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RESEARCH LETTER

Inhibitive and adsorption properties of ethanol extract of *Hibiscus sabdariffa* calyx for the corrosion of mild steel in 0.1 M HCl

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The inhibitive and adsorption properties of ethanol extract of *Hibiscus sabdariffa* calyx were studied using gravimetric, gasometric, thermometric, and Fourier transform infrared methods of monitoring corrosion. The results obtained indicated that ethanol extract of *Hibiscus sabdariffa* calyx is a good adsorption inhibitor for the corrosion of mild steel in HCl solutions. The adsorption of the inhibitor on mild steel surface is spontaneous and supports the Langmuir adsorption model. From the calculated values of free energy of adsorption, the activation energy, and the variation of inhibition efficiency with temperature, it can be concluded that the initial mechanism for the adsorption of ethanol extract of *Hibiscus sabdariffa* calyx on mild steel surface is physical adsorption. Analysis of spectra obtained from the Fourier transform infrared spectrophotometer indicated that there is an interaction between iron in mild steel and the inhibitor.

Keywords: corrosion; green inhibitor; *Hibiscus sabdariffa* calyx

Nomenclature

C	concentration of the inhibitor
CR	corrosion rate of mild steel (in $\text{g cm}^{-2} \text{h}^{-1}$)
E_{exp}	inhibition efficiency obtained from experiments
ΔG_{ads}^0	free energy of adsorption
k_1	first-order rate constant
K_{ads}	adsorption equilibrium constant
R	gas constant ($R = 8.314 \text{ kJ mol}^{-1}$)
t	period of immersion
$t_{1/2}$	half-life of mild steel
T	temperature (in K)
θ	degree of surface coverage of the inhibitor

Introduction

Mild steel is widely used in the manufacturing of installations for the petroleum, fertilizers, and in other industries. In most cases, processes within these industries such as pickling, acid cleaning, and acid descaling involve contact between mild steel and aggressive solution (such as acids, salts, and bases) 1–5. Therefore, the metal is prone to corrosion. In view of the viability of mild steel and its high cost of production and installation, several steps are taken to prolong the lifespan of the metal in most industries. However, the most practical and preferred method is

the use of inhibitors (6, 7). Most efficient inhibitors are organic compounds containing electronegative functional groups and π -electrons in triple or conjugated double bond. The presence of heteroatoms such as sulfur, phosphorus, nitrogen, and oxygen as well as aromatic rings in their chemical structure is the major center for the adsorption of the inhibitor.

In spite of the broad spectrum of organic compounds available as corrosion inhibitors, there is increasing concern about the toxicity of most corrosion inhibitors because they are toxic to living organism and may also poison the earth (8). These have prompted searches for green corrosion inhibitors. According to Eddy et al. (9), green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. The successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment has been reported by some research groups 10–15.

Also, some studies have been carried out on the use of *Hibiscus sabdariffa* as a corrosion inhibitor for some metals. Noor (16) studied the inhibitory potentials of aqueous extract of *Hibiscus sabdariffa* calyx for the corrosion of mild steel in 0.5 M NaOH using chemical and electrochemical techniques. Electrochemical measurements indicated that the aqueous

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extract of *Hibiscus sabdariffa* acted as a mixed inhibitor; the adsorption of the inhibitor on aluminum surface supported the mechanism of physical adsorption and was best described by the Langmuir and Dubinin–Radushkevich adsorption isotherms. Oguzie (17) also studied the inhibitory potentials of calyx extract of *Hibiscus sabdariffa* for the corrosion of mild steel in HCl and H₂SO₄ solutions, using gasometric (hydrogen evolution) method and found that the inhibition efficiency of the extract increased with increasing concentration. The adsorption of the inhibitor on mild steel surface supported the Langmuir adsorption model and followed the mechanism of physical adsorption. Khamis and AlAndis (18) also studied the inhibitory potentials of some herbs including *Hibiscus sabdariffa* and found that the leaf extract of *Hibiscus sabdariffa* is a good adsorption inhibitor for the corrosion of steel in acidic media. In spite of the above studies, there is still much to investigate on the inhibition and adsorption potentials of *Hibiscus sabdariffa* calyx for the corrosion of mild steel in HCl. For example, there is need to investigate the average inhibitory potentials of the calyx using different extract concentrations and experimental methods. Literature is also scanty on the active chemical constituents of the calyx extract of *Hibiscus sabdariffa* that are responsible for its corrosion inhibition properties. Therefore, the objective of the present study is to investigate the inhibitive and adsorption properties of ethanol extracts of *Hibiscus sabdariffa* calyx for the corrosion of mild steel in HCl. Gravimetric methods shall be used to investigate the average inhibition efficiency of the extract, gasometric and thermometric methods shall be used to investigate the instantaneous inhibition efficiency of the plant, while Fourier transform infrared (FTIR) method shall be used to study the functional groups responsible for the adsorption of the inhibitor on mild steel surface.

Figure 1 shows the *Hibiscus sabdariffa* plant and the dried samples of the flowers that were used for the study.

Primarily, the plant is cultivated for the production of bast fiber using the stem of the plant. The fiber may be used as a substitute for jute in making burlap. *Hibiscus*, specifically Roselle, has been used in folk medicine as a diuretic, mild laxative, and in treatment of cardiac and nerve diseases and cancer. The red calyces of the plant are increasingly exported to America and Europe, where they are used as food colorings. The green leaves are a spicy version of spinach.

In East Africa, the calyx infusion is taken to relieve coughs. Roselle juice, with salt, pepper, asafetida, and molasses, is taken as a remedy for

biliousness. The heated leaves are applied to cracks in the feet and on boils and ulcers to speed maturation. The seeds are said to be diuretic and tonic in action and the brownish-yellow seed oil is claimed to heal sores on camels. In India, a decoction of the seeds is given to relieve dysuria, strangury, and mild cases of dyspepsia. Brazilians attribute stomachic, emollient, and resolutive properties to the bitter roots. Many parts of the plant are also claimed to have various medicinal values. The plants are rich in anthocyanins as well as in protocatechuic acid. The dried calyces contain the flavonoids gossypetin, hibiscetine, and sabdaretine. The major pigment in *Hibiscus sabdariffa* is daphniphylline. The plant is also rich in myrtillin (delphinidin 3-monoglucoside), chrysanthenin (cyanidin 3-monoglucoside), and delphinidin.

Results and discussions

Effect of the ethanol extract of Hibiscus sabdariffa calyx

Table 1 presents the corrosion rates of mild steel, degrees of surface coverage, and inhibition efficiencies of various concentrations of ethanol extract of *Hibiscus sabdariffa* calyx in various media. From Table 1, it is evident that the corrosion rate of mild steel in the blank solution (0.1 M HCl) is higher than those obtained for solutions of HCl containing various concentrations of the calyx extract of *Hibiscus sabdariffa*. This indicates that the corrosion of mild steel in solution of HCl is inhibited by various concentrations of ethanol extract of *Hibiscus sabdariffa* calyx. The corrosion rate of mild steel was also found to decrease with increasing concentration of ethanol extract of *Hibiscus sabdariffa* calyx. Therefore, the inhibition of the corrosion of mild steel in HCl solutions by ethanol extracts of *Hibiscus sabdariffa* calyx is concentration-dependent (19).

Figure 2 shows the variation of weight loss with time for the corrosion of mild steel in 0.1 M HCl containing various concentrations of ethanol extract of *Hibiscus sabdariffa* calyx. From the figure, it can be seen that weight loss of mild steel for the blank is higher than those obtained for solutions containing various concentrations of ethanol extracts of *Hibiscus sabdariffa* calyx. This also indicates that ethanol extracts of *Hibiscus sabdariffa* calyx inhibited the corrosion of mild steel in HCl solutions. The figure also reveals that weight loss of mild steel decreases with increase in the concentration of the inhibitor, which also indicates that the inhibition potentials of ethanol extracts of *Hibiscus sabdariffa* calyx increase with increasing concentration. Figure 3 is a plot showing the variation of inhibition efficiency of calyx



Hibiscus sabdariffa plant

Dried *Hibiscus sabdariffa* calyx

Figure 1. *Hibiscus sabdariffa* plant and calyx.

extract of *Hibiscus sabdariffa* with concentration. From the figure, it is evident that the inhibition efficiency of the inhibitor increases with increasing concentration.

The inhibition efficiencies of various concentrations of ethanol extract of *Hibiscus sabdariffa* calyx were also found to decrease with increase in temperature. Therefore, the adsorption of ethanol extract of *Hibiscus sabdariffa* calyx supports the mechanism of physical adsorption. These findings are consistent with those reported by Noor (16), Oguzie (17), and Khamis and AlAndis (18). However, values of inhibition efficiencies obtained from gasometric and thermometric experiments are relatively higher than those reported by Oguzie (17). This may be due to the fact that the concentration of HCl used by Oguzie (17) was 2 M while we used 2.5 M in our study. On the other hand, the inhibition efficiencies obtained

from gravimetric methods are comparable to those obtained by Noor (16).

It is also interesting to note that the inhibition efficiencies obtained from gasometry and thermometric methods correlated strongly ($r=0.8189$ and 0.95211 for gasometric and thermometric, respectively) with those obtained from the gravimetric method. However, values of inhibition efficiencies obtained from thermometric and gasometric methods are relatively higher than those obtained from the gravimetric method, indicating that the instantaneous inhibition efficiency of ethanol extract of *Hibiscus sabdariffa* calyx is better than the average inhibition efficiency of the extract. This is because the gravimetric method measures average inhibition efficiency while thermometric and gasometric methods measure instantaneous inhibition efficiency.

Table 1. Corrosion rate (CR) of mild steel, inhibition efficiencies (%*I*), and degree of surface coverage (θ) of ethanol extract of *Hibiscus sabdariffa* calyx in various media.

Systems	CR $\times 10^{-5}$ (g h ⁻¹ cm ²)	% <i>I</i>			θ
		Grav	Gasm	Therm	
Blank (0.1 M HCl) at 303 K	10.3	–	–	–	–
0.1 g L ⁻¹ of <i>Hibiscus sabdariffa</i> calyx extract at 303 K	4.15	59.72	72.12	73.43	0.5972
0.2 g L ⁻¹ of <i>Hibiscus sabdariffa</i> calyx extract at 303 K	4.06	60.62	74.32	75.23	0.6062
0.3 g L ⁻¹ of <i>Hibiscus sabdariffa</i> calyx extract at 303 K	4.00	61.12	79.22	80.28	0.6112
0.4 g L ⁻¹ of <i>Hibiscus sabdariffa</i> calyx extract at 303 K	3.69	64.20	81.23	83.25	0.6420
0.5 g L ⁻¹ of <i>Hibiscus sabdariffa</i> calyx extract at 303 K	3.56	65.48	86.34	86.44	0.6548
Blank (0.1 M HCl) at 333 K	28.35	–	–	–	–
0.1 g L ⁻¹ of <i>Hibiscus sabdariffa</i> calyx extract at 333 K	23.34	17.67	32.45	–	0.1767
0.2 g L ⁻¹ of <i>Hibiscus sabdariffa</i> calyx extract at 333 K	20.34	28.25	36.47	–	0.2825
0.3 g L ⁻¹ of <i>Hibiscus sabdariffa</i> calyx extract at 333 K	19.89	29.84	38.21	–	0.2984
0.4 g L ⁻¹ of <i>Hibiscus sabdariffa</i> calyx extract at 333 K	19.73	30.41	43.22	–	0.3041
0.5 g L ⁻¹ of <i>Hibiscus sabdariffa</i> calyx extract at 333 K	18.02	36.44	47.34	–	0.3644

Note: Grav, results obtained from gravimetric analysis; Gasm, results obtained from gasometric analysis; Therm, results obtained from thermometric measurements.

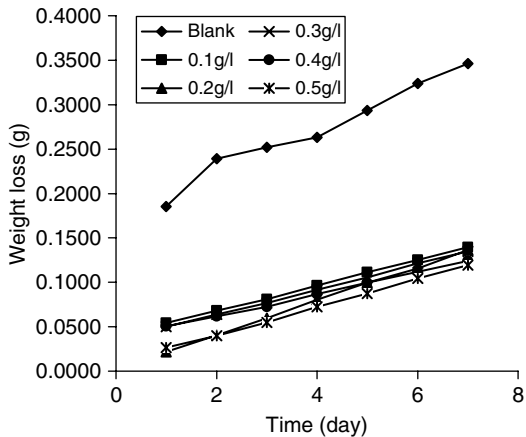


Figure 2. Variation of weight loss with time for the corrosion of mild steel in 0.1 M HCl containing various concentrations of ethanol extract of *Hibiscus sabdariffa* calyx at 303 K.

Effect of the period of contact

In order to test the stability of the inhibitors over a period of time, the inhibition efficiencies of the inhibitor were calculated after every 24 h of immersion. The results obtained from the calculations were used to develop plots for the variation of inhibition efficiency with time, as shown in Figure 4. From Figure 5, it can be seen that the inhibitor can retain more than 60% of its efficiency after 168 h of immersion. Hence, the ethanol extract of *Hibiscus sabdariffa* calyx is a good inhibitor for the corrosion of mild steel in HCl solutions.

Kinetic study

In order to investigate the kinetic model for the inhibition of the corrosion of mild steel in HCl

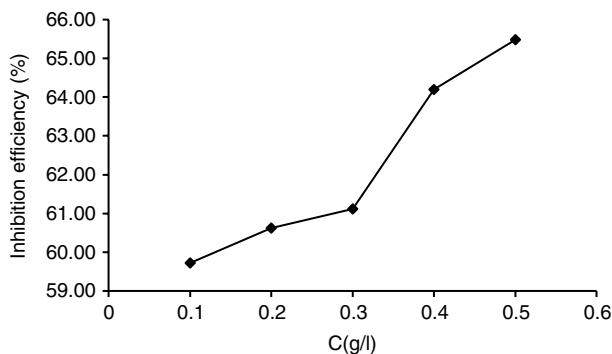


Figure 3. Variation of inhibition efficiencies (obtained from gravimetric, gasometric, and thermometric methods) of ethanol extracts of *Hibiscus sabdariffa* calyx with concentration for the corrosion of mild steel in 0.1 M HCl at 303 K.

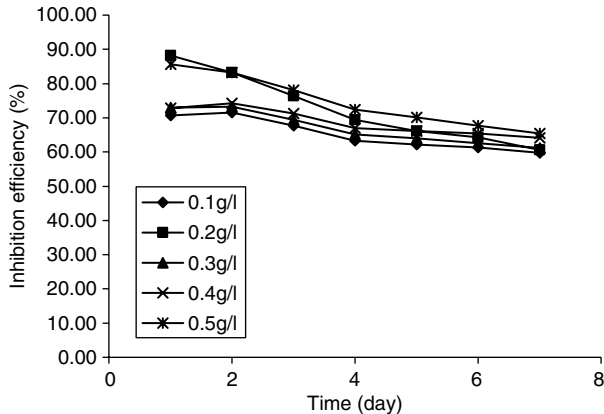


Figure 4. Variation of inhibition efficiencies of ethanol extract of *Hibiscus sabdariffa* calyx with time.

solution by *Hibiscus sabdariffa*, data obtained from weight loss measurements were used to fit curves for different kinetic orders. The tests revealed that the plots of $-\log(\text{weight loss})$ versus time yielded straight lines. Therefore, the corrosion of mild steel in 0.1 M HCl (in the absence and presence of ethanol extract of *Hibiscus sabdariffa* calyx) is consistent with a pseudo-first-order kinetic, which can be expressed as follows (20):

$$-\log(\text{weight loss}) = \frac{k_1 t}{2.303}, \tag{1}$$

where k_1 is the first-order rate constant and t is the period of contact. Figure 5 shows the variation of $-\log(\text{weight loss})$ with time for the corrosion of mild steel in HCl solutions containing ethanol extract of *Hibiscus sabdariffa* calyx. Values of rate constants calculated from the slopes of the plots are presented in Table 2. The results obtained indicate that the rate constants decrease with increasing concentration of the inhibitor. Also, the first-order rate constant is related to the half-life of the reaction according to the following equation:

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

where $t_{1/2}$ is the half-life of the corrosion reaction of mild steel. Using Equation (2), the half-lives of mild steel in HCl solutions were calculated and are also presented in Table 2. The results obtained revealed that the half-life of mild steel for the blank is lower than those obtained for the inhibited systems, indicating that the inhibitor increases the half-life of mild steel in HCl solutions. The half-lives were also found to increase with increasing concentration of the inhibitor.

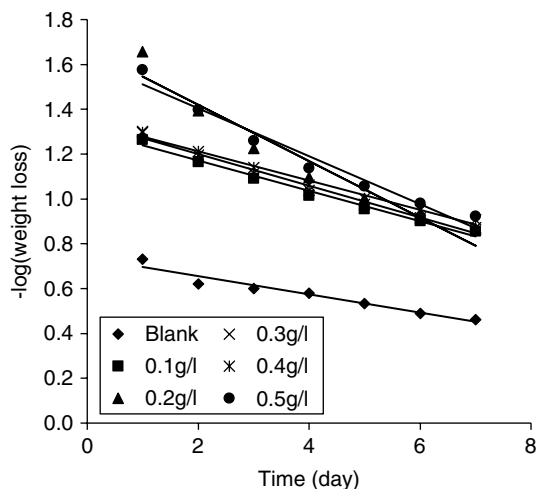


Figure 5. Variation of $-\log(\text{weight loss})$ versus time for the corrosion of mild steel in 0.1 M HCl containing various concentrations of ethanol extract of *Hibiscus sabdariffa* calyx.

Effect of temperature

The Arrhenius equation was used to study the effect of temperature on the corrosion of mild steel in solutions of HCl. The Arrhenius equation gives the relation between the minimum energy required for the corrosion reaction to proceed (i.e. activation energy) and the rate of the reaction and can be written as follows (21):

$$\text{CR} = A \exp(-E_a/RT), \quad (3)$$

where CR is the corrosion rate of mild steel, A is the Arrhenius or the preexponential factor, R is the gas constant, and T is the temperature. Assuming that the corrosion rates of mild steel (CR_1 and CR_2) at two different temperatures (T_1 and T_2) are known, Equation (3) can be transformed as follows:

$$\log \frac{\text{CR}_2}{\text{CR}_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right). \quad (4)$$

Table 2. Kinetics and thermodynamic parameters for the adsorption of ethanol extract of *Hibiscus sabdariffa* calyx on mild steel surface.

C (g L ⁻¹)	E_a (kJ mol ⁻¹)	Q_{ads} (kJ mol ⁻¹)	ΔS_{ads} (kJ mol ⁻¹)	$\Delta G_{\text{ads}}^{\circ}$ (kJ mol ⁻¹)	K_1	$t_{1/2}$ (days)	R^2
Blank	28.35	–	–	–	1.56	0.45	0.9427
0.1	48.35	–40.54	0.10	–11.11	0.29	2.40	0.9843
0.2	45.12	–28.60	0.06	–11.21	0.25	2.81	0.9351
0.3	44.91	–27.42	0.05	–11.26	0.16	4.24	0.9836
0.4	46.94	–29.62	0.06	–11.59	0.15	4.61	0.9878
0.5	45.41	–25.10	0.04	–11.73	0.09	7.38	0.9641

The activation energies obtained from Equation (3) (Table 2) are lower than the threshold value of 80 kJ mol⁻¹ required for a chemical adsorption mechanism. Therefore, the adsorption of ethanol extract of *Hibiscus sabdariffa* calyx supports the mechanism of physical adsorption.

Adsorption/thermodynamic considerations

The heat of adsorption of ethanol extract of *Hibiscus sabdariffa* calyx on mild steel surface was calculated using the following equation (22):

$$Q_{\text{ads}} = 2.303R \left[\log \left(\frac{\theta_2}{1 - \theta_2} \right) - \log \left(\frac{\theta_1}{1 - \theta_1} \right) \right] \times \left(\frac{T_1 \times T_2}{T_2 - T_1} \right) \text{kJmol}^{-1}, \quad (5)$$

where θ_2 and θ_1 are the degrees of surface coverage of the inhibitor at the temperatures 333 (T_2) and 303 K (T_1), respectively, and R is the gas constant. Calculated values of Q_{ads} (in kJ mol⁻¹) are also presented in Table 2. From the results obtained, it can be seen that the adsorption of the inhibitor on mild steel surface is exothermic.

The free energy of adsorption of ethanol extract of *Hibiscus sabdariffa* calyx on mild steel surface was calculated using the following equation (23):

$$\Delta G_{\text{ads}}^0 = -2.303RT \log(55.5K_{\text{ads}}), \quad (6)$$

where $K = \theta/(1 - \theta) \times [C]$, T is the temperature, R is the gas constant, θ is the degree of surface coverage of the inhibitor, and K_{ads} is the equilibrium constant of adsorption. Calculated values of the free energies are presented in Table 2. From the calculated values of ΔG_{ads}^0 , the entropies for the adsorption of the inhibitor were also calculated using the Gibb–Helmholtz equation, which can be written as follows:

$$\Delta G_{\text{ads}}^0 = \Delta H_{\text{ads}}^0 - T\Delta S_{\text{ads}}^0. \quad (7)$$

Calculated values of ΔS_{ads}^0 are also presented in Table 2. The results obtained indicated that ΔS_{ads}^0 values are positive and relatively lower when compared with values of ΔH_{ads}^0 and ΔG_{ads}^0 , indicating that the degree of disorderliness for the inhibited systems is low.

In order to study the adsorption characteristics of ethanol extract of *Hibiscus sabdariffa* calyx on mild steel surface, data obtained for the degree of surface coverage were used to fit curves for different adsorption isotherms, including Langmuir, Temkin, Flory–Huggins, Frumkin, Freundlich, and Brockris–Swinkel adsorption isotherms. The tests indicated that the Langmuir adsorption isotherm best described the adsorption characteristics of ethanol extract of *Hibiscus sabdariffa* calyx on mild steel surface.

The Langmuir adsorption model relates the degree of surface coverage of the inhibitor (θ) to its concentration as follows (24):

$$\theta = \frac{K_{\text{ads}} C \times 1}{(1 + K_{\text{ads}} C)}, \quad (8)$$

where K_{ads} designates the adsorption equilibrium constant and C is the concentration of the inhibitor in the bulk electrolyte. From the rearrangement of Equation (8), the following equations are obtained (25):

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

$$\log(C/\theta) = \log C - \log K_{\text{ads}}. \quad (10)$$

Using Equation (10), plots of $\log(C/\theta)$ versus $\log C$ were linear, indicating that the assumptions establishing the Langmuir adsorption isotherm are valid for the presence system. Figure 6 shows the Langmuir isotherm for the adsorption of ethanol extract of *Hibiscus sabdariffa* calyx on mild steel surface. Values of adsorption parameters deduced from the plots are presented in Table 3. From the results obtained, it can be seen that the slopes and R^2 values are very close to unity, indicating a strong adherence of the adsorption data to the assumptions establishing the Langmuir model.

The average free energies for the adsorption of ethanol extract of *Hibiscus sabdariffa* calyx on mild steel surface were also calculated using the value of the equilibrium constant of adsorption (K_{ads}) obtained from the Langmuir adsorption isotherm. K_{ads} is related to the equilibrium constant of adsorption according to the following equation (26):

$$\Delta G_{\text{ads}}^0 = -2.30RT \times \log(55.5K_{\text{ads}}), \quad (11)$$

where K_{ads} is the equilibrium constant of adsorption, 55.5 is the molar concentration of water, ΔG_{ads}^0 is the

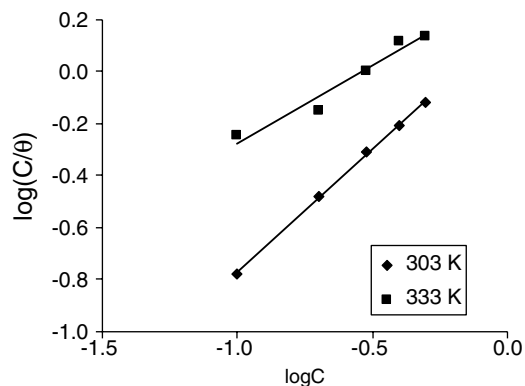


Figure 6. Langmuir isotherm for the adsorption of ethanol extract of *Hibiscus sabdariffa* calyx on mild steel surface.

free energy of adsorption of the inhibitor, R is the gas constant, and T is the temperature. The free energies calculated from Equation (10) are presented in Table 3. There is no significant difference between the average value of the free energies obtained from Equations (7) and (11) ($p > 0.5$), which implies that either of the two methods can be used to estimate the free energy of adsorption of the inhibitor. In both cases, the free energies are negatively less than the threshold value (-40 kJ mol^{-1}) required for chemical adsorption. Therefore, the adsorption of ethanol extract of *Hibiscus sabdariffa* calyx on mild steel surface is spontaneous and supports the mechanism of physical adsorption.

Photochemical constituents of the inhibitors

Table 4 presents the phytochemical constituents of ethanol extracts of *Hibiscus sabdariffa* calyx. From the results, it is significant to note that the ethanol extract of *Hibiscus sabdariffa* flower contains saponins, terpenes, tannins, flavonoids, phlobatanins, anthraquinones, cardiac glycoside, and alkaloids. In addition to the above listed phytochemicals, Mahaderan et al. (27) also reported that the ethanol extract of *Hibiscus sabdariffa* calyx contains thiamine, xylose, niacin, pectin, fat, rhamnogalacturans, riboflavin, β -caroene, phylosterols, carboxylic acids (notably, citric acid, ascorbic acid, malic acid, maleic acid, tartaric acid, oxalic acid, glycolic acid, nicotinic acid, hiniscic

Table 3. Langmuir adsorption parameters for the inhibition of the corrosion of mild steel by ethanol extract of *Hibiscus sabdariffa* calyx.

Temperature (K)	Slope	log K	ΔG (kJ mol $^{-1}$)	R^2
303	0.9176	0.2487	-11.54	0.9968
333	0.5948	0.3198	-13.13	0.9554

Table 4. Phytochemical constituents of ethanol extract of *Hibiscus sabdariffa* calyx.

Phytochemical	<i>Hibiscus sabdariffa</i> calyx
Saponins	+++
Terpenes	+++
Tannins	+
Flavonoid	++
Phlobatannins	+++
Anthraquinones	+++
Cardiac glycoside	+++
Alkaloids	+++

Note: (+++) highly present; (++) moderately present; (+) present in minute quantity.

acid, ultalonic acid, and protocatechui acid), hibiscetin, and sabdaretic, among others. Figure 7 presents the chemical structures of some of these phytochemicals. From the point of view of corrosion inhibition, it is evident from Figure 7 that these phytochemicals

are expected to be good corrosion inhibitors because they are organic compounds having heteroatoms in aromatic systems. Several studies have also implicated carboxylic acids as potential corrosion inhibitors (28). Therefore, the inhibition of the corrosion of mild steel by ethanol extract of *Hibiscus sabdariffa* calyx is due to the formation of chelates between iron in the mild steel and some phytochemicals constituents of the extract.

FTIR study

Figure 8 shows the FTIR spectrum of the corrosion product of mild steel. From the spectrum, it is evident that the corrosion product of mild steel does not show any useful adsorption peaks; therefore, the corrosion product of mild steel is not IR-active.

Figure 9 shows the FTIR spectrum of ethanol extract of *Hibiscus sabdariffa* calyx, while Figure 10 shows the FTIR spectrum of the corrosion product of mild steel when the extract was used as an inhibitor.

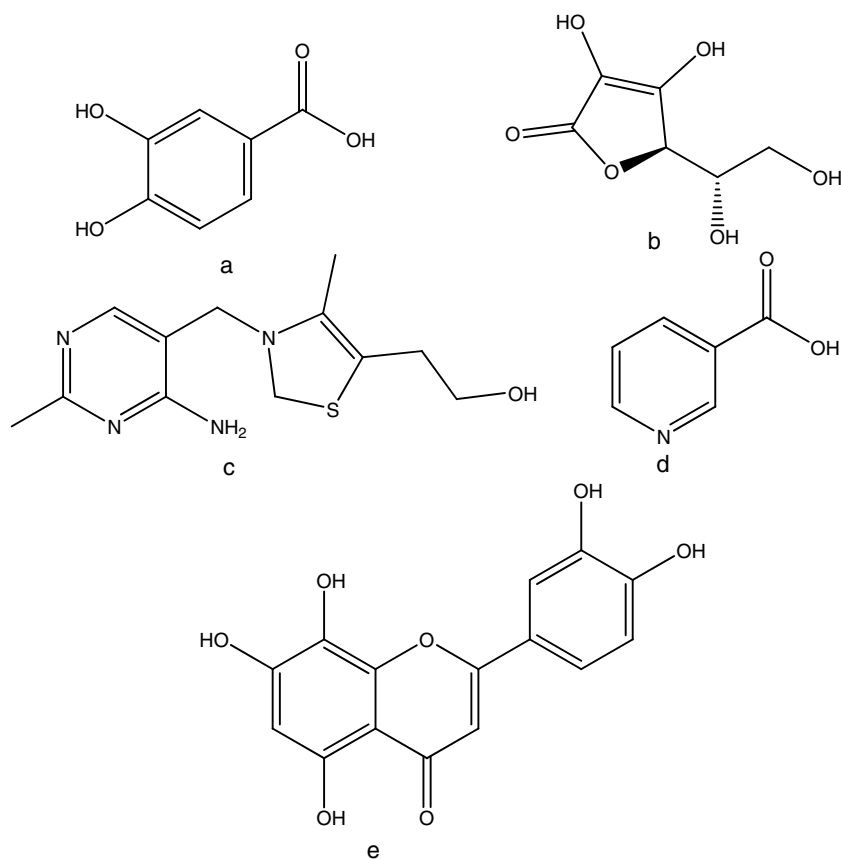


Figure 7. Chemical structures of some photochemical constituents [(a) 3,4-dihydroxybenzoic acid; (b) (*R*)-5-((*S*)-1,2-dihydroxyethyl)-3,4-dihydroxyfuran-2(5H)-one; (c) 2-(3-((4-amino-2-methylpyrimidin-5-yl)methyl)-4-methyl-2,3-dihydrothiazol-5-yl)ethanol; (d) nicotinic acid; (e) (*R*)-5-((*S*)-1,2-dihydroxyethyl)-3,4-dihydroxyfuran-2(5H)-one; (f) 2-(3,4-dihydroxyphenyl)-5,7,8-trihydroxy-4H-chromen-4-one] of ethanol extract of *Hibiscus sabdariffa* calyx.

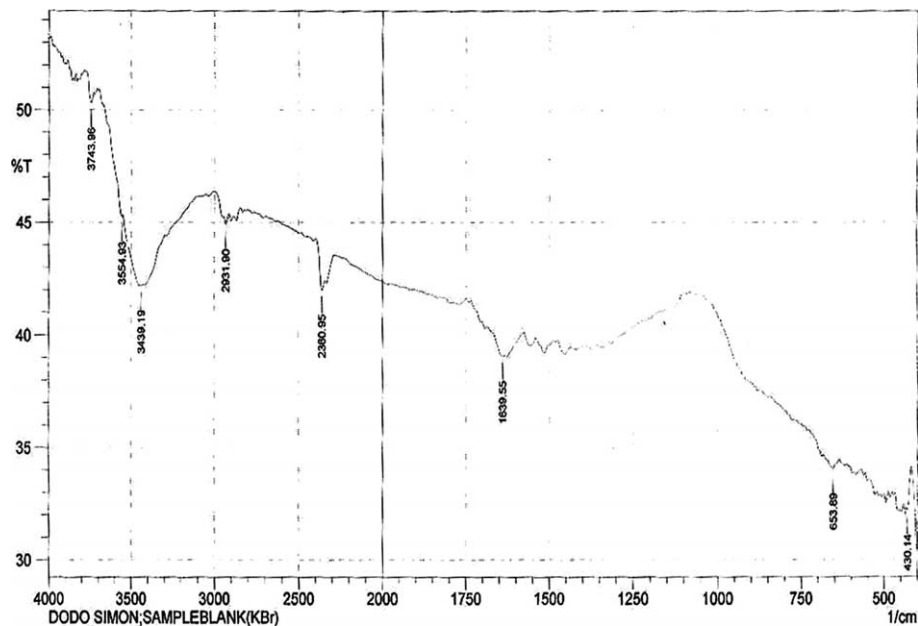


Figure 8. FTIR spectrum of the corrosion product of mild steel.

Frequencies and peaks of IR adsorption for both cases are presented in Table 5. From the results obtained, it can be seen that the C–Cl stretch at 705.97 cm^{-1} is shifted to 569.02 cm^{-1} , the C–H “oop” at 862.21 cm^{-1} is shifted to 669.32 cm^{-1} , the C=C stretch at 1637.62 cm^{-1} is shifted to 1649.19 cm^{-1} , the C–H stretch at 2926.11 cm^{-1} is shifted to 2928.04 cm^{-1} , and the –OH stretch at 3410.26 cm^{-1} is shifted to 3435.34 cm^{-1} . These shifts indicate that there is interaction between Fe in the mild steel and

some of the inhibitor’s molecules. Also the C=O stretch at 1739.85 cm^{-1} , the C–N stretch at 1217.12 cm^{-1} , and the C–O stretch at 1072.99 cm^{-1} were missing in the spectrum of the corrosion product, indicating that these bonds might have been used for bonding between the inhibitor’s molecules and Fe in mild steel. However, the new bonds formed were the O–H bend at 950.94 cm^{-1} and C–Cl and C–C stretches at 522.73 and 1417.73 cm^{-1} , respectively. It is also evident from the analyzed FTIR spectra that

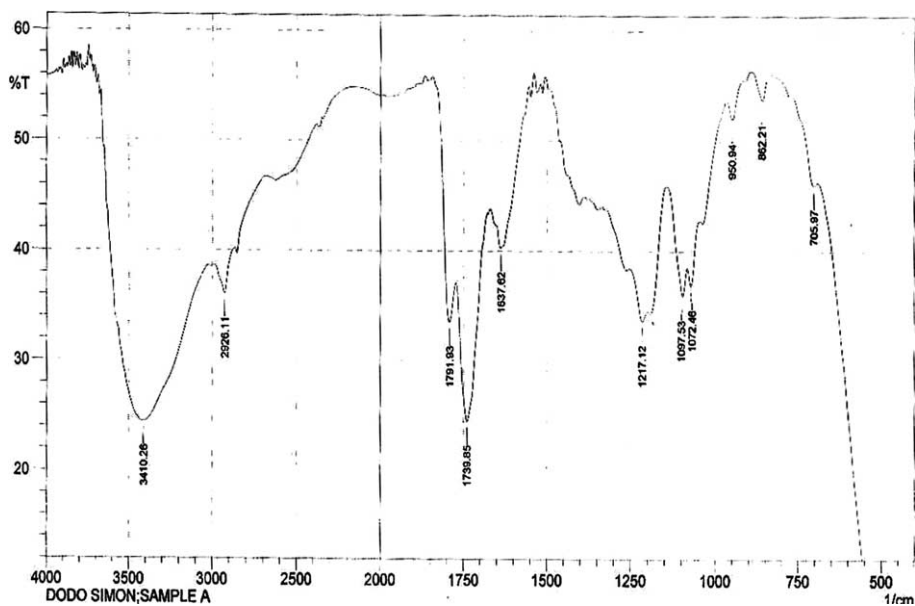


Figure 9. FTIR spectrum of the ethanol extract of *Hibiscus sabdariffa* calyx.

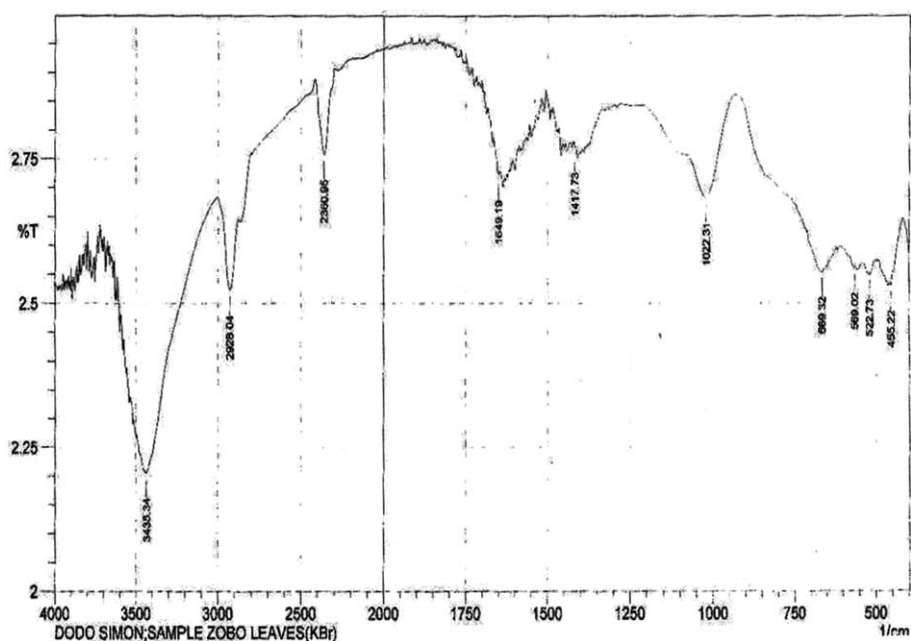


Figure 10. FTIR spectrum of the corrosion product of mild steel in the presence of ethanol extract of *Hibiscus sabdariffa* calyx.

after the initial mechanism of physical adsorption, chemical adsorption of the inhibitor's molecules on Fe (in mild steel) also occurred.

Experimental

Materials

Quantimetry determined that the composition of mild steel used for the study was Mn (0.6%), P (0.36%), C (0.15%), Si (0.03%), and Fe (98.96%). The sheet was mechanically pressed and cut into different coupons, each of dimension $5 \times 4 \times 0.11$ cm. Each coupon was washed with ethanol, rinsed in acetone, and allowed to dry in the air before preservation in a desiccator. Analar grade reagents

and double distilled water were used for the study. In gravimetric study, the concentration of HCl used was 0.1 M, but in gasometric and thermometric methods, HCl concentration used was 2.5 M.

Extraction of the calyx

Samples of *Hibiscus sabdariffa* calyx were obtained from a botanical garden located within the Ahmadu Bello University, Zaria, Kaduna State, Nigeria. The calyx were sun-dried, grounded, and soaked in a solution of ethanol for 48 h. After 48 h, the samples were cooled and filtered. The filtrates were subjected to evaporation at 352 K in order to leave the sample free of the ethanol. The stock solutions of the extract

Table 5. Frequencies and peaks of adsorption of IR by ethanol extract of *Hibiscus sabdariffa* calyx.

Pure extract			Extract adsorbed on mild steel		
Frequency (cm^{-1})	Height (cm)	Assignment	Frequency (cm^{-1})	Height (cm)	Assignment
705.97	769.62	C-Cl stretch	522.73	526.58	C-Cl stretch
862.21	895.00	C-H "oop"	569.02	584.4	C-Cl stretch
950.94	968.30	O-H bend	669.32	715.61	C-H "oop"
1072.46	1084.03	C-O stretch			
1097.53	1143.03	C-O stretch	1022.31	1093.67	C-O stretch
1217.12	1253.77	C-N stretch			
1637.62	1651.12	-C = C- stretch	1417.73	1421.58	C-C stretch
1739.85	1772.64	C = O stretch	1649.19	1664.62	-C = C- stretch
2926.11	2991.69	C-H stretch	2928.04	3005.20	C-H stretch
3410.26	3417.98	OH stretch	3435.34	3444.98	OH stretch

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 1 L solution of 2.5/0.1 M of HCl, respectively.

Gravimetric method

In the gravimetric experiment, a weighed mild steel coupon was completely immersed in 250 mL of the test solution in an open beaker. The beaker was covered with aluminum foil and maintained at 303 K in a water bath for 24 h. After every 24 h, the sample was withdrawn from the test solution and washed with distilled water containing 50% NaOH and 100 g L⁻¹ of zinc dust. The washed coupon was rinsed in acetone and dried in the air before reweighing. The experiment was repeated at 333 K. In each case, the difference in weight for a period of 168 h was taken as the total weight loss. From the average weight loss (mean of three replicate analyses) results, the inhibition efficiency (%I) of the inhibitor, the degree of surface coverage (θ), and the corrosion rate of mild steel (CR) were calculated using the following equations (29):

$$\%I = (1 - W_1/W_2) \times 100 \quad (12)$$

$$\theta = 1 - W_1/W_2 \quad (13)$$

$$CR = \Delta W/At, \quad (14)$$

where W_1 and W_2 are the weight losses (in g) for mild steel in the presence and absence of the inhibitor, θ is the degree of surface coverage of the inhibitor, $\Delta W = W_2 - W_1$, A is the area of the mild steel coupon (in cm²), t is the period of immersion (in h), and ΔW is the weight loss of mild steel after time t .

Gasometric method

Gasometric methods were carried out at 303 K using a gasometer. The volume of hydrogen liberated per minute was recorded until constant values were obtained. From the volume of hydrogen gas evolved per minute, inhibition efficiencies were calculated using the following equation (30):

$$\%I = \left(1 - \frac{V_{H_2}^1}{V_{H_2}^0}\right) \times 100, \quad (15)$$

where ΔG_{ads}^0 and $V_{H_2}^0$ are the volumes of H₂ gas evolved at time “ t ” for inhibited and uninhibited solutions, respectively.

3.5. Thermometric method

Thermometric experiments were carried out using a thermometric flask, equipped with temperature (30). The temperatures of the system containing mild steel and the respective test solution were recorded after every minute until a steady temperature value was obtained. From the temperature rise, the reaction number was calculated using the following equation:

$$RN \left(^\circ\text{C min}^{-1}\right) = \frac{T_m - T_i}{t}, \quad (16)$$

where RN is the reaction number (in $^\circ\text{C min}^{-1}$), T_m and T_i are the maximum and initial temperatures attained by the systems, respectively, and “ t ” is the time (in min) taken to attain the maximum temperature. From the reaction number, the inhibition efficiency (%I) of the inhibitor was calculated using the following equation:

$$\%I = \frac{RN_{\text{aq}} - RN_{\text{wi}}}{RN_{\text{aq}}} \times 100, \quad (17)$$

where RN_{aq} is the reaction number in the absence of inhibitors (blank solution) and RN_{wi} is the reaction number of 2.5 M H₂SO₄ containing the studied inhibitor.

Chemical analysis

Phytochemical analysis of the ethanol extract of the sample was carried out according to the method reported by Odiongenyi et al. (31). Frothing and Na₂CO₃ 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 glycosides, while Dragendorf, Hagger, and Meyer reagents were used for the identification of alkaloid.

Infrared analysis

FTIR analysis of the corrosion product of mild steel and the ethanol extract of the sample were carried out at the National Research Institute of Chemical Technology, Zaria, Kaduna State, Nigeria, using an FTIR spectrophotometer. The sample was prepared in KBr powder and the scanning was done between the wavenumber of 4000 and 500 cm⁻¹.

Conclusions

The results obtained from gravimetric, gasometric, and thermometric studies revealed that ethanol extracts of *Hibiscus sabdariffa* calyx is a good

adsorption inhibitor for the corrosion of mild steel in HCl solutions. The adsorption characteristic of the inhibitor is best described by the Langmuir adsorption isotherm. The adsorption of the inhibitors on mild steel surface is spontaneous and supports the mechanism of physical adsorption at the initial stage.

The inhibition efficiency of ethanol extract of *Hibiscus sabdariffa* calyx is attributed to joint adsorption of some of its phytochemical constituents. Therefore, the use of ethanol extract of *Hibiscus sabdariffa* calyx as an inhibitor for the corrosion of mild steel in HCl is recommended.

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