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Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of mild steel

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ABSTRACT

Corrosion inhibition of mild steel in 2 M HCl and 1 M H_2SO_4 by extracts of selected plants was investigated using a gasometric technique at temperatures of 30 and 60 °C. The studied plants materials include leaf extracts *Occimum viridis* (*OV*), *Telferia occidentalis* (*TO*), Azadirachta indica (*AI*) and *Hibiscus sabdariffa* (*HS*) as well as extracts from the seeds of *Garcinia kola* (*GK*). The results indicate that all the extracts inhibited the corrosion process in both acid media by virtue of adsorption and inhibition efficiency improved with concentration. Synergistic effects increased the inhibition efficiency in the presence of halide additives. Inhibition mechanisms were deduced from the temperature dependence of the inhibition efficiency as well as from assessment of kinetic and activation parameters that govern the processes. Comparative analysis of the inhibitor adsorption behaviour in 2 M HCl and 1 M H_2SO_4 as well as the effects of temperature and halide additives suggest that both protonated and molecular species could be responsible for the inhibiting action of the extracts.

1. Introduction

Acid solutions are often used in industry for cleaning, decaling and pickling of steel structures, processes which are normally accompanied by considerable dissolution of the metal. A useful method to protect metals and alloys deployed in service in aggressive environments against corrosion is addition of species to the solution in contact with the surface in order to inhibit the corrosion reaction and reduce the corrosion rate. A number of organic compounds [1–8] are known to be applicable as corrosion inhibitors for steel in acidic environments. Such compounds typically contain nitrogen, oxygen or sulphur in a conjugated system and function via adsorption of the molecules on the metal surface, creating a barrier to corrodent attack. The adsorption bond strength is dependent on the composition of the metal and corrodent, inhibitor structure and concentration as well as temperature. Despite the broad spectrum of organic compounds, the final choice of the appropriate inhibitor for a particular application is restricted by several factors. One is increased environmental awareness and the need to promote environmentally friendly processes. Another factor is the vast variety of possible corrosion systems coupled with the specificity of action of most acid inhibitors, which often necessitates use of combinations of additives to provide the multiple services required for effective corrosion inhibition. Consequently there exists the need to develop a new class of corrosion inhibitors with low toxicity and good efficiency.

The exploration of natural products of plant origin as inexpensive eco-friendly corrosion inhibitors is an essential field of study. In addition to being environmentally friendly and ecologically acceptable, plant products are low-cost, readily available and renewable sources of materials. The extracts from their leaves, barks, seeds, fruits and roots comprise of mixtures of organic compounds containing nitrogen, sulphur and oxygen atoms and some [9–14] have been reported to function as effective inhibitors of metal corrosion in different aggressive environments. Gunasekaran and Chauhan [10] assessed the influence of extracts from *Zenthoxylum alatum* plant on the corrosion of mild steel in phosphoric acid. Li and co-workers investigated the inhibitive effect of beberine, extracted from *Coptis chinensis* on mild steel corrosion in 1 M sulphuric acid [13]. El-Etre et al. [14] studied the inhibiting action of *Lawsonia* extract on the corrosion of different metals. The corrosion inhibition efficacy of these extracts is normally ascribed to the presence, in their composition, of complex organic species such as tannins, alkaloids and nitrogen bases, carbohydrates and proteins as well as their acid hydrolysis products.

Despite the great availability and varieties of plant materials, only relatively few have been thoroughly investigated. The present report continues to focus on the broadening application of plant extracts for metallic corrosion control and collates some of the findings in our laboratory on the inhibiting effect of some plant materials including leaf extracts of *Occimum viridis* (*OV*) [15], *Telferia occidentalis* (*TO*) [16], *Azadirachta indica* (*AI*) [17] and *Hibiscus sabdariffa* (*HS*) [18] as well as extracts from the seeds of *Garcinia kola* (*GK*) [19] on mild steel corrosion in acidic solutions. This study has dual purpose; first to further establish the

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effectiveness of plant extracts as corrosion inhibitors and next to attempt deduction of the inhibition mechanism and possible adsorption modes of the extract active components vis-à-vis a number of experimental observations. SEM, AFM, XPS and FTIR investigations of the studied systems is envisaged in subsequent studies to ascertain the corrosion morphology and also determine the active components in the adsorbed layer.

2. Experimental

2.1. Materials

The experiments were performed on mild steel sheets with weight percentage composition as follows; C – 0.05, Mn – 0.6 P – 0.36, Si – 0.03 and thickness 0.14 cm. The metal specimen were prepared, degreased and cleaned as previously described [19–21].

All chemicals and reagents used were of analytical grade. The blank corrodents were, respectively, 2 M HCl and 1 M H_2SO_4 solutions. Stock solutions of the plant extract were prepared by boiling weighed amounts of the dried and ground plant material for 3 h in the 2 M HCl and 1 M H_2SO_4, respectively. The solutions were cooled and then filtered and stored. From the respective stock solutions, inhibitor test solutions were prepared in the concentration range 10–50 v/v% using excess acid as solvent. The effect of halide additives was studied by introducing 5.0 mM of the halide salts KCl, KBr and KI.

2.2. Gasometric experiments

The gasometric set up is essentially an apparatus that measures the volume of gas evolution from a reaction system. A two-necked flask was connected via a delivery tube to a burette which was in turn connected to a reservoir of paraffin oil. Test solution (250 ml) was then introduced into the reaction vessel and the initial volume of air in the burette recorded. Thereafter, two mild steel test coupons were dropped into the test solution and the reaction vessel immediately closed. The volume of hydrogen gas evolved by the corrosion reaction was estimated by the volume change in the level of the paraffin oil in the burette. The progress of the corrosion reaction was monitored by careful volumetric measurement of the evolved hydrogen gas at fixed time intervals. Experiments were conducted at 30 and 60 °C.

3. Results and discussion

3.1. Hydrogen evolution and corrosion rates

The anodic dissolution of iron in acidic solutions has been reported to proceed according to the mechanism [22]

$$Fe + OH^- \rightleftharpoons FeOH_{ads} + H^+ + e \tag{1a}$$

$$FeOH_{ads} \rightarrow FeOH^+ + e \tag{1b}$$

$$FeOH^+ + H^+ \rightleftharpoons Fe^{2+} + H_2O \tag{1c}$$

accompanied by the conjugate cathodic reaction

$$2H^+ + 2e \rightarrow H_2 \tag{2}$$

Accordingly, the progress of the corrosion reaction was followed by measuring the volume of evolved H_2 gas. This technique apart from its experimental rapidity ensures a more sensitive monitoring, in situ, of any perturbation by an inhibiting additive vis-à-vis gas evolution at the metal-corrodent interphase [23,24]. Results obtained by the gasometric method are corroborated by other well established methods including weight loss and thermometric [11], potentiostatic polarization [12], and impedance spectroscopy [25].

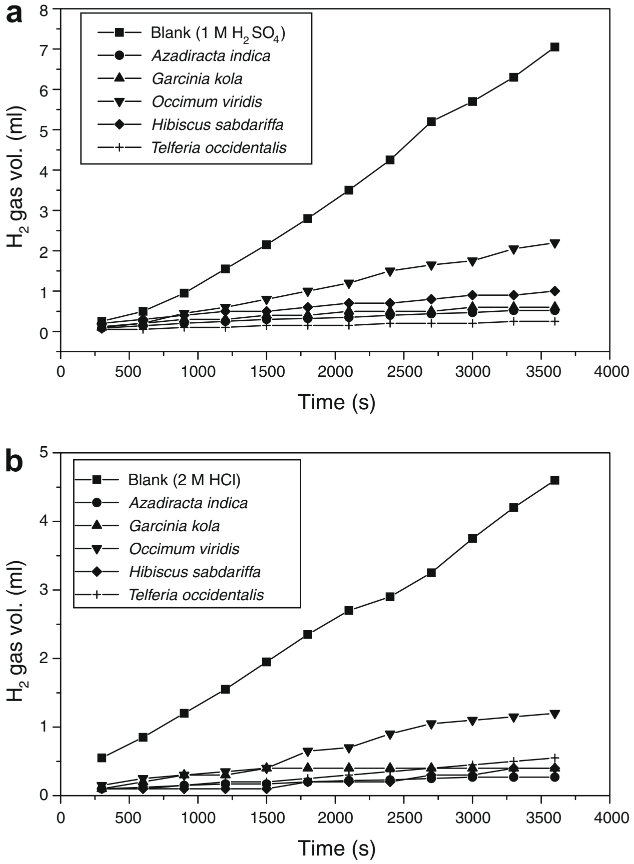

Fig. 1. Hydrogen evolution from mild steel corrosion in (a) 1 M H_2SO_4 and (b) 2 M HCl in absence and presence of different plant extracts at 30 °C.

Typical hydrogen evolution data for uninhibited and inhibited steel containing the extract from the different plant materials, in 1 M H_2SO_4 and 2 M HCl are illustrated in Fig. 1. The volume of evolved H_2 gas is observed to vary linearly with reaction time as follows:

$$V = Kt \tag{3}$$

where V is the volume of evolved H_2 gas in time t and K is the specific rate constant of the corrosion reaction. The results show that the extracts diminished the H_2 gas evolution rate and hence inhibited mild steel corrosion in both acid solutions. For all the studied extracts, the rates of H_2 gas evolution generally decreased with increasing extract concentration, suggesting that the inhibiting action was concentration dependent. The trend of corrosion rate with time for uninhibited and inhibited steel with *A. indica* extract is illustrated in Fig. 2. These plots were derived from linear fitting of the volume of evolved H_2 gas as a function of the square of the natural logarithm of time, as shown in Fig. 3, according to the relationships [26]

$$V = k_o \ln^2 t + k_i \tag{4}$$

$$\frac{dV}{dt} = 2k_o \frac{\ln t}{t} \tag{5}$$

where V is the H_2 gas volume (ml), t the time (min), k_o and k_i are the slope and intercept, respectively. Corrosion rates in the presence of the extract are markedly reduced, again indicating a corrosion inhibiting effect.

3.2. Inhibition efficiency and adsorption considerations

The characterization of the free corrosion of mild steel in the different inhibitor/corrodent solutions was carried out by an

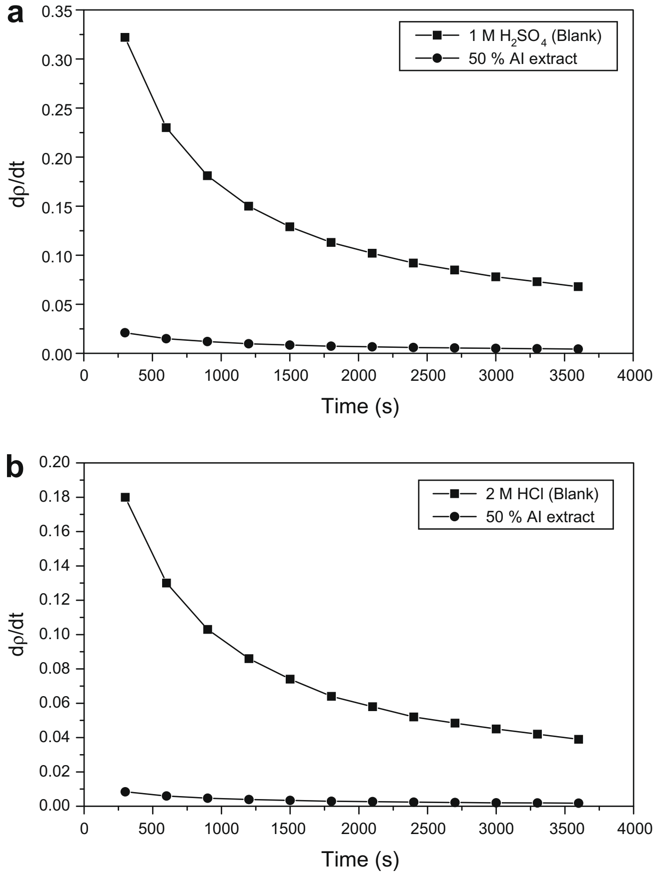

Fig. 2. Variation of mild steel corrosion rate with time in absence and presence of *Azadirachta indica* extract in (a) 1 M H_2SO_4 and (b) 2 M HCl.

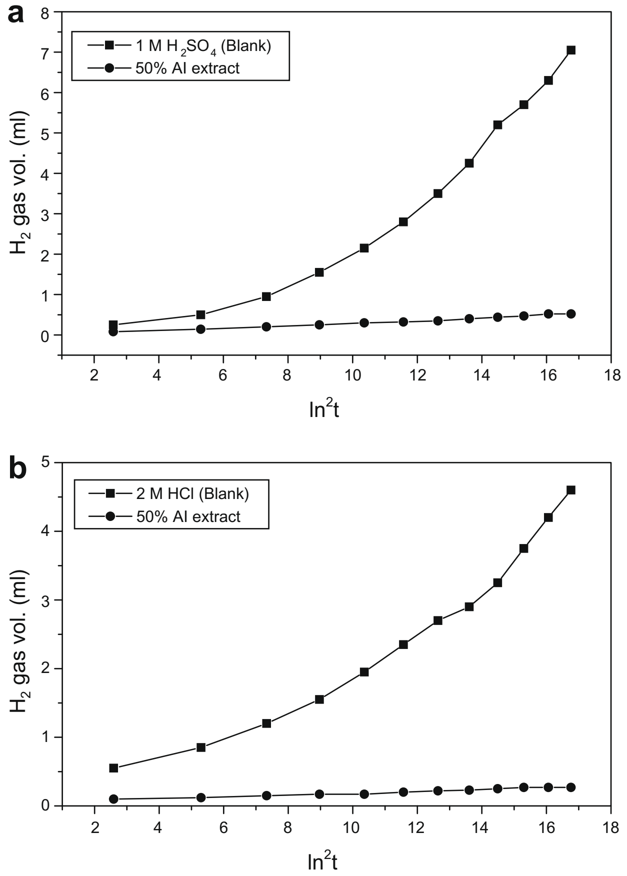

Fig. 3. Evolved hydrogen gas as a function of the natural logarithm of time for mild steel corrosion in the absence and presence of *Azadirachta indica* extract in (a) 1 M H_2SO_4 and (b) 2 M HCl.

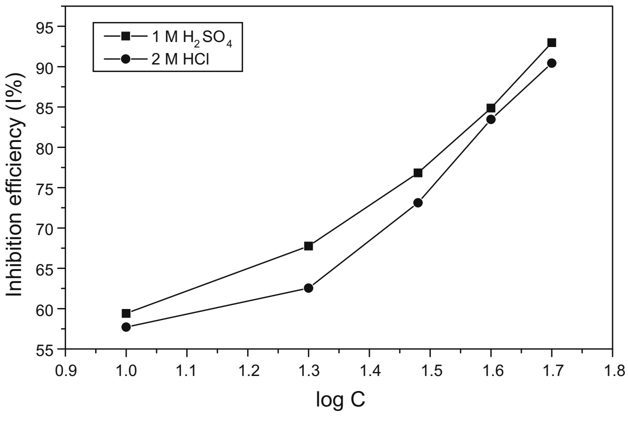

Fig. 4. Variation of inhibition efficiency with *Hibiscus sabdariffa* extract concentration in 1 M H_2SO_4 and 2 M HCl.

assessment of the degree of surface coverage (θ) of the metal surface by the inhibitor as well as the inhibition efficiency ($I\%$) as follows:

$$\theta = 1 - \frac{\rho_{\text{inh}}}{\rho_{\text{blank}}} \tag{6}$$

$$I\% = \left(1 - \frac{\rho_{\text{inh}}}{\rho_{\text{blank}}}\right) \times 100 \tag{7}$$

where ρ_{inh} and ρ_{blank} correspond to the corrosion rates in the presence and absence of inhibitor, respectively. Figs. 4–6 show plots of inhibition efficiency versus logarithmic concentration of inhibitor for HS, GK and AI, which represents the adsorption isotherms for the extracts on mild steel from 1 M H_2SO_4 and 2 M HCl. The results indicate that these plant materials retard mild steel dissolution in the examined media by adsorption of the active components on the metal surface and efficiency of inhibition generally increased with concentration. Table summarizes the efficiencies of the highest and lowest concentrations of the studied plant extracts at different temperatures. It is obvious that the additives display remarkable protective ability in the examined media. Inhibition efficiency in 1 M H_2SO_4 is in the order: OV (70.2%) < GK (91.0%) < HS (93.0%) < AI (93.8%) < TO (97.3%) at the upper concentration limit and OV (71.1%) < HS (90.4%) < GK (93.1%) < TO (94.8%) < AI (95.6%) in 2 M HCl. Thus apart from OV, all the others exhibit efficiencies >90% (Fig. 7).

In accounting for the observed protective effect, it should be noted that the extracts comprise a mixture of organic and resinous matter (Table 1) some of which are known to exhibit good corrosion inhibiting abilities. The complex chemical compositions make it rather difficult to assign the inhibiting action to a particular constituent or group of constituents. Nevertheless, the net adsorption of the extract organic matter on the metal surface creates a barrier to charge and mass transfer, thus protecting the metal surface from corrodent attack. The degree of protection varies for the different extracts, but generally increased with an increase in extract concentration due to higher degree of surface coverage resulting from enhanced adsorption of the extract organic matter. From Table 1, we observe some similarities in the phytochemical components of the extracts, particularly tannins and glycosides, which could be responsible for the comparable inhibitive effect observed in

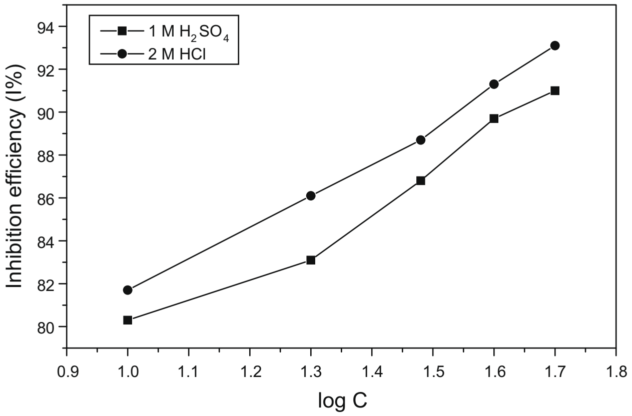

Fig. 5. Variation of inhibition efficiency with *Garcinia kola* extract concentration for mild steel corrosion in 2 M HCl and 1 M H_2SO_4.

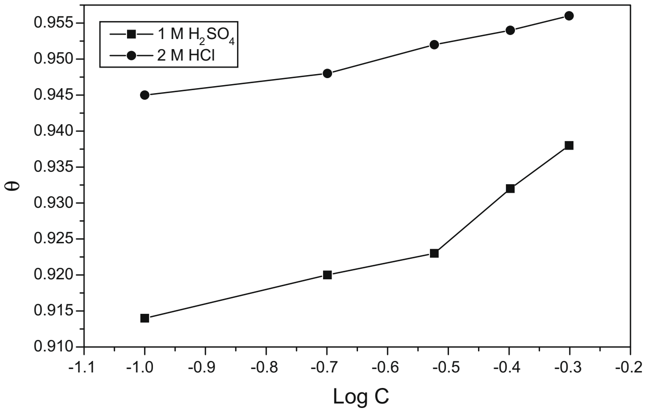

Fig. 6. Langmuir isotherm for *Azadirachta indica* adsorption from 1 M H_2SO_4 and 2 M HCl.

some cases. The inhibitive properties of tannins has been attributed to the reaction of the polyphenolic fraction of the tannin molecule with ferric ions, thereby forming a highly cross-linked network of ferric tannate moieties [27], which ensures effective protection of the metal surface. The triterpenoid and other constituents also possess functional groups which are capable of chelating with ferric ions and thus facilitate strong coordination on the steel surface. The resulting Fe–extract complexes may, depending on their relative solubility, inhibit or even catalyse further metal dissolution. The present results indicate a pervasiveness of the inhibitive effect, which implies that the Fe–extract complexes formed an insoluble surface layer which isolated the metal surface from the corrodent. The integrity of this protective film has been shown to be quite sensitive to the extract concentration [28]. Possible synergistic interactions between the different adsorbed constituents could also contribute to the high inhibition efficiencies observed.

Having ascertained the effectiveness of these plant materials, precise interpretation of the nature and composition of the adsorbed inhibitor layer will be achieved from in depth studies of the corrosion morphology and characterization of the active materials in the adsorbed layer.

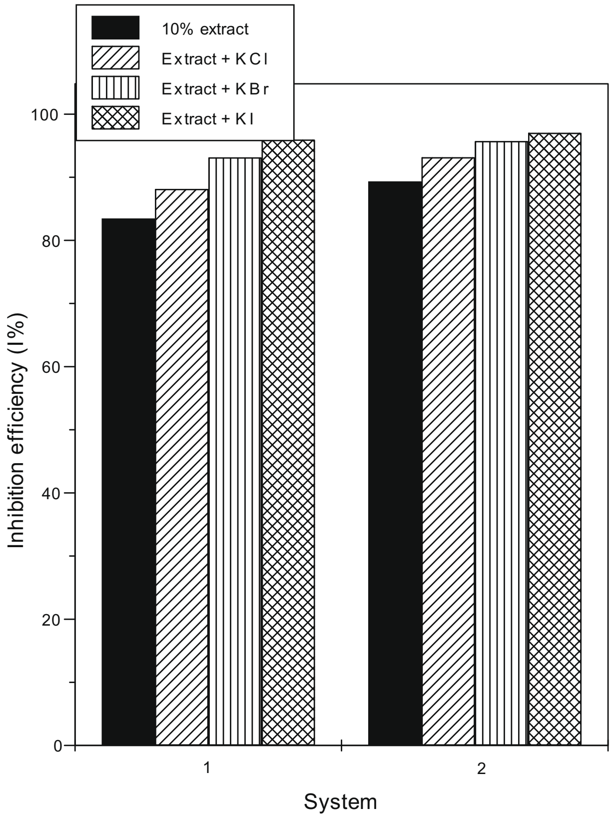

Fig. 7. Effect of halide salts on the inhibition efficiency of 10% *Telfaria occidentalis* extract (1 = 2 M HCl; 2 = 1 M H_2SO_4).

Table 1
Major chemical constituents of the studied plants

Plant	Major constituent
Occimum viridis	Mono and triterpenoids, ascorbic acid, carotenoids, aromatic oils
Azadirachta indica	Tannins, triterpenoids
Hibiscus sabdariffa	Ascorbic and amino acids, flavonoids, β-carotene
Telferia occidentalis	Amino acids, flavonoids
Garcinia kola	Primary and secondary amines, flavonoids, unsaturated fatty acids

3.3. Effect of temperature

Two main types of interaction often describe adsorption of organic inhibitors on a corroding metal surface viz: chemical adsorption and physical adsorption. It has been suggested [29,30] that physisorbed molecules are attached to the metal at local cathodes and essentially retard metal dissolution by stifling the cathodic reaction whereas chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached. The more efficient inhibitors appear to protect anodic areas preferentially by chemisorption. Initial deduction of the adsorption mechanisms in this study involved the assessment of the effects of varying system temperature between 30 and 60 °C on corrosion and inhibition processes. The variation of inhibition efficiency with temperature is given in Table 2. The apparent activation energies (E_a) for the corrosion process in absence and presence of inhibitor were evaluated from Arrhenius equation

$$\log\frac{\rho_2}{\rho_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{8}$$

whereas estimates of the heats of adsorption (Q_{ads}) were obtained from the trend of surface coverage with temperature as follows [31]:

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] \times \frac{T_1T_2}{T_2 - T_1} \tag{9}$$

Table 2
Inhibition efficiency (*I*%) of different plant extracts on mild steel corrosion in 1 M H_2SO_4 and 2 M HCl at different temperatures

Extract concentration (v/v%)	1 M H_2SO_4		2 M HCl	
	30 °C	60 °C	30 °C	60 °C
Occimum viridis				
10	69.2	63.3	66.9	56.1
50	70.2	79.9	71.1	65.0
Telferia occidentalis				
10	89.3	63.4	83.5	28.8
50	97.3	90.2	94.8	40.6
Azadirachta indica				
10	91.4	91.0	94.5	89.1
50	93.8	96.2	95.6	96.2
Hibiscus sabdariffa				
10	59.4	65.5	57.7	48.6
50	93.0	93.3	90.4	73.9
Garcinia kola				
10	80.3	50.0	81.7	75.8
50	91.0	76.8	93.1	80.1

ρ_1 and ρ_2 are the corrosion rates at temperatures T_1 and T_2, respectively while θ_1 and θ_2 are the degrees of surface coverage at temperature T_1 and T_2 and R is the gas constant. The calculated values of E_a and Q_{ads} are given in Table 3. Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies in absence and presence of inhibitor gives some insight into the possible mechanism of inhibitor adsorption. A decrease in inhibition efficiency with rise in temperature, with analogous increase in corrosion activation energy in the presence of inhibitor compared to its absence, is frequently interpreted as being suggestive of formation of an adsorption film of physical (electrostatic) nature. The reverse effect, corresponding to an increase in inhibition efficiency with rise in temperature and lower activation energy in the presence of inhibitor, suggests a chemisorption mechanism [3,6,32]. From the foregoing, the trend for *A. indica* suggests physisorption of inhibiting species at lower concentration while chemisorption is favoured at higher concentration while the results for *H. sabdariffa* suggest chemical adsorption of organic matter on the steel surface in 1 M H_2SO_4 and physical adsorption in 2 M HCl. For *T. occidentalis* and *G. kola*, the data suggest a predominant effect of physisorption. The observed behaviour could be ascribed to the existence of both protonated and molecular species in the complex acid extractions under study, inhibiting the cathodic and anodic reactions to different extents.

Table 3
Calculated values of activation energy (E_a) and heat of adsorption (Q_{ads}) for various plant extracts during mild steel corrosion in 2 M HCl with and 1 M H_2SO_4

Extract concentration (v/v%)	1 M H_2SO_4		2 M HCl	
	E_a (kJ mol^{-1})	Q_{ads} (kJ mol^{-1})	E_a (kJ mol^{-1})	Q_{ads} (kJ mol^{-1})
Blank				
–	56.4	–	49.3	–
Occimum viridis				
10	62.9	−7.3	53.7	−12.8
50	56.9	1.5	51.1	−7.3
Telferia occidentalis				
10	89.0	−44.1	96.5	−70.7
50	96.6	−38.1	123.9	−92.1
Azadirachta indica				
10	58.9	–	83.7	–
50	45.0	–	49.6	–
Hibiscus sabdariffa				
10	50.2	8.37	51.7	−10.1
50	53.4	1.4	74.3	−32.2
Garcinia kola				
10	94.0	−45.5	100.2	−10.0
50	94.0	−38.2	121.9	−31.2

Further elucidation of adsorption mechanisms from the experimental data requires estimation of the adsorption modes of the inhibiting species (whether molecular or ionic). The predominant adsorption mode will be dependent on factors such as the extract composition, type of acid anion, chemical changes to the extract and the nature of the surface charge on the metal. A negative surface charge will favour the adsorption of cations whereas anion adsorption is favoured by a positive surface charge. A corroding mild steel specimen carries a positive surface charge in both sulphuric and hydrochloric acid solutions and as such, protonated species should be poorly adsorbed. On the other hand, the ability of Cl^- ions in hydrochloric acid to be strongly adsorbed on the metal surface and hence facilitate physical adsorption of inhibitor cations is an important consideration. Accordingly, a comparison of the inhibiting characteristics of the extract in 2 M HCl and 1 M H_2SO_4 could very well give an idea of the mode of adsorption of the inhibiting species since both solutions have identical anion concentration. If corrosion inhibition is due exclusively to protonated species which adsorb electrostatically, the inhibitor should be more effective in 2 M HCl, alternatively, if they adsorb as molecules, the inhibiting effect in both acid solutions should be comparable. A further consideration involves assessment of the effect of halide additives on inhibition efficiency. It is generally accepted that halide ions facilitate adsorption of organic cations during mild steel corrosion in acidic media by forming intermediate bridges between the metal surface and the positive end of the organic inhibitor. Again, if the inhibiting effect of the extract is due exclusively to the protonated species, a synergistic increase in inhibition efficiency should be observed in the presence of the halide additives. On the other hand, if molecular species in the extract have a predominating effect, the halide additives will have negligible effect. Table 4 illustrates the effect of 5.0 mM solutions of the halide salts KCl, KBr, and KI on the inhibition efficiency of *O. viridis* and *H. sabdariffa* as well as KI on *G. kola* while Fig. 5 depicts the data for *T. occidentalis*. It is observed that halide ions generally have a beneficial effect upon the performance of all the extracts. The synergistic effect increased in the order; $Cl^- < Br^- < I^-$, suggesting a possible role by ionic radii of the halides which also increase in the same order.

The data in Table 2 show close similarities in the efficiency of each extract in both acid solutions, suggesting chemisorption of

Table 4
Influence of halide additives (0.5 mM) on the inhibition efficiency of different plant extracts

System	Inhibition efficiency			
	1 M H_2SO_4		2 M HCl	
	30 °C	60 °C	30 °C	60 °C
Occimum viridis				
10% extract	69.1	63.3	66.9	56.1
Extract + KCl	87.0	79.9	−8.2	54.3
Extract + KBr	87.5	87.8	87.1	57.5
Extract + KI	94.5	90.0	91.6	56.7
Hibiscus sabdariffa				
10% extract	59.4	65.5	57.7	48.6
Extract + KCl	90.0	86.8	83.6	71.2
Extract + KBr	91.3	90.2	83.7	76.4
Extract + KI	95.0	94.8	87.9	82.1
Garcinia kola				
10% extract	80.3	50.0	81.7	75.8
Extract + KI	93.2	80.9	92.9	89.9

the organic matter. On the other hand, halide ions remarkably enhanced efficiency in both acid solutions, which implies a role by cationic species, which adsorption becomes favoured in the presence of the halide ions resulting in enhanced surface coverage and hence high inhibition efficiencies observed. This behaviour is comparable to reports [14,28] that certain plant extracts function as mixed-type inhibitors of the acid dissolution of mild steel. Some similarities are evident in the inhibiting action of the studied extracts (Tables 1 and 2 and Fig. 1). It is possible that the protein hydrolysis products of the extracts have identical effect on the cathodic reaction [28]. The variations in inhibition efficiency may then be attributed to differences in the extents to which the extracts affect the anodic dissolution reaction.

4. Conclusions

The extracts from studied plant materials were found to be effective green inhibitors of mild steel corrosion in 1 M H_2SO_4 and 2 M HCl. The corrosion process was inhibited by adsorption of the extract organic matter on the steel surface. Analyses of all the results yield some interesting observations. The synergistic action of the halides point to physisorption of protonated organic species on the other hand, the close similarity in inhibition efficiency values in both acid solutions at 30 °C suggests chemical adsorption of molecular species. This possibly suggests the participation of both protonated and neutral species in the inhibiting action of the extracts. Further investigation is required to assess the corrosion morphology and ascertain the active species in the adsorption layer.

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