



Original scientific paper

## Electrochemical and adsorption study of environmentally friendly inhibitor used for low-carbon steel

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### Abstract

Low-carbon steel is susceptible to corrosion in various technical applications, particularly in the petroleum industry. Typically, classic approaches like coatings have downsides, including toxicity and environmental issues. Plant-based corrosion inhibitors are emerging as new, green, and affordable corrosion preventatives. In this study, an inhibitor of *Portulaca oleracea* roots was extracted and added in different concentrations of 200, 400, 600, 800 and 1000 ppm to study the adsorption mechanism at low carbon steel in 3.5 % NaCl. The effectiveness of inhibition and the rate of corrosion were assessed by using the potentiometric polarization method. Corrosion rate measurements showed a decrease from 0.149 to 0.021 mm year<sup>-1</sup>, respectively, and the maximum efficiency of 85.7 % was obtained at 1000 ppm of *Portulaca oleracea* extract. The data were tested for Langmuir, Flory-Huggins, El-Awady and Freundlich isotherms, and the Langmuir isotherm provided the best fit, indicating that the layer of inhibitor formed on the metal surface is a monolayer. According to the findings, the extract of *Portulaca oleracea* is very effective for suppressing corrosion of low-carbon steel in a 3.5 % NaCl solution.

### Keywords

Mild steel; green corrosion inhibitor; *Portulaca oleracea* extract; corrosion rate; Langmuir adsorption isotherm

### Introduction

Metal corrosion is a significant problem that has existed since the beginning of the industrial revolution. Corrosion can occur in different systems, including cooling systems, oil production units, oil storage tanks, pipeline protection, refinery units, etc. [1,2]. Most importantly, corrosion can cause infrastructure and mechanical damage, which can be costly to repair. costly in terms of lost sales from contaminated items, (costly-deleted) in terms of environmental damage, and possibly even costly to human safety [3]. Thus, corrosion threatens the industry's stability and endangers the safety of those who live there. To generate degradation of materials and their properties, corrosion is a mechanism that involves chemical or electrochemical reactions between materials, metals, and

their environment [3-5]. Factually, the most often used material for flow lines and transmission pipelines in the oil industry is low-carbon steel (LCS) [6].

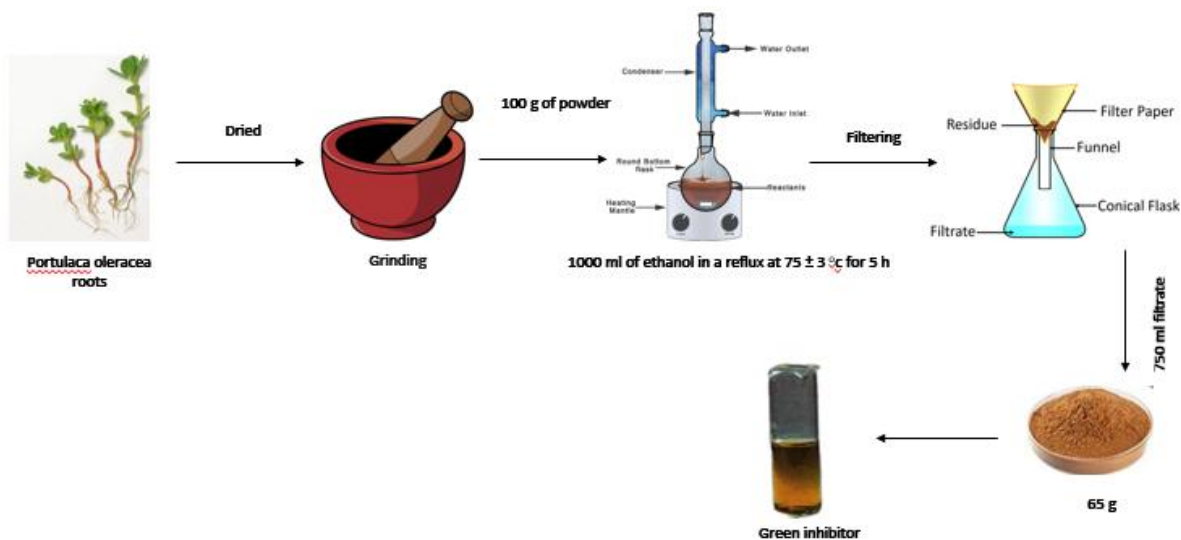
However, in corrosive settings associated with the oil industry, LCS has limited corrosion resistance [6,7]. There are various methods used for the corrosion protection of metals, including metal modification, surface modification, coatings, and the use of corrosion inhibitors [3,8-10]. One of the most popular methods for reducing the corrosion rate (CR) is the use of corrosion inhibitors, which is generally considered the most popular technique for preventing metal corrosion. This way of corrosion reduction does not require any specialized equipment and is inexpensive and simple to use [11]. However, it is crucial to note that due to their toxicity, many corrosion inhibitors have adverse effects on human health and/or the environment. The essential part of the inhibitors' mechanism is the alteration of metal surfaces caused by the adsorption of inhibitor molecules, which is followed by the development of a protective layer. However, the rising widespread concerns over health risks and environmental pollution promote the use of various categories of inhibitors. This ecological awareness stimulated the creation of green corrosion inhibitor compounds that are affordable, efficient, and have little or no harmful environmental effects [11,12]. Thus, based on published research [13-21], leaves from plants including margosa, *Murray koenigii*, *Ervatamia coronaria*, herb, *Bauhinia purpurea*, and olives prevent the corrosion of metals in an acidic medium [12]. Adejo *et. al.* [13] studied the effects of the extracts of leaves of *Portulaca oleracea* as corrosion inhibitors for the mild steel surface in sulfuric acid ( $H_2SO_4$ ) medium at the range of temperatures 305 to 315 K, using different adsorption isotherms. Our innovative work focuses on creating an eco-friendly, affordable corrosion inhibitor with superior performance, using *Portulaca oleracea* extract synthesized for seawater applications, thus broadening its industrial potential. In response to this, the objective of the current study is to examine the corrosion rate of low-carbon steel in salt solution (3.5 % NaCl) using the root extract of *Portulaca oleracea* as a corrosion inhibitor. Furthermore, the active chemical groups of the *Portulaca oleracea* were studied to ascertain the inhibitor's effectiveness and its corrosion inhibition mechanism. Testing of the obtained results with Langmuir, Flory-Huggins, El-Awady, and Freundlich adsorption isotherms should provide a description of the adsorbing process of the inhibitor on the surface of mild steel.

## Experimental

The *Portulaca oleracea* roots were gathered from the field in Iraq, dried, and ground into powder for extraction. 100 g of powder was added to 1000 ml of ethanol in a reflux condenser for 5 hours at a reflux temperature of  $75\pm 3$  °C. The extract was filtered when the extraction process was complete and then dried to produce a solid mass. Filtering yielded roughly 750 ml, which was used to create various concentrations of green inhibitor by diluting the stock solution. After drying, the solid mass weighed around 65 g because some compounds were dissolved in the ethanol. Figure 1 shows a procedure for preparation of the inhibitor.

### Fourier transform infrared spectroscopy analysis

The most effective method for identifying functional groups in various substances is likely one that utilizes an infrared spectrophotometer by placing the inhibitor specimen in a Fourier transform infrared (FTIR) spectrometer and allowing it to operate at room temperature. Additionally, an examination test of FTIR (resolution 16, optical path difference 0.125, number of data points 4096, data interval 7.72 and Aperture Diameter open/Shimadzu) was done in the range of 4000 to 400  $cm^{-1}$  wavelength.



**Figure 1.** Preparing the inhibitor using *Portulaca oleracea* roots

### Preparation of the specimens and solutions

Specimens were prepared from low carbon steel with dimensions of (2×1×1 cm) and ground with emery papers of (400, 600, 800 and 1000 grades) of wet silicon carbide papers. Next, the specimens were cleaned with acetone and distilled water and then dried in air. For preparing specimens for electrochemical tests, a chemical analysis of low-carbon steel is carried out by the X-ray fluorescence (XRF) technique, and the results are shown in Table 1. The corrosive solution for electrochemical tests was prepared by weighing 35 g of laboratory table salt and dissolving it in 1 liter of distilled water to obtain a concentration of 3.5 M sodium chloride.

**Table 1.** The chemical composition of low-carbon steel

Element	Content, wt.%
Fe	99.060
C	0.090
Mn	0.490
P	0.020
S	0.012
Si	0.043
Cr	0.040
Cu	0.130
Ni	0.060
W	0.010
Mo	0.020

### Electrochemical measurements

To evaluate the effectiveness of the *Portulaca oleracea*-inhibitor, the electrochemical glass cell containing three electrodes was used. The working electrode was a low-carbon steel specimen, the auxiliary electrode was a platinum electrode, and the reference electrode was a saturated calomel electrode (SCE). Software electrochemical systems 4.9 (GPES) was employed to draw curves of potentiometric polarizations. Electrochemical tests were done in a 3.5 % NaCl solution containing 200, 400, 600, 800 and 1000 ppm of *Portulaca oleracea* extract.

For the electrochemical examination, the prepared low-carbon steel specimens were used. The scan potential is  $\pm 300$  mV from OCP ( $-630$  mV vs. SCE). All potential measurements in this work will be referred to relative to the potential of SCE. The scan rate of  $1 \text{ mV s}^{-1}$  was applied to measure the

corrosion potential. Also, the Tafel method was used to determine corrosion potential ( $E_{corr}$ ), corrosion current density ( $j_{corr}$ ), and cathodic and anodic Tafel slopes ( $\beta_c$  and  $\beta_a$ ). The inhibitor efficiency (IE, %) was determined using Equation (1) [22]:

$$IE = \frac{j_0 - j_i}{j_0} 100 \quad (1)$$

where  $j_0$  is the current density in the absence of the inhibitor, while  $j_i$  represents the current density in the presence of the inhibitor.

Corrosion rate (CR, mm year<sup>-1</sup>) was calculated by Equation (2) [23]:

$$CR = \frac{0.00327 E_q j_{corr}}{\rho} \quad (2)$$

where  $E_q$  is the equivalent weight of metal,  $j_{corr} / \mu\text{A cm}^{-2}$  is current density and  $\rho / \text{g cm}^{-3}$  is metal density.

### Adsorption isotherm

Adsorption isotherm studies provide a description of the adsorption process of organic inhibitors on metal surfaces [24-28]. Langmuir, Flory-Huggins, El-Awady, and Freundlich adsorption isotherms were used to determine which of these different adsorption isotherm models corresponds best with the current results. The following equations describe four tested adsorption models:

Langmuir adsorption isotherm is described by Equation (3) [24,25]:

$$\frac{c}{\theta} = \frac{1}{k} + C \quad (3)$$

Flory-Huggins adsorption isotherm is described by Equation (4) [26]:

$$\log\left(\frac{\theta}{C}\right) = \log K + x \log(1-\theta) \quad (4)$$

The adsorption isotherm model of El-Awady is given by Equation (5) [13]:

$$\log\left(\frac{\theta}{1-\theta}\right) = \log K + x \log(1-\theta) \quad (5)$$

Freundlich adsorption isotherm is described by Equation (6) [27]:

$$\log \theta = \log K + n \log C \quad (6)$$

Common parameters in Equations (3 to 6) are  $\theta$ ,  $C$  and  $K$ , which are defined as the degree of surface coverage, concentration of adsorbent, and adsorption-related constant, respectively. The parameter  $x$  is specific for a particular isotherm, describing ease of adsorption, or the number of active sites in Equations (4) and (5). Equation (6) shows that  $n$  is a constant for adsorption strength.

### Surface characterization

Scanning electron microscopy (SEM, Thermo Fisher/USA) was used to examine the specimen's surface morphology before and after inhibitor addition, analysing surface changes on corroded specimens after adding the chosen inhibitor.

## Results and discussion

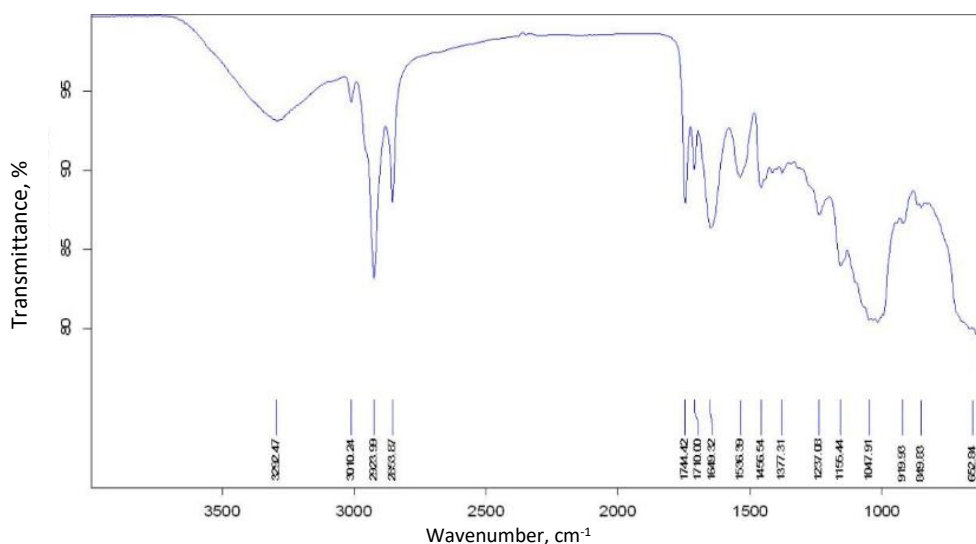
### Fourier transform infrared analysis of *Portulaca oleracea* extract

The functional groups included in the extract were identified using FTIR analysis. Figure 2 shows the FTIR spectrum of the *Portulaca oleracea* extract. The strong, broad peak at 3292.47 cm<sup>-1</sup> is related to alcohol-induced O-H stretching. On the other hand, the strong broad peak of O-H

stretching in a carboxylic acid was determined to be the cause of the peaks at  $3010.24\text{ cm}^{-1}$ , and  $2923.99$  and  $2853.87\text{ cm}^{-1}$ . In addition, peaks at  $1744.42$  and  $1710.00\text{ cm}^{-1}$  are attributed to the C-H stretching of the aromatic ring. At  $1619.32\text{ cm}^{-1}$ , the C=O stretching was observed. Peaks at  $1536.39$  and  $1456.54\text{ cm}^{-1}$  are ascribed to have N-O stretch in the nitro compound. The aromatic group and the alkyl aryl ether show strong C-O stretching bands at  $1377.31$  and  $1237.08\text{ cm}^{-1}$ . Medium C-N stretches appear in the amine group. They are at  $1155.44$  and  $1047.91\text{ cm}^{-1}$ . The strong peaks at  $919.93$  and  $819.83\text{ cm}^{-1}$  in the C=C bending mode of the alkene group. The peak strength of C-Br stretching at  $652.84\text{ cm}^{-1}$  in the halo compound. All these bands of chemical molecular groups are constructed in the barrier layer to protect the steel surface from corrosion. Organic compounds are composed of various heteroatoms such as nitrogen (N), oxygen (O), sulphur (S) and phosphorus (P). These compounds have been shown to be highly effective in suppressing aqueous corrosion due to the formation of a coating on the metal surface, resulting from adsorption.

Didouh *et al.* [28] explored the potential of *Portulaca oleracea* as a biocide and corrosion inhibitor for low-carbon steel. The extract exhibited strong anodic inhibition, as confirmed by electrochemical analysis. Reducing the anodic reaction by 80 % reduces carbon steel corrosion, which is especially relevant in environments rich in thiosulfate-reducing bacteria. Hayajneh *et al.* [29] examined the possibilities of *Portulaca Oleracea L.* in corrosion mitigation. Leaf extract (POLE) was used to protect mild steel from corrosion in 1 M HCl. Corrosion inhibition was investigated using potentiodynamic polarization and weight loss techniques, and all tests showed that POLE is a good green inhibitor of mild steel corrosion in acid conditions.

These results suggested a high potential of these compounds as eco-friendly corrosion inhibitors, warranting further investigation.

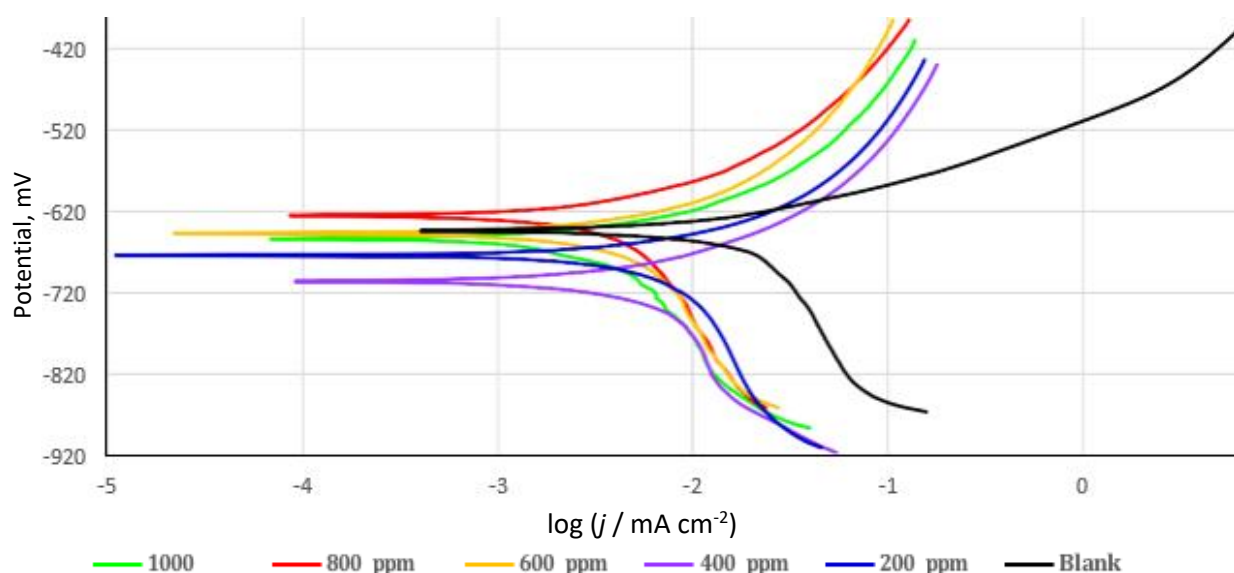


**Figure 2.** FTIR spectrum of *Portulaca oleracea* extract

### Electrochemical measurements

Figure 3 shows the polarization curves of *Portulaca oleracea* extract at concentrations of 200, 400, 600, 800 and 1000 ppm in 3.5 % NaCl. It can be noticed from Figure 3 that polarization curves move to the positive side (anodic) with increasing inhibitor concentrations. Many researchers [28-33] stated that the inhibitor can be categorized as either cathodic or anodic, if the difference in  $E_{\text{corr}}$  values ( $\Delta E_{\text{corr}} = E_{\text{corr}}$  without inhibitor-  $E_{\text{corr}}$  with inhibitor) is higher than 85 mV. If  $\Delta E_{\text{corr}}$  is less than 85 mV, the inhibitor is categorized as a mixed type. In this study, all concentrations of inhibitor showed  $\Delta E_{\text{corr}}$  values less than 85 mV, which confirms that *Portulaca oleracea* extract is a mixed type of inhibitor [28,29]. Polarization

curves in Figure 3 demonstrate that corrosion curves with increasing concentration of inhibitor led to a decrease in the corrosion potential, which resulted in a decrease in the corrosion rate. The highest positive shift in corrosion potentials was obtained at concentrations of inhibitor of 800 and 1000 ppm. The corrosion parameters extracted from Figure 3 are presented in the first part of Table 2. The value of the corrosion current density in the absence of an inhibitor is 12.78  $\mu\text{A cm}^{-2}$  and decreases when an inhibitor is added, attaining 1.83  $\mu\text{A cm}^{-2}$  at 1000 ppm of *Portulaca oleracea* extract. Since both the anodic ( $\beta_a$ ) and cathodic ( $\beta_c$ ) Tafel slopes of polarization curves changed with inhibitor concentration, the inhibitors are referred to as mixed-type inhibitors because they had an impact on both reactions and these results agree with [28,33]. The fact that these inhibitors are thought to be of the mixed type, with predominating anodic behaviour, is further supported by the larger values of  $\beta_a$  compared to  $\beta_c$  at each concentration of the inhibitor.



**Figure 3.** Polarization results for low carbon steel in 3.5 % NaCl solution influenced by different amounts of extract of *Portulaca oleracea*

The parameters listed in the last two columns of Table 2 are the inhibition efficiencies and corrosion rates, calculated using Equations (1) and (2), respectively. Table 2 shows that corrosion rates were reduced with *Portulaca oleracea* extract at various concentrations, versus a high corrosion rate observed without an inhibitor. The results showed that adding *Portulaca oleracea* extract enhances inhibitor efficiency. These results align with those of El-Etre and Abdullah [34]. It is important to mention that the addition of 1000 ppm of *Portulaca oleracea* extract yielded the strongest inhibition with an efficiency value of 85.7 %. An increase in the inhibitor's concentration up to 1000 ppm results in a reduction in the rate of corrosion, as shown in Table 2. This trend is explained by the fact that when the extract concentration rises, more surface area is covered by adsorbed extract particles of green corrosion inhibitor.

**Table 2.** Polarization results of the corrosion process on carbon steel in 3.5 % NaCl inhibited by the extract of *Portulaca oleracea*

C / ppm.	$E_{corr}$ / mV	$j_{corr}$ / $\mu\text{A cm}^{-2}$	$\beta_c$ / mV dec <sup>-1</sup>	$\beta_a$ / mV dec <sup>-1</sup>	CR, mm year <sup>-1</sup>	Inhibitor efficiency, %
0 (blank)	-650	12.78	-168.1	52.8	0.149	---
200	-690	3.29	-118.1	54.1	0.038	74.2
400	-710	2.89	-93.7	64.7	0.034	77.4
600	-660	2.28	-104	60	0.026	82.1
800	-630	2.15	-115	59	0.025	83.2
1000	-635	1.83	-78.8	59.8	0.021	85.7

The above results are consistent with Abdulhussein *et al.* [35], who reported that the corrosion rate of low carbon steel is reduced clearly by using pectin as a green corrosion inhibitor and inhibition efficiency increased with an increase in the inhibitor concentration. The inhibition efficiency was 92 % at the maximum concentration of inhibitor (10 g l<sup>-1</sup>).

Abdulhussein *et al.* [36] showed that the corrosion resistance of carbon steel A285 grade C is improved using different concentrations (0.2, 0.4, 0.6, 0.8 and 1 g L<sup>-1</sup>) of nanoparticles of SiO<sub>2</sub> as green corrosion inhibitor in acid solution. The nanoparticles of SiO<sub>2</sub> were extracted from natural sand using a chemical method. The corrosion rate was improved in the presence of a nano inhibitor. Also, the results indicated the formation of a thin film of SiO<sub>2</sub> on the metal surface. This thin film of SiO<sub>2</sub> protects the metal from corrosion by preventing any activity of the corrosion.

#### *Adsorption isotherm behaviour*

Basic knowledge regarding the interaction between the inhibitor and the carbon steel surface is provided by adsorption isotherms [27]. A thin shielding layer develops on shielded metal surfaces, and the surface coverage ( $\theta$ ) of this layer can be used to represent it. Surface coverage has the following relationships with inhibitory effectiveness (IE, %) described by equation (8) [37]:

$$IE = 100 \theta \quad (8)$$

The calculated values of  $\theta$  are listed in the first column of Table 3. It can be noticed from Table 3 that the higher the concentration of the inhibitor, the greater the value  $\theta$ , and these results are confirmed by the results of the corrosion rates, where corrosion current density was obtained from the polarization curves. The highest surface coverage was 0.857 at the highest concentration of the extract of *Portulaca oleracea* inhibitor of 1000 ppm. Also, the highest inhibitor efficiency was 85.7 % at the highest concentration of the extract of *Portulaca oleracea* inhibitor of 1000 ppm. The effect of surface coverage on corrosion rate is to create the adsorbate barrier layer on the metal surface; this layer improves the corrosion rate of low-carbon steel.

The Langmuir isotherm, which uses two parameters to empirically describe adsorption, assumes that adsorption occurs in a thickness with a localized molecule unaffected by nearby molecules, resulting in a homogeneous layer [27,37]. According to the Flory-Huggins model, adsorption is a spontaneous process that is predictable by the Gibbs free energy and equilibrium constant. The adsorption isotherm of El-Awady *et al.* [27,37] thermodynamic/kinetic model offers crucial hints about the nature of the metal-inhibitor interactions. The adsorption processes that occur on heterogeneous surfaces can be explained by the Freundlich isotherm. An expression for the surface heterogeneity and exponential distribution of the active sites and their energy is provided by this isotherm [28,37].

The several adsorption isotherm models considered in this work are shown in Figure 4. The most appropriate model was chosen based on the coefficient of determination ( $R^2$ ) values for each isotherm model. The  $R^2$  is the mean variation in the data, which indicates the success of fitting the kinetic and isotherm models.

It is seen in Figure 4 that the obtained data are fitted well into all isotherms, but the Langmuir isotherm provides the best fit. Therefore, the adsorption mechanism of *Portulaca oleracea* extract on low carbon steel in 3.5 % NaCl medium is best described by the Langmuir isotherm, which has the highest  $R^2$  value of about 0.9991. Accordingly, the Langmuir adsorption isotherm can be used to calculate the  $K_{ads}$  value for the adsorption equilibrium constant. Table 3 displays the adsorption equilibrium constant ( $K_{ads}$ ) calculated from the intercept of the Langmuir curve at various inhibitor concentrations. Positive adsorption  $K_{ads}$  values suggest the viability of the inhibitor's adsorption on the metal surface till 1000 ppm, the adsorption equilibrium constant rises with inhibitor concentration.

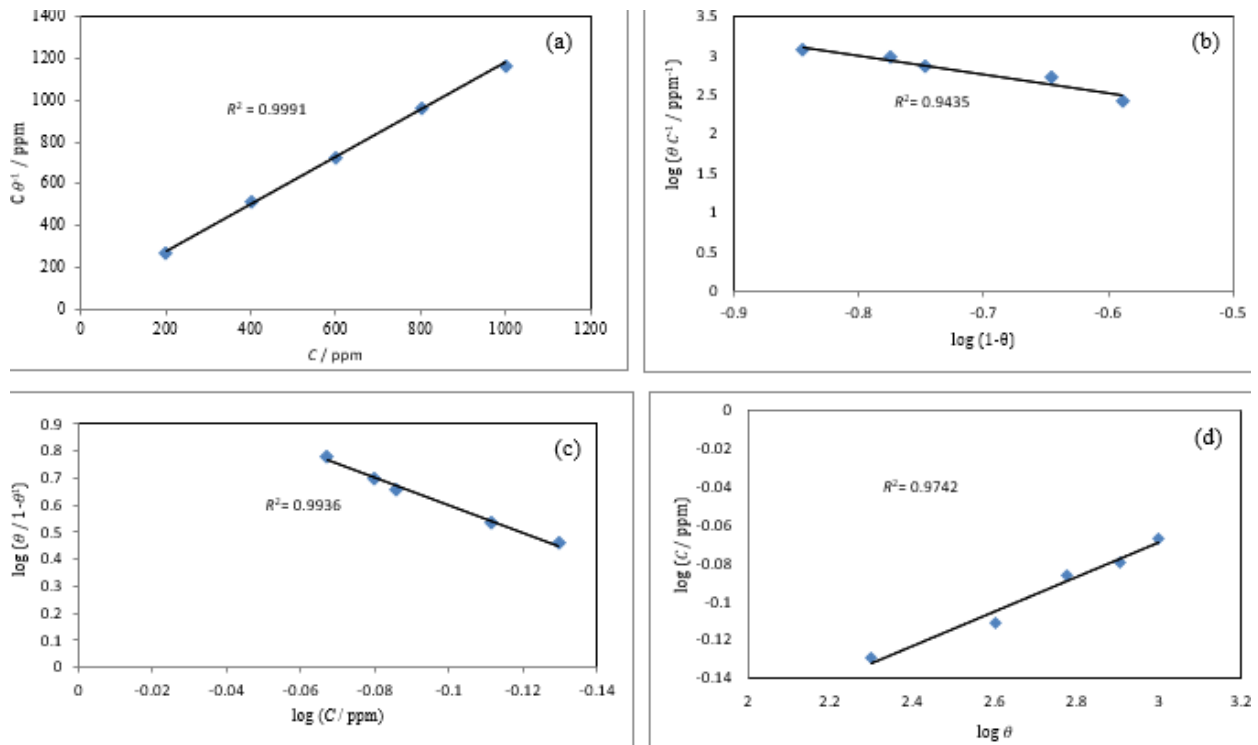


Figure 4. Several adsorption isotherm models: (a) Langmuir (b) Flory-Huggins (c) El-Awady and (d) Freundlich

Table 3. Values of surface coverage ( $\theta$ ) and  $K_{ads}$  of the Langmuir isotherm for *Portulaca oleracea* extract at different dosages

C / ppm	$\theta$	$K_{ads}$ / ppm <sup>-1</sup>
200	0.742	0.005779
400	0.774	0.008562
600	0.821	0.007644
800	0.832	0.00619
1000	0.857	0.005993

Scanning electron microscopy

Scanning electron microscopy (SEM) analysis reveals distinct morphological differences between specimens exposed to a 3.5% NaCl solution, with and without *Portulaca oleracea*. Without the inhibitor, the specimen shows accelerated corrosion, evident in pits and cracks as in Figure 5a.

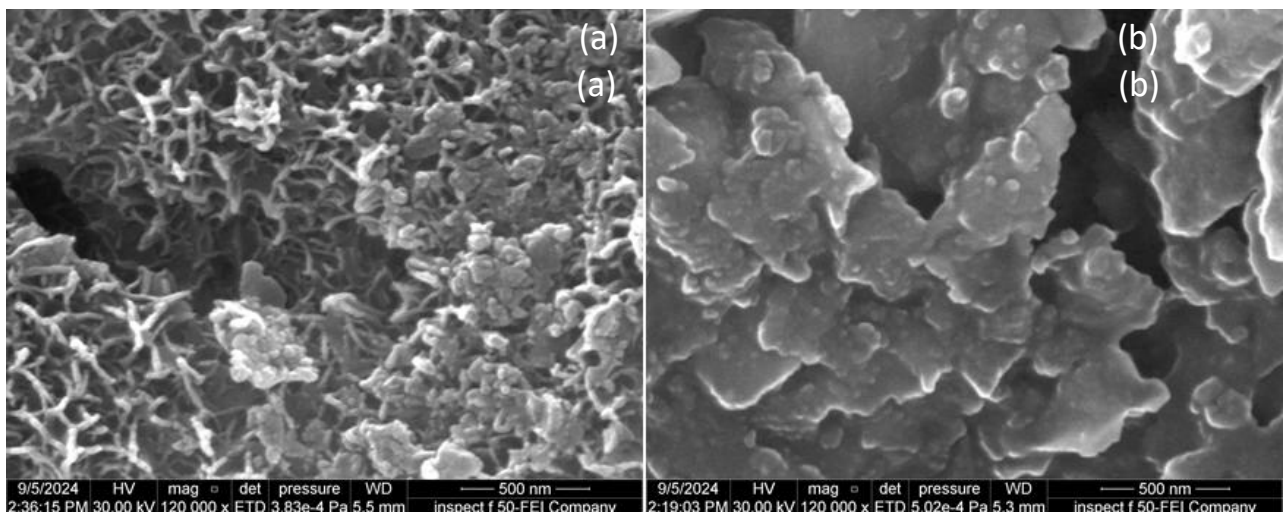


Figure 5. SEM images of the specimen surface exposed to sodium chloride solution without (a) and (b) with 1000 ppm of inhibitor

Figure (5b) shows an SEM image of a specimen with 1000 ppm of the inhibitor. SEM surface measurements confirm a protective inhibitor molecule coating on the steel. It is seen in Figure 5b that at 1000 ppm of inhibitor, the steel's protective coating is smooth and complete, lacking imperfections. This result agrees with high inhibition efficiency (85.7%) for *Portulaca oleracea*, supporting its potential as a corrosion inhibitor.

## Conclusions

Corrosion inhibitors from plants are becoming popular because they are safe and good for the environment. In the current examination, the extract of *Portulaca oleracea* roots has demonstrated considerable corrosion inhibition activity on low-carbon steel in 3.5 % NaCl. Electrochemical studies and tests were used to determine the inhibitor concentration-dependent protective efficacy. Inhibitor effectiveness has peaked at 85.7 % at 1000 ppm of *Portulaca oleracea* extract. According to polarization analysis in this study, the extracts inhibitor mechanism is of mixed-type with mostly cathodic inhibitive action. Ultimately, the study has proved that the Langmuir isotherm is the best fit to demonstrate monolayer surface coverage of the inhibitor on low-carbon steel. Using this inhibitor is advised, as it is very effective, reasonably priced, and environmentally friendly.

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