***Sargassum* seaweed extract as a novel green corrosion inhibitor for API-5L carbon steel**

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Abstract

Sargassum extract was studied as a novel green corrosion inhibitor against the corrosion of API-5L carbon steel in 0.1 M HCl solution. The inhibiting action of this extract was investigated using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). In addition, FTIR was employed to identify the main compound of *Sargassum* extract. The *Sargassum* extract was prepared by the maceration process. The maceration process takes 72 h to produce the filtrate. To obtain the *Sargassum* extract, the filtrate that resulted from the maceration process was evaporated. The inhibitor concentration was varied from 50 ppm, 100 ppm, 200 ppm, 400 ppm, to 500 ppm. Furthermore, the temperature and exposure time were also varied to determine their effect on the inhibitor efficiency. The temperature was varied as follows: room temperature, 40°C, and 50°C. The specimens were measured with two conditions, *i.e.*, with and without pre-exposure for 30 min. The inhibitor efficiency increased when inhibitor concentration, temperature, and exposure time increased according to the polarization test results. Interestingly, *Sargassum* extract (500 ppm) manifested inhibition efficiency up to 95% with 30 min exposure time. Moreover, the presence of aromatic rings (C=C), hydroxide (O–H), and organic compounds (C–H) was confirmed by FTIR. The results indicate that *Sargassum* seaweed extract is a good green corrosion inhibitor.

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Introduction

API-5L carbon steel is the most adopted material in industries owing to its outstanding mechanical properties, low cost, and ease of supply [1]. However, API-5L carbon steel is prone to corrosion attack, especially in acid environments [2]. Corrosion of a metal is the degradation due to reactions with its environment [3, 4]. Corrosion can be controlled by modifying the environment by addition of an inhibitor [5, 6].

A corrosion inhibitor is a chemical substance that reduces the corrosion rate [7]. Recently, the development of green inhibitors has attracted enormous attention because the use of inorganic inhibitors, particularly those containing phosphate, chromate, and other heavy metals, is now being gradually restricted by environmental regulations [8, 9]. In

addition, the use of synthetic organic inhibitors is now being limited due to their toxicity and high cost of manufacturing [10].

Green corrosion inhibitors are biodegradable and do not contain toxic or heavy metals [11]. In this study, *Sargassum* seaweed was used for the first time as a green corrosion inhibitor to decrease the corrosion rate of API-5L and take advantage of the massive amounts of this biomass, which has been found in recent years on the beach coasts of Indonesia [12]. The aim of this research was to evaluate *Sargassum* extract as a novel green corrosion inhibitor under potentiodynamic polarization, electrochemical impedance (EIS), and FTIR studies. Further, the effects of temperature, concentration, and exposure time on the inhibition efficiency were compared.

Materials

API-5L carbon steel with the chemical composition (wt.%: C = 0.05; Si = 0.13; Mn = 0.73; P = 0.02; S = 0.004; Fe – remainder) was utilized to prepare the specimens used in this work. The microstructure of API-5L carbon steel is shown in Figure 1. API-5L carbon steel was cut into $1 \times 1 \text{ cm}^2$ pieces and then connected with a cable wire. Prior to exposure in the HCl solution, the specimens were mounted with a resin and abraded using 120–1200 grit silicon carbide emery paper.

Figure 1. Microstructure of API-5L carbon steel.

Sargassum extract and solution

Sargassum extract was prepared via the maceration process. Prior to the maceration process, *Sargassum* was cleaned with tap water then dried for five days at room temperature. The dried *Sargassum* was chopped and collected in 70% of ethanol (maceration process) for 72 h at a *Sargassum*:ethanol ratio of 1:3. The maceration result was filtered and evaporated to

obtain the extract. FTIR was employed to determine the compounds present in the *Sargassum* extract.

Hydrochloric acid (HCl) 0.1 M was used as a solution in this experiment. *Sargassum* extract with concentrations from 0, 50, 100, 200, 400, to 500 ppm was added to 0.1 M HCl. All specimens were immersed in the solution with and without exposure for 30 min before the test. The temperature of the solution was also varied (room temperature, 40°C, and 50°C) to study the effect of temperature on the corrosion rate.

Potentiodynamic polarization and EIS test

Potentiodynamic polarization and EIS tests were performed using a Gamry G-750 Corrosion Monitoring System in a typical three-electrode cell [13]. The cell components were a standard calomel electrode (SCE) as a reference electrode, a platinum counter electrode, and a previously mounted API-5L specimen as a working electrode. All electrodes were immersed in 0.1 M HCl with and without *Sargassum* extract during the test. Potentiodynamic polarization was performed in the potential range from –250 mV to +250 mV vs the established electrode potential at a scan rate of 1 mV/s. The EIS tests were conducted in the frequency range from 100 kHz to 10 mHz with an amplitude of 10 mV.

Result and Discussion

Potentiodynamic polarization measurements

Figures 2–4 display the potentiodynamic polarization curves of API-5L in 0.1 M HCl with and without the inhibitor at different concentrations and temperatures. It is seen that the corrosion potential (E_{corr}) tends to become a little nobler upon increasing the inhibitor concentration according to the polarization curves recorded without preliminary exposure (Figures 2(a)–4(a)). However, polarization curves recorded after 30 min exposure (Figures 2(b)–4(b)) show that the potential is nearly the same at various inhibitor concentrations due to the adsorption of the inhibitor. The similar values of the corrosion potential upon increasing inhibitor concentration indicated that *Sargassum* extract is a mixed-typed corrosion inhibitor [6].

Based on Figures 2–4, the corrosion current density (I_{corr}) decreases on increasing the inhibitor concentration. This proves that *Sargassum* extract can improve the corrosion resistance of API-5L in an acid medium [14]. Furthermore, the smallest corrosion current density (I_{corr}) is seen on the polarization curve with 500 ppm of the inhibitor and 30 min exposure time. Therefore, at 500 ppm and 30 min exposure time, the corrosion rate of API-5L is lower than in the other cases due to adsorption of *Sargassum* extract that inhibits the corrosive attack [15].

Table 1 lists the electrochemical parameters obtained from the polarization curves at room temperature. From Table 1, the corrosion current density is directly proportional to the corrosion rate. The corrosion current density and corrosion rate decrease with an increase in the inhibitor concentration. In addition, 30 min of exposure give *Sargassum* extract

sufficient time to adsorb on the API-5L surface. Thus, the corrosion rate after 30 min of exposure is lower than that without the exposure.

Figure 2. Potentiodynamic polarization curves of API-5L in 0.1 M HCl and various inhibitor concentrations at room temperature (a) without exposure and (b) with exposure for 30 min.

Figure 3. Potentiodynamic polarization curves of API-5L in 0.1 M HCl and various inhibitor concentrations at 40°C (a) without exposure and (b) with exposure for 30 min.

Figure 4. Potentiodynamic polarization curves of API-5L in 0.1 M HCl and various inhibitor concentrations at 50°C (a) without exposure and (b) with exposure for 30 min.

Table 1. Electrochemical parameters obtained from polarization curves at room temperature.

Inhibitor concentration (ppm)	Without exposure			Exposure for 30 min		
	E_{corr} (mV)	I_{corr} (A/m ²)	Corrosion rate (mpy)	E_{corr} (mV)	I_{corr} (A/m ²)	Corrosion rate (mpy)
0	−532	$6.65 \cdot 10^{-4}$	304.70	−532	$6.65 \cdot 10^{-4}$	304.70
50	−528	$4.91 \cdot 10^{-4}$	224.90	−506	$2.30 \cdot 10^{-4}$	105.50
100	−523	$4.05 \cdot 10^{-4}$	185.70	−500	$1.01 \cdot 10^{-4}$	48.70
200	−491	$1.52 \cdot 10^{-4}$	69.39	−482	$9.99 \cdot 10^{-4}$	45.78
400	−488	$1.14 \cdot 10^{-4}$	52.20	−496	$4.09 \cdot 10^{-4}$	18.73
500	−475	$8.76 \cdot 10^{-5}$	40.12	−506	$3.30 \cdot 10^{-4}$	15.12

The inhibitor efficiency can be calculated from corrosion rate data using Equation 1 [16].

$$\text{Inhibitor Efficiency (\%)} = \frac{CR - CR_{\text{in}}}{CR} \cdot 100\% \quad (1)$$

Where CR is corrosion rate without the inhibitor and CR_{in} is the corrosion rate with the inhibitor. Figure 5 illustrates the inhibitor efficiency for all the specimens. According to Figure 5, the inhibitor concentration, exposure time, and temperature boost the inhibitor efficiency. The efficiency of *Sargassum* extracts is up to 95% at an inhibitor concentration of 500 ppm and an exposure time of 30 min. An increase in temperature accelerates the corrosion process as indicated by the increase in the corrosion rate. However, the inhibitor efficiency also increases with increasing temperature because temperature improves the surface chemisorption of *Sargassum* inhibitor [17].

Figure 5. Inhibitor efficiency.

EIS test

Besides potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) was employed to investigate the inhibition performance of *Sargassum* extract. Figures 6–8 show the Nyquist plots of API-5L in 0.1 M HCl at various inhibitor concentrations and temperatures that resulted from the EIS test. It can be seen that the diameter of the semicircle increases with an increase in inhibitor concentration and the existence of exposure at each temperature. The diameter of the semicircle on the Nyquist plot represents the impedance of the system [18, 19] – the greater the impedance, the lower the corrosion rate. Therefore, the corrosion resistance of API-5L boosts with increasing inhibitor concentration and exposure time.

Figure 6. Nyquist plot of API-5L in 0.1 M HCl with various inhibitor concentrations at room temperature.

Figure 7. Nyquist plot of API-5L in 0.1 M HCl with various inhibitor concentrations at 40°C.

Figure 8. Nyquist plot of API-5L in 0.1 M HCl with various inhibitor concentrations at 50°C.

To obtain more details on the electrochemical processes taking place during the test, an equivalent electrical circuit (Figure 9) was used to fit the Nyquist plot shown in Figure 6–8. The equivalent electrical circuit is composed of solution resistance (R_s), charge transfer resistance (R_{ct}), and a constant phase element (CPE). The CPE element includes Y_0 and “ α ” as the shift phase angle parameter [20]. The charge transfers resistances (R_{ct}) of all the specimens displayed in Figure 10. The value of R_{ct} reveals the total corrosion resistance performance [21]. According to Figure 10, the R_{ct} value increases with increasing inhibitor concentration and with pre-exposure.

Figure 9. Equivalent electrical circuit.

Figure 10. R_{ct} value.

FTIR result

Figure 11 shows Fourier Transform Infrared (FTIR) spectra of *Sargassum* seaweed extract. The intense peaks close to 2923, 2856, and 1457 cm^{-1} are associated with the stretching vibrations of the C–H bond. The absorption peaks at 1561 and 721 cm^{-1} are attributed to the C=C bond. The two bands at 3381 and 3339 cm^{-1} correspond to O–H. In addition, the peak at 1171 cm^{-1} is related to C–O. Finally, the presence of C=O bonds is testified by the stretching vibrations occurring at a wavenumber of 1734 cm^{-1} . Hence, *Sargassum* extract contains O, C, and H elements with asymmetric methyl and aromatic rings, which are attracted to the metal surface due to the existence of free electrons.

Figure 11. FTIR spectra of *Sargassum* seaweed extract.

Conclusion

Sargassum seaweed extract inhibits the corrosion of API-5L carbon steel in the acid medium based on potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) results. The concentration of *Sargassum* extract, temperature, and exposure time improve the efficiency of the inhibitor, with the highest value up to 95%. According to EIS, the impedance or R_{ct} also increase with an increase in inhibitor concentration. Furthermore, *Sargassum* seaweed extract includes the organic compound, aromatic and asymmetric methyl functional group based on FTIR results. Therefore, *Sargassum* seaweed was successfully used for the first time as a green corrosion inhibitor for API-5L carbon steel.

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