

## The Effect of *Alyssum floribundum* Boiss. & Balansa (Brassicaceae) Leaves Extract on the Corrosion of Mild Steel in an Acidic Medium

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The purpose of this research was to examine how *Alyssum floribundum* Boiss. & Balansa can prevent the corrosion of mild steel. For this purpose, electrochemical measurements were taken in a 1 M H<sub>2</sub>SO<sub>4</sub> solution. The experimental results demonstrated that the extract of *Alyssum floribundum* had significant inhibitory effects. Based on the potentiodynamic polarization measurements, it was found that the inclusion of the inhibitor caused a shift in the corrosion potential towards negative values and reduced the current in both the cathodic and anodic potential regions. The highest inhibition efficiency (98%) was observed when a 1 M H<sub>2</sub>SO<sub>4</sub> solution was used, which contained 20 g l<sup>-1</sup> of plant extract. Based on the electrochemical impedance spectroscopy (EIS) measurements taken in the same solution, the polarization resistance was determined to be 827 ohm cm<sup>2</sup>. This finding shows that the extract of *A. floribundum* could adsorb on the surface of mild steel and protect the metal from corrosion. Polarization measurements were carried out at various temperatures between 27 °C and 60 °C to establish the temperature dependence and activation energy of the corrosion inhibition process. The inhibition efficiency decreased with an increase in the temperature of the corrosive medium. Furthermore, the activation energies were found to be 33.56 kJ mol<sup>-1</sup> in a 1 M H<sub>2</sub>SO<sub>4</sub> solution and 96.98 kJ mol<sup>-1</sup> in the presence of the inhibitor (1 M H<sub>2</sub>SO<sub>4</sub> + 20 g ml<sup>-1</sup>). It was observed that the Langmuir adsorption isotherm was suitable for the adsorption of *A. floribundum* leaf extract on the surface of mild steel in an acidic solution.

**Keywords:** Mild steel, Electrochemical impedance spectroscopy, Inhibitor, *Alyssum floribundum* leaves, Adsorption

### INTRODUCTION

Corrosion refers to the gradual degradation and deterioration of materials, typically metals, due to chemical or electrochemical reactions with their environment. It is a natural and electrochemical process that causes the metal to lose its structural integrity, strength, and appearance over time. In the context of the industry, corrosion is a significant concern as it can lead to substantial economic losses and safety hazards. Industries rely heavily on metals for building infrastructure, equipment, and machinery. Corrosion-induced damage can compromise the functionality of these assets, leading to costly repairs, replacements, and even

failures, which, in turn, causes production downtime and safety risks. Industries such as oil and gas, marine, automotive, aerospace, construction, and manufacturing are particularly vulnerable to the detrimental effects of corrosion [1]. It is estimated that corrosion costs hundreds of billions of dollars worldwide annually.

Steel is the most widely used metal in industry, so it is essential to protect it from corrosion. The main cause of steel corrosion is exposure to acid solutions, which are often used in industry to remove mill scale from metal surfaces [2-4]. Preventing and mitigating corrosion is critical in the industry. It is essential to maintain the reliability and longevity of equipment. Various corrosion prevention strategies are employed, such as the use of corrosion-resistant materials, coatings, inhibitors, cathodic protection systems, and regular

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inspection and maintenance routines. The most practical approach to prevent metal corrosion in acidic solutions is the utilization of inhibitors [5]. Inhibitors achieve this by adsorbing onto the metallic surface and interfering with the electrochemical reactions that drive the corrosion process. Thus, they play a critical role in reducing the rate of corrosion by effectively inhibiting both anodic and/or cathodic reactions. Corrosion is an electrochemical process that involves two main reactions: anodic (oxidation) and cathodic (reduction). Anodic reactions involve the dissolution of metal ions into the environment while cathodic reactions involve the reduction of another species, typically oxygen or hydrogen ions. Inhibitors function by adsorbing onto the metal surface and creating a barrier to protect it. This barrier prevents the reactants involved in the electrochemical reactions from reaching the metal surface and interfering with the corrosion process. By blocking these reactions, inhibitors effectively reduce the corrosion of steel and extend its life in industrial applications. In addition, corrosion reactions require reactants, such as water, oxygen, and other corrosive substances, to reach the metal surface. Inhibitors can slow down the rate of diffusion of these reactants to the metal surface, thus making it more difficult for corrosion to occur. In addition, inhibitors have the ability to form an insulative layer on the metal surface, which results in an increase in its electrical resistivity [6].

It is important to note that inhibitors can be either organic or inorganic and their effectiveness can vary depending on their properties, the specific metal, and the corrosive environment. Proper selection and application of inhibitors are essential to ensure the effective protection of metal assets against corrosion. When selecting an inhibitor, factors such as toxicity, environmental friendliness, and cost should be taken into account. Organic compounds containing O, S, and N groups have been proven to be effective inhibitors. However, many of these compounds are synthetic and highly toxic to both humans and the environment. For this reason, more studies have recently focused on the use of various environmentally friendly plant extracts as corrosion inhibitors [7-18]. Using plant extracts to reduce corrosion offers several advantages. They are not only readily soluble in acidic media [12] but also environmentally friendly and cost-effective compared to synthetic organic compounds.

The presence of heterocyclic constituents, such as

alkaloids and flavonoids, in plant extracts is believed to contribute to their corrosion inhibition activity. Additionally, tannins, cellulose, and polycyclic organic compounds can form a protective layer on metals, shielding them against corrosion [14]. These phytochemicals consist of numerous electron-rich polar functional groups and multiple bonds, which facilitate their adsorption on metallic surfaces. As a result, they can effectively protect the metals from corrosion [15]. A thorough literature review led to the identification of relevant studies on natural extract-based corrosion inhibitors and their potential applications. Kaya *et al.* [16] investigated the corrosion inhibition effect of aqueous extracts of *Rheum ribes* extract and found promising results for mild steel in acidic environments. Singh *et al.* [17] explored the corrosion-inhibitory effects of *Aloe vera* gel on mild steel and reported its effectiveness in reducing the corrosion rate under acidic conditions. In addition, simulation studies have provided valuable understanding of how to prevent corrosion. For instance, Thakur *et al.*'s [18] study on the interaction between Vicia Sativa weed aerial extract and metal surface shed light on the adsorption behaviour and inhibition efficiency of the plant.

In this study, the extract of *A. floribundum*, a plant species known for its metal accumulation properties, was used as a corrosion inhibitor. *A. floribundum* belongs to the genus *Alyssum* in the Brassicaceae family [19-21]. Certain species of *A. floribundum* have been found to accumulate nickel in approximately 3% of the leaf dry mass, indicating its potential economic value. Metal accumulation in plants can occur through the formation of thiolate compounds, facilitated by cysteine-rich peptides. Cysteine (Cys, C) is one of the 20 amino acids found in proteins and contains a sulphur group in its side chain. Sulphur compounds have a strong affinity for metals. Therefore, the aim of this study was to investigate the inhibitory potential of *A. floribundum* extract on mild steel corrosion.

## EXPERIMENTAL

The aim of this study was to investigate the corrosion inhibition properties of *A. floribundum* extract on mild steel in a corrosive medium containing 1 M H<sub>2</sub>SO<sub>4</sub>. A three-electrode cell setup was used to conduct the experiments. The working electrode consisted of cylindrical mild steel rods cut

into 5 cm lengths with a surface area of 1 cm<sup>2</sup> and a balanced specific chemical composition (wt%) of C: 0.125-0.300, Mn: 0.57-0.62, Si: 0.03, P: 0.012-0.018, S: 0.039-0.045, and Fe. To prepare the working electrode, the mild steel rods were coated with polyester, leaving the base exposed. Before each use, the mild steel electrode was ground with 1200 g sandpaper. After etching, the electrodes were washed with distilled water and ethanol to ensure a clean surface. Immediately before the electrochemical measurements, the electrode was washed again with distilled water. In the experimental setup, a platinum (Pt) plate (1 cm<sup>2</sup>) was used as the counter electrode and an Ag/AgCl electrode as the reference electrode. The corrosive medium used was 1 M H<sub>2</sub>SO<sub>4</sub>, and different amounts (20, 15, 10, and 5 g l<sup>-1</sup>) of *A. floribundum* leaf extract were added to the solution to test the inhibitory effects. *A. floribundum* leaf samples were collected from the Müğlü stream, located at 36°49' N, 034°19' E in the vicinity of İçmeler, C5 Mersin, Turkey.

The inhibitor solution was prepared from the leaf samples as follows:

- 1- The leaf samples were cleaned with distilled water;
- 2- Then, the washed leaf samples were dried at 100 °C for 24 h;
- 3- After drying, 20 g of the dried leaf samples were ground to a fine powder;
- 4- The ground leaf sample (20 g) was boiled in 1 l of 1 M H<sub>2</sub>SO<sub>4</sub> (sulphuric acid) for 1 h using a Soxhlet extraction apparatus;
- 5- After boiling, the extract obtained was allowed to cool. After cooling, it was filtered to remove any solid residue;
- 6- To compensate for the loss of water during the boiling process, the volume of the filtered solution was adjusted back to 1 l.

The final solution obtained after these steps was used as the stock inhibitor solution. This stock inhibitor solution was used without dilution in the experiments and diluted to the desired concentrations using 1 H<sub>2</sub>SO<sub>4</sub> acid.

The electrochemical measurements in this study were carried out using a Gamry ZRA 600 series electrochemical instrument equipped with the 5.8 software package. Two main techniques, electrochemical impedance spectroscopy (EIS) and potentiodynamic polarisation, were used to determine the corrosion process of mild steel in inhibitor-free and inhibitor-enhanced media. To determine the polarisation

resistance (R<sub>p</sub>) of mild steel, linear polarisation curves were generated by sweeping the electrode potential ±10 mV around the open circuit potential (E<sub>corr</sub>). The sweep rate used for this measurement was 0.5 mV s<sup>-1</sup>, and the slope of the resulting current-potential curve provided the polarisation resistance value, which was indicative of the corrosion behaviour of mild steel. In order to provide a more comprehensive analysis of the corrosion process, potentiodynamic polarisation curves were recorded by scanning ±300 mV around the corrosion potential (E<sub>corr</sub>). A scan rate of 5 mV s<sup>-1</sup> was used to allow the researchers to study the corrosion behaviour of mild steel both in the presence and absence of the inhibitor.

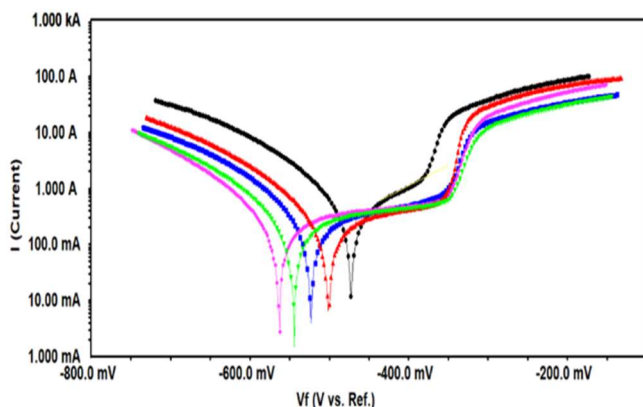
EIS measurements were performed in the frequency range of 2 MHz to 3 × 10<sup>-2</sup> Hz, with an amplitude of 5 mV at open circuit potential. EIS is a useful technique for understanding the impedance behaviour of a system and gives information on the kinetics and mechanisms of corrosion inhibition.

To examine how temperature could impact the corrosion of mild steel, the researchers conducted potentiodynamic polarisation measurements at various temperatures, ranging from 27 °C to 60 °C. This range of temperatures helped determine the activation energy needed for the corrosion reaction of mild steel, providing more insight into the thermodynamics and kinetics of the corrosion process in both inhibitor and non-inhibitor conditions.

## RESULTS AND DISCUSSIONS

### Potentiodynamic Polarization Measurements

Figure 1 shows the polarisation curves of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> solution without inhibitor and with different inhibitor concentrations (20, 15, 10, and 5 g l<sup>-1</sup>). Table 1 shows the kinetic parameters such as corrosion potential (E<sub>corr</sub>), corrosion current (i<sub>corr</sub>), anodic and cathodic Tafel slope (β<sub>a</sub> and β<sub>c</sub>), and inhibition efficiency (IEI) of mild steel obtained from the above current-potential curves. According to the experimental results, it was clear that the addition of inhibitors shifted the corrosion potential towards negative values and reduced the current in the cathodic and anodic potential regions (as shown in Fig. 1). However, the decrease in the current was more pronounced in the cathodic region, indicating the inhibition of the cathode reaction. The impact



**Fig. 1.** Polarization curves of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> in the absence (●-blank) and presence of the inhibitor (extracts of ▲-5 g l<sup>-1</sup>, ■- 10 g l<sup>-1</sup>, ▼-15 g l<sup>-1</sup>, and ◆-20 g l<sup>-1</sup> *A. floribundum* leaves).

of the inhibitor became stronger with an increase in its concentration.

In the cathodic region, the current changes with potential corrosion resulted in parallel Tafel lines, indicating that the cathodic reaction was activation-controlled. In an acidic solution, a hydrogen reduction reaction takes place at the cathode. The β<sub>c</sub> value did not change significantly upon the addition of the inhibitor (as shown in Fig. 1 and Table 1), suggesting that the mechanism of the cathodic reaction remained unaltered by the *A. floribundum* leaves extract. This phenomenon can be attributed to the barrier effect of inhibitor molecules, which hinder the access of hydrogen ions to the metal surface for reduction. On the other hand, the current decreased in the anodic side of the polarization curves as did the anodic Tafel slopes (β<sub>a</sub>) in the presence of

*A. floribundum* leaves extract (Table 1). The modification of the anodic reaction, which involved mild steel dissolution, can be responsible for the change in the anodic slope. Therefore, it can be stated that the *A. floribundum* leaves extract acts as a corrosion inhibitor in both the anodic and cathodic regions, with a greater effect observed in the latter region. These observations suggest that the *A. floribundum* leaves extract functions as a mixed-type inhibitor.

The Stern-Geary equation, used to calculate the corrosion current (*i*<sub>corr</sub>), was given by Eq. (1):

$$i_{corr} = \left( \frac{1}{R_{pl}} \right) \left( \frac{\beta_a \beta_c}{\beta_a + \beta_c} \right) \quad (1)$$

where *R*<sub>pl</sub> is the polarization resistance determined by scanning the working electrode (± 10 mV) and corrosion potential (*E*<sub>corr</sub>) with a 0.5 mV s<sup>-1</sup> scan rate in all corrosive media (Table 1). Equation (1) allowed the estimation of the corrosion current based on the Tafel slopes, corrosion potential, and other parameters related to the electrochemical behaviour of the system. The concentration of the inhibitor was found to have a decreasing effect on the corrosion current (*i*<sub>corr</sub>).

The inhibition efficiency (IE<sub>1</sub>) of *A. floribundum* leaves extract on mild steel corrosion was calculated using the corrosion currents (*i*<sub>corr\_inhibited</sub> (*i*<sub>corr</sub>) and *i*<sub>corr\_uninhibited</sub> (*i*<sub>corr</sub><sup>0</sup>)) obtained for inhibited and uninhibited mild steel corrosion in 1 M H<sub>2</sub>SO<sub>4</sub> at 300 K. The formula used to calculate the inhibition efficiency was as follows:

$$IE_1 = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100 \quad (2)$$

**Table 1.** Electrochemical Parameters of Inhibition of Mild Steel Corrosion Obtained from the Polarization Measurements in 1 M H<sub>2</sub>SO<sub>4</sub> Containing Different Inhibitor Concentrations

| Concentration (g l <sup>-1</sup> ) | <i>E</i> <sub>corr</sub> (mV/Ag,AgCl) | <i>i</i> <sub>corr</sub> (mA cm <sup>-2</sup> ) | ba (dec/V) | bc (dec/V) | IE <sub>1</sub> % | R <sub>p</sub> (ohm) |
|------------------------------------|---------------------------------------|---|------------|------------|-------------------|----------------------|
| Blank                              | -473                                  | 8.1 × 10 <sup>-2</sup>                          | 7.21       | 14.88      | -                 | 60                   |
| 5                                  | -504                                  | 8.2 × 10 <sup>-3</sup>                          | 3.57       | 15.42      | 90                | 353                  |
| 10                                 | -521                                  | 4.9 × 10 <sup>-3</sup>                          | 2.94       | 14.73      | 94                | 497                  |
| 15                                 | -545                                  | 2.9 × 10 <sup>-3</sup>                          | 2.11       | 14.81      | 96                | 625                  |
| 20                                 | -562                                  | 1.2 × 10 <sup>-3</sup>                          | 1.14       | 14.49      | 98                | 853                  |

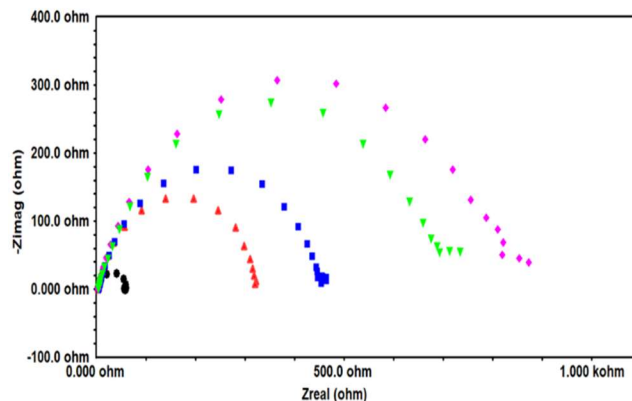
\*IE<sub>1</sub> = The inhibition efficiency obtained from polarization measurements.

By substituting the respective values of  $i_{\text{corr\_inhibited}}$  and  $i_{\text{corr\_uninhibited}}$  from Table 1 into Eq. (2), the inhibition efficiency was calculated in percentage. The inhibition efficiency showed the extent to which the *A. floribundum* leaves extract inhibited mild steel corrosion, with higher values indicating a greater inhibitory effect. Table 1 shows that the inhibitory effect of *A. floribundum* leaves extract changed based on the concentration of the extract. The best inhibition was observed at a concentration of  $20 \text{ g l}^{-1}$ , resulting in a 98% efficiency rate. By adding this inhibitor to a 1 M  $\text{H}_2\text{SO}_4$  solution, the corrosion of mild steel was inhibited. The inhibition process involved the attaching of the inhibitor to the metal surface, forming a barrier that obstructed the transfer of charge and mass during the anodic and cathodic reactions, resulting in corrosion. These results align with the previously mentioned experimental findings. Based on the results, it appears that higher concentrations of *A. floribundum* leaves extract, as an inhibitor, can have a stronger inhibitory effect on the corrosion of mild steel in an acidic medium.

### Electrochemical Impedance Spectroscopy Measurements

To study how mild steel corroded in a 1 M  $\text{H}_2\text{SO}_4$  solution, the EIS technique was used. First, the open circuit potential was determined. Then, Nyquist plots were drawn for the acidic solution with varying amounts of inhibitor (Fig. 2). The Nyquist plots exhibited a depressed, rather than a perfect, semicircle. This depression can be attributed to various factors, such as the distribution of active sites on the metal surface, surface roughness, adsorption of inhibitors, surface inhomogeneity, the formation of porous layers, and other non-ideal conditions [22-23]. As the concentration of *A. floribundum* extract increased, the depressed semicircle grew in size, indicating a more powerful inhibitory effect. Moreover, the  $R_p$  value, which was initially  $58 \text{ ohm cm}^2$  in a medium without inhibitors, increased when inhibitors were added, reaching  $828 \text{ ohm cm}^2$  at the highest inhibitory concentration.

In addition, Nyquist plots showed a short diffusion tail in the presence of the inhibitor. This tail became more pointed as the inhibitor concentration increased, as shown in Fig. 2. The capacitive semicircle observed at higher frequencies in Nyquist plots can be attributed to the interfacial charge



**Fig. 2.** The EIS diagram of mild steel in 1 M  $\text{H}_2\text{SO}_4$  in the absence (●-blank) and presence of the inhibitor (extracts of ▲- $5 \text{ g l}^{-1}$ , ■- $10 \text{ g l}^{-1}$ , ▼- $15 \text{ g l}^{-1}$ , and ◆- $20 \text{ g l}^{-1}$  *A. Floribundum* leaves).

transfer reaction [24-25]. Diffusion tails observed at lower frequencies are associated with mass transfer. This behaviour suggests that *A. floribundum* extract can act as a barrier, inhibiting charge transfer during the metal dissolution process and delaying the diffusion of corrosion products from the metal surface into the bulk solution.

Overall, the EIS results confirmed that the *A. floribundum* extract effectively inhibited the corrosion of mild steel by impeding both the charge transfer and the diffusion processes involved in the corrosion mechanism.

Based on the observed results, it can be concluded that the corrosion of mild steel is controlled by the diffusion step in the presence of the *A. floribundum* extract. Polarization resistance ( $R_p$ ) values were determined from the Nyquist plots obtained through the EIS. It was observed that the diameter of the Nyquist plot increased in the presence of the extract and that the size of the plot increased with higher concentrations of the extract. The highest polarization resistance (*i.e.*,  $827 \text{ ohm cm}^2$ ) was recorded when the 1 M  $\text{H}_2\text{SO}_4$  solution contained  $20 \text{ g l}^{-1}$  of the *A. floribundum* extract. In contrast, for the inhibitor-free medium (1 M  $\text{H}_2\text{SO}_4$ ), the polarization resistance ( $R_p$ ) was found to be  $58 \text{ ohm cm}^2$ . Polarization resistance values indicated the inhibitory effect of the *A. floribundum* extract on the corrosion process. Higher polarization resistance values obtained in this study signify a stronger hindrance to the flow of current during the corrosion process, showing greater

corrosion inhibition. Therefore, the significant increase in polarization resistance values in the presence of the *A. floribundum* extract suggests its effective role in inhibiting the corrosion of mild steel in the acidic medium. The relationship between inhibition efficiency ( $IE_2$ ) and polarization resistance can be expressed as follows and is shown in Table 2:

$$IE_2 = \frac{R_p - R_p^0}{R_p} \times 100 \quad (7)$$

With an increase in the concentrations of the *A. floribundum* extract, the inhibition efficiency ( $IE_2$ ) increased as well, reaching a maximum value of 93% in the studied corrosive medium with the highest concentration of the inhibitor. This indicates that the *A. floribundum* extract formed a protective layer and had an excellent inhibitory effect against the corrosion of mild steel in 1 M  $H_2SO_4$ . The calculated inhibition efficiencies obtained from the two techniques, polarization measurements ( $IE_1$ ) and EIS ( $IE_2$ ), were in good agreement.

To analyze the experimental data, the Nyquist plots were fitted to a simplified Randles equivalent circuit model, which was suitable for describing the interaction between the mild steel and the acidic solution containing the *A. floribundum* extract (see Fig. 2). In this model, a non-homogeneous phase constant element (CPE) was used instead of a double-layer capacitance (Cdl) [22] to compensate for the non-uniformity of the system caused by surface roughness, porosity, adsorption, or diffusion [26-27]. The CPE values were determined by fitting the experimental data to the estimated circuit model using Gamry electrochemical analyzer software, and the obtained values are presented in Table 2.

As shown in Table 3, the CPE values decreased significantly while the polarization resistance ( $R_p$ ) values increased. This decrease in CPE values can be attributed to an increase in the layer thickness or a decrease in the local dielectric constant due to the adsorption of inhibitors on the metal surface [28]. These findings suggest that the *A. floribundum* extract formed a protective layer on the surface of the mild steel, leading to improved corrosion resistance and inhibition efficiency.

**Table 2.** Electrochemical Parameters of Inhibition of Mild Steel Corrosion Obtained from EIS Measurements in 1 M  $H_2SO_4$  Containing Different inhibitor Concentrations

| Concentration (g l <sup>-1</sup> ) | $R_p$ (ohm cm <sup>2</sup> ) | CPE (F cm <sup>-2</sup> ) | $IE_2\%$ |
|------------------------------------|------------------------------|---------------------------|----------|
| Blank                              | 58                           | $47.7 \times 0$           | -        |
| 5                                  | 321                          | $18.6 \times 10^{-5}$     | 82       |
| 10                                 | 453                          | $17.4 \times 10^{-5}$     | 87       |
| 15                                 | 694                          | $16.8 \times 10^{-5}$     | 92       |
| 20                                 | 827                          | $14.7 \times 10^{-5}$     | 93       |

\* $IE_2$  = The inhibition efficiency obtained from EIS measurements.

**Table 3.** The Corrosion Parameters of Mild Steel in 1 M  $H_2SO_4$  in the Absence and Presence of Inhibitors at Different Temperatures

| Temperature (°C) | 1 M $H_2SO_4$   |                                   | 1 M $H_2SO_4$ + 20 g l <sup>-1</sup> inhibitor |                 |                                   |          |          |
|------------------|-----------------|-----------------------------------|--|-----------------|-----------------------------------|----------|----------|
|                  | $E_{corr}$ (mV) | $i_{corr}$ (mA cm <sup>-2</sup> ) | $R_p$  | $E_{corr}$ (mV) | $i_{corr}$ (mA cm <sup>-2</sup> ) | $R_{pl}$ | $IE_1\%$ |
| 27               | -473            | $8.1 \times 10^{-2}$              | 60   | -563            | $1.2 \times 10^{-3}$              | 853      | 98       |
| 40               | -463            | $1.1 \times 10^{-1}$              | 46   | -502            | $9.6 \times 10^{-3}$              | 231      | 91       |
| 50               | -451            | $2.5 \times 10^{-1}$              | 38   | -482            | $2.3 \times 10^{-2}$              | 120      | 90       |
| 60               | -447            | $2.7 \times 10^{-1}$              | 25   | -466            | $5.9 \times 10^{-2}$              | 56       | 78       |

\* $IE_1$  = The inhibition efficiency obtained from polarization measurements. \* $IE_2$  = The inhibition efficiency obtained from EIS measurements.

### Adsorption Isotherm

The inhibition of the corrosion process typically occurs through the adsorption of inhibitor molecules on the metal surface, either chemically or physically. Physical adsorption is a result of van der Waals or dispersion forces and can also involve electrostatic interactions at the metal surface. However, chemisorption takes place when a bond is formed between the organic molecules of the inhibitor and the metal surface. This bond is created through the sharing of a pair of electrons between the inhibitor and the metal [29].

Understanding the adsorption isotherm is essential in identifying how the inhibitor interacts with the metal surface. This information is crucial in determining the surface coverage ( $\theta$ ) or the amount of inhibitor adsorbed on the metal surface. To understand the type of interaction between the inhibitor and the metal surface, surface coverage ( $\theta$ ) can be utilized. The adsorption isotherm, which explains the correlation between the inhibitor concentration and surface coverage, is a valuable tool for obtaining information about the aforementioned interaction.

The value of surface coverage ( $\theta$ ) was obtained from linear polarization measurements at 300 K using Eq. (8) [29]:

$$\theta = \frac{i^0 - i}{i^0} \quad (8)$$

To determine the corrosion current densities, we measured the  $i^0$  and  $i$  values in a 1 M  $\text{H}_2\text{SO}_4$  solution with and without an inhibitor, respectively. After testing different adsorption isotherms, it was found that the Langmuir adsorption isotherm was the most accurate. This isotherm correlates the inhibitor concentration ( $C$ ) to the surface coverage ( $\theta$ ) and is expressed as follows:

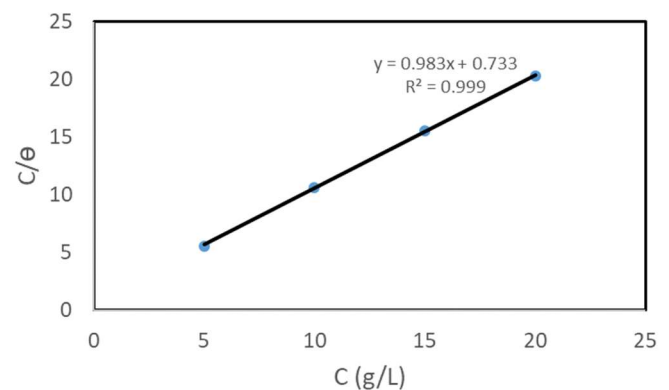
$$C/\theta = 1/k_{\text{ads}} + C \quad (9)$$

Equation (9) contains three variables:  $\theta$  is surface coverage,  $C$  is inhibitor concentration, and  $K_{\text{ads}}$  is the Langmuir adsorption constant. According to the Langmuir adsorption isotherm, the process of adsorption takes place on a surface that is homogeneous and has a limited number of adsorption sites. It suggests that the maximum coverage ( $\theta_{\text{max}}$ ) can be achieved when all adsorption sites are occupied.

The Langmuir adsorption constant ( $K_{\text{ads}}$ ) represents the affinity between the inhibitor molecules and the metal surface.

Based on the findings, the surface coverage ( $\theta$ ) and the bulk concentration of the inhibitor ( $C$ ) were linearly related. This suggests that the adsorption behaviour of the substance followed the Langmuir isotherm. Additionally, the correlation coefficient was estimated to be 0.999, which clearly indicates that the experimental data fitted well with the Langmuir adsorption model (Fig. 3).

The slope of the linear plot in Fig. 3 represents the adsorption coefficient ( $K_{\text{ads}}$ ) in the Langmuir equation. Based on the data, it was found that the slope was  $1.01 \text{ l g}^{-1}$ . It appears that there was a significant connection between the inhibitor molecules and the metal surface.  $K_{\text{ads}}$  is expressed in  $\text{g}^{-1}$  unit because the molecular weight of the extract is unknown. Determining the average molecular weight could impact the  $K_{\text{ads}}$  value and potentially result in a higher value. The term “ $K_{\text{ads}}$ ” refers to the attraction between inhibitor molecules and the metal surface, and is indicative of the strength of adsorption. Therefore, a higher  $K_{\text{ads}}$  value indicates a stronger bond between the inhibitor and the metal surface, leading to better corrosion inhibition. With a higher  $K_{\text{ads}}$  value, a lower concentration of the inhibitor in the solution is required to achieve a significant coverage on the metal surface. At lower concentrations, the inhibitor can still be effective in preventing corrosion because the inhibitor



**Fig. 3.** The Langmuir adsorption isotherm for the adsorption of *A. floribundum* extract (concentration ranging from 5 to 20  $\text{g l}^{-1}$ ) in  $\text{M H}_2\text{SO}_4$  at 300 K.

forms a strong bond with the metal surface, creating a dense and stable layer of inhibitor molecules that act as a protective shield against corrosive agents and, consequently, reduce the susceptibility of the metal to corrosion.

The relationship between the free energy ( $\Delta G_{\text{ads}}$ ) and adsorption coefficient ( $k$ ) is given below:

$$K_{\text{ads}} = 1/55.5 \exp(-\Delta G_{\text{ads}}/RT) \quad (10)$$

where  $R$  is ideal gas constant,  $\Delta G_{\text{ads}}$  is free energy, and  $K_{\text{ads}}$  is the adsorption coefficient.

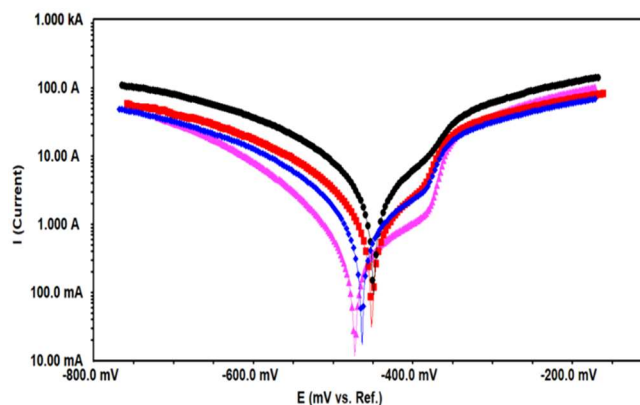
The calculated value of  $-9.98 \text{ kJ g}^{-1}$  for the free energy ( $\Delta G_{\text{ads}}$ ) indicates that the adsorption of inhibitor molecules from the *A. floribundum* extract onto the mild steel surface was a spontaneous process [30]. The negative value of  $\Delta G_{\text{ads}}$  suggests that the adsorption was energetically favourable and that the inhibitor molecules had a strong affinity for the metal surface. It should be noted that the unit of  $\text{kJ g}^{-1}$  was used in the above calculation because the exact molecular weight of the *A. floribundum* extract was not known. However, considering the typical molecular weights of organic compounds [31-32], it is likely that the value of  $\Delta G_{\text{ads}}$  would be higher if expressed in  $\text{kJ mol}^{-1}$ .

### The Effect of Temperature

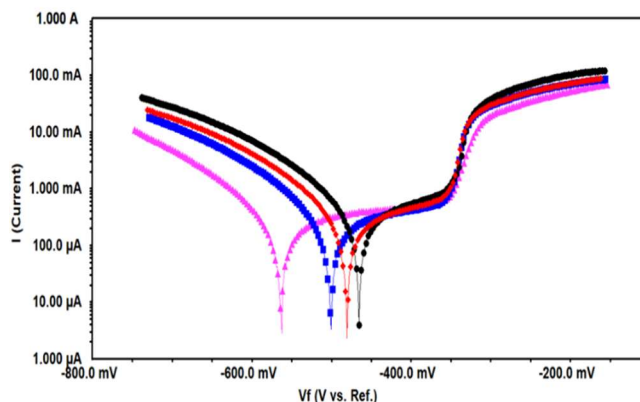
The effect of temperature on the inhibition of mild steel corrosion was investigated in this study. Potentiodynamic polarization measurements were conducted at temperatures ranging from 27 to 60 °C and using two corrosive solutions as follows: 1 M  $\text{H}_2\text{SO}_4$  and 1 M  $\text{H}_2\text{SO}_4$  containing 20  $\text{g l}^{-1}$  *A. floribundum* extract. The results are presented in Figs. 4 and 5, respectively.

Based on the data presented in Figs. 4 and 5, it is possible to determine how temperature influenced the corrosion behaviour of mild steel in the presence and absence of the inhibitor. The results show that the effectiveness of the inhibitor was influenced by temperature, with some variations in corrosion parameters as the temperature changed. This result can provide insights into the temperature-dependent performance of the *A. floribundum* extract as a corrosion inhibitor for mild steel in a sulphuric acid solution.

The electrochemical parameters obtained from the polarization curves at different temperatures are presented in



**Fig. 4.** Polarization curves of mild steel at different temperatures in 1 M  $\text{H}_2\text{SO}_4$  (●-20, ■-35, ◆-45, and ▲-55 °C).



**Fig. 5.** Polarization curves of mild steel at different temperatures in the presence of 20  $\text{g l}^{-1}$  of *A. floribundum* extract (●-20, ◆-35, ■- 45, and ▲-55 °C).

Table 3. As the temperature increased, the calculated corrosion current also increased, which is the expected behaviour as higher temperatures generally accelerate the corrosion process. The corrosion potentials were observed to shift towards more positive values, indicating a decrease in the corrosion tendency. The inhibition efficiencies, determined from the corrosion current values, showed a decreasing trend with increasing temperature. This suggests that the effectiveness of the inhibitor in preventing corrosion decreased as the temperature increased. Activation energy ( $E_a$ ) is an important parameter that provides insight into the inhibition mechanism. The relationship between the medium temperature ( $T$ ) and activation energy ( $E_a$ ) can be expressed

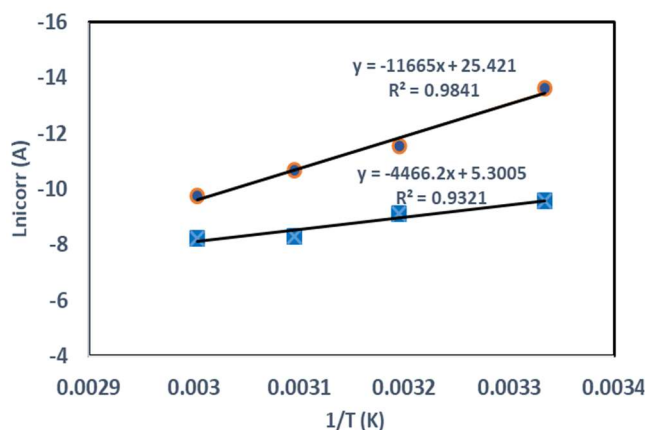


using the Arrhenius equation:

$$\ln i_{\text{corr}} = -E_a/RT + A \quad (11)$$

In the above equation,  $A$  is the Arrhenius pre-exponential factor, and  $R$  is the universal gas constant. By plotting the natural logarithm of the corrosion current ( $\ln(i_{\text{corr}})$ ) against the inverse of the absolute temperature ( $1/T$ ), the activation energy can be determined from the slope of the linear relationship. The activation energy provides information about the energy barrier for the corrosion process and can help explain the inhibitory effect of the *A. floribundum* extract. The calculated activation energy values can shed light on the temperature dependence of the corrosion inhibition process and provide insights into the mechanism by which the *A. floribundum* extract inhibits the corrosion of mild steel in a sulphuric acid solution.

Figure 6 illustrates the Arrhenius plot obtained by plotting the reciprocal of temperatures against the corresponding logarithm of current densities. The activation energy of the corrosion process was calculated from the slope of this plot. In the 1 M  $\text{H}_2\text{SO}_4$  solution, the activation energy was determined to be  $33.56 \text{ kJ mol}^{-1}$  while in the 1 M  $\text{H}_2\text{SO}_4$  solution containing  $20 \text{ g l}^{-1}$  of *A. floribundum* extract, the activation energy was found to be  $96.98 \text{ kJ mol}^{-1}$ . It is important to note that the activation energy increased when the extract was added to the corrosive medium.



**Fig. 6.** Arrhenius plots for the process of corrosion of mild steel in 1 M  $\text{H}_2\text{SO}_4$  (■) and in the presence of  $20 \text{ g l}^{-1}$  of *A. floribundum* extract (●).

When a corrosion inhibitor is present in the corrosive medium, it interacts with the metal surface and creates a protective layer that hinders the reaction between the metal and the corrosive environment. This protective layer can either physically block the reactants from coming into contact with the metal surface or chemically modify the metal surface to make it less susceptible to corrosion [33]. Higher activation energies imply that more energy is required for the corrosion reaction to proceed in the presence of the inhibitor. This increase in energy barrier hinders the movement of corrosive species and their interaction with the metal surface. As a result, the corrosion rate is reduced, and the inhibitor can effectively slow down the corrosion process.

## CONCLUSIONS

In this study, the potential of *A. floribundum* extract as an eco-friendly corrosion inhibitor was investigated, and its effectiveness was evaluated using electrochemical techniques. The *A. floribundum* extract showed an exceptional inhibitory effect at a concentration of  $20 \text{ g l}^{-1}$ . According to potentiodynamic polarisation and EIS measurements at 300 K, the extract achieved 98% and 93% efficiencies, respectively. The experimental data clearly showed that the inhibition efficiency increased with higher concentrations of the extract, which makes the extract a promising option for practical applications. The inhibitor functioned by adhering to the surface of mild steel, successfully preventing both the cathodic and anodic reactions that lead to corrosion. The decrease in anodic and cathodic current values, as seen in the potentiodynamic polarization curves, suggests that the inhibitor adhered to the mild steel surface in an ionic or molecular manner, ultimately reducing the corrosion rate. The adsorption behaviour of the extract aligned with the Langmuir adsorption isotherm.

According to the results obtained from the EIS, a single-frequency capacitively suppressed semicircle was observed in the Nyquist plots. The size of the semicircle increased with higher concentrations of the inhibitor, showing an improvement in the formation of a protective layer on the surface of the mild steel by adsorption. This protective layer proved to be effective in preventing corrosion, evidenced by the calculated polarisation resistance and inhibition efficiency. Through polarisation measurements, it was

observed that the corrosion process had a certain activation energy. However, when an inhibitor was present, the activation energy increased, which indicated that the inhibitor was able to fortify the barrier effect and decelerate the corrosion rate of mild steel. These findings show the effectiveness of the *A. floribundum* extract as a corrosion inhibitor in reducing mild steel corrosion and offer useful information for developing corrosion protection and control methods in diverse industrial settings.

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