf000892m>
16. S.-H Lee and B.-J Choi, Mechanical Properties of ASTM A572 Grades 50 and 60 Steels at High Temperatures, *Applied Sciences*, **11**, 11833 (2021). Doi: <https://doi.org/10.3390/app112411833>
17. A.R Torres, M.G.V Cisneros, C.C Arteaga and M.A.V Rodríguez, Study of Green Corrosion Inhibition on AISI 1018 Carbon Steel in Sulfuric Acid Using *Crataegus mexicana* as Eco-Friendly Inhibitor, *Journal of Materials and Environmental Science*, **10**, 101 (2019).
18. P. Khadke, T. Tichter, T. Boettcher, F. Muench, W. Ensinger, and C. Roth, A simple and effective method for the accurate extraction of kinetic parameters using differential Tafel plots, *Scientific reports*, **11**, 8974 (2021). Doi: <https://doi.org/10.1038/s41598-021-87951-z>
19. N. Bhardwaj, P. Sharma, and V. Kumar, Phytochemicals as steel corrosion inhibitor: An insight into mechanism, *Corrosion Reviews*, **39**, 27 (2021). Doi: <https://doi.org/10.1515/corrrev-2020-0046>
20. P.B. Raja, M. Fadaeinasab, A.K. Qureshi, A.A. Rahim, H. Osman, M. Litaudon, and K. Awang, Evaluation of green corrosion inhibition by alkaloid extracts of *Ochrosia oppositifolia* and isoreserpiline against mild steel in 1 M HCl medium, *Industrial and Engineering Chemistry Research*, **52**, 10582 (2013). Doi: <https://doi.org/10.1021/ie401387s>
21. C. Verma, M. A. Quraishi, K. Kluza, M. Makowska-Janusik, L. O. Olasunkanmi, and E. E. Ebenso, Corrosion inhibition of mild steel in 1M HCl by D-glucose derivatives of dihydropyrido [2,3-d:6,5-d] dipyrimidine-2, 4, 6, 8(1H,3H, 5H,7H)-tetraone, *Scientific Reports*, **7**, 44432 (2017). Doi: <https://doi.org/10.1038/srep44432>
22. M.M Khowdiary, N.A Taha, N.M Saleh, and A.A Elhenawy, Synthesis of Novel Nano-Sulfonamide Metal-Based Corrosion Inhibitor Surfactants, *Materials*, **15**, 1146 (2022). Doi: <https://doi.org/10.3390/ma15031146>
23. A. K. Singh and M. A. Quraishi, Effect of Cefazolin on the corrosion of mild steel in HCl solution, *Corrosion Science*, **52**, 152 (2010). Doi: <https://doi.org/10.1016/j.corsci.2009.08.050>
24. M. Afrok, S. Baroud, Y. Kerroum, A. Hatimi, S. Tahrouch, I. Sadki, I. Warad, A. Guenbour, A.

CORROSION INHIBITION OF CARBON STEEL IN SULFURIC ACID USING CYMBOPOGON CITRATUS AS A GREEN CORROSION INHIBITOR

Bellaouchou, M. Tabyaoui, and A. Zarrouk, Green approach to corrosion inhibition of carbon steel by fucus spiralis extract in 1 M HCl medium, *Biointerface*

Research in Applied Chemistry, **12**, 7075 (2022). Doi: <https://doi.org/10.33263/BRIAC125.70757091>