Exploration of *Eucheuma* Seaweed Algae Extract as a Novel Green Corrosion Inhibitor for API 5L Carbon Steel in Hydrochloric Acid Medium

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**ABSTRACT**

Regarding the issue of green chemistry and the vision of human sustainability, a novel corrosion inhibitor for API 5L carbon steel was explored from *Eucheuma* seaweed algae. The inhibiting performance of *Eucheuma* extract was studied by electrochemical measurements such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). In this work, the Fourier Transform Infra-Red (FTIR) was also employed to confirm the main phenolic compounds of *Eucheuma* extract. The electrochemical measurement result indicated that the *Eucheuma* extract was an efficient corrosion inhibitor in reducing corrosion attacks of API 5L carbon steel in hydrochloric acid medium. The improved corrosion resistance is attributed to the complicated items, including extract concentration and holding time. *Eucheuma* inhibitor efficiency up to 90% (96.4%) with concentration 500ppm and 30min holding time indicated that *Eucheuma* could be used as a green inhibitor. It was found that the *Eucheuma* extract was a mixed-type corrosion inhibitor that inhibit both the cathodic and anodic corrosion reaction. This study was helpful to discover the seaweed algae that was abundant in Indonesia’s marine for inhibiting corrosion of API 5L carbon steel in an aggressive environment.

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**NOMENCLATURE**

| CR | Corrosion rate, mils per year (mpy) |
|----|------------------------------------|
| EIS | Electrochemical Impedance Spectroscopy |
| FTIR | Fourier Transform Infra Red |
| OCP | Open Circuit Potential |
| $R_c$ | Charge transfer resistance (Ω) |
| $R_s$ | Solution resistance (Ω) |
| $I_{corr}$ | Corrosion current density (A/m²) |
| $E_{corr}$ | Corrosion potential (V) |

1. INTRODUCTION

Low carbon steel such as API 5L is one of the most widely materials used and extensively applied for oil and gas exploration, drilling, and production [1]. These steels are important due to their low cost, easily fabrication, excellent welding, and forming abilities. However, they are vulnerable to corrosion attack when exposed to corrosive agents [2].

Hydrochloric acid (HCl) is one of the corrosive agents commonly used in industries for acid cleaning, descaling, and pickling. Corrosion inhibitors can be useful for avoiding the corrosion caused by hydrochloric acid [3].

In the last few years, the use of natural and organic extract as green corrosion inhibitors has attracted many researchers’ attention. The green corrosion inhibitors have many advantages such as biodegradable, non-toxic, environmentally friendly and ecologically acceptable, inexpensive, readily available, renewable and safe to use compared to the chemical ones [4].

There are several previous works about environmentally-friendly corrosion inhibitors in a hydrochloric acid medium, such as reviewed by Yang ang Yang [5] and research conducted by Jiddawi et
al. [6] that used organic compound aniline and phenol. Besides that, some researchers used natural sources Rosmarinus officinalis plant [7], Hyalomma insect [8], and the waste from sunflower seedhull [3] as corrosion inhibitors. In contribution to the research on the natural compound for effective corrosion inhibition in HCl medium, this present work uses Eucheuma seaweed algae as the new resource.

Eucheuma is a group of red seaweed algae usually found in Indonesia [5]. Eucheuma extract has potential to be used as a green corrosion inhibitor due to the exhibits high growth rates and contains high polyphenol [6]. However, this algae has never been studied before as corrosion inhibitors. Due to the purposes below, this research aims to explore Eucheuma seaweed algae extracts to inhibit the corrosive impact on API 5L carbon steel in hydrochloric acid (0.1 M HCl). Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and FTIR were used to assess this work.

2. MATERIALS AND METHODS

2. 1. Materials Carbon steel API 5L specimens having a chemical composition in wt % (C, 0.05; Si, 0.13; Mn, 0.73; P, 0.02; S, 0.004; Fe remainder) were used. Carbon steel was cut with a size of 1 cm x 1 cm x 1 cm, connected with cable wire, and mounted with an exposed area of 1 cm². Prior the experiment, the specimens were mechanically abraded using different grades (120 – 1200) of silicon carbide emery paper and subsequently cleaned with acetone, then rinsed with distilled water.

2. 2. Eucheuma Extract and Medium For the Eucheuma seaweed algae extract process, at first, seaweed was cleaned with tap water and dried at room temperature for five days. The dried Eucheuma was chopped and collected in 70% of ethanol (maceration) for 72h. The ratio between dried Eucheuma and ethanol for the maceration process was 1:3, respectively. The maceration result was filtrated and evaporated to obtain the extract. To investigate the chemical composition of the Eucheuma extract, FTIR was employed.

The hydrochloric acid medium that used in this experiment was 0.1 M HCl. Eucheuma extract with various concentration i.e. 0, 50, 100, 200, 400, and 500 ppm was mixed into 0.1 M HCl. All specimens were immersed in the medium without and with 30 min of holding time before electrochemical measurement. The temperature of the medium also varied (room temperature, 40°C, and 50°C) to evaluate the influence of temperature on the corrosion rate.

2. 3. Electrochemical Measurement Electrochemical measurements were performed using GAMRY Series G-750 Corrosion Measurement System. For measurement, the three-electrode corrosion cell was used [7]. API 5L specimens with an exposed area of 1 cm² were utilized as a working electrode. A platinum and SCE (saturated calomel electrode) electrode were acted as counter and reference electrodes, respectively.

Potentiodynamic polarization was carried out in the potential range of ±250 mV from the OCP potential. The scanning rate of the polarization curve was about 1 mV/s. The electrochemical impedance spectroscopy (EIS) measurements were conducted with the frequency range of 100 kHz and 0.1 mHz. The measurements were done with a signal of 10 mV peak to peak. In addition, the impedance results were fitted to obtain the charge transfer resistance (Rct). All the electrochemical measurements were recorded in triplicate.

3. RESULT AND DISCUSSION

3. 1. Polarization Test Result Figure 1 illustrates the cathodic and anodic polarization curves for API 5L carbon steel immersed in 0.1 M HCl containing various concentrations of Eucheuma green inhibitor at different temperatures without holding time. In addition, potentiodynamic polarization curves for API 5L in 0.1 M HCl solution at various temperatures and concentrations of Eucheuma extract with 30 min of holding time are represented in Figure 2. It is observed that by adding inhibitor, the potential tends to be a similar value but current shifts toward less current. Hence, it is indicated that Eucheuma extract was a mixed-type corrosion inhibitor and improved the corrosion resistance of API 5L in the hydrochloric acid medium [8]. From Figures 1 and 2, the polarization curve of the specimen without inhibitor at 50°C has the lowest potential value and the highest current. Therefore, the greatest corrosion rate is specimen without inhibitor at 50°C.

![Figure 1](link-to-image)
In this study, the electrochemical corrosion parameters such as corrosion potential (Ecorr) and corrosion current densities (Icorr) were automatically calculated based on Butler–Volmer and Tafel equations [9]. Tafel slope analysis and fitting of the polarization curves were performed using Echem analyst software to obtain the corrosion rate of API 5L carbon steel. Table 1 listed the parameters of API 5L in 0.1 M HCl and various inhibitor concentrations at room temperature with 30 min of holding time that resulted from polarization test.

According to Table 1, corrosion current density (Icorr) and corrosion rate decrease significantly with increasing inhibitor concentration. Figure 3 summarizes the corrosion rate of API 5L in 0.1 M HCl with various concentrations of Eucheuma inhibitor at different temperatures. All specimens with a low inhibitor concentration have a higher corrosion rate than specimens with higher inhibitor concentration. When “30 min holding time” was used, the corrosion rate was lower than “no holding time” specimens. This behavior could justify the adsorption process of inhibitors on the steel surface. The holding time gives a chance to the inhibitor for covering the steel surface. Corrosion rate also boosts with the increasing of temperature based on Figure 3.

**TABLE 1. Parameters obtained from polarization test**

| Concentration (ppm) | Ecorr (mV) | Icorr (mA/cm²) | Corrosion rate (mpy) |
|---------------------|-----------|----------------|----------------------|
| 0                   | -532      | 6.65E-4        | 304                  |
| 50                  | -523      | 4.65E-4        | 212.9                |
| 100                 | -513      | 2.22E-4        | 101.5                |
| 200                 | -494      | 9.58E-5        | 43.88                |
| 400                 | -481      | 5.63E-5        | 25.77                |
| 500                 | -514      | 5.28E-5        | 24.17                |

Inhibition efficiency (η) can be formulated by Equation (1):

$$\eta = \frac{CR - CR(in)}{CR} \times 100\%$$  \hspace{1cm} (1)

where CR and CR(in) are corrosion rate without and with the presence of inhibitor, respectively. Figure 4 showed the inhibitor efficiency of all specimens. Compared to “no holding time”, specimens with holding time presented a more pronounced inhibition effect.

Inhibitor efficiency increase with an increase in inhibitor concentration and temperature. The highest inhibition efficiency (96.4%) was specimen containing a *Eucheuma* inhibitor with a concentration of 500 ppm with 30 min holding time at 50°C. It is seen that the corrosion rate decreases by adding inhibitor so that it is reduced by 28 times at 500 ppm concentration of the inhibitor. Therefore, it is obvious that the *Eucheuma* extract inhibitor is useful [13].

### 3. 2. EIS Test Results

The inhibition performance of *Eucheuma* extract on API 5L carbon steel was further...
analyzed by means of electrochemical impedance spectroscopy (EIS) measurements under different experimental conditions.

Figure 5 showed a Bode plot for API 5L in 0.1 M HCl environment with and without inhibitor at different temperatures. The peak in the Bode plot indicated the existence of the relaxation time. The higher impedance was obtained for API 5L with the highest concentration of inhibitor in each temperature. Furthermore, the corrosion resistance of steel substrate increased when the concentration of *Eucheuma* extract increased, as the total impedance obviously increased due to the results in Figure 5. According to Figure 5 (a), the phase angles increased from -40 to -60°. The increasing of phase angle with the increasing of inhibitor concentration indicated that the *Eucheuma* inhibitor was physically adsorbed on the surface [14].

Nyquist plot for API 5L carbon steel in 0.1 M HCl and various inhibitor concentrations with and without holding time at different temperatures presented in Figure 6. Based on Figure 6, all impedance spectra implied a single depressed capacitive semicircle, indicating that the steel dissolution is related to the charge transfer process [15]. In addition, the diameter of the Nyquist plot’s semicircle increases with the increasing concentration of *Eucheuma* extract. This phenomenon revealed that *Eucheuma* extract inhibits the corrosion process due to the electronegative charge of the heteroatoms contained in the extracts and the electropositive charge on the steel surface [16].

Electrical circuit model used to interpret EIS data. The suggested electrical circuit model for API 5L in 0.1M HCl and *Eucheuma* inhibitor is shown in Figure 7. The electrical circuit model in Figure 7 includes Rs as solution resistance, Rct as charge transfer resistance, and CPE as constant phase element. In this study, CPE was used instead of capacitance (C) for the circuit model due to all angles of phases are less than 90° based on Figure 5 [10]. CPE was introduced as “capacitance dispersion” that related to capacity of the material surface area of complex surface roughness and inhomogeneous reaction [17]. The CPE element has a fixed phase shift angle and its impedance describes the expression: ZCPE= 1/Y₀(jω)ⁿ, where Y₀ and ‘a’ are the parameters related to the shift phase angle [18].

Figure 8 depicts the charge transfer resistance value obtained using the fitting of the electrical circuit model. Charge transfer resistance (Rct) value increase with the increase of inhibitor concentration, as shown in Figure 8. Holding time also increases the Rct value. The increasing Rct value indicates that charge transfer from solution to the steel surface and vice versa inhibited by more inhibitor concentration [17].
3. Thermodynamics of the Electrochemical Process

The thermodynamics result of the electrochemical process at various temperature and concentration are listed on the Table 2. The 500 ppm *Eucheuma* inhibitor at 50°C shows superior inhibition as it has the greatest surface coverage area (0.964).

It has been reported that organic inhibitors are absorbed on the metal surface and adsorption are fitted with Langmuir adsorption isotherms and prevents corrosion. The fundamental details of *Eucheuma* inhibitor also were explored using Langmuir adsorption isotherm, according to the following equation:

$$ \frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + \frac{C_{inh}}{K_{ads}} \tag{2} $$

where $\theta$ equals to $\eta/100$, $K_{ads}$ is the equilibrium constant of the adsorption process, and $C_{inh}$ represents to the inhibitor concentration. Figure 9 depicts plot $C_{inh}$ vs $C_{inh}/\theta$ based on Equation (2). The intercept of this plot represents the $K_{ads}$ value. Figure 9 reveals that *Eucheuma* inhibitor follows the Langmuir adsorption inhibitor because the high value of $R^2$. Therefore, it can be described that the molecules of *Eucheuma* inhibitor are absorbed in a single-layer on the metal surface.
TABLE 2. Thermodynamic parameters

| T (K) | Cinh (ppm) | θ   | Kads (L/mol) | ∆G (kJ/mol) | ∆H (kJ/mol) | ∆S (J/mol) |
|-------|------------|-----|--------------|-------------|-------------|-------------|
|       |            | 298 | 200          | 0.856       | 0.023       | -24.84      |
|       |            | 400 | 0.915        | 66          | 0.023       | -24.84      |
|       |            | 500 | 0.920        | 66.12       | 0.023       | -24.84      |
| 313   | 200        | 0.827|              | 14.82       | 133         |
|       | 400        | 0.954|              | -26.74      | 14.82       | 133         |
|       | 500        | 0.962|              | -26.74      | 14.82       | 133         |
| 323   | 200        | 0.855|              | 14.82       | 133         |
|       | 400        | 0.963|              | -26.74      | 14.82       | 133         |
|       | 500        | 0.964|              | -26.74      | 14.82       | 133         |

\[ \Delta G = -R \cdot T \cdot \ln (10^5 \cdot K_{ads}) \]  
\[ \ln K_{ads} = \ln \frac{1}{C_{solvent}} - \frac{\Delta H}{R \cdot T} + \frac{\Delta S}{R} \]  

\( \Delta H \) and \( \Delta S \) are slope and intercept of \( \ln K_{ads} \) vs \( T^{-1} \) curve respectively. These two parameters are presented in Table 2. The positive value of \( \Delta H \) indicates an increase in irregularities due to desorption of \( H_2O \) molecules from surface and adsorption of the inhibitors molecules in each site [3]. The positive amount of entropy elicits that the thermal stability of the film increases at elevated temperature and their irreversibility process [20].

3. 4. FTIR Test Results

The FTIR of the *Eucheuma* extract is represented in Figure 10. A broad peak with the wavenumber value of 3372.68 cm\(^{-1}\) has corresponded to OH bonds. Besides, the strong peak of 2922.28 and 2856.7 cm\(^{-1}\) are related to the binding of C-H group. It is also clear that the peaks at 1729.26 and 1631.85 cm\(^{-1}\) are related to the vibrational mode of the bindings of C=O and C=C, respectively. The wavenumber values of 1452.46 and 1412.92 cm\(^{-1}\) are depicted the bond of O-H. The peak at 1167.95 and 1049.32 cm\(^{-1}\) belonged to C-O.

Consequently, it can be concluded that *Eucheuma* extract contained elements of O, H, and C with a cyclic group of carbon or polyphenol compound which attracted the steel substrates according to have free electrons. This behavior could justify the decrease in the corrosion rate of API 5L substrate in HCl solution in the presence of *Eucheuma* extract as a green inhibitor.
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چکیده
با توجه به موضوع شیمی سبز و چشم انداز پایداری انسان، یک بازدارنده خوردگی جدید برای فولاد کربنی API 5L از جلبک جلبک دریایی Eucheuma مورد بررسی قرار گرفت. عملکرد بازدارنده عصاره Eucheuma با اندازه‌گیری‌های الکتروشیمیایی مانند قطبش پتانسیودینامیک و طیف‌سنجی امپدانس الکتروشیمیایی (EIS) به کار گرفت. نتایج امپدانس الکتروشیمیایی Eucheuma در محیط اسید هیدروکلریک API 5L نشان داد که عصاره Eucheuma یک بازدارنده خوردگی کارآمد در کاهش حملات خوردگی فولاد کربنی API 5L در محیط تهاجمی فراوان بوده، از جمله غلظت عصاره و زمان نگهداری اصلی عصاره ی Eucheuma به کار گرفته شد. نتایج نشان داد که عصاره Eucheuma به عنوان یک بازدارنده خوردگی کربنی API 5L می‌تواند به عنوان یک بازدارنده خوردگی نوع کاتدی و بسیار موثر در محیط‌های تهاجمی فراوان مورد استفاده قرار گیرد. مشخص شد که عصاره Eucheuma یک بازدارنده خوردگی نوع مخلوط است که هم‌اکنون در اندونزی راه می‌یابد. در نهایت، این مطالعه نشان داد که عصاره Eucheuma یک بازدارنده خوردگی نوع مخلوط در محیط‌های تهاجمی فراوان مورد استفاده قرار می‌گیرد و می‌تواند به عنوان یک بازدارنده خوردگی نوع مخلوط در محیط‌های تهاجمی فراوان مورد استفاده قرار گیرد.