Study of curcuma xanthorrhiza extract as green inhibitor for API 5L X42 steel in 1M HCl solution

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Abstract. The inhibitory effects of *Curcuma xanthorrhiza* extract on the corrosion of API 5L X42 steel in 1M HCl solution was investigated by using weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy methods. In this study the concentration of *C. xanthorrhiza* extract used was 100, 250, 500, and 1000 ppm. The results show that *C. xanthorrhiza* inhibit the steel corrosion and acted as mixed type inhibitors. The corrosion rate decreased with the increasing of inhibitors concentrations. At the same time, inhibition efficiency increased with the increase of inhibitors concentrations. The adsorption of the extract on the steel surface was found to obey Langmuir’s adsorption isotherm. The free energy value (ΔG_{ads}) indicated that the adsorption of the inhibitor molecules was typical of physisorption. It can be concluded that *C. xanthorrhiza* extract could be used as an alternative and environmental friendly inhibitor for API 5L X42 steel in acidic environment.

1. Introduction

Carbon steels are widely used in petroleum industry, chemical processing, marine applications, chemical processing, mining and metal processing equipment. The type of carbon steel commonly used on the oil and gas industry is API 5L. One reason the use of carbon steel as pipe is because the price that is considered relatively cheaper than the other type of steel. However, the low corrosion resistance of carbon steel will cause corrosion that can lead to damage with more expensive repairs cost [1]. The corrosion inhibitor is one of the best options for corrosion prevention in a closed-loop system. Corrosion inhibitors mostly come from organic and inorganic compounds containing groups which have free electron pairs such as nitrite, chromate, fospat, urea, phenylalanine, imidazoline, and amine compounds. Synthetic chemicals such as phosphate and chromate are not only expensive but also harmful to humans and the environment. Therefore, researchers have conducted research on eco-friendly corrosion inhibitors from plant extracts such as morinda citrifolia [2] and purple sweet potato extracts [3]. One of the plant extract in Indonesia that contains antioxidant substances is “temulawak” (*C. xanthorrhiza*) [4]. So, in the present study, *C. xanthorrhiza* extract was investigated as green inhibitors of API 5L X42 steel corrosion in 1 M HCl using weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy measurements. The adsorption isotherm was also studied.
2. Materials and method

2.1. Preparation of Steel Specimen
In this research, API 5L X42 steel with a chemical composition (wt%) of 0.178% C, 0.270% Si, 0.519% Mn, 0.014% P, 0.005% Ni, 0.012% Cu and Fe balance was used. The steel specimens were abraded using 80 to 600 grades of abrasive papers. The specimens were well cleaned using distilled water and then again by acetone. The steel specimens with a specific size (30 x 20 x 5 mm) were used for the weight loss method and another specific size (10x10x6 mm) were used for the electrochemical studies.

2.2. Preparation of Test Solution
The test solution was 350 ml 1M HCl, which was prepared by the dilution of technical grade 32% m/v HCl with distilled water. Curcuma xanthorrhiza extracts were added to the acid solution at the varied concentrations 100, 250, 500, and 1000 ppm, and the solution in the absence of inhibitor was taken as blank for comparison purposes.

2.3. Weight Loss Measurement
In the weight loss measurements test, each sample was immersed in 350 ml 1M HCl containing inhibitors with the concentrations of 0 ppm (blank), 100 ppm, 250 ppm, 500 ppm, and 1000 ppm. The sample was immersed for 7 days. Then the corrosion rate was calculated using Eq. 1

\[ CR (\text{mm/yr}) = \frac{87.6 \times w}{D \times A \times t} \]  

(1)

Where, \( w \) is calculated from the initial weight minus the final weight (mg), \( A \) is the specimen area (cm\(^2\)), \( t \) is the immersion time (hour) and \( D \) is the density of steel in gcm\(^{-3}\).

The Inhibition efficiency (IE) was calculated using Eq. 2

\[ IE (%) = \frac{CR - CR'}{CR} \times 100 \]  

(2)

Where, \( CR' \) and \( CR \) are the corrosion rate of steel with and without inhibitor.

2.4. Potentiodynamic Polarization Measurement
Autolab PGSTAT302N instrument equipped with Nova 1.10 software was used for the electrochemical measurements by recording Tafel polarization curve. All measurements were done using a 150 ml corrosion cell in which a reference electrode (Ag/AgCl electrode), a counter electrode (C electrode), a working electrode (API 5L X42). Potentiodynamic polarization testing was performed using a scanning rate of 0.01 Vs\(^{-1}\) and an open circuit potential (OCP) reading was performed for 120 seconds. The IE was calculated using Eq. 3

\[ IE (%) = \frac{i_{\text{corr}} - i'_{\text{corr}}}{i_{\text{corr}}} \times 100 \]  

(3)

Where, \( i_{\text{corr}} \) and \( i'_{\text{corr}} \) are current densities (A) of corrosion with and without the inhibitors, respectively.

2.5. Electrochemical Impedance Spectroscopy Measurements
The electrochemical experiments were performed using the PGSTAT302N instrument which was installed GPES and FRA software provided by Autolab. EIS testing was performed using an AC signal with the amplitude of 0.01 and with a frequency range from 0.1 kHz to 10 MHz. This test produces a Nyquist diagram that formed a semicircle graph. The inhibition efficiency (IE) was calculated from the electrochemical impedance diagrams, as described by Eq. 4

\[ IE (%) = 100 \left(1 - \frac{R_p}{R_p'} \right) \]  

(4)
Where, $R_p$ is the polarization resistance ($\Omega$) with inhibitor, and $R_p'$ is the polarization resistance ($\Omega$) without inhibitor.

3. Result and Discussion

3.1. Weight Loss Measurement

The effect of *C. xanthorrhiza* extract addition on the corrosion of API 5L X42 in 1M HCl solution was studied by weight loss measurements after 7 days of immersion period. And the calculation results of inhibition efficiency and corrosion rate are summarized in Table 1.

| Inhibitor Concentration (ppm) | $W_o$ (g) | $W_i$ (g) | Weight Loss (g) | Corr Rate (mm/yr) | IE (%) |
|------------------------------|----------|----------|----------------|-----------------|-------|
| 0                            | 32.7397  | 31.2029  | 1.5368         | 5.86            | 0     |
| 100                          | 33.0140  | 32.6527  | 0.3613         | 1.37            | 76    |
| 250                          | 28.0764  | 27.8226  | 0.2538         | 0.97            | 83    |
| 500                          | 31.8669  | 31.6500  | 0.2169         | 0.83            | 86    |
| 1000                         | 31.4752  | 31.3373  | 0.1379         | 0.50            | 91    |

Table 1 shows that the corrosion rate values were decreased with the increasing of inhibitor concentrations. This indicates that increased concentration will increase the surface area of metal covered by *C. xanthorrhiza* extract, resulting in a decrease in corrosion rate of steel to reach its lowest value, ie 0.50 mm/yr. While the highest IE value reached 91% occurred when the concentration of *C. xanthorrhiza* extract is 1000 ppm. This phenomenon can occur due to steel surface was covered by the curcumin molecule of *C. xanthorrhiza* extract, via an adsorption mechanism. Therefore, the redox reactions between the steel surface with the acid will be inhibited and corrosion can be prevented. That is why, it can be said that xanthorrhiza extract can be used to protect the API 5L X42 steel in 1M HCl solution.

3.2. Potentiodynamic Polarization Measurement

Figure 1 show the Tafel polarization curve of API 5L X42 steel in 1 M HCl with different concentrations of *C. xanthorrhiza* extract. The extrapolation of anodic and cathodic lines were used to determine various electrochemical parameters such as anodic and cathodic Tafel slopes ($ba$ and $bc$), potential ($E_{corr}$), and current density of corrosion ($i_{corr}$) as given in Table 2. Table 2 shows the $i_{corr}$ value decreases with increasing *C. xanthorrhiza* extract concentrations. As shown by Figure 1, the inhibitors affects both the cathodic and anodic parts of the Tafel curves, and decreases both the cathodic and anodic current densities. Therefore, the presence of *C. xanthorrhiza* extract inhibits the hydrogen evolution and the anodic dissolution processes [5]. This result indicates that the *C. xanthorrhiza* extract act as mixed type corrosion inhibitors. In addition, the maximum displacement in $E_{corr}$ was 32.59 mV. This results show that *C. xanthorrhiza* extract act as mixed type inhibitors since the displacement of $E_{corr} < 85$ mV.
The results obtained by potentiodynamic polarization measurements show that \textit{C. xanthorrhiza} extract are effective inhibitors against API 5L X42 steel corrosion in 1 M HCl. The IE increases with the increase in the \textit{C. xanthorrhiza} extract concentrations to attain 97% at 1000 ppm. These result is in accordance with the results indicated by weight loss measurements.

**Table 2.** Polarization parameters of API 5L X42 steel in 1 M HCl without and with different concentrations of \textit{C. xanthorrhiza} extract.

| Inhibitor Concentration (ppm) | \(ba\) (mV/dec) | \(bc\) (mV/dec) | \(E_{corr}\) (mV) | \(i_{corr}\) (\(\mu\)A) | Corr Rate (mm/yr) | IE (%) |
|-------------------------------|----------------|----------------|------------------|-----------------------|-----------------|--------|
| 0                             | 35.077         | 42.802         | -401.44          | 476.23                | 5.53            | 0      |
| 100                           | 6.2786         | 14.175         | -411.96          | 106.82                | 1.24            | 78     |
| 250                           | 12.644         | 14.949         | -418.81          | 66.795                | 0.78            | 86     |
| 500                           | 14.932         | 13.947         | -434.03          | 24.125                | 0.28            | 95     |
| 1000                          | 12.55          | 9.8129         | -432.91          | 12.69                 | 0.15            | 97     |

3.3. **Electrochemical Impedance Spectroscopy Measurement**

The Nyquist plot of API 5L X42 steel in 1 M HCl solution with different concentrations of \textit{C. xanthorrhiza} extract are shown in Figure 2. Various parameters obtained from impedance measurements as \(R_p\), \(R_c\), \textit{CPE}, \textit{N} and \textit{IE} are given in Table 3.
The \( R_p \) values increased with increasing the inhibitor concentration. Increasing of \( R_p \) values indicated the adsorption of the inhibitor molecules on metal surface form a protective electrochemical double layer. Furthermore, the formation of the protective double-layer may decrease the electron transfer between the metal surface and the corrosive medium. Finally, the corrosion was inhibited.

**Table 3.** EIS test results in the absence and presence of different concentrations of \( C. \) Xanthorrhiza extract.

| Inhibitor Concentration (ppm) | \( R_s \) (mΩ) | \( R_p \) (Ω) | CPE (μMho) | \( N \) | \( IE \) (%) |
|------------------------------|----------------|--------------|------------|--------|------------|
| 0                            | 642            | 14.6         | 1720       | 0.611  | 0          |
| 100                          | 519            | 34.5         | 791        | 0.749  | 58         |
| 250                          | 843            | 80.7         | 605        | 0.772  | 82         |
| 500                          | 997            | 110          | 473        | 0.801  | 87         |
| 1000                         | 852            | 149          | 229        | 0.813  | 90         |

Table 3 shows that the values of CPE decrease with the increase in \( C. \) xanthorrhiza extract concentrations, which consequently may decrease the electrical capacity and/or increase in the thickness of the electrical double layer.

Table 3 shows a decrease in CPE values along with increased concentrations of \( C. \) xanthorrhiza extract, resulting in the decreasing of electrical capacity and / or increasing in the thickness of
electrical double layer [6]. This electrical double layer was formed by the C. xanthorrhiza extract adsorption at the metal-solution interface and replaced water molecules gradually [7].

The maximum IE value based on this EIS reaches 90% at 1000 ppm C. xanthorrhiza extract, and the EIS results are also in line with the results indicated by both polarization and weight loss data.

4. Conclusion
Curcuma Xanthorrhiza extract are good inhibitors for API 5L X42 in 1M HCl solution. The C. xanthorrhiza extract acts as a mixed type inhibitor where the reactions on both cathode and anode were inhibited by xanthorrhiza molecules adsorbing on the metal surface. A maximum efficiency 97% was obtained with the addition of inhibitor 1000 ppm in the potentiodynamic polarization studies. Weight loss method obtained 91% efficiency inhibition of 1000 ppm inhibitor in 7 days immersion time. EIS method obtained 90% efficiency inhibition of 1000 ppm inhibitor.

5. Acknowledgement
The authors wish to thank the Ministry of Research Technology and Higher Education and Directorate of Research and Community Engagement, Universitas Indonesia, under PITTA Research Grants Contract No. 790/UN2.R3.1/ HKP05.00/2017 for the financial support of this research.

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