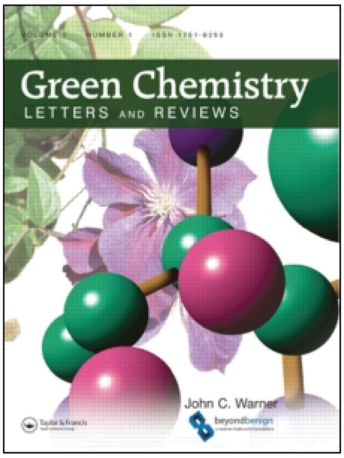

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Nnabuk Okon Eddy[a]; Patricia A. Ekwumemgbo[a]; Paul A. P. Mamza[a]
[a] Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

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RESEARCH ARTICLE

Ethanol extract of *Terminalia catappa* as a green inhibitor for the corrosion of mild steel in H_2SO_4

Nnabuk Okon Eddy*, Patricia A. Ekwumemgbo and Paul A.P. Mamza

Department of Chemistry, Ahmadu Bello University, Zaria, Nigeria

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The inhibitive and adsorption properties of ethanol extract of *Terminalia catappa* for the corrosion of mild steel in H_2SO_4 were investigated using weight loss, hydrogen evolution, and infra red methods of monitoring corrosion. Ethanol extract of *T. catappa* is a good adsorption inhibitor for the corrosion of mild steel in H_2SO_4. The inhibition efficiency of the inhibitor increases with increasing concentration but decreases with increasing temperature. The inhibition potential of ethanol extract of *T. catappa* is attributed to the presence of saponnin, tannin, phlobatin, anthraquinone, cardiac glycosides, flavanoid, terpene, and alkaloid in the extract. The adsorption of the inhibitor on mild steel surface is exothermic, spontaneous and is best described by Langmuir adsorption model. From the calculated values of activation energy, free energy of adsorption and the trend in the variation of inhibition efficiency with temperature, the mechanism of adsorption of the inhibitor is physical adsorption.

Keywords: corrosion; green inhibitors; *Terminalia catappa*

Introduction

Mild steel is widely used in the manufacturing of installations for the petroleum, fertilizer, water treatment plants, and other industries (*1–5*). Most often, this metal is made to come in contact with aggressive solutions (such as acid, alkaline, and salt solutions) during industrial processes such as pickling, acid cleaning, and acid descaling (*6*). Consequently, the metal is prone to attack by corrosion, which depends on the concentration of the aggressive medium, operating temperature, period of contact, the presence or absence of inhibitors, etc. (*7*).

Due to the viability of mild steel, its high cost of production and installations, several steps have been adopted to protect the metal against corrosion. However, one of the most practical and preferred methods are the use of corrosion inhibitors (*8–15*). Most efficient inhibitors are organic compounds containing electronegative functional groups and π-electrons in triple or conjugated double bonds. The presence of heteroatoms such as sulfur, phosphorus, nitrogen, and oxygen as well as aromatic rings in their structures is the major adsorption centers (*16,17*). However, it has been found that the inhibition efficiency of an organic inhibitor does not only depend on structural characteristics of the inhibitor, but also on the nature of the metal and the environment. Therefore, the selection of a suitable inhibitor for a particular system is a difficult task because of the selectivity of the inhibitor and environmental requirments. In recent times, there is increasing concern about the toxicity of most corrosion inhibitors because the toxic effects do not only affect living organisms, but also poison the environment (*18–23*). According to Eddy and Ebenso (*18*), green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. The successful use of naturally occurring substances for the inhibition of the corrosion of metals in acidic and alkaline media has been reported by some research groups (*24–41*). In spite of the large numbers of green corrosion investigated and tested, literature is scanty on the inhibitive and adsorptive properties of ethanol extract of *Terminalia catappa* for the corrosion of mild steel in H_2SO_4. Therefore the objective of our study is to investigate the inhibitive and adsorptive properties of ethanol extract of *T. catappa* leaves for the corrosion of mild steel.

The plant: *Terminalia catappa*

T. catappa is a large tropical tree in the Leadwood tree family, Combretaceae (*42*). The tree has been spread widely by humans and the native range is uncertain. It has long been naturalized in a broad belt extending

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*Corresponding author. Email: nabukeddy@yahoo.com

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from Northern Australia and New Guinea through Southeast Asia and Micronesia into the Indian Subcontinent. More recently, the plant has been introduced to parts of Africa and the Americas. Common names include Indian almond, Bengal almond, Singapore almond, Malabar almond, Tropical almond, Sea almond, Talisay tree, and Umbrella tree. It grows to 35 meters (110 ft) tall, with an upright, symmetrical crown, and horizontal branches. The *T. catappa* has corky, light fruit that is dispersed by water. The nut within the fruit is edible when fully ripe, tasting almost like almond. As the tree gets older, its crown becomes more flattened to form a spreading, vase shape. Its branches are distinctively arranged in tiers. The leaves are large, 15–25 cm long and 10–14 cm broad, ovoid, glossy dark green, and leathery. They are dry-season deciduous; before falling, they turn pinkish–reddish or yellow–brown, due to pigments such as violaxanthin, lutein, and zeaxanthin (*43*).

The flowers are monoecious, with distinct male and female flowers on the same tree. Both are 1 cm in diameter, white–greenish, inconspicuous with no petals; they are produced on auxiliary or terminal spikes. The fruit is a drupe 5–7 cm long and 3–5.5 cm broad, green at first, then yellow and finally red when ripe, containing a single seed (*44*).

T. catappa is widely grown in tropical regions of the world as an ornamental tree, grown for the deep shade its large leaves provide. The fruit is edible, tasting slightly acidic. The wood is red, solid, and has high water resistance; it has been utilized in Polynesia for making canoes. The leaves contain several flavonoids (such as kamferol or quercetin), several tannins (such as punicalin, punicalagin, or tercatin), saponines, and phytosterols. Due to this chemical richness, the leaves (and also the bark) are used in different traditional medicines for various purposes. For instance, in Taiwan fallen leaves are used as herbs for the treatment of liver diseases. In Suriname, a tea made from the leaves is prescribed against dysentery and diarrhea. It is also thought that the leaves contain agents for prevention of cancers (although they have no demonstrated anticarcinogenic properties) and antioxidant as well as anticlastogenic characteristics (*45,46*).

Results and discussion

Effect of concentration of acid/inhibitor

Figure 1 shows the variation of weight loss with time for the corrosion of mild steel in various concentrations of H_2SO_4. From Figure 1, it is evident that weight losses of mild steel increases with increase in the concentration of H_2SO_4 and with the period of contact indicating that the rate of corrosion of mild steel increases with increasing concentration of H_2SO_4.

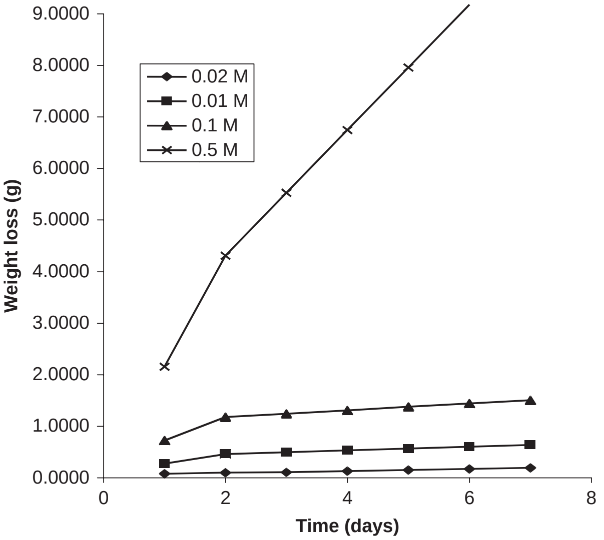

Figure 1. Variation of weight loss with time for the corrosion of mild steel in various concentrations of H_2SO_4.

Figure 2 shows the variation of weight loss with time for the corrosion of mild steel in 0.1 M H_2SO_4 containing various concentrations of ethanol extract of *T. catappa* at 303 K. Figure 2 reveals that weight loss of mild steel decreases with increasing concentration of ethanol extract of *T. catappa* which indicates that ethanol extract of *T. catappa* is an adsorption inhibitor for the corrosion of mild steel. At 333 K, plots of weight loss versus time (plots not shown) were similar to those obtained at 303 K. However, values of weight loss were relatively higher than those obtained at 303 K indicating that the inhibition efficiency of ethanol extract of *T. catappa* decreases with increasing temperature. This also suggests that the adsorption of

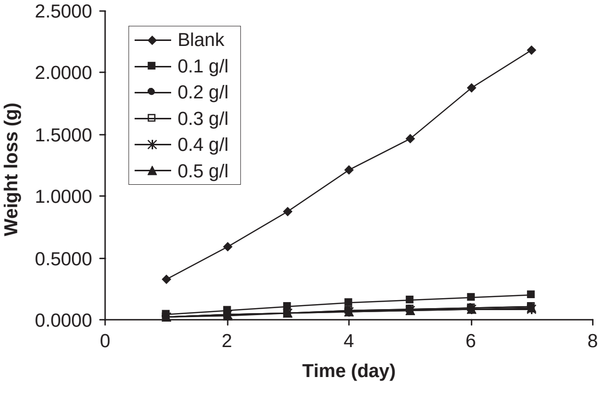

Figure 2. Variation of weight loss with time for the corrosion of mild steel in 0.1 M tetraoxosulphate (VI) acid containing various concentrations of ethanol extract of *T. catappa*.

ethanol extract of *T. catappa* on mild steel surface is consistent with the mechanism of physical adsorption.

In order to further sustain our findings, we calculated the inhibition efficiencies of ethanol extract of *T. catappa* and the corrosion rates of mild steel in H_2SO_4 in the absence and presence of ethanol extract of *T. catappa* (as an inhibitor). From the results obtained (Table 1), we observed that the corrosion rate of mild steel decreases with increasing concentrations of the extract while the inhibition efficiency increases with increasing concentration of the extract. These findings imply that ethanol extract of *T. catappa* retarded the rate of corrosion of mild steel in H_2SO_4. Results obtained from hydrogen evolution measurments are also recorded in Table 1. Values obtained from this source are relatively higher than those obtained from weight loss measurments implying that the instantaneous inhibition efficiency of ethanol extract of *T. catappa* is better than its average inhibition efficiency.

Kinetic study

In order to study the kinetics of the corrosion of mild steel in 0.1 M H_2SO_4 (containing various concentrations of ethanol extract of *T. catappa*, values of log(weight loss) were plotted versus time (t) for various combinations of inhibitor–H_2SO_4 solutions as shown in Figure 3. The plots are linear, with R^2 values very close to unity. Therefore, the kinetic of the corrosion of mild steel in H_2SO_4 can be represented according to the equation given below (*51*):

$$-\log(\text{weight loss}) = k_1 t/2.303 \tag{5}$$

where k_1 is the first order reaction rate constant and t is the time in day. Values of k_1 obtained from the slopes of the plots (at various concentrations of the inhibitor) are presented in Table 2. Also, for a first order reaction, the relationship between the rate constant and half life can be written as follows (*51*):

$$t_{1/2} = 0.693/k_1. \tag{6}$$

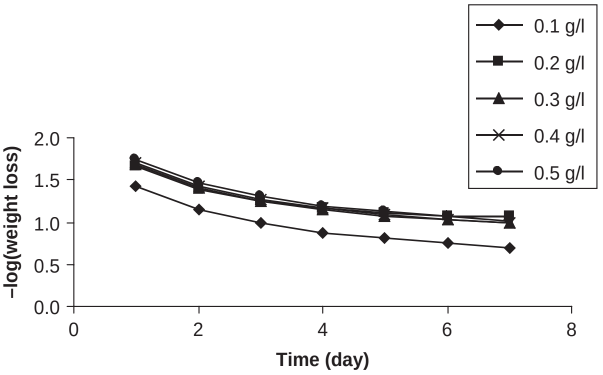

Figure 3. Kinetic plots for the inhibition of the corrosion of mild steel by ethanol extract of *T. catappa*.

Calculated values of $t_{1/2}$ are also presented in Table 2. From the results obtained, it is significant to note that the half life increases with increasing concentration of ethanol extract of *T. catappa* which suggests that the half life of mild steel in H_2SO_4 increases with increasing concentration of the inhibitor.

Effect of temperature

The Arrhenius equation was used to investigate the effect of temperature on the rate of corrosion of mild steel in H_2SO_4 (containing various concentrations of ethanol extract of *T. catappa*). The Arrhenius equation which can be written as Equation 7 arises from the fact that, before a reaction can proceed, a minimum energy input (activation energy) is required (*51*).

$$\log\frac{\mathrm{CR}_2}{\mathrm{CR}_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{7}$$

where CR_1 and CR_2 are the corrosion rates at temperatures, T_1 (303 K) and T_2 (333 K), R is the gas constant and E_a is the activation energy. Values of E_a calculated from Equation (7) are presented in Table 2. Calculated values of E_a are lower than the threshold value of 80 KJ mol^{-1} required for chemical

Table 1. Corrosion rates (CR) of mild steel and inhibition efficiencies (%*I*) of ethanol extract of *T. catappa*.

	$\mathrm{CR} \times 10^{-5}$ ($\mathrm{gh}^{-1}\mathrm{cm}^{-2}$)		%*I* (Weight loss)		%*I* (Hydrogen evolution)
C (g/L)	303 K	333 K	303 K	333 K	303 K
Blank	6.51	14.54	–	–	–
0.1	5.91	10.02	90.92	31.09	92.36
0.2	3.1	9.33	95.23	35.83	96.77
0.3	3.06	7.23	95.3	50.28	97.01
0.4	2.59	6.33	96.02	56.46	98.22
0.5	2.88	6.01	95.56	58.67	98.89

Note: *C*, concentration of ethanol extract of *T. catappa*; CR, corrosion rate obtained from weight loss measurement; %*I*, the inhibition efficiency.

Table 2. Some kinetics and thermodynamic parameters for the adsorption of ethanol extract of *T. catappa* on mild steel surface.

C (gdm^{-3})	E_a (KJ mol^{-1})	Q_{ads} (KJ mol^{-1})	K_1	$t_{1/2}$ (day)	R^2
Blank	22.50	–	0.3068	2.3	0.9497
0.1	14.78	−3.40	0.2589	2.7	0.897
0.2	30.85	−3.92	0.2547	2.7	0.8924
0.3	24.07	−3.28	0.2612	2.7	0.8947
0.4	25.02	−3.20	0.2490	2.8	0.8334
0.5	20.60	−2.98	0.2139	3.2	0.8994

adsorption, hence the adsorption of ethanol extract of *T. catappa* on mild steel surface is consistent with the mechanism of physical adsorption.

Thermodynamic/adsorption considerations

The heat of adsorption (Q_{ads}) of ethanol extract of *T. catappa* on the surface of mild steel was calculated using the following equation (*51*):

$$Q_{ads} = 2.303R[\log(\theta_2/1 - \theta_2) - \log(\theta_1/1 - \theta_1)] \times (T_1 \times T_2)/(T_2 - T_1) \qquad (8)$$

where R is the gas constant, θ_1 and θ_2 are the degrees of surface coverage of the inhibitor at temperatures, T_1 (303 K) and T_2 (333 K) respectively. Calculated values of Q_{ads} are also presented in Table 2. These values range from -2.98 to -3.92 KJ mol^{-1} which indicate that the adsorption of ethanol extract of *T. catappa* on mild steel surface is exothermic.

The adsorption characteristics of ethanol extract of *T. catappa* were studied by fitting data obtained from weight loss measurments into different adsorption isotherms. The test indicates that Langmuir adsorption isotherm best described the adsorption characteristics of ethanol extract of *T. catappa*. The assumptions of Langmuir adsorption isotherm are as given by Equation (9), which can also be written as Equation (10) (*52*):

$$C/\theta = 1/K + C \qquad (9)$$

$$\log(C/\theta) = \log C - \log K \qquad (10)$$

where C is the concentration of the inhibitor in the bulk electrolyte, θ is the degree of surface coverage of the inhibitor and K is the equilibrium constant of adsorption of the inhibitor. Using Equation (10), plots of $\log(C/\theta)$ versus $\log C$ were linear and is presented in Figure 4. Values of adsorption parameters deduced from Langmuir adsorption isotherms are recorded in Table 3. The results obtained indicate that the slopes and R^2 values are very close to unity indicating a strong adherence of the adsorption characteristics of the inhibitor to the model of Langmuir.

Generally, four types of adsorption may take place, involving organic molecules at the metal solution interface, namely (*54*): (i) the electrolytic attraction between charged molecule and the charged metal; (ii) interaction of unshared electron pairs in the molecules with the metal; (iii) interaction of S electrons with metal; and (iv) combination of the above. Inhibition efficiency depends on several factors such as the number of adsorption sites and their charge density, molecular size, heat of hydrogenation, mode of interaction with the metal surface, and the formation of metallic complexes. Due to adsorption, inhibitor molecules block the reaction sites and reduce the rate of corrosion reaction. The inhibitor molecules inhibit the corrosion of mild steel by adsorption on the mild steel-solution surface. The adsorption provides the information about the interaction around the adsorbed molecules themselves as well as their interaction with electrode surface (*53*). From the present results, the increase in inhibition efficiency with concentration indicates that there is increasing ease of adsorption of the inhibitor on the surface of mild steel. This may be attributed to the increase in the number of molecules approaching the surface of mild steel as the concentration increases.

The equilibrium constant of adsorption (K) obtained from the Langmuir equation (Equation 11) is related to the free energy of adsorption (ΔG_{ads}) as follows (*54–56*):

$$\Delta G_{ads} = -2.303RT\log(55.5K) \qquad (11)$$

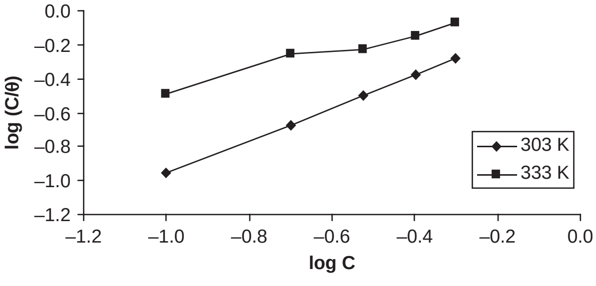

Figure 4. Langmuir isotherm for the adsorption of ethanol extract of *T. catappa* on mild steel surface.

Table 3. Langmuir adsorption parameters for the adsorption of ethanol extract of *T. catappa* on the surface of mild steel.

Langmuir	Temperature (K)	Log K	Slope	ΔG_{ads} (KJ mol^{-1})	R^2
	333	0.0006	0.9689	-10.10	0.9997
	303	0.0931	0.7666	-11.69	0.9641

Calculated values of ΔG_{ads} are also recorded in Table 3. These values are less in magnitude than the threshold value of -40 KJ mol^{-1} required for chemical adsorption hence the adsorption of ethanol extract of *T. catappa* on mild steel surface supports the mechanism of physical adsorption.

Stability of the inhibitor

We also studied the stability of ethanol extract of *T. catappa* for the corrosion of mild steel in H_2SO_4 (over a time range) by plotting values of inhibition efficiency versus the period of contact as shown in Figure 5. The plots indicate that at 303 K ethanol extract of *T. catappa* retained more than 87% of its inhibition efficiency even after 168 hours of immersion.

Phytochemical constituents/infra red (IR) study

Table 4 shows the phytochemical composition of ethanol extract of *T. catappa*. The results obtained, indicate that saponnin, tannin, phlobatin, anthraquinone, cardiac glycosides, flavanoid, terpene, and alkaloid are present in ethanol extract of *T. catappa* hence the inhibition efficiency of ethanol extract of *T. catappa* may be attributed to the phytochemical constituent of the extract (*57*).

Figure 6 shows the infra red (IR) spectrum of the corrosion product of mild steel without the inhibitor. The spectrum reveals that the corrosion product of mild steel is not IR active. On the other hand, the IR spectrum of ethanol extract of *T. catappa* shown in Figure 7 reveals the existence of some adsorption bands at different wave numbers. The peaks, wave number of IR adsorption and the assign functional groups, deduced from Figure 7 are recorded in Table 5. Also, Figure 8 shows the IR spectrum of the corrosion product of mild steel when ethanol extract of *T. catappa* was used as an inhibitor. The functional groups assigned to each adsorption band are also recorded in Table 5. A close examination of Figures 7 and 8 reveal that the –OH stretch (in the spectrum of the extract) at 3379.41 cm^{-1} is shifted to 3393.87 cm^{-1} in addition to a new –OH stretch formed at 2924.86 cm^{-1} (spectrum of the corrosion product when the extract is used as inhibitor). Other functional groups in the spectrum of ethanol extract of *T. catappa* are N–H bend, C–H bend, C–O stretch, and C–H$_{oop}$ at wave numbers of 1627.54, 1459.78, 1108.53, and 885.85 cm^{-1} respectively. These shifts or changes in the IR spectrum of the corrosion product (as opposed to the spectrum obtained for the ethanol extract of *T. catappa*) indicate that there is interaction between mild steel and ethanol extract of *T. catappa*.

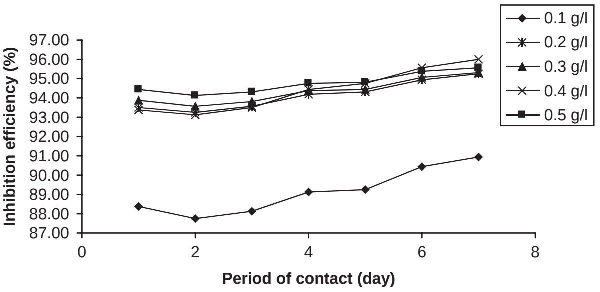

Figure 5. Variation of inhibition efficiency of ethanol extract of *T. catappa* with the period of contact.

Experimental

Materials

Materials used for the study were mild steel sheet of composition (wt%) Mn (0.6), P (0.36), C (0.15), and Si (0.03) and the rest Fe (determined by quantiometric method). The sheet was mechanically pressed cut into different coupons, each of dimension, 5 × 4 × 0.11 cm. Each coupon was degreased by washing with ethanol, rinsed with acetone and allowed to dry in air before they were preserved in a desiccator. All reagents used for the study were analar grade and double distilled water was used for their preparation.

Table 4. Phytochemical composition of ethanol extract of *T. catappa*.

Phytochemicals	
Saponin	+ + +
Tannin	+ + +
Phlobatanin	+ +
Anthraquinone	+ +
Cardiac glycosides	+ + +
Flavanoid	+ +
Terpene	+ + +
Alkaloid	+ + +

Note: + present in trace quantity; + + moderately present; + + + present in large quantity.

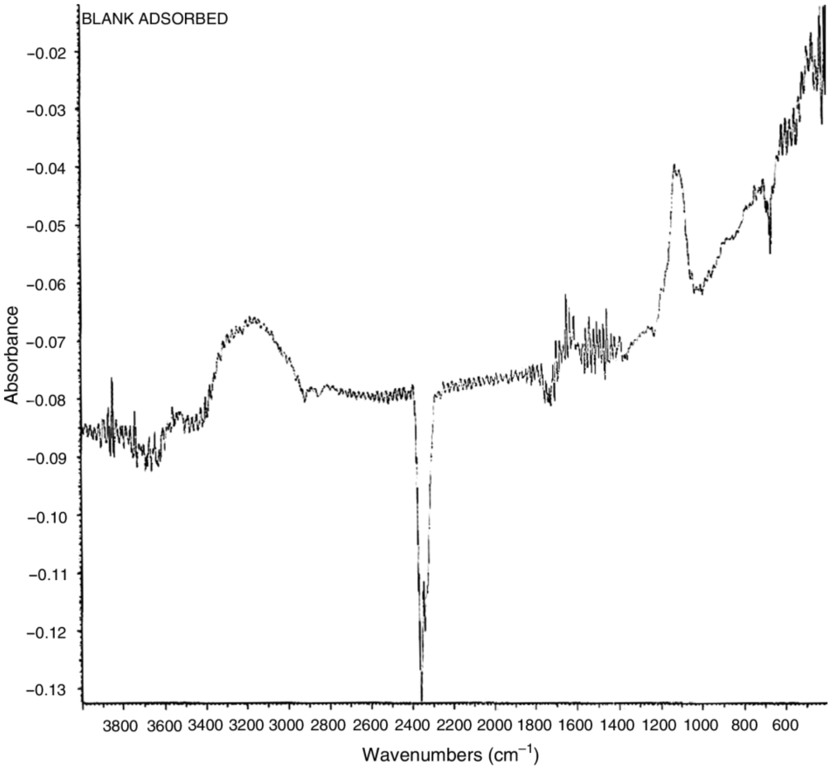

Figure 6. IR spectrum of the corrosion product of mild steel.

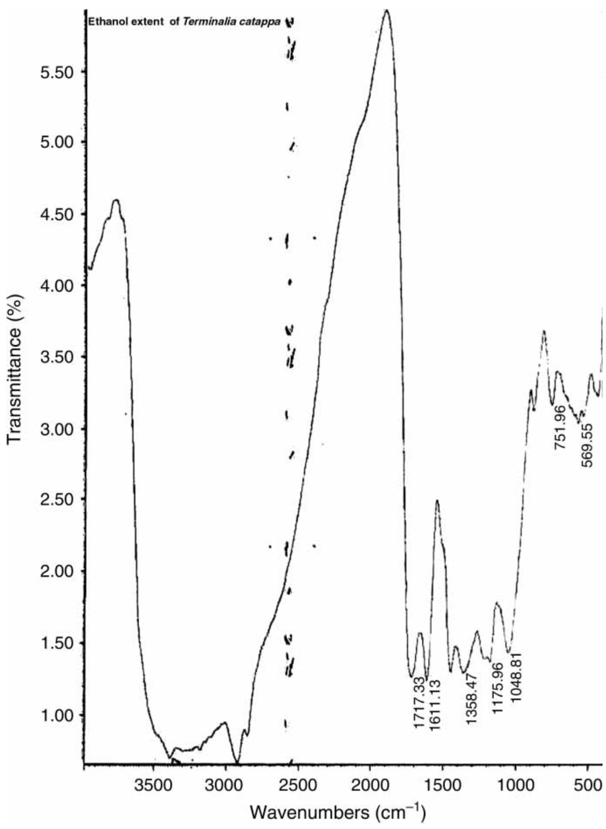

Figure 7. IR spectrum of ethanol extract of *T. catappa.*

Extraction of plants

Samples of *T. catappa* leaves were obtained from the same locations within Ahmadu Bello University, Samaru campus, Zaria. The leaves were dried, ground, and soaked in a solution of ethanol for 48 hours. After 48 hours, the samples were cooled and filtered. The filtrates were further subjected to evaporation at 352 K in order for the sample to be free of ethanol. The stock solutions of the extract so obtained were used in preparing different concentrations of the extract by dissolving 0.1, 0.2, 0.3, 0.4, and 0.5 g of the extract in 1L of 2.5 M H_2SO_4, respectively. For gravimetric analysis, the concentration of H_2SO_4 used for the preparation of the inhibitor–acid solutions was 0.1 M.

Chemical analysis

Phytochemical analysis of the ethanol and aqueous extract of the sample was carried out according to the method reported by Ebenso et al. (*47*). Frothing and Na_2CO_3 tests were used for the identification of saponin, bromine water, and ferric chloride tests were used for the identification of tannin, Leberman's and Salkowski's tests were used for the identification of cardiac glycodises while Dragendorf, Hagger, and Meyer reagent tests were used for the identification of alkaloid.

Table 5. Functional groups assigned to adsorption of ethanol extract of leaves of *T. catappa* and the corrosion product when the extract is used as inhibitor.

Ethanol extract			Corrosion product		
Wave number (cm^{-1})	Height	Bond	Wave number (cm^{-1})	Position	Bond
3754.78	21.03		3393.87	0.68	–OH stretch
3379.41	11.98	O–H stretch	2924.86	0.64	–OH stretch
2371.04	21.12		1717.33	1.23	C = O stretch
1627.54	22.82	N–H bend	1358.47	1.28	C–H rock
1459.78	26.56	C–H bend	1048.81	1.43	C–N stretch
1108.53	17.22	C–O stretch	751.96	3.16	C–Cl stretch
885.85	23.62	C–H oop	569.55	3.03	C–Br stretch

Infra red (IR) analysis

IR analysis of ethanol extract of the *T. catappa* and the corrosion products of mild steel were carried out using BUCK model 500 M IR spectrophotometer. The sample was prepared using KBr and the analysis was done by scanning the sample through a wave number range of 400–4000 cm^{-1}.

Gasometric method

Gasometric methods were carried out at 303 and 333 K as described in elsewhere (*48*). From the volume of hydrogen evolved per minute, inhibition efficiency (%*I*) was calculated using Equation (1):

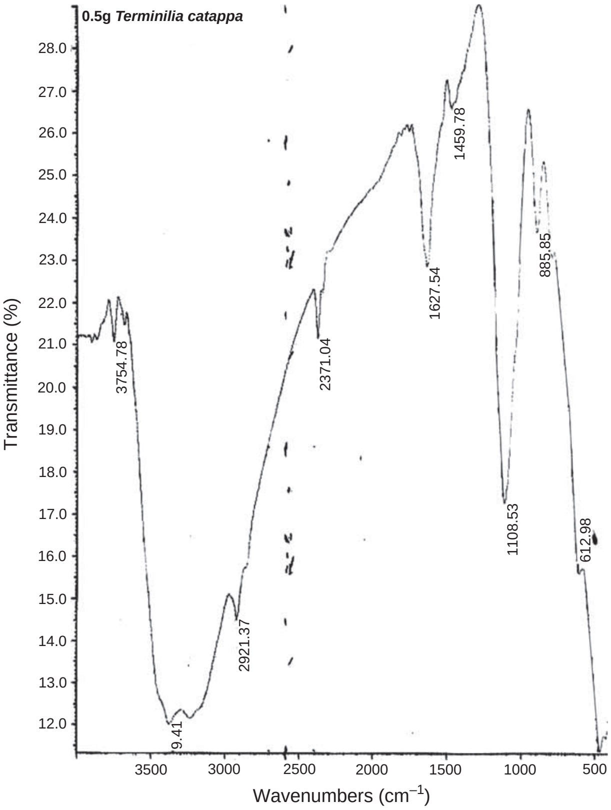

Figure 8. IR spectrum of the corrosion product of mild steel when ethanol extract of *T. catappa* is used as inhibitor.

$$\%I = \left(1 - \frac{V^1_{Ht}}{V_{Ht}{}^0}\right) \times 100 \tag{1}$$

where V^1_{Ht} is the volume of hydrogen gas evolved at time "*t*" for inhibited solution and V^0_{Ht} for uninhibited solution.

Gravimetric analysis

In gravimetric experiment, a previously weighed metal (mild steel) coupon was completely immersed in 250 ml of the test (in an open beaker). The beaker was inserted into a water bath maintained at a temperature of 303 K. After every 24 hours, each sample was withdrawn from the test solution, washed in a solution containing 50% NaOH and 100 g/L of zinc dust. The washed steel coupon was rinsed in acetone and dried in air before re-weighing. The difference in weight for a period of 168 hours was taken as the total weight loss. Similar experiments were repeated at 333 K. From the weight loss results, the inhibition efficiency (%*I*) of the inhibitor was calculated using the formula (*49*):

$$\%I = (1 - W_1/W_2) \times 100 \tag{2}$$

where W_1 and W_2 are the weight losses (g/dm^3) of mild steel in the presence and absence of inhibitor (in 0.1 M H_2SO_4) solution, respectively. The degree of surface coverage (θ) was calculated using Equation (3):

$$\theta = 1 - W_1/W_2. \tag{3}$$

The corrosion rates (CR) of mild steel in different concentrations of the acid and other media was determined using Equation (4) (*50*):

$$CR(gh^{-1}cm^{-2}) = W/At \tag{4}$$

where W = weight loss (in grams), A = area of specimen (in cm^2), and t = period of immersion (in hours).

Conclusion

Ethanol extract of *T. catappa* is a good adsorption inhibitor for the corrosion of mild steel in H_2SO_4. The inhibition potential of this inhibitor is attributed to the presence of saponnin, tannin, phlobatin, anthraquinone, cardiac glycosides, flavanoid, terpene, and alkaloid in the extract. Its inhibition potentials can be optimized by taking advantage of temperature, period of contact, and inhibitor's concentration. Kinetic, thermodynamic, and adsorption models can sufficiently be used to explain the adsorption behavior of ethanol extract of *T. catappa* on mild steel surface.

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