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Corrosion Inhibition of Mild Steel in Sulphuric Acid Solution with *Tetradenia riparia* Leaves Aqueous Extract: Kinetics and Thermodynamics

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Abstract: One of the most successful ways for maximizing profit and lowering costs is to use mild steel over other corrosion-resistant alloys. As a result, mild steel is the most commonly used metallic material in many industries, and its corrosion resistance has received a lot of attention. The mild steel corrosion inhibition using compounds derived from plants is the most practicable and preferable technique because of their linked low cost and green chemistry credentials. This study reports on the kinetics and thermodynamics of mild steel corrosion inhibition in sulphuric acid media utilizing *Tetradenia riparia* leaves aqueous extract as a potential green inhibitor. The investigations were carried out using the gasometric technique. The findings indicated that the corrosion inhibition efficiency (IE) increased with increasing inhibitor concentration with an optimal value of 90.6% at 500-ppm. The increase in temperature 298 to 338 K lowered the corrosion inhibition efficiency by only 4%. The adsorption kinetics of the extract on the mild steel fit into Langmuir, Temkin, EL-awady, and Freundlich models, but the Langmuir was the best. The results of this investigation show that adsorption of the extracted chemicals on mild steel in a sulphuric acid solution is feasible and most likely involves a combination of physical and chemical adsorption.

Keywords: mild steel, corrosion kinetics, corrosion thermodynamics, Tetradenia Riparia, sulphuric acid.

1. Introduction

Corrosion is a prevalent problem that affects applications of metallic substances in various industries, including construction and manufacturing. Corrosion is a naturally occurring electrochemical process that causes characteristics of metallic materials to deteriorate. As a result, substantial damage to bridges, buildings, pipelines, and other infrastructures may occur, resulting in financial costs associated with the repair, replacement, product losses, safety, and environmental contamination. The cost resulting from the maintenance and replacement of corroded materials alone is estimated to amount to about 3-4% of national growth product (GNP) [1].

Mild steel is one of the metallic materials used for a wide range of applications such as manufacturing reactors, storage vessels, gathering pipelines, drilling equipment, and other apparatuses due to superior mechanical properties and thermal conductivity. However, mild steel corrosion has been a serious global problem for many decades, causing massive economic losses in a vast number of fields. Particularly, the impacts of MS corrosion in acidic media are considerable due to industrial processes such as acid pickling, acid descaling, industrial cleaning, and oil well acidizing [2,3]. Therefore, the protection of MS against corrosion in acidic conditions is attracting significant recent attention.

The use of inhibitors is one of the most practical and cost-effective methods of minimizing/controlling corrosion rates and extends a lifetime of metallic materials [4]. The inhibitor can be defined as a chemical substance added in small amounts to reduce the extent to which the metallic materials are exposed to corrosive environments. Both organic and synthetic compounds have shown acceptable efficacy in corrosion inhibition [5]. However, most conventional compounds such as chromates and phosphates are reported to cause harm to organisms and the environment due to their toxic nature, consequently, are regarded as environmentally unfriendly [5,6]. Therefore, the use of green compounds that are biodegradable and not causing harm to the environment and organisms is of practical importance.

Natural products such as plant extracts, proteins, and natural polymers are known for effective corrosion inhibition [7,8]. Among these, plants have been recognized as a good source of many extractable organic compounds that are inexpensive, biodegradable, eco-friendly, and non-toxic [9]. Consequently, there is a recent increasing trend of using compounds from plants and biomass wastes as potential green corrosion inhibitors [5,10]. Most organic compounds containing heteroatoms such as nitrogen, sulfur, phosphorous, and oxygen are reported to contain corrosion inhibition properties due to their ability to chemically interact with metal surfaces and form a passive thin film [11-14]. Therefore, the compounds such as tannins, flavonoids, phenols, steroids, and triterpenoids have shown an acceptable efficacy in metal corrosion inhibition [5,15]. *Tetradenia riparia* (Tr) leaves contain numerous compounds containing lipophilic and polar functional groups such as OH [16], which is an important feature for corrosion inhibitors. To my knowledge, no result on the efficacy of Tr extracts in metal corrosion inhibition has been documented in the literature. In this study, the aqueous extract of Tr leaves as a source of environmentally friendly organic compounds for the mild steel corrosion inhibition in an acidic solution was investigated using a gasometric method.

2. Materials and Methods

2.1. Inhibitor preparation.

Tetradenia reparia (Hochst.) plant, also known as the ginger bush, belongs to a Lamiaceae (Labiate) family. The plant parts, such as leaf and stem, are useful for medicinal purposes because they contain broad-spectrum antibacterial compounds [17]. The leaves of this plant were collected from a garden at the Sokoine University of Agriculture (SUA), Morogoro, Tanzania. They were then rinsed in distilled water to remove any adsorbed particles before being dried in the shade. The dried leaves were ground into a powder, and 10 g of it was refluxed for 4 hours in 100 mL of distilled water at the temperature of 60 °C. The resultant solution was filtered to remove undissolved materials, and the filtrate was dried overnight in the oven. The resultant solid brown substance was dissolved in 50 mL of 2 M H_2SO_4 to prepare a stock solution from which working solutions with extract concentrations ranging from 0 to 500 ppm were made.

2.2. Gasometric method.

The gasometric technique was carried out according to procedures previously published [18]. Mild steel specimens with the known chemical composition [19] measuring 2 cm x 1 cm and 0.0920 cm were physically abraded with sandpapers of different grit 100, 800, and 2400 before being washed with distilled water and acetone. The specimens were then immersed for 60 minutes in a glass tube containing 10 mL of a 2 M H_2SO_4 solution as a corrosive medium. The hydrogen gas liberated was collected in a burette with a delivery tube, and the volume of displaced water was measured every 2 minutes. The corrosion inhibition efficiency (IE%) was determined using corrosion rate using Eqn. 1&2.

$$\text{CR} = \frac{V_t - V_i}{t_t - t_i} \quad (1)$$

$$\text{IE\%} = \frac{CR^0 - CR^i}{CR^0} \times 100 \quad (2)$$

where V_t and V_i are volume of hydrogen at time t and i and CR^0 and CR^i are corrosion rates before and after addition of inhibitors, respectively.

2.3. Determination of activation energy (Ea)

The activation energy (E_a) is determined using the Arrhenius equation presented in Eqn. 3 [20]. The plot of Ln (*CR*) versus the reciprocal of temperature (*1/T*) in Eqn. 3 gives a slope from which the activation energy is calculated.

$$\text{Ln(CR)} = \frac{-E_a}{RT} + Ln(A) \quad (3)$$

where R is the gas constant (8.3144621 $J.K^{-1}.mol^{-1}$), E_a is the activation energy, T is the temperature in Kelvin, and A is the exponential factor.

2.4. Determination of enthalpy change

The change in enthalpy was evaluated using an alternate formula for the Arrhenius equation in the transition state (Eqn. 4).

$$\text{CR} = \frac{RT}{Nh}\exp\left(\frac{\Delta S}{R}\right)\exp\left(-\frac{\Delta H}{RT}\right) \quad (4)$$

Eqn. 4 can be linearized to form Eqn 4a, which can be further modified to produce Eqn. 5.

$$\text{Ln}\ \frac{\text{CR}}{T} = \text{Ln}\frac{R}{Nh} + Ln\left\{\exp\left(\frac{\Delta S}{R}\right)\right\} + Ln\left\{\left(-\frac{\Delta H}{RT}\right)\right\} \quad (4a)$$

$$\text{Ln}\ \frac{\text{CR}}{T} = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + \left[\text{Ln}\frac{R}{Nh} + \left(\frac{\Delta S}{R}\right)\right] \quad (5)$$

where h is Planck's constant (6.626176 × 10^{-34} J.s), N is the Avogadro's number (6.02252 × 10^{-23} mol^{-1}); ΔS is the entropy change and ΔH the enthalpy change.

The enthalpy change was determined from the slope of the plot of *CR/T* against *1/T*.

3. Results and Discussion

3.1. Fourier transform Infrared spectroscopy (FT-IR).

The functional groups present in a compound play critical roles in determining the chemical interactions between the inhibitor molecules and the metal surface. The phytochemicals containing heteroatoms or unsaturated bonds can be adsorbed on the metal surface to produce a corrosion protective layer. The adsorption process can be facilitated by coordination between the lone pairs/ π-electrons and empty orbital of metals. Thus, the analysis of functional groups contained in the aqueous crude extract of Tr leaf was performed using the FT-IR spectrometer in the wavelength range of 500- 4000 cm^{-1}. The findings shown in Figure 1 indicated the presence of OH (3224), CH (2920), C-O (1562), C=C (1399), and C-O (1021) functional groups. This suggests that the Tr leaf extract contains compounds capable of chemically interacting with a metal surface through the lone pair on oxygen heteroatom or π-electrons (double bond) to produce a corrosion protective layer. The identified functional groups were consistent with reported corrosion inhibitors [5,21]. Thus, the extract was used for subsequent corrosion inhibition experiments.

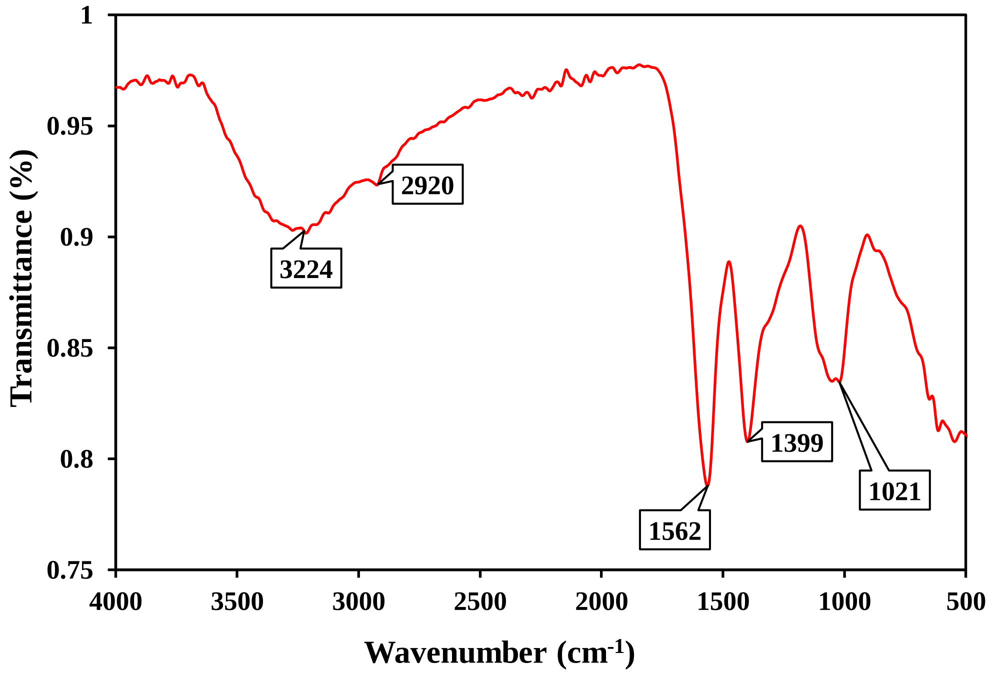

Figure 1. FT-IR spectrum of crude aqueous extract of Tr leaf.

3.2. Influence of inhibitor concentration.

The concentration of chemical molecules adsorbed on the surface of mild steel affects the performance of the inhibitor because it determines the extent to which the metal surface is isolated from a corrosive solution through the formation of protective films. Thus, the effect of the concentration of Tr leaves aqueous extract in the range of 0 to 500 ppm on the mild steel corrosion inhibition was studied. The results in Figures 2 & Table 1 showed that corrosion rate decreased, and inhibition efficiency (IE) increased with increasing inhibitor concentrations. The inhibition efficiency of 60% was observed with just 100-ppm of the extract. This observation indicates that the extract contains high corrosion inhibition ability chemical compounds. The increase of inhibitor concentration increases the number of inhibitor molecules adsorbed on a metal surface (surface coverage, ø), producing a passive film (barrier) that prevents a direct attack of acid. This is a possible explanation for decreasing corrosion rate and increasing IE% with inhibitor concentrations. The lowest corrosion rate (12×10^{-3} mL/min) and highest corrosion inhibition efficiency (90.6%) were observed at the Tr concentration of 500-ppm. The performance of the Tr inhibitor was similar to other reported plant extracts, as presented in Table 2. Therefore, the Tr concentration of 500-ppm was regarded as the optimal inhibitor concentration for the subsequent corrosion experiments.

Table 1. Effect of Tr leaf aqueous extract concentration on mild steel corrosion in 2 M H_2SO_4 at 298 K.

[Tr] ppm	CR (mL/min) 10^{-3}	IE%	Coverage (ø) 10^{-3}
0	138	0	0
100	54	60.5	605
200	28	80.4	804
300	23	84.1	841
400	21	86.3	863
500	12	90.6	906

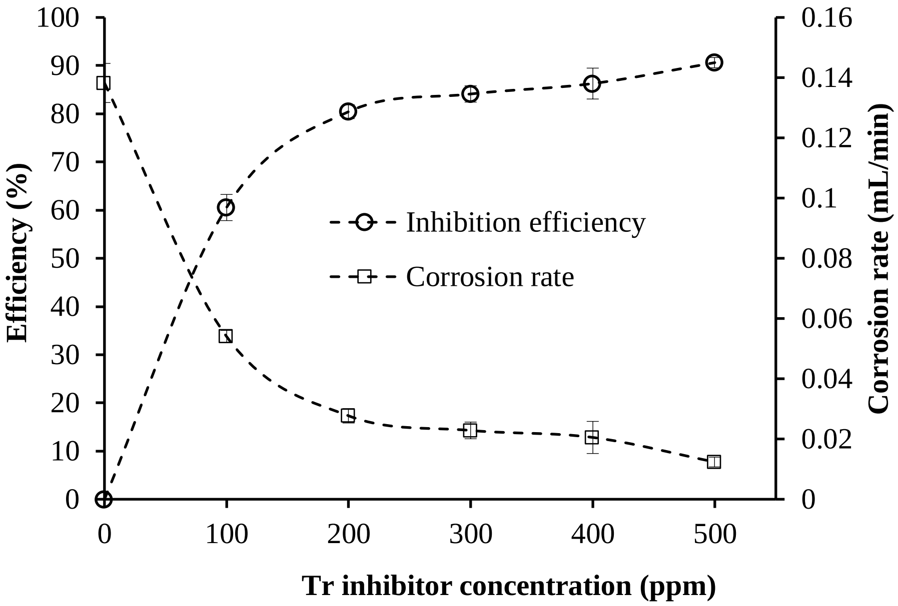

Figure 2. Effect of Tr inhibitor concentration in the range of 100 – 500 ppm on mild steel corrosion rate and efficiency in 2 M H_2SO_4 solution at 298 K.

Table 2. The inhibition efficiency of Tr aqueous extract on the corrosion of mild steel in sulphuric acid solution compared with the performance of other plant leaf extracts. The molarity in brackets indicates the concentration of sulphuric acid solutions.

Plant name	Optimal concentration	IE%	Reference
Eriobotrya japonica (Lindl.) leaves (0.5 M)	100 % v/v	96	[22]
Citrus aurantium leaves (1 M)	10 ml/L	89	[23]
Acacia nilotica leaves (0.5 M)	50 ppm	89	[24]
Athyrium filix-femina leaf extract (1 M)	1.0 g/L	85.5	[25]
Raphinus sativus Linn. (Cruciferae) (0.5 M)	300 ppm	93	[26]
Africa parquetina leaves extract (2 M)	0.5 g/L	87.8	[27]
Tephrosia Purpurea (*T. purpurea*) (1 N)	300 ppm	93	[28]
Medicago sativa leaf (1 M)	500 ppm	92	[29]
Tetradenia riparia leaves (2 M)	500 ppm	90.06	This study

3.3. Kinetics and thermodynamics parameters.

The chemical kinetics of a metal corrosion process in the presence of various extract concentrations can be explored using equation 6 [30], which can be modified further to Eqn. 7 [31,32].

$$\mathrm{CR} = k[\mathrm{Tr}]^n \quad (6)$$

$$\log \mathrm{CR} = \log k + n \log[\mathrm{Tr}] \quad (7)$$

where n is the order of reaction, k specific rate constant in the present work conditions, CR corrosion rate.

The plot of log CR and log [Tr] shown in Figure 3 shows good linearity with the correlation coefficient close to 1 (0.983). This indicates the reaction for the corrosion process in the present study obeys first-order kinetics.

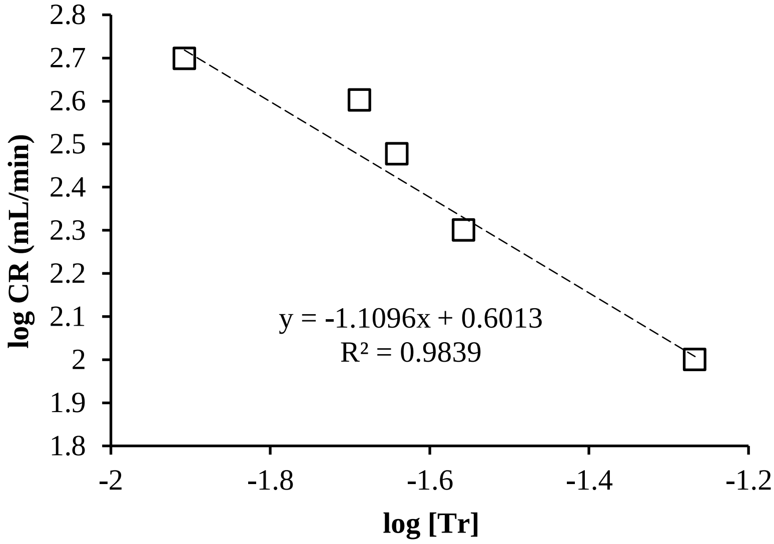

Figure 3. log CR vs. log [Tr] plot for the corrosion of mild steel in 2 M H_2SO_4 at 298 K.

The influence of temperature has a significant role in understanding corrosion inhibition mechanisms. Thus, the effect of temperature in the range of 298-338 K on the performance of the extract was investigated using the blank and optimal inhibitor concentration of 500-ppm. The results displayed in Figure 4 & Table 3 show that the corrosion rate increased with the increase in temperature for both uninhibited and inhibited solutions. The observation is a possible indicator of the effect of temperature on increasing kinetics of corrosion chemical reaction.

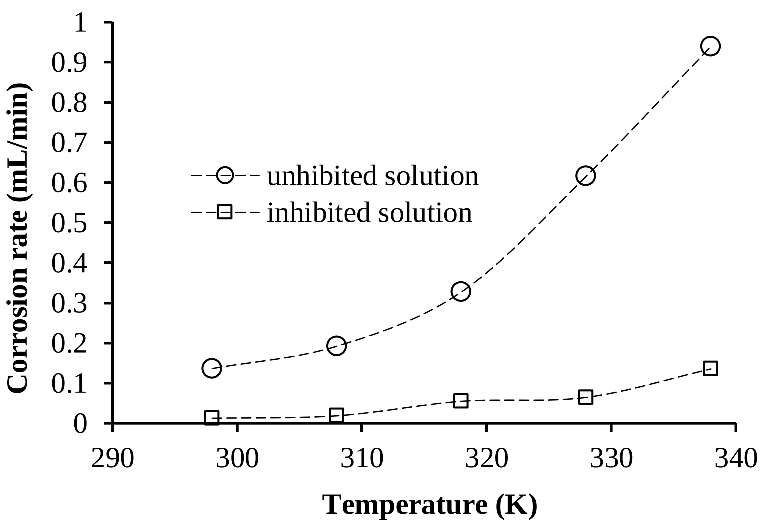

Figure 4. Influence of temperature on the performance of Tr leaf aqueous extract in the presence and absence of 500 ppm in 2 M H_2SO_4 and temperature range 298-338 K.

It was further noted that the increase in corrosion rates was lower for the inhibited solution compared to the uninhibited solution. This suggests that even at high temperatures, the film formed by adsorbed molecules effectively prevented metal corrosion. The increase in the corrosion rate for the uninhibited solution was initially slow (298-318 K), and the rapid increase was observable in the temperature range of 318-338 K. This is attributed to the deposition of corrosion products on the mild steel surface, such as Fe-oxides and Fe-hydroxide, which produces a coating that protects the mild steel from a direct attack of the corrosive acidic solution and slows the corrosion process [33,34]. However, as the temperature rises, the corrosion products dissolve, exposing more metal surfaces to the corrosive solution, resulting in greater metal corrosion.

Table 3. Influence of temperature (298-338 K) on the mild steel corrosion inhibition in the presence and absence of 500 ppm Tr leaf aqueous extract in 2 M H_2SO_4.

T (K)	CR^o	CR^i	IE%	Øx10^{-3}
298	0.136	0.012	90.6	906
308	0.192	0.018	89.1	891
318	0.327	0.054	86.0	860
328	0.615	0.064	87.1	871
338	0.939	0.135	86.3	863

The performance of the extract at elevated temperature can be further evaluated by IE%, as shown in Figure 5 and Table 3. The results show that the IE% decreased with increasing temperature. This is a likely consequence of the partial desorption of the inhibitor molecules at the elevated temperature due to the increased kinetic energy of molecules that increases the metal surface area exposed to the corrosive solution. The decrease in IE% with increasing temperature has been previously associated with the physical adsorption process [35,36].

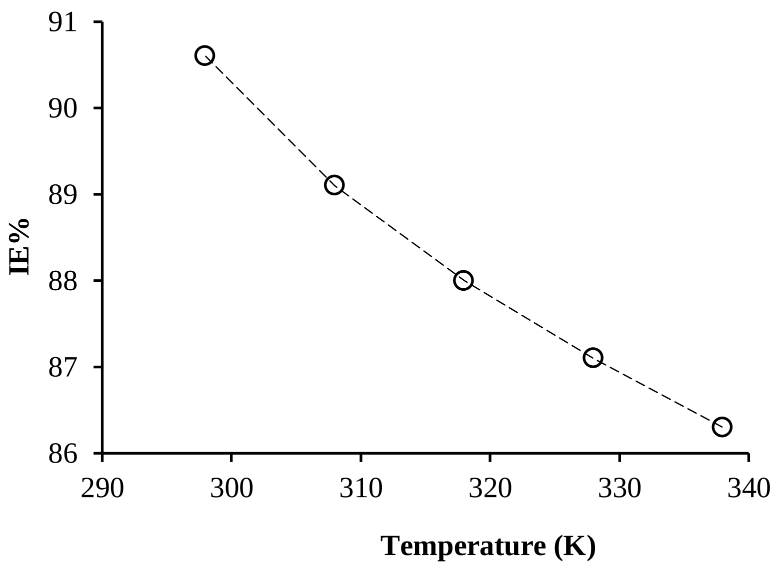

Figure 5. Influence of temperature (298 - 338 K) on the performance of Tr leaf aqueous extract (500 ppm) for mild steel corrosion inhibition in 2 M H_2SO_4.

However, the presence of chemical adsorption in the current study cannot be completely ruled out due to the complex nature of the Tr leaf extract. The extract contains molecules with diversified chemical properties capable of producing both types of adsorptions [16]. The observation that only a small decrease in IE (4.3%) as temperature decreased from 298 to 338 K could be a possible indicator of the presence of the desorption to a small extent. In chemisorption, increasing temperature increases the collision between the molecules and the metal surface, leading to increased adsorption strength. This is a possible explanation for the small decrease in the IE%. It can be concluded that the mild steel corrosion inhibition by Tr leaf extract is characterized by mixed adsorption processes of chemisorption and physisorption. The findings indicate that the extract effectively inhibits mild steel corrosion even at elevated temperatures.

The adsorption mechanism can be further examined based on the activation energy (E_a) determined using the Arrhenius Equation (Eqn. 3). A plot of log corrosion rate against the reciprocal of absolute temperature (Figure 6) indicates good linearity for both inhibited and uninhibited solutions with the linear regression coefficients (R2) very close to 1, 0.987, and 0.964, respectively. This observation confirms that the corrosion of mild steel in the sulphuric acid solution in the absence and presence of the inhibitor could be elucidated by the Arrhenius kinetic model [37]. The determined values of activation energy and pre-exponential factor are presented in Table 4. The results show that the apparent activation energy was higher for the inhibited solution compared to the uninhibited solution. Similarly, the value of the pre-exponential factor is higher for inhibited than uninhibited solutions. The decrease in the corrosion rates for the inhibited solutions can be explained based on the increased activation energy for the corrosion reaction [38]. Thus, the corrosion inhibition is a likely outcome of increased activation energy in the presence of Tr aqueous leaf extract.

$$Ea - \Delta Ha = RT \quad \textbf{(8)}$$

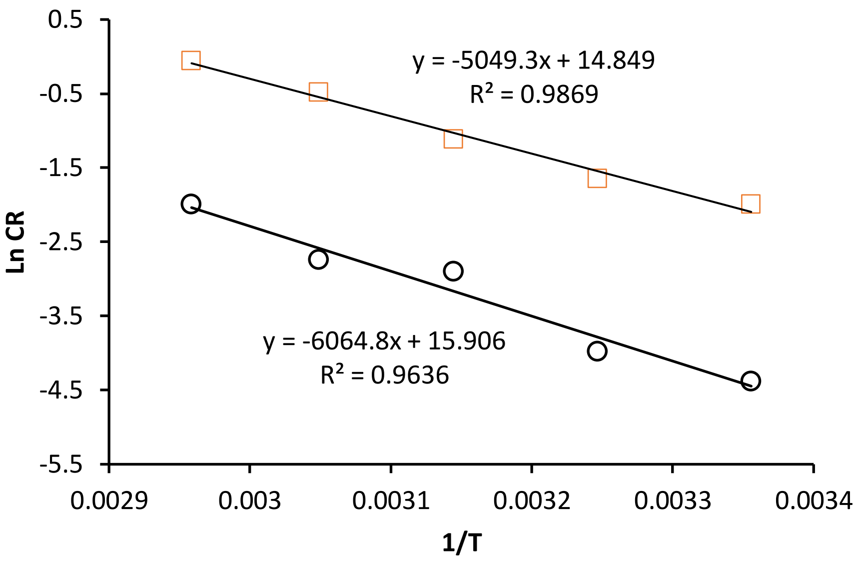

Figure 6. Transition-state plot for mild steel corrosion rate (CR) in 2 M H_2SO_4 in the presence and absence of 500-ppm Tr leaf aqueous extract.

The change in enthalpy determined from a plot (Figure 7) is positive, indicating that the mild steel corrosion process is endothermic. This observation indicates that Tr molecules adsorb on the metal surface through chemisorption [35,39]. The activation enthalpy increased by about 8 kJ/mol for the inhibited solution compared to the uninhibited solution. The average value of the difference between activation energy and change in the activation enthalpy (E_a - ΔH_a) is 2.64 kJ/mol, which is the exact value of the product of gas constant (R=8.314 J/mol.K) and average temperature (T= 318 K). The obtained value is in agreement with previously reported results [30,31]. Thus, the corrosion process in this study is likely to involve a unimolecular gas-phase reaction described by Eqn. 8 [31].

Table 4. Thermodynamical influence of Tr inhibitor concentrations on the mild steel corrosion inhibition in 2 M H_2SO_4.

[Tr] ppm	Fig.6 slope	Fig.7 slope	Ea (kJ/mol)	A (mL/mol)	ΔH (kJ/mol)
0 ppm (Blank)	5049.3	4732.3	41.98	2.81×10^6	39.34
500 ppm	6064.8	5747.7	50.42	8.09×10^6	47.79

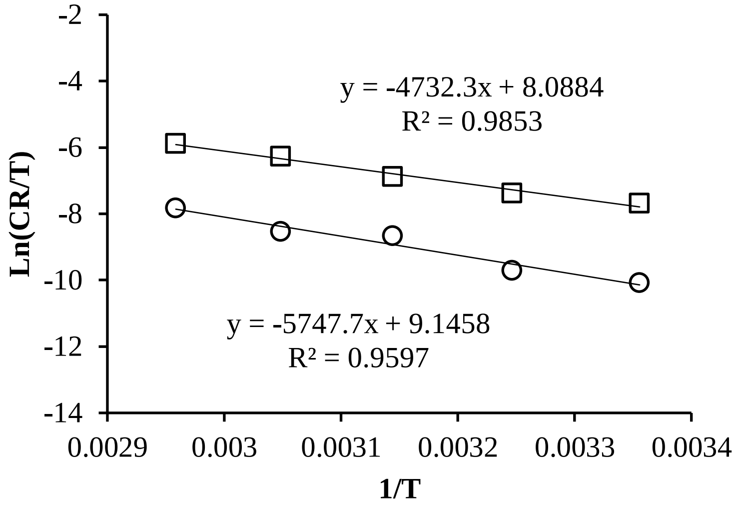

Figure 7. Transition-state plot for mild steel corrosion rate (CR) in 2 M H_2SO_4 in the presence and absence of 500-ppm Tr aqueous extract.

3.4. Adsorption isotherm.

Adsorption isotherms are important to describe interactions existing between inhibitor molecules and metal surfaces. Thus, the selected adsorption isotherm models, namely: Langmuir, Temkin, EL-awady's, and Freundlich, were used to assess the inhibition performance of the Tr extract. The determined values of the linearity regression coefficient (R^2) in Figure 8 were used to determine the most appropriate model to describe the adsorption process occurring in this study. The findings indicate that the experimental data fit into Langmuir, Temkin, EL-awady's, and Freundlich's adsorption isotherm models. Among these, the Langmuir isotherm model gives the best fit with the R^2 very close to 1 (0.99). This model signifies that the extract adsorbs on the metal surface, forming a monolayer film with no interactions between the adsorbed molecules [40].

The model was used to determine the equilibrium constant (K_{ads}) and Gibb's free energy (ΔG°_{ads}) using equations 9 and 10, respectively. The value of the equilibrium constant (**Table 5**) is similar to a previous study on the corrosion inhibition of low carbon steel using *Eucalyptus globulus* [36]. The value of the equilibrium constant indicates the presence of strong adsorption of Tr molecules on the mild steel surface. The value of the determined Gibb's free energy is negative, indicating that the adsorption of the Tr extract on the mild steel is stable and spontaneous. The value of ΔG°_{ads} was between 20 and 40 kJ/mol, suggesting that the adsorption of the extract involves a complex process of physical (electrostatic interaction) and chemical adsorption [41]. The mixed adsorption processes can be associated with the complexity of the plant extract containing numerous chemical compounds with various chemical properties [16]. Thus, the chemicals contained in the extract are likely to adsorb on the metal surface through physical and chemical interactions to produce the corrosion-resistant film, as previously mentioned in the current study.

$$\frac{C}{\phi} = C + \frac{1}{K_{ads}} \quad (9)$$

$$\Delta G_{ads} = -RT\ln(1000K_{ads}) \quad (10)$$

where C is the concentration of the inhibitor in (g/L) and K_{ads} is the adsorption-desorption equilibrium constant. The constant value 1000 is the water concentration in solution in g/L.

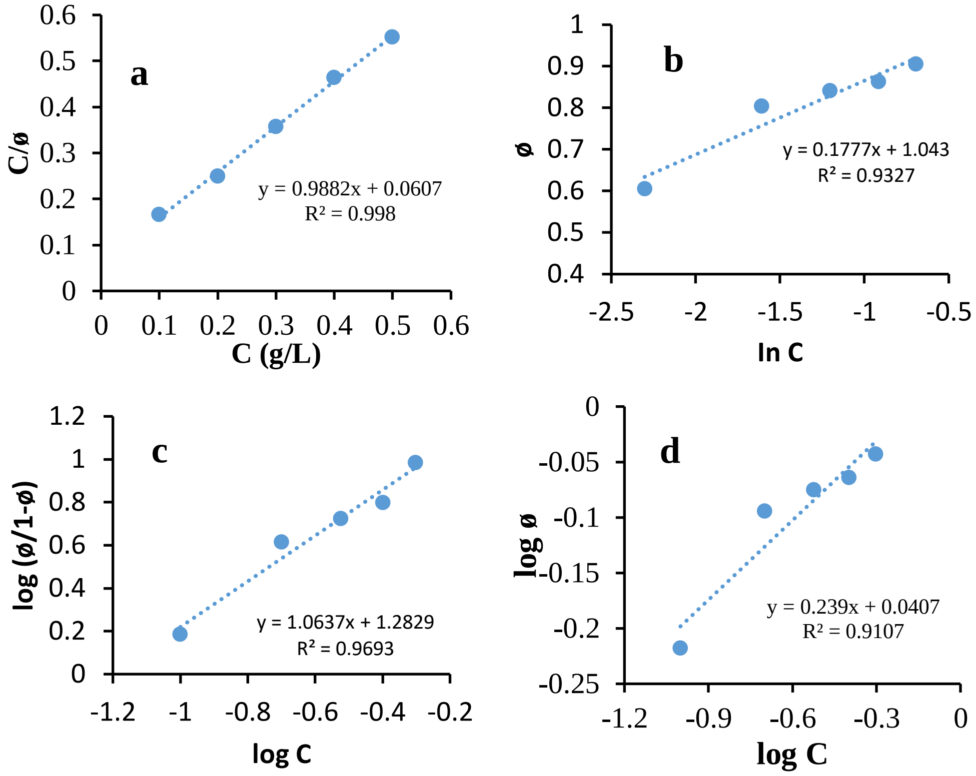

Figure 8. Isotherm plots for the adsorption of Tr aqueous extract on mild steel in 2 M H_2SO_4 at 298 K; (**a**) Langmuir; (**b**)Temkin; (**c**) EL-awady's; (**d**) Freundlich.

Table 5. Thermodynamic parameters for Tr aqueous extract on mild steel in 2 M H_2SO_4 at 298 K.

Inhibitor	Slope	K_{ads} (L/g)	R^2	ΔG°_{ads} (kJ/mol)
Tr	0.988	16.471	0.998	-24

4. Conclusions

The aqueous extract from *Tetradenia riparia* leaves was successfully used for the corrosion inhibition of mild steel in the sulphuric acid solution. The corrosion inhibition efficiency increased with the extract concentration up to 90.6% at 500-ppm. The inhibition efficiency decreased by 4.3% as temperature increased from 298 to 338 K. The adsorption of the Tr inhibitor molecules on the metal surface followed the Langmuir isotherm model indicating the inhibitor forms a monolayer protective film there is no interaction existing between adsorbed molecules. The positive sign for the change in activation enthalpy indicated that the adsorption of the inhibitor involved the chemisorption process. In contrast, the small decrease in the IE% with increasing temperature indicated that the adsorption involved physical interactions. The magnitude of Gibb's free energy indicated that the adsorption is a combination of chemical and physical interactions. Thus, the adsorption of the Tr inhibitor molecules on the mild steel likely involved a combination of chemical and physical interactions. The findings from this study suggest that the Tr aqueous extract can form a corrosion-resistant film on a mild steel surface and serve as a potential green corrosion inhibitor in the acidic solution.

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Conflicts of Interest

The authors declare no conflict of interest.

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