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Corrosion Behaviour, Kinetic and Thermodynamic Studies of Water Hyacinth Extract as a Corrosion Inhibitor for Low-Carbon Steel

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Abstract

Corrosion inhibitors are widely used in industry to reduce the corrosion rate of metals and alloys. Corrosion inhibitors adsorb onto metallic surfaces and insulate them from deterioration. Plants abundant in nature offer a cost-effective replacement for toxic chemical inhibitors on the market. The current research used the potentiostatic polarization technique at room temperature to explore the inhibitory impact of water hyacinth extract on the corrosion of low-carbon steel specimens in a 3.5% NaCl solution. The Tafel curve was used to assess corrosion inhibition activity, with the best inhibition efficiency reaching 79.36% at a concentration of 200 ppm. Cyclic polarization indicated the type of corrosion was general corrosion. The surface of carbon steel was investigated using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). FTIR analysis reveals the presence of alkaloid compounds, which are known corrosion inhibitors. In addition, the polarization behavior indicates that this inhibitor acts as a mixed-type inhibitor. Kinetic and thermodynamic parameters have been obtained from temperature studies. The higher activation energy than the blank (26.17 kJ/mol to 46.4 kJ/mol) suggests that an inhibitor has been deposited on the metal surface that is corroding, providing a resist layer to prevent corrosion. The low-carbon steel dissolution process is exothermic, as evidenced by the negative enthalpy of activation value. A positive increase in the activation entropy during the formation of the film layer suggests more disordering.

1. Introduction

Corrosion is the term used to describe the deterioration of metal due to a chemical attack or reactivity with its surroundings. It is regarded as an ongoing problem that is usually challenging to resolve fully. When the protective layer is compromised, corrosion processes quickly become apparent. They are accompanied by several reactions that change the composition and characteristics of the metal surface and the surrounding environment [1,2].

Corrosion inhibitors are small concentrations of substances added to corrosive media to decrease or prevent the reaction of metal with corrosive media. Cooling systems, refinery units, chemicals, oil and gas production units, and boilers are used inhibitors. Corrosion inhibitors can be organic or inorganic substances that adsorb on the metallic structure, isolating it from its surrounding environment and thereby preventing the oxidation-reduction process [3,4]. Inorganic inhibitors are composed of metallic compounds that form protective films on metal surfaces, such as phosphates, chromates, nitrates, and molybdates. While organic inhibitors are composed of organic compounds such as alcohols, amines, and amino acids, the protective mechanism of organic inhibitors relies on their ability to adsorb on metal surfaces, removing water molecules to create a compact barrier [5]. The molecules of organic inhibitors contain nonbonded (lone pair) electrons that can transfer from the inhibitor to the metal surface to create a coordinated covalent bond. The strength of the chemisorption bond depends upon the electron density on the donor atom of the functional group and also the polarizability of the group. The electron density in the metal at the point of attachment changes resulting in the retardation of the cathodic or anodic reactions. The factors that contribute to the action of the inhibitor are chain length, size of the molecule, bonding, aromatic/conjugate, strength of bonding to the substrate, cross-linking ability, and solubility in the environment [1,6]. Although chemical inhibitors have been considered to be excellent anticorrosion materials, their toxicity poses a threat to the environment. Therefore, natural plant extracts have lately been preferred to avoid any negative effects of chemicals. Plant extracts are now widely used since they are cheap, easily available, renewable sources of ingredients that are also environmentally friendly. Plant products are organic in nature, and some of the constituents include tannins, organic and amino acids, alkaloids, and pigments are known to have inhibitory effects. Additionally, they are easily and cheaply extractable [7]. Various parts of plants such as leaves, stems and roots have been stated as corrosion inhibitors. The inhibition ability depends on compounds on their part of the plant [8]. Water hyacinth (Eichhornia crassipes) is a water weed that causes blockages in irrigation channels because of the rapid growth of the plant and it is capable of competing to other aquatic plants [9]. However, scholars reported the presence of anti-oxidant ingredients in water hyacinth extracts such as alkaloids, flavonoids, steroids, and saponins. The ingredients possess a role in the protection of metals from corrosion [10].

Water hyacinth spread can reduce dissolved oxygen levels in bodies of water, reducing aquatic fish productivity. Water hyacinth is particularly efficient in absorbing Calcium, Magnesium, copper, Ferric, Manganese, Aluminum, Boron, Sulfur, Molybdenum, Zinc, Nitrogen, Phosphorus, and Potassium, which allows it to grow faster than other aquatic plants [11]. All scientists recognized plants as waste due to the unfavorable effects of their massive development. Therefore, the researchers used this plant's stems, roots, and leaves to make beneficial products. Oloruntoba et al. (2012) studied using water hyacinth leaves extracts as an inhibitor of high carbon steel alloy (AISI 1030) in a water environment. The findings demonstrated that when the concentration of water hyacinth increased, the rate of corrosion decreased. The sample of carbon steel was inhibited with 20 ml of 20g of water hyacinth leaves extract and the inhibition efficiency was 89.63% in 45 days of the exposure period [12]. According to Salman et al. (2022), The roots of the water hyacinth plant, which were extracted using hexane solvent, can be used to prevent carbon steel from corroding in acidic environments (one molarity of hydrochloric acid). The findings showed that increasing the concentration to 500 ppm boosted the inhibitory efficiency to 91% [9]. Abraham et al. (2022) investigated the corrosion of gray cast iron utilizing hot water digested water hyacinth plant extract as an inhibitor in an alkaline environment (0.5 M of NaOH). They used various concentrations of inhibitors to determine the rate of corrosion at a scan rate of 10 mV/s. Through electrochemical polarization, the rate of corrosion sharply reduced compared to the control specimen [13].

This work aims to prepare a green inhibitor extract using a water hyacinth plant (Eichhornia crassipes), to analyze the impact of green inhibitor on the rate of corrosion on carbon steel specimens by electrochemical polarization under the prevailing research conditions. Also, the effect of temperature on corrosion of the inhibition process was studied.

2. Experimental Procedure

2.1. Preparation Water Hyacinth Extract

Water hyacinth plant was gathered from the Diyala River in southeast Baghdad. The leaves of the water hyacinth were used to prepare the extract after being gently rinsed under water to remove any dirt or debris. The leaves were dried, then ground into a fine powder using an electric grinder. This technique aids in the breakdown of the cell walls and enables active compound extraction. Then add 50 g of the ground leaves to a glass conical flask

(1000 ml) along with 1000 ml of ethyl alcohol (99%), and stir the mixture using a hot plate stirrer at 50 °C to ensure adequate mixing after being stirred for 48 hours in a glass conical flask. The extract was filtered by filter paper (Watman No. 1) in a Buchner funnel to get a clear solution free of impurities and plant residues. Concentrate the filtrate containing the desired compounds dissolved in ethyl alcohol by using a rotary evaporator under vacuum at 45 °C. After concentrating the extract with a rotary evaporator, the final product was dried in an oven at a temperature of 45 °C. A paste of 4 g of the extract was obtained. Then a standard aqueous solution of the extract with a concentration of 1% was prepared by adding 396 ml of distilled water to 4 g of the ethanolic extract paste. In this way, an extract with a standard concentration of 1% was obtained to be ready for subsequent experiments.

2.2. Preparation Samples of the Working Electrode

The low-carbon steel was used in this study as a working electrode. The carbon steel coupons were polished using emery paper with grade degrees 500, 800, and 1200 using a polishing machine to provide a smooth surface suitable for the electrochemical polarization test. Then the coupons were washed with absolute ethanol and kept until used. The chemical composition of the carbon steel coupon is shown in Table (1).

Table (1): Chemical compositions of carbon steel coupon.

Elements	Concentration (wt%)
Fe	99.3
C	0.2
Si	0.07
Mn	0.16
P	0.034
Cu	0.157
Cr	0.042
Ni	0.02
Co	0.01
W	0.01

The salt solution was prepared by taking 35g of sodium chloride and diluted by 1000 ml of distilled water to obtain a solution (3.5% salt). Different concentrations of water hyacinth extract inhibitor (50, 100, 150, 200 ppm) were taken to study the effect. The electrochemical measurements were achieved using potentiostat (MLab 200) with a three-electrode system. The working electrode was a carbon steel coupon as mentioned before. Whereas the counter electrode was Platinum (Pt) with saturated Ag/AgCl as a reference electrode. The open circuit potential (E_{corr}) was monitored for 15 min. The corrosion efficiency was calculated by the following equation [14] :

$$IE\% = \frac{I_{corr} - I_{inh\,corr}}{I_{corr}} * 100\% \qquad (1)$$

Where I_{corr} corrosion current density (µA/cm^2) in the absence of inhibitor, $I_{inhcorr}$ corrosion current density (µA/cm^2) in the presence of inhibitor. Tafel plots were recorded for corrosion rate measurement by scanning the potential ±200 mV around the open circuit potential at the rate of 3 mV/sec.

2.3. Surface Characterization

Fourier Transform Infrared Spectroscopy (Shimadzu, Japan) was used to determine the functional group of water hyacinth extract and metal surface (corrosion product). The spectrum range of the FTIR was the mid-infrared region, which covers the frequency ranges of 400- 4000 cm^{-1}. The surface topography of carbon steel was measured and analyzed by SEM.

3. Results and Discussion

3.1. Corrosion Measurements

Figure (1) shows anodic and cathodic polarization curves for the corrosion of carbon steel in simulated seawater solution with different concentrations of water hyacinth plant extract at ambient temperature. The employed method was extrapolation for polarization curves and the data of corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic and anodic Tafel slopes and percentage of inhibition efficiency (IE%) are listed in Table (2). As shown in Figure (1) the addition of different concentrations of water hyacinth extract plant leaves affects both the cathodic and anodic of the Tafel curves and decreases the current densities [9]. The current density (I_{corr}) values were shifted to more active potential and at 150 ppm reached 570.9 mV, which means that water hyacinth extract works as a cathodic inhibitor. In addition, it was clear that the Tafel plots of 200 ppm concentration shifted toward lower corrosion density values, confirming the role of water hyacinth protection as an inhibitor. Table (2) presents Tafel slopes b_c and b_a also affected by adding inhibitor since decreased the values of slopes compared with the blank solution referring to reducing the reactions of cathodic and anodic sites and decreasing the change in current corresponded to change in potential through the corrosion process.

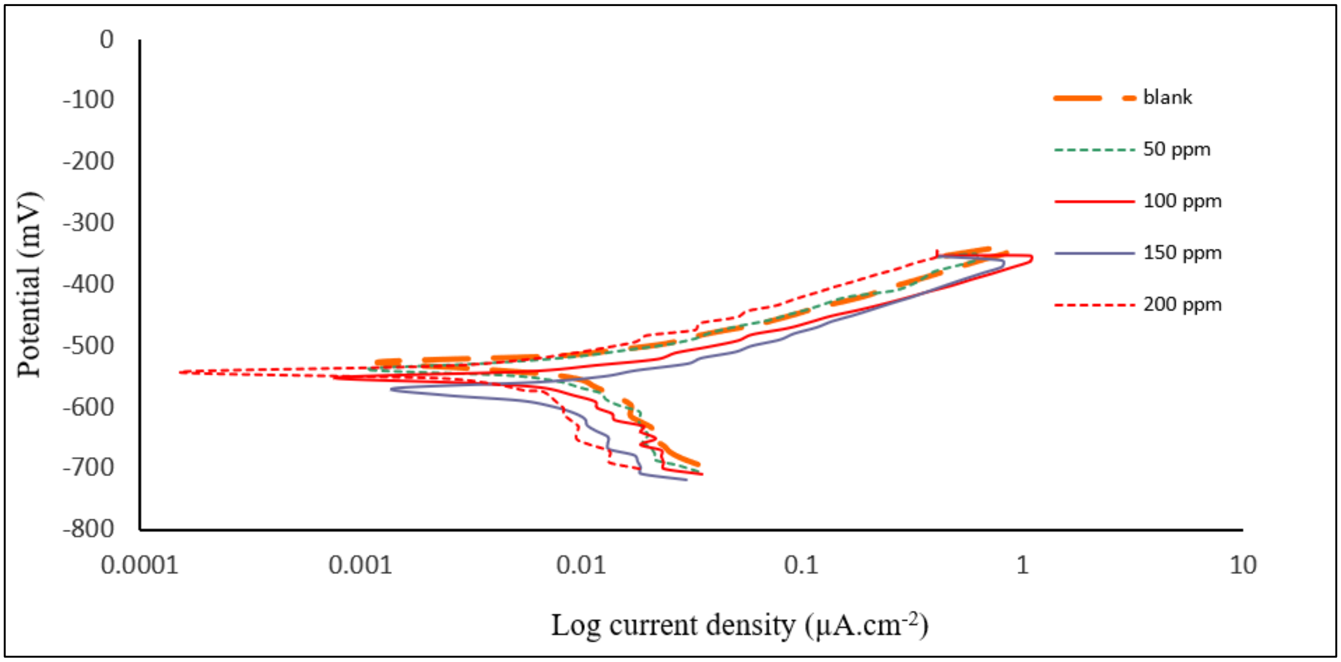

Figure (1): Potentiostatic polarization curves (Tafel plots) for different concentration.

Table (2): Polarization parameters for different concentration.

	Conc. (ppm)	-E (mV)	$I_{corr.}$ (μA/cm^2)	b_a (mV/D_{ec})	$-b_c$ (mV/D_{ec})	IE%
1	Blank	528.3	7.27	67.6	179.8	-
2	50	538.3	5.85	74.4	126.2	19.5
3	100	544.0	4.7	66.8	190.4	35.35
4	150	570.9	3.7	45.7	136.7	49.1
5	200	539.5	1.5	40.9	50.3	79.36

The probability of pitting corrosion was investigated by cycling polarization procedure. Figure (2) shows the cyclic voltagrams and the histories loop that have formed during the polarization for low carbon specimens without inhibitor and with water hyacinth extract as an inhibitor at a concentration of 200 ppm. It is clear no pitting corrosion is observed and the histories loop indicate that general corrosion occurred.

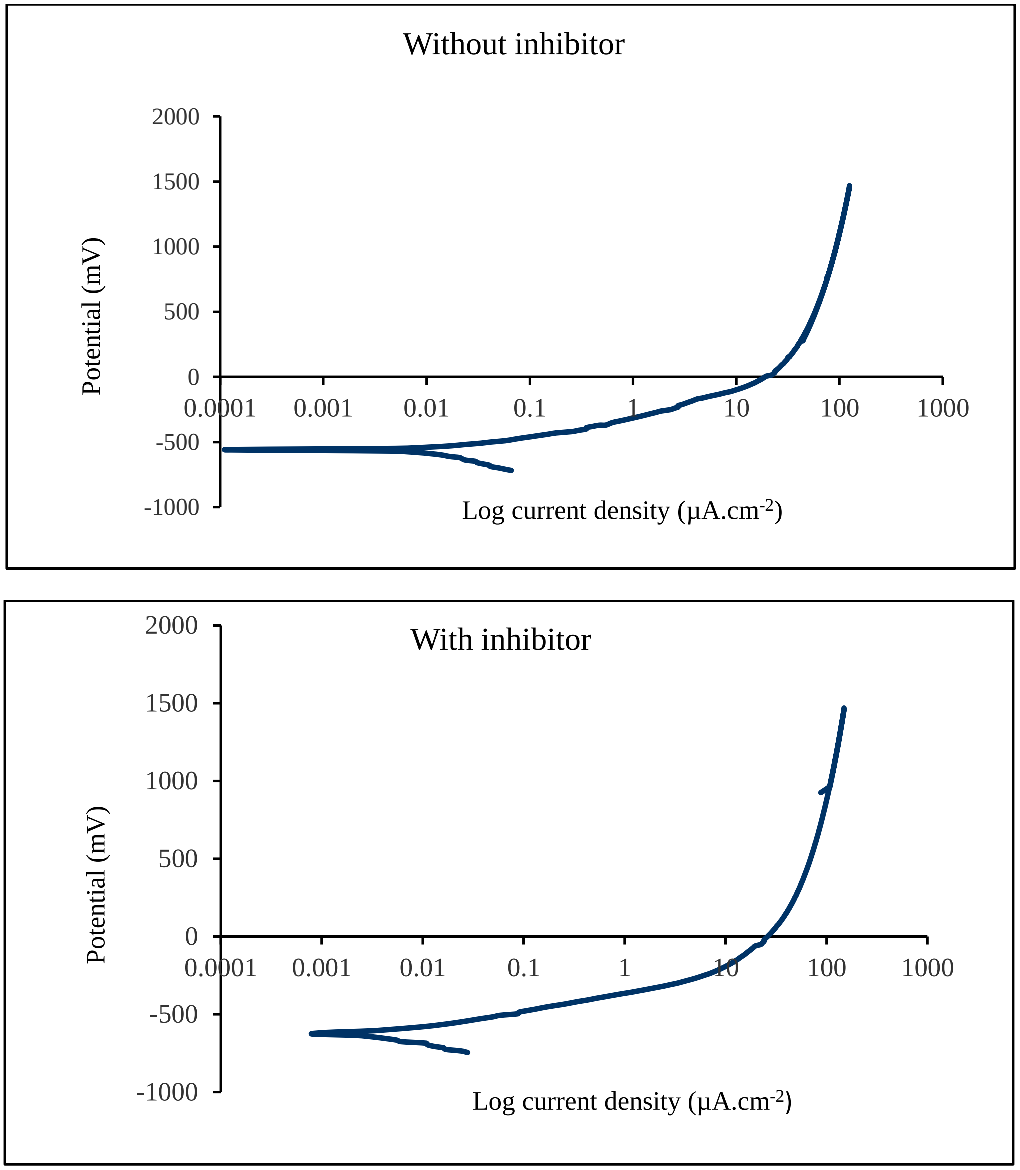

Figure (2): Cyclic polarization of low carbon steel specimens without inhibitor and with inhibitor.

3.2. Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared spectroscopy test was performed to study the chemical functional groups shifting for water hyacinth extract and the corrosion product. Figures (3 & 4) display the main functional groups between the extract and corrosion product which represent the metal surface. The water hyacinth extract shows characteristic vibrational modes at 3550-3200 cm^{-1} for the O-H stretching in alcohol, 1730-1715 cm^{-1} for the C=O stretching in unsaturated ester, 1275-1200 cm^{-1} for the C-O stretching in alkyl aryl ether, 1124-1087 cm^{-1} for the C-O stretching in secondary alcohol, 850-550 cm^{-1} for the C-Cl stretching in halo compound. In addition, there are two wave numbers 1627.81 and 1458.08 cm^{-1} indicating the existence of N-H bending function groups which refer to the presence of alkaloid compounds which is used as a corrosion inhibitor [15]. It is clear from the comparison between FTIR spectra for water hyacinth and its film on the carbon steel metal (corrosion product) as shown in Table (3) that all functional groups have been shifted to lower values due to the force of binding between the interface of the metal surface and the inhibitor.

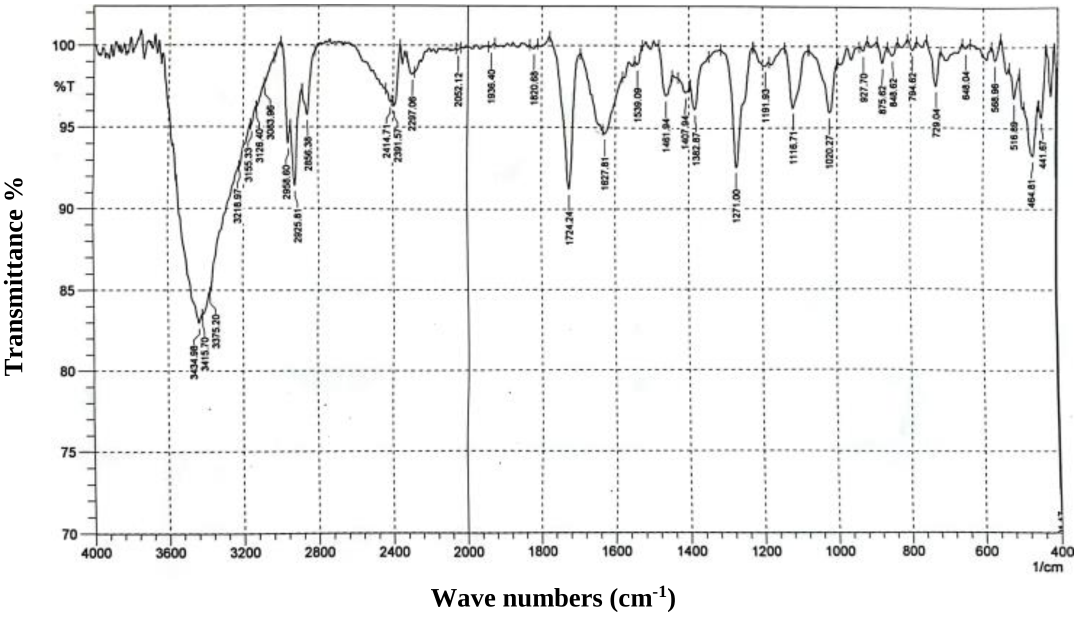

Figure (3): FTIR spectra of water hyacinth extract.

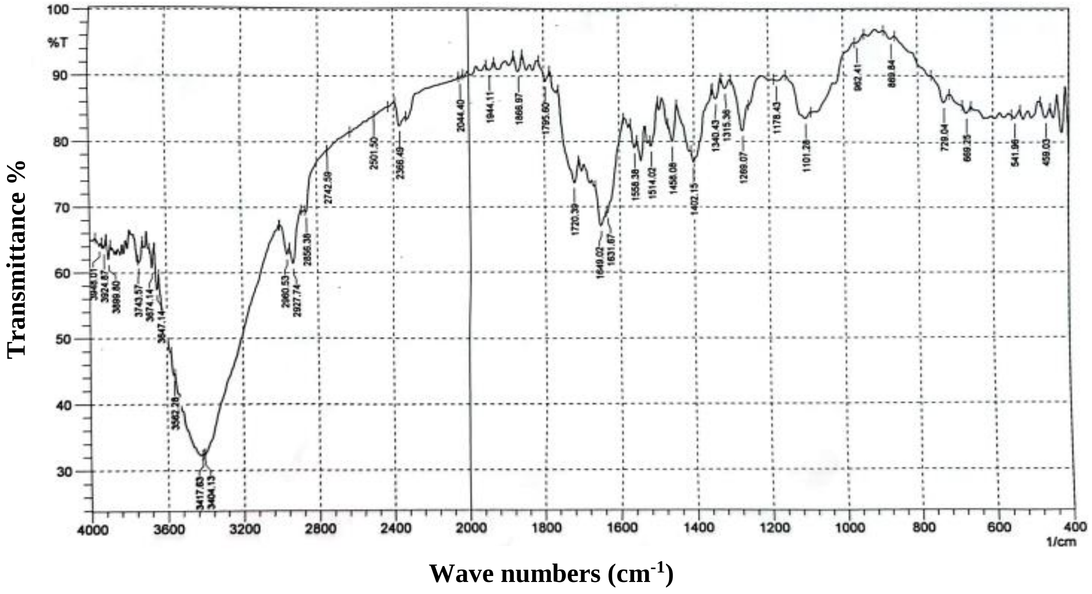

Figure (4): FTIR spectra of corrosion product.

Table (3): Summary of characteristic FTIR for water hyacinth and corrosion product.

Extract wave number(cm^{-1})	Corrosion product wave number (cm^{-1})	Vibrational modes range wave number (cm^{-1})	Appearance	Group
3434.98	3417.63	3550-3200	Strong	O-H stretching
1724.24	1720.39	1730-1715	Strong	C=O stretching
1271	1269.09	1275-1200	Strong	C-O stretching
1116.71	1101.28	1124-1087	Strong	C-O stretching
729.04	729.04	850-550	Strong	C-Cl stretching

3.3. Scanning Electron Microscope (SEM) Analysis

Surface analysis studies by SEM for the low carbon steel before and after corrosion test in pure simulated seawater and in inhibited seawater with optimum concentration (200 ppm) have been represented in Figure (5a, b, & c), respectively. SEM analysis technique gives two-dimensional (2D) visual information about the performance of the insight inhibitor toward the metal corrosion. Figure (5a) shows the surface of carbon steel before the corrosion test after polished, where observed that the surface is clear and smooth with a small scratch [16]. From Figure (5b), it can be observed that the higher damage X50 surface fulfilled with corrosion product while, with Figure (5c), after adding the optimum concentration of inhibitor, the X50 surface becomes smoother and freer compared to the surface of carbon steel in pure seawater, and it can be observed the particle of extracted inhibitor were adsorbed on the surface of carbon steel, this inferred the inhibition action of water hyacinth via blocking the active centers of the metal surface.

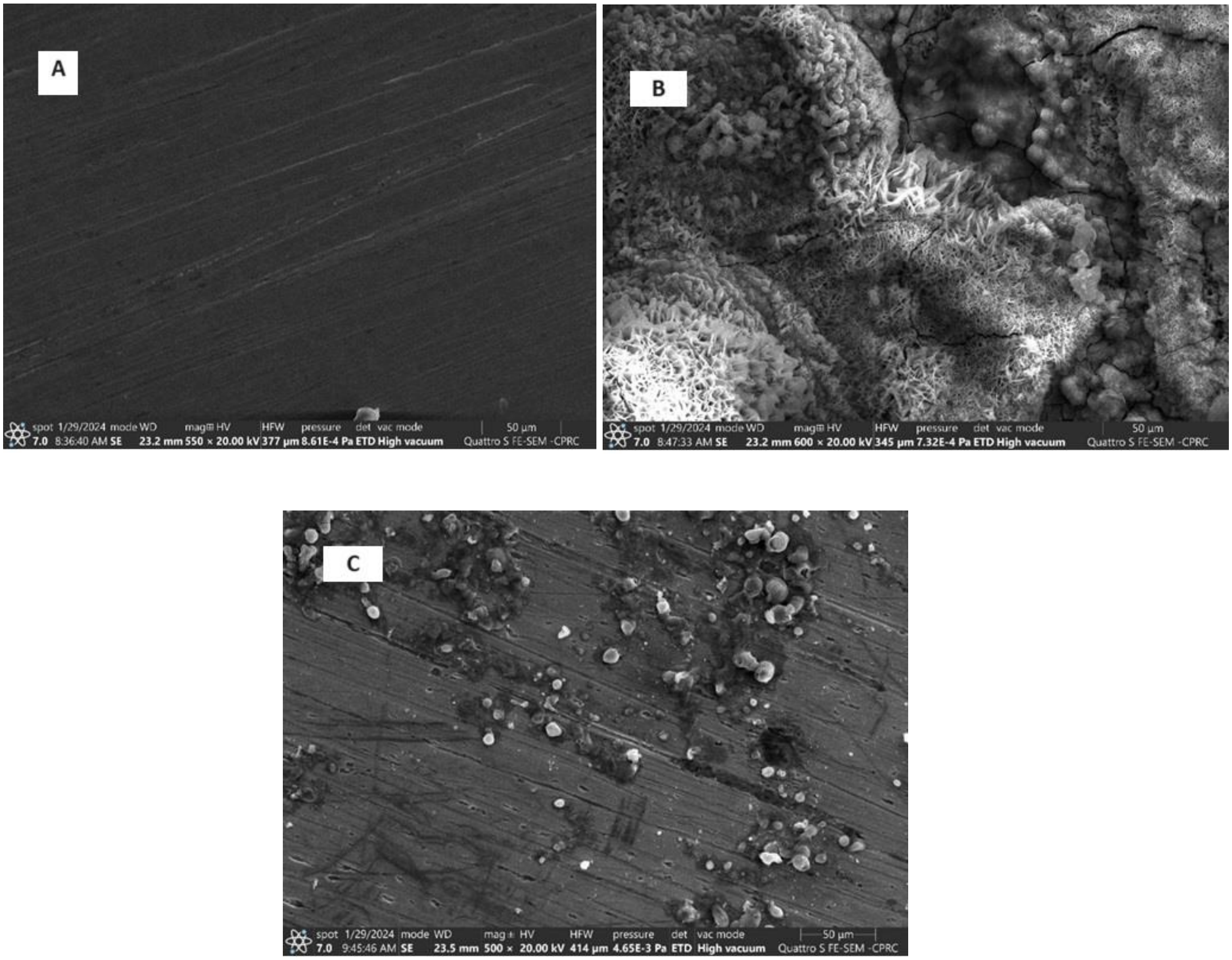

Figure (5): SEM surface analysis micrograph of the X50 carbon steel a) before, b) after the corrosion test in pure seawater, and c) in inhibited seawater with optimum concentration (200 ppm).

3.4. The Kinetic and Thermodynamic Study

The effect of temperature on the rate of corrosion of low carbon steel coupons in 3.5% NaCl solution in the presence and absence of inhibitor at a range of temperatures (298–338 K). The Arrhenius equation has been utilized to calculate the activation energy from the following equation [17]:

$$\boldsymbol{log i_{corr}} = \log A - \frac{E_a}{2.303\,RT} \qquad (2)$$

Where i_{corr} is the corrosion current density, A is the pre-exponential factor, *Ea* is the apparent activation energy, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K), *Ea* is the activation energy.

Figure (6) presents the Arrhenius plots of the natural logarithm of the corrosion current density vs. 1/T in the absence and presence of water hyacinth extract at a concentration of 200 ppm. The calculated values of activation energy are given in Table (4). The increased activation energy in inhibited solutions (from 26.17- 46.4kJ.mol^{-1}) compared to the blank indicates that the inhibitor is physically deposited on the corroding metal surface and poses a resist layer against corrosion [18]. Arrhenius factor *A* increased which refers to an increase in the number of corrosion sites with the existence of water hyacinth extract [19].

Temperature has an impact on thermodynamic parameters, which can be used to evaluate the enthalpy (ΔH) and entropy (ΔS) of the corrosion process activation. The enthalpy and entropy of the corrosion process's activation were calculated using the equation [19]:

$$\boldsymbol{log}\frac{i_{corr}}{T} = \log\left[\frac{R}{Nh} + \frac{\Delta S*}{2.303R}\right] - \frac{\Delta H*}{2.303\,RT} \qquad (3)$$

Where i_{corr} is the corrosion current density, A is the pre-exponential factor, Ea is the apparent activation energy, R is the universal gas constant (8.314 J mol^{-1} K^{-1}), T is the temperature (K). N: the Avogadro's number (6.022 x 1023 mol^{-1}), h: Plank's constant (6.626176 x 10-34 J.s), ΔS*: the entropy of activation, ΔH*: the enthalpy of activation. From the slope and the intercept, ΔH and ΔS were calculated as shown in Figure (7). The enthalpy of activation value was negative, which reflects the exothermic nature of the low carbon steel dissolution process. The entropy of activation was increased positively, which indicates increased disordering when the film layer formed [2].

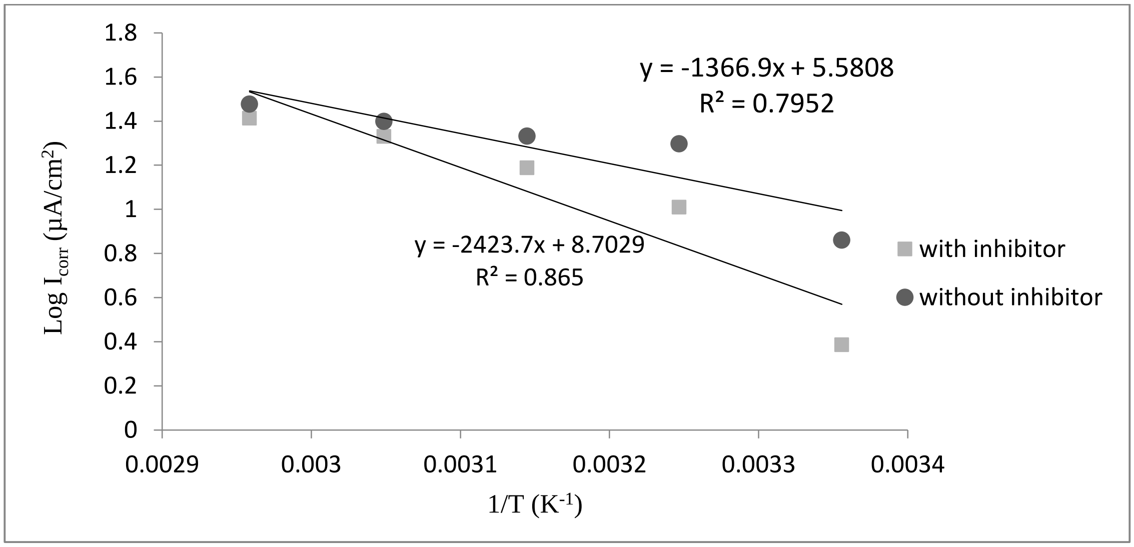

Figure (6): Arrhenius Plot of log I_{corr} Versus 1/T for the corrosion of low-carbon steel.

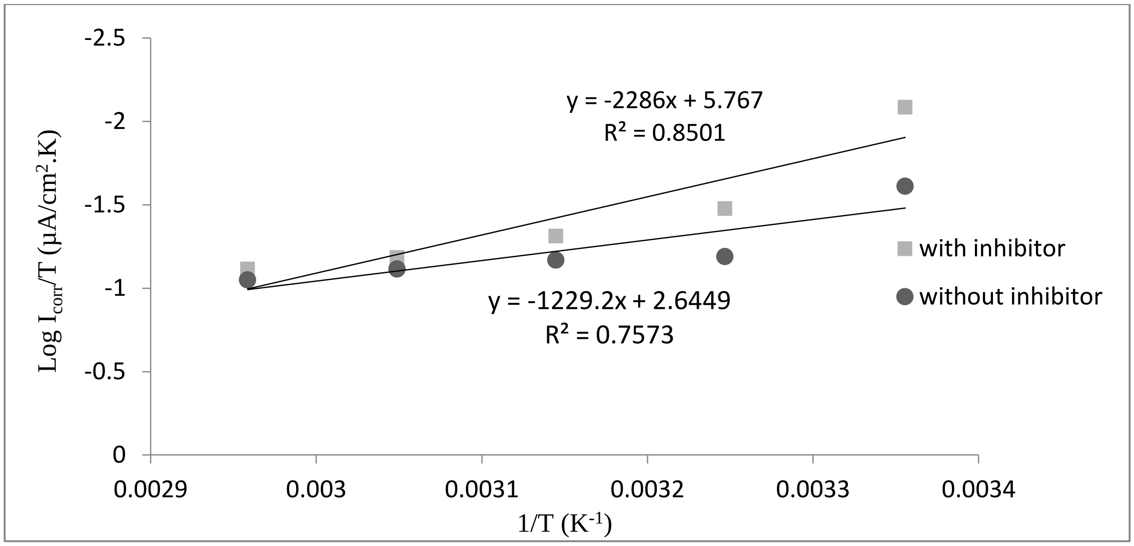

Figure (7): A plot of log I_{corr}/T Versus 1/T for the corrosion of low-carbon steel.

Table (4): Transition state thermodynamic parameter at different temperatures.

	ΔH* (kJ)	**ΔS* (kJ)**	**Ea (kJ.mol^{-1})**	**A (Molecules.cm^{-2}.S^{-1})**
Blank	-23.535	-0.146	26.17	2.29×10^{29}
Inhibitor	-43.77	0.871	46.4	3.3×10^{32}

4. Conclusion

Based on the experimental findings, several observations can be made. Water hyacinth extract proves effective in inhibiting corrosion on carbon steel surfaces. Cyclic polarization analysis indicates that general corrosion is predominant. FTIR analysis confirms the presence of NH bending groups, indicating the existence of alkaloid compounds. In addition, the FTIR result indicated that the actual adsorption of the inhibitor is a result of a donation of a single pair of electrons in an alkaloid structure to the metal that leads to the formation of complexes on the metal surface. Kinetics and thermodynamic studies were carried out to estimate the binding/adsorption mechanism of the molecules of inhibitor onto the surface of the carbon steel. Corrosion inhibition of the water hyacinth extract on the carbon steel surface occurred by physical adsorption mechanism. This was proved by the values of activation energy that was obtained in an inhibited medium which was higher than in the blank solution. It was observed that the maximum inhibition efficiency of 79.36% was attained when the inhibitor concentration was 200 ppm. Thermodynamic parameters show that the interaction on low-carbon steel surfaces with inhibitors is exothermic and promotes increased disordering.

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Conflict of Interest: The authors declare that there are no conflicts of interest associated with this research project. We have no financial or personal relationships that could potentially bias our work or influence the interpretation of the results.

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