

Utilization of secang heartwood (caesalpinia sappan l) as a green corrosion inhibitor on carbon steel (API 5L Gr. B) in 3.5% NaCl environment

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Abstract. This research objective was to investigate secang heartwood extract (caesalpinia sappan l) as a corrosion inhibitor on carbon steel metal (API 5L Gr B) in 3.5% NaCl environment. This research utilized polarization linier for the measurement method. Secang extract was adequate to reduce corrosion rate by 53.18% efficiency (based on polarization measurement). The most effective concentration of inhibitor secang was 2.0 ml/400 ml 3.5% NaCl. Furthermore, inhibitor efficiency of secang has tended to decrease by increasing of temperature. From polarization study, secang was indicated as mixed type inhibitor, with predominant cathodic effectiveness. In addition, the inhibition mechanism of secang was shown as physisorption mechanism and obeys Langmuir Isotherm model.

1. Introduction

Corrosion inhibitor is one of methods for corrosion control. As material point of view, corrosion inhibitor is divided into two types : organic inhibitor and inorganic inhibitor types [1]. Organic inhibitors have many atoms (heteroatoms) including O (oxygen), N (nitrogen), and S (sulfur). O, N, and S is the center absorption activation process on the metal surface. The research reports show that the organic inhibitor is absorbed on metal surface by the turn of the water molecules and form a barrier compact. The performance of an organic inhibitor related to chemical structure and physicochemical properties of the compound as a functional group, electron density in the atom donor, p-orbital characters and the electron structure of the molecule. Inhibition can be caused by absorption of molecules or ions on anodic or cathodic sites, potential increasing on cathodic and or anodic, a barrier layer / protector forming. Absorption inhibitor mechanism can be through as following ways : physisorption, caused by electrostatic forces between ions which inhibit and electric charge on metal surface; chemisorption, caused by interaction between pairs free electrons with the metal to form a bond , this takes place during availability of a heteroatom such as P, Se, S, N and O will be pair with electrons itself or aromatic rings in molecule absorption; then the combination of physisorption and chemisorption[2].

Secang heartwood (caesalpinia sappan l) can be considered as environmentally friendly corrosion inhibitor on the metal material of carbon steel in sea water containing 3.5% NaCl, because the phenolic



compounds contained in the secang heartwood, ie brazilin, chalcone, protossappanin and homoisoflavonoid [3], are expected to inhibit corrosion through physisorption mechanisms.

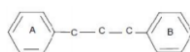


Figure 1. The organic structure of flavonoids.

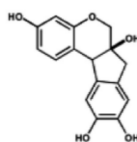


Figure 2. The organic structure of brazilin.

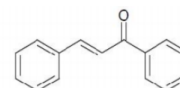


Figure 3. The organic structure of chalcone.

The purpose of this study is to determine the inhibition efficiency of the secang extract as corrosion inhibitor in a 3.5% NaCl solution, find out most effective concentrations of secang extract inhibiting corrosion rate, find out the solution temperature change effects to the inhibitor performance, and to understand the mechanism of secang (*caesalpinia sappan* l) extract inhibition on metal surface. Evaluation of corrosion rate and inhibition mechanism has been evaluated by linear polarization methods.

This study uses a variation of extract concentration and temperature as following parameters: extract concentration variation ranging from 0 to 2.5 ml / 400 ml NaCl at temperature 25, 35, and 45°C. Then this study is limited by the following conditions: operating pressure during the experiment is assumed to constant (1 atm), NaCl concentration is 3.5%.

2. Experimental work

2.1. Materials and Solution

Metal samples of carbon steel API 5L Gr. B with composition (%) 0.147 C, 0.199 Si, 0.004 S, 0.013 P, 0.424 Mn, <0.005 Ni, 0.01 Cr, 0.008 Mo, <0.002 Ti, 0.007 Cu, <0.002 Nb, <0.002 V, 0.002 Al and free Fe used in this study.

Secang extract was prepared by mixing of secang's slicing with methanol for minimum 3 days, then the initial extract result continued by evaporation to remove methanol and water contents. The evaporation using equipment rotary vacuum evaporator with pressure parameters of 185 bar at room temperature (27-28°C). While NaCl solution was prepared by mixing of salt and distilled water to obtain 3.5% NaCl solution.

2.2. Linear Polarization Measurements

Electrochemical measurements utilized Metrohm Instruments Autolab Potentiostat/Galvanostat PGSTAT302N with NOVA 1.10 software. The cell contained three electrodes; the working, counter and reference electrodes, comprised of mild steel, a carbon bar and AgCl (saturated with KCl) respectively.

2.3. FTIR Measurement

FTIR is used to identify the functional groups contained in the extract of secang's heart-wood. FTIR measurement is also conducted to ascertain whether the functional groups contained in the wooden cup extract can be adsorbed well on the steel surface and form an inhibition layer which would inhibit the corrosion reaction. For this purpose FTIR measurement was done 2 times; the extract of secang heart-wood and a metal surface that has been immersed in a solution of 3.5% NaCl were added to extract the wooden cup at the optimal concentration.

3. Results and Discussions

3.1. Linear Polarization

The polarization measurements result as shown in Figure 4 shows the inhibition effect on the material API 5L Gr. B in 3.5% NaCl environment, while Table 1 is polarization parameters of inhibitor

concentration variations. Parameters results on Table 1 show decreasing of current density (I_{corr}) corresponding addition of inhibitor concentrations up to concentration of 2.0 ml ($I_{corr} = 12.88 \mu A \cdot cm^{-2}$), then current density rising again at concentration of 2.5 ml with $I_{corr} = 16.94 \mu A \cdot cm^{-2}$.

The same pattern also applied in corrosion rate (CR) value, the inhibitor concentration addition will reduce the CR of up to 2.0 ml inhibitor concentration (CR= 0.150 MPY) then the CR will increase at concentration of 2.5 ml.

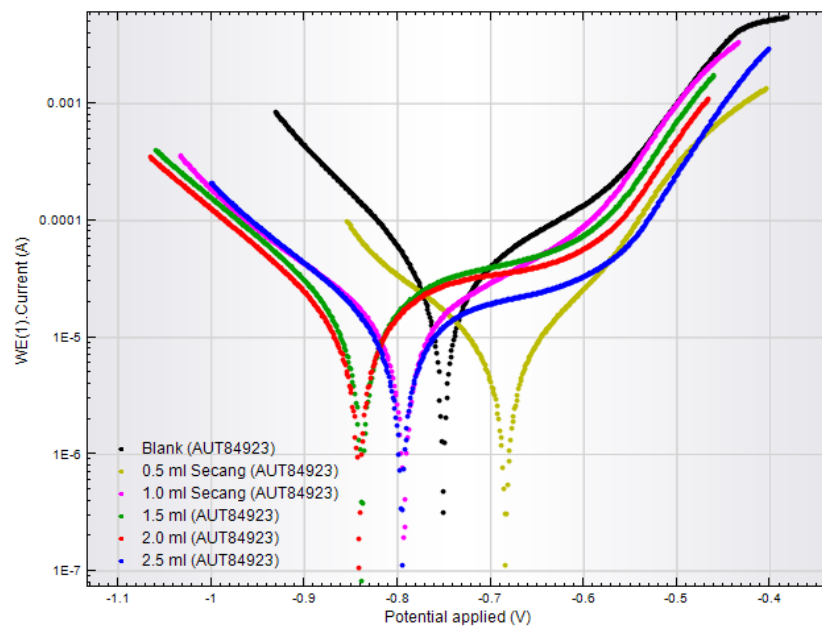


Figure 4. Polarization curve for 3.5% NaCl solution with inhibitor concentration variation.

The inhibition efficiencies for different inhibitor concentrations were calculated from the following equation [6]:

$$\eta_p = \frac{i_{corr(uninh)} - i_{corr(inh)}}{i_{corr(uninh)}} \times 100 \quad (1)$$

Where, i_{corr} is corrosion current densities.

Table 1. Polarization parameters of inhibitor concentration variations in 400ml NaCl 3.5%.

Secang extract volume (ml)	E_{corr} (mV)	I_{corr} ($\mu A \cdot cm^{-2}$)	b_a (mVdec ⁻¹)	b_c (mVdec ⁻¹)	C_R (mpy)	EI, η (%)
Blank	-747.51	27.49	121.69	210.19	0.32	0.00
0.5 ml	-683.57	20.05	379.87	333.15	0.23	27.07
1.0 ml	-794.05	17.23	221.39	290.48	0.20	37.33
1.5 ml	-831.16	13.86	152.01	166.89	0.16	49.58
2.0 ml	-837.41	12.88	157.67	196.88	0.15	53.14
2.5 ml	-784.91	15.20	194.79	350.60	0.18	44.71

As the investigation, concentration of 2.0 ml/400 ml NaCl is most effective inhibitor concentration with highest efficiency of 53.14%, the lowest current density (I_{corr}) and the lowest corrosion rate (CR). In another words, the inhibitor concentration of 2.0 ml /400 ml NaCl solution is the most effective

concentration reducing or inhibit corrosion rate on metal sample API 5L Gr B in the 3.5% NaCl environment.

In accordance to Figure 4, polarization curves tend to shift to more negative potential values (cathodic area). Based on Table 1, corrosion potential (E_{Corr}) parameter at concentration of 0.5 ml inhibitor shows shifting to anodic area with value of -683.57 mV, while other inhibitors concentration shifts toward cathodic area ranging from -794.05 mV up to -837.41 mV, maximum E_{Corr} is showed at inhibitor concentration of 2.0 ml. As the investigation, E_{Corr} shifting until 89.9 mV of blank E_{Corr} . According to Ambrish Singh [7], Mc Caferty [8], Bramley [9], secang is cathodic inhibitor type due to E_{Corr} shifting exceeds value of 85 mV.

From Table 1, value of the anodic Tafel constants (b_a) and cathodic Tafel constants (b_c) look change due to inhibitor concentration increasing. Changes value of b_c and b_a indicate that absorption process of inhibitor extract able to change cathodic solubility mechanism [10]. According to Li [11] and Rahmad [12], changes of b_c and b_a due to inhibitor volume changes also indicate an absorption process on both anodic and cathodic areas.

As above review, secang heartwood is mixed type inhibitor, with predominant cathodic effectiveness.

3.2. Thermodynamic Aspect

Inhibition and absorption mechanism of the inhibitor molecules were investigated using temperature variations measurement. The resulted curve and parameters of linear polarization measurements are shown in Figure 5.

Based on Table 1, Figure 6 and Figure 7 temperature increasing will raise the current density (I_{Corr}), corrosion rate (CR), and reduce inhibitor efficiency. Such tendencies also occur in other plant extracts such as *Morinda citrifolia* [4], *Mentha pulegium* [5], *Thymus algeriensis* [6], and *Santolina chamaecyparissus* [7]. The increasing of temperature will damage the inhibitor bonding on to surface, then reduce inhibition performance between the inhibitor with metal surface.

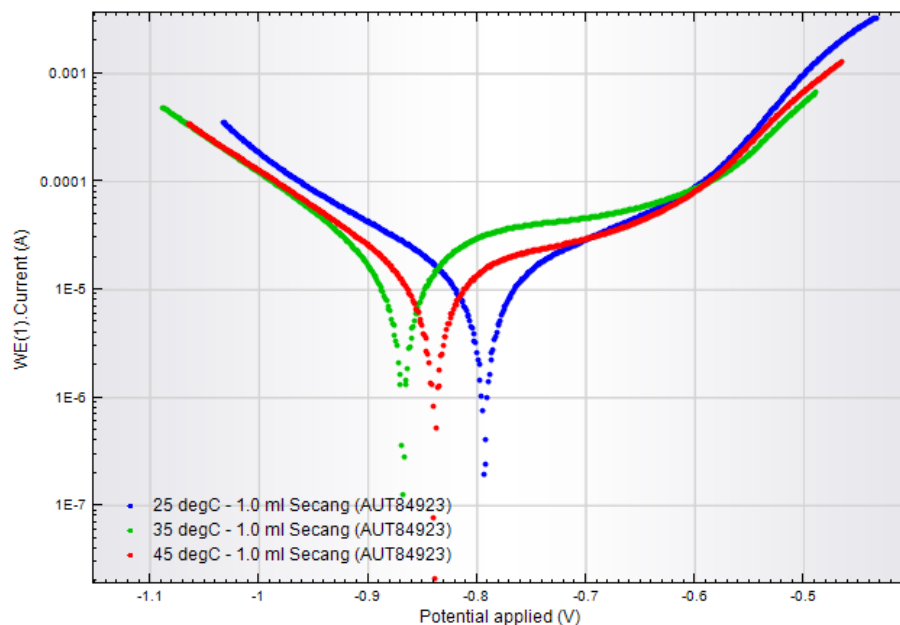


Figure 5. Polarization curve of 3.5% NaCl solution with inhibitor at temperature 25, 35, and 45°C.

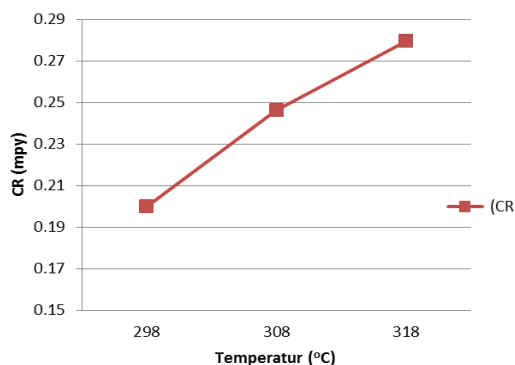


Figure 6. Corrosion Rate (CR) at temperature variations.

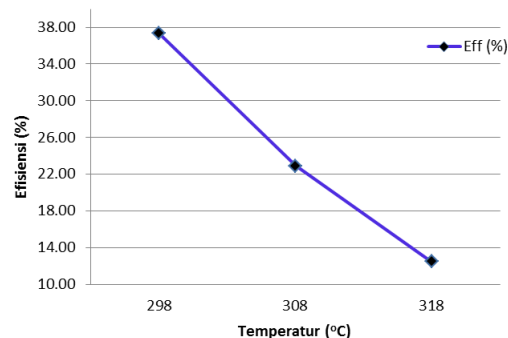


Figure 7. Inhibitor Efficiency at temperature variations.

According to Olivares et al. [8] and Kairi et al. [9], inhibitor efficiency reduction due to temperature increasing proved that absorption mechanism of secang inhibitor molecules acted as physically (physicorption).

3.3. Absorption Mechanism

Absorption process of the inhibitor molecule will obey the Langmuir modeling based on figures 5 because the correlation coefficient (degree of conformity) of modeling Langmuir has a value > 0.95 . As investigation result by Yurt et al. [10], organic molecules to be adsorbed as a monolayer on metal surfaces without any interaction with other adsorbed molecules, and according to Behpour investigation result [11], there is only one site (area) where the absorption of molecules. Therefore, molecules of secang inhibitors in this study are strongly indicated run into the formation of a single layer (monolayer) on the metal surface.

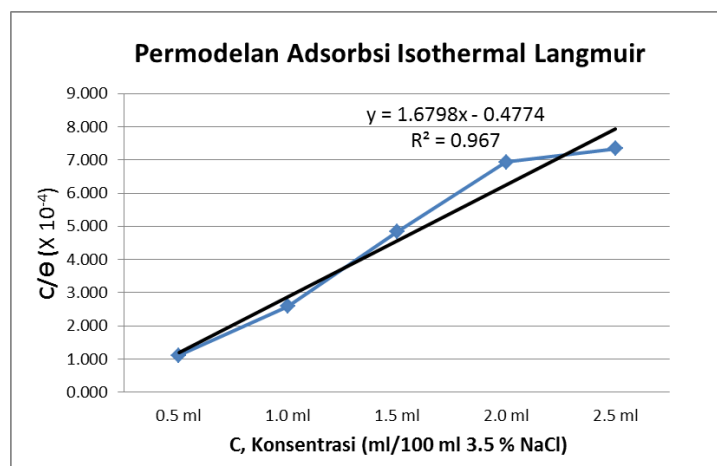


Figure 8. Isotherm Langmuir for secang inhibitor absorption on metal API 5L Gr. B surfaces in 3.5% NaCl solution.

Negative values in the free energy show the corrosion reaction runs spontaneously. According to Ahmed Musa Y. et al [12], when the interaction free value was reached -40kJmol^{-1} , then the interaction of adsorption is chemisorptions where there is charge exchange of organic molecules to the metal surface forming the coordinate bond.

Based on the resulted parameters in above Table 1, absorption mechanism of secang heartwood inhibitor was indicated to react as physicorption because of free energy value is below -40kJmol^{-1} .

3.4. FTIR Measurement

FTIR Measurement result (spectra) of secang inhibitor absorption layer on the metal surface can be seen in Figure 9.

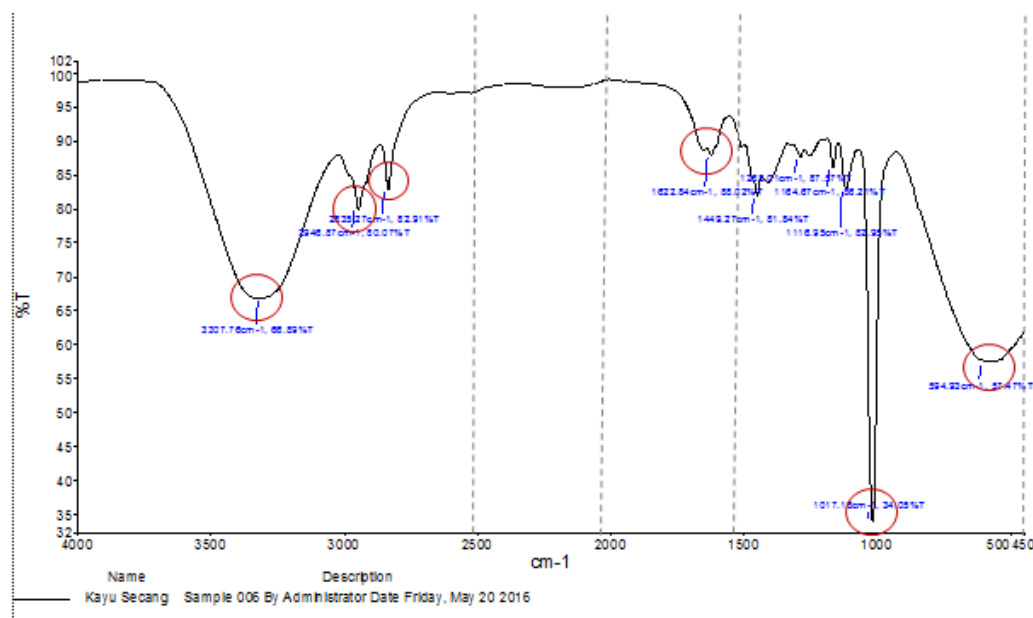


Figure 9. FTIR spectrum of secang absorption on metal API 5L Gr B surface.

As Figure 9 shows absorption widened at wave number 3308 cm^{-1} is the absorption of O-H hydroxyl (single), then looks weak absorptions between area $2947\text{ dan }2950\text{ cm}^{-1}$ are typical C-H aldehyde. Furthermore, the weak absorptions double C = O stretch looked at wave number of 1622 cm^{-1} . Then there is strong absorption of the carbonyl group C-O at wave number 1017 cm^{-1} .

Above facts confirm that secang heartwood extract contain braziline compounds [13,14] which has a functional group of O-H and chalcone compounds which has group of C-H and the double bond of C=O act as antioxidant that can be used to inhibit corrosion rate on metal surfaces by absorption mechanism.

4. Conclusion

Secang heartwood extract can be utilized as an alternative of corrosion inhibitor because the inhibitor is proven to inhibit corrosion on metal samples API 5L Gr. B in 3.5% NaCl environment; polarization study indicate secang heartwood is mixed type inhibitor with predominant cathodic effectiveness; inhibition efficiency is influenced by concentration and temperature, the higher inhibitor concentration the higher inhibition efficiency while conversely the higher temperature the lower inhibition efficiency; the inhibitor concentration of 2.0 ml / 400 ml NaCl is the best effective inhibitors concentration reducing corrosion rate; the highest inhibition efficiency is 53.18% based on Polarization evaluation. And, the secang heartwood inhibitor reacts as physisorption and obeys Langmuir Isotherm model.

5. Acknowledgement

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