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Inhibitory Effect of *Stachytarpheta mutabilis* Extracts on the Corrosion of Mild Steel in Acidic Media

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Keywords

- Stachytarpheta mutabilis; Isotherms; Kinetics; Thermodynamics; Corrosion inhibition; Efficiency

Abstract

The anticorrosive potential of *Stachytarpheta mutabilis* leaf extract (SMLE) as a corrosion inhibitor for corrosion of mild steel (MS) in 1 M HCl was investigated using weight loss measurement as well as gasometric techniques at 30 and 60 °C. Relevant thermodynamic equations were employed to estimate the activation energy, enthalpy change and entropy change. The adsorption isotherms were used to determine the Gibbs free energy change. Results obtained showed that SMLE functioned as an excellent corrosion inhibitor for mild steel in the acidic environment. Temperature studies revealed a decrease in inhibition efficiency with increase in temperature and activation energies increased in the presence of the extract. The adsorption of SMLE on mild steel was approximated using Freundlich, Flory-Huggins, Frumkin, El-Awary's and Temkin isotherms but Langmuir gave the best fit. Both kinetic and thermodynamic parameters governing the adsorption process were calculated and discussed. The adsorption followed a first order kinetics. As concluded from the results, the adsorption of *S. mutabilis* on mild steel in 1M HCl medium is feasible, spontaneous and it occurred by physical adsorption. From the experimental results obtained, it can be concluded that SMLE inhibit corrosion effectively when compared well with many reported green inhibitors for MS corrosion.

INTRODUCTION

The corrosion of metals in many industrial operations has become a serious problem that requires a broad-reaching approach due to ; cost of maintenance, replacement of damaged component, labour cost as well as the cost incurred during installation .Companies loss billions of dollars as a result of corrosion of iron and steel in the oil and drilling sector due to contamination of product, loss productivity via product delays and failures to meet specification, efficiency, litigation and taxes and overhead imposed on corroded portion of goods and services [1]. In order to prevent or minimize corrosion, organic and /or inorganic substances referred to as inhibitors are usually added to the system to inhibit corrosion via chemisorptions and/or physisorption mechanism on the metal surface or by reacting with metal ions and forming a barrier precipitate that keeps the interface away from corrosion agents [2]. These inhibitors based on their functional properties mitigate corrosion by; increasing the electrical resistance at the metal-electrolyte interface and hydrogen overvoltage, shifting the corrosion potential/polarization of the metal surface to either cathodic or anodic end or both and decreasing the permeation of ions onto the metal interface [3,4].The use of plant extracts as an anticorrosive inhibitors have been validated by their elemental and electronic configurations such as oxygen, nitrogen or sulphur, and multiple bonds presence, which allow an adsorption on the metal surface [5,6].

Several investigators have reported the use of myriads of synthetic organic compounds as inhibitors such as benzylaminopurine [7], S-triazole-triazole derivatives [8], azoles (Popova et al., 2007), Schiff base [9], pyridine derivatives [10], pyrazole derivatives [11], bipyrazole derivatives [12], pyrimidine derivatives [13], and benzimidazole derivatives [14,15] as effective corrosion inhibitors in acidic media. Nevertheless, most of these inhibitors are not environmentally friendly but toxic and expensive with attendant safety issues. Therefore, the study of non-toxic or environmentally friendly corrosion inhibitors is important to overcome this challenge. Recent literatures highlighting the use of plant extract from *Carica papaya*, *Rosmarinus Officinalis*, *Damsissa*, *Murrayakoenigii*, cashew, mango, *Uncaria gambir*, *Fiscusycomorus*, Gum Arabic, *Raphia hookeri*, *Ipomoea invulcrata*, *Vigna unguiculata*, *Pachylobus edulis*, Ginseng root, *Dacroydes edulis* and *Zenthoxylum alatum* had been investigated and [16-22] Ogunleye et al., 2018; [23-30] to mention but a few have been found to exhibit anticorrosion inhibiting effect for metal in acidic/alkaline media. In our continuous quest to explore, verify and validate more natural products of plant origin as corrosion inhibitors, the present study is on *Stachytarpheta mutabilis* leaf extract. Perusals of literatures however, revealed that the anticorrosive inhibiting action of *Stachytarpheta mutabilis* has not been tested for metals in acidic/alkaline media to the best of our knowledge.

Stachytarpheta mutabilis belongs to the family Verbenaceae.

The verbena family has more than 2600 species and 100 genera with *Stachytarpheta mutabilis* as the most popular and abundant species [31]. It is commonly called 'Red porterweed', 'pink snakeweed', 'coral poterweed' or 'red snakeweed' [32]. *Stachytarpheta mutabilis* has been known to exhibit antibacterial and hypoglycemic effect on living tissues and as a result, have been well employed in the treatment of malaria, stomach-ache and cholera. It has also been used as a vermifuge or purging vehicle, in the treatment of eye trouble, heart trouble, yellow fever and gonorrhoea [33]. It has been reported elsewhere that *Stachytarpheta mutabilis* has an anti-viral activity against chronic and acute hepatitis [34]. Several literatures have reported that sulphur containing compounds in *Stachytarpheta mutabilis* are responsible for its pharmacological properties. These compounds include alkaloids, flavonoids, tannins etc [35-37]. Consequent upon this, the extracts of this plant, which contains numerous naturally environmentally organic compounds, may be utilized as eco-friendly corrosion inhibitors.

To gain insight on the working and applicability of *S. mutabilis* for commercial purposes, the inhibition mechanism, kinetics and process thermodynamics were examined. This present study deployed gravimetric and gasometric techniques at 30 and 60 °C to evaluate another eco-friendly material *Stachytarpheta mutabilis* leaves extract (SMLE), for use as an engineering inhibitor on MS submerged in a 1 M HCl solution. The kinetics and thermodynamic parameters for maximum corrosion inhibition using SMLE were established.

MATERIALS AND METHODS

Materials preparation

The mild steel sheets used in this work were obtained from St. Iyke Iron and Steel, Mutala Mohammed Highway Calabar, Cross River State, Nigeria. Small piece of 5cm x 4cm and 4cm x 2cm coupons were cut off from a full sheet of about 1mm in thickness for the weight loss and hydrogen evolution technique respectively. Before taking measurements, all the mild steel samples were mechanically polished using emery paper of upto 600 grits, degreased with absolute ethanol, dried in acetone and stored in moisture free desiccators before their use in corrosion studies.

Preparation and extraction of *S. mutabilis* leaf extract (SMLE)

The procedure for the preparation of the leaf extracts is similar to that reported by Okafor et al., (2028). The leaves of *Stachytarpheta mutabilis* were collected as required from a local bush of Parliamentary in Ikot Ishie, Calabar Municipality, Cross River State, Calabar, Nigeria and were authenticated at the herbarium of the University of Calabar, Calabar, Nigeria. The leaves were oven dried in a N53C – Genlab Laboratory oven at 323K, to avoid denaturing. The undenatured sample was blended with a commercial blender until it became powdery in nature. The weight was taken and stored in an air tight sample bottle for future use.

Dried and powdered leaves of *S. mutabilis* were extracted with absolute ethanol in Soxhlet apparatus for 2 hrs. After completion of extraction, the extract was filtered and heated on a water bath at 60 °C until most of the ethanol evaporated. 10g of the ethanol extract was digested in 1L of 1 M HCl solutions (for weight loss and gasometric technique respectively). The resultant solution was kept for 24 hours. From the stock solution obtained, solutions of different concentrations of (0.5g/l, 1.0g/l, 2.0g/l, 4.0g/l, 6.0g/l, 8.0g/l, and 10.0g/l) were prepared. The blank solution was also prepared.

Gravimetric measurements

Gravimetric-based method such as weight loss provides integrated weight loss information from corrosion that has occurred over some period of time. Weight loss measurements were investigated under total immersion using 250 mL capacity beakers containing 200 mL test solution at (303± 1K) maintained in a thermostated water bath. The mild steel coupons were weighed and suspended in the beaker with the aid of rod and hook. The coupons were withdrawn at 24 hrs interval progressively for 168 hrs (7days), scrubbed with bristle brush using ethanol, rinsed severally in deionized water, cleaned, dried in acetone, and re-weighed. The weight losses of the coupon in grammes, was taken as the difference in the weight of the mild steel coupons (MS) before and after immersion in different test solutions. Then the tests were repeated at different temperatures. In order to get good reproducibility, experiments were carried out in triplicate. In this present investigation, the standard deviation values among parallel triplicate experiments were found to be less than 5%, depicting good reproducibility. However, experiments were conducted at 30 °C for weight loss and 30 and 60 °C for hydrogen evolution measurements.

The corrosion rate (ρ) in $mgcm^{-2}hr$ was evaluated from the following equation [38,39]:

$$\rho = \frac{\Delta W}{St} \quad (1)$$

where W is the average weight loss of three mild steel sheets, S the total area of one mild steel specimens and t is the immersion time (168 h). With the calculated corrosion rate, the inhibition efficiency (%) was calculated as follows [40,41]:

$$\%I = \left(\frac{\rho_1 - \rho_2}{\rho_1} \right) \times 100 \quad (2)$$

Where ρ_1 and ρ_2 are the corrosion rates of the mild steel coupons in the absence and presence of SMLE, respectively.

Gasometric technique

The volume of hydrogen evolved was determined following the procedures previously described elsewhere [42,43]. The measurements were performed at temperatures of 303 ± 1K and 333± 1K respectively. A test solution of 1M blank HCl was introduced into the reaction vessel connected to a burette through a delivery tube. A coupon was dropped into the blank

solution of HCl and the reaction vessel quickly closed to prevent any escape of hydrogen gas. The volume of hydrogen gas evolved from the corrosion reaction vessel was examined by the volume changes in the level of the paraffin oil in the burette at 60s (1min) interval for 45 min (2700s). The same procedure was repeated in the presence of inhibitor (SMLE) having concentrations range of 0.5g/l, 1.0g/l, 2.0g/l, 4.0g/l, 6.0g/l, 8.0g/l, 10.0g/l with a corrodent (HCl) concentration of 1M.

The inhibition efficiency (%) was calculated using the equation:

$$\%I = \left(1 - \frac{V_{Ht}^1}{V_{Ht}^0} \right) \times 100 \quad (3)$$

Where V_{Ht}^1 is the volume of hydrogen evolved at time "t" for inhibited solution and V_{Ht}^0 for uninhibited solution. The rate of evolution of hydrogen gas R_H ($ml/cm^2 \text{ min}^{-1}$) was determined from the slope of the graph of volume of hydrogen gas evolved per surface area ($mlcm^{-2}$) against immersion time (min).

Solutions

The aggressive solutions, 1 M HCl were prepared by dilution of analytical grade 36% HCl with distilled water. The concentration ranges of SMLE (0.5g/l, 1.0g/l, 2.0g/l, 4.0g/l, 6.0g/l, 8.0g/l, and 10.0g/l) were prepared for corrosion inhibition study.

Phytochemical studies

The phytochemical analysis of alkaloids, saponins, flavonoids, polyphenols, phlobatinins, antraniods, anthraquinones, cardiac glycoside and tannins was carried out by using the methods of (Gopal et al., 2015 [44]; Hampel 1976[45]; Harold 1971 [46]; Henth 1971 [47]; Herbert 1978 [48] and Harbone (1973) [49].

RESULTS AND DISCUSSION

Effect of SMLE on corrosion

The effect of extract of *Stachytarpheta mutabilis* leaves towards the corrosion inhibition of mild steel (MS) in aggressive 1M HCl was investigated using weight loss technique at 30 °C. The results obtained are presented in Table 1. Figure 1 shows the variation of weight loss versus time for mild steel corrosion in 1M HCl without and with different SMLE concentrations (0.5g/L, 1.0g/L, 2.0g/L, 4.0g/L, 6.0g/L, 8.0g/L, 10.0g/L) at 30 °C. Inspection of the plot revealed that the weight loss of the mild steel was reduced in the presence of the inhibitor compared to its absence; an indication of inhibitive effect of acid corrosion of mild steel (MS). Further inspection of the plot showed that the weight loss of MS in the different SMLE test solutions increased with time. The non-linearity of the plot of weight loss versus time may be due to the heterogeneous nature of the process and presence of mill scale on the MS surface involving several steps [50]. Similar report has been reported elsewhere [51].

The effect of SMLE on the corrosion rate of MS with temperature at 30 °C in the absence and presence of different

concentrations of SMLE are depicted in Figure 2, and the calculated values are presented in Table 1. Inspection of Table 1 and Figure 2, revealed that the corrosion rate in the presence of SMLE increases with rise in temperature. This may be due to the fact that corrosion of MS in acidic environments necessitates the evolution of hydrogen gas and a rise in temperature increases hydrogen gas evolution which invariably results in higher dissolution rate of MS. Figure 2 also revealed that the corrosion rate was reduced in the presence of the different SMLE concentrations with the lowest value obtained at 8.0g/L of SMLE solution used at 30 °C. Decrease in corrosion rate of MS in the presence of SMLE solution depicts the inhibitive and anticorrosive effect of SMLE on the corrosion of mild steel (MS) coupons. The inhibitive effect of SMLE in retarding the corrosion of mild steel in 1M HCl was obtained by comparing the corrosion of MS in the inhibited and uninhibited acid solution and is denoted in terms of the inhibition efficiency (%I). The influence of temperature on percentage inhibition efficiency was studied by conducting weight loss measurements at 30 °C containing different SMLE concentrations (Table1). Inspection of (Table1) revealed that the percentage inhibition efficiency increases with concentration but decreases with temperature. The increase in percentage inhibition efficiency (%I) with increase in extract concentration may be due to an increase in the phytochemical constituents in the crude extract adsorbed on the mild steel-solution interface blocking the active sites, in which direct acid attacks occur and effectively isolate the mild steel from corrosion attack [52 ,53]. Similarly, views have been held by other researchers elsewhere. The increase in percentage inhibition efficiency of SMLE with extract concentration may be due to the adsorption of SMLE onto the mild steel – solution surface through non-bonding election pairs present on the heteroatoms as well as π - electrons with the d- orbitals on the mild steel surface [54]. Similarly, it can be seen that the percentage inhibition efficiency decreases with increase in temperature (Table 2). Such functional display may be due to an increase in the rate of desorption of SMLE from the MS surface at higher temperature [55].

Hydrogen evolution measurements

The corrosion of mild steel coupons in 1M HCl in the presence and absence of *S. mutabilis* leaves extract was investigated at 30 and 60 °C using hydrogen evolution technique. The plot profiling the volume of hydrogen gas evolved in the inhibited and uninhibited acid solution against the reaction time (t, mins) of the MS coupons are depicted in Figure 3,4 and the estimated inhibition efficiency of the systems at different temperatures are presented in Table 2 respectively. Inspection of the Figures showed that the volume of hydrogen gas evolved varies directly with the reaction time. The plot also indicates that the volume of hydrogen gas evolved increase with increase in temperature in the absence and presence of the SMLE while it decreased with increasing SMLE concentration. The values of the corrosion rates of MS coupons in the inhibited and uninhibited sample solution were assessed from the linear portion of the hydrogen evolution plot and the corresponding values for the different systems investigated are presented in Table 2. Figure 5 portrayed that

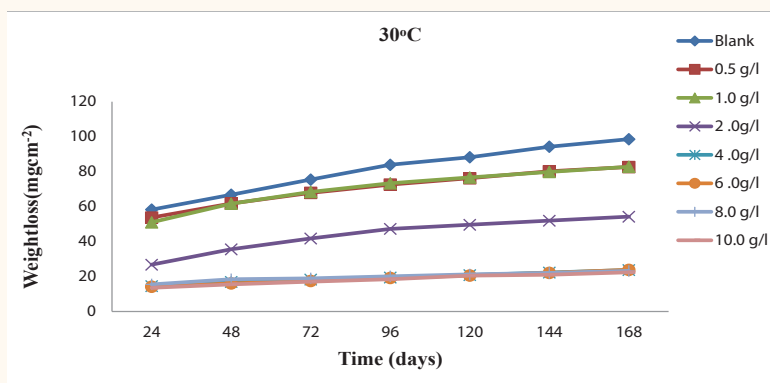


Figure 1 Variation of weight loss with time for mild steel corrosion in 1M HCl in the absence and presence of different concentrations of extract at 30 °C

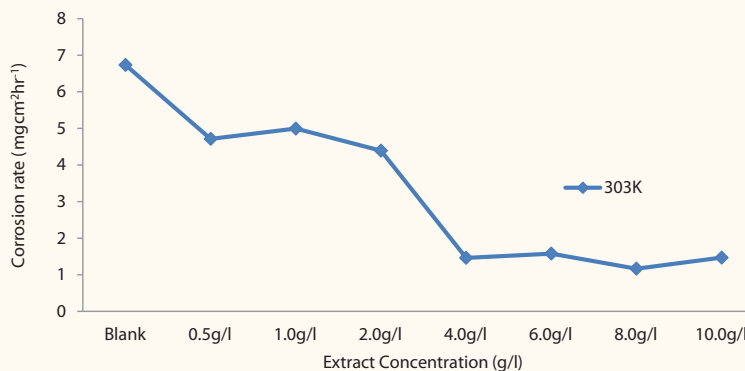


Figure 2 The relationship between corrosion rate and extract concentration in the absence and presence of SMLE at 30 °C

Table 1: Calculated values of corrosion rate, inhibition efficiency, rate constant and half-life for mild steel coupons in the presence and absence of SMLE in 1 MHCl (using the weight loss technique) at 30 °C

System/Concentration	Corrosion rate (mgcm ⁻² hr ⁻¹)	Inhibition efficiency (%)	Rate constant ×10 ⁻³ (day ⁻¹)	Half-life (days)
Blank (1 MHCl)	6.74	-	10.60	65.38
1 MHCl +0.5g/l SMLE	4.71	30.02	7.30	94.93
1 MHCl +1.0g/l SMLE	4.10	25.84	7.80	88.85
1 MHCl +2.0g/l SMLE	4.39	34.80	6.30	110.00
1 MHCl +4.0g/l SMLE	1.46	78.30	2.00	346.50
1 MHCl +6.0g/l SMLE	1.58	76.57	2.20	315.00
1 MHCl +8.0g/l SMLE	1.17	82.69	1.60	433.13
1 MHCl +10.0g/l SMLE	1.47	78.20	2.00	346.50

Table 2: Calculated values of corrosion rate, inhibition efficiency, activation energy and heat of adsorption for mild steel coupons in the acid media containing extracts from *Stachytarpheta mutabilis* (using the gasometric technique)

System/Concentration	Corrosion rate (mgcm ⁻² hr ⁻¹)		Inhibition efficiency (%)		E _a (KJmol ⁻¹)	(KJmol ⁻¹)
	30 °C	60 °C	30 °C	60 °C		
Blank (1 MHCl)	0.06	0.40	-	-	53.44	Q _{ads}
1 MHCl +0.5g/l SMLE	0.04	0.33	24.6	13.72	57.21	-20.04
1 MHCl +1.0g/l SMLE	0.04	0.27	31.4	30.22	53.96	-2.62
1 MHCl +2.0g/l SMLE	0.03	0.21	53.63	45.12	58.16	-10.11
1 MHCl +4.0g/l SMLE	0.02	0.15	65.13	59.49	57.64	-7.13
1 MHCl +6.0g/l SMLE	0.01	0.14	76.81	62.32	67.02	-20.10
1 MHCl +8.0g/l SMLE	0.02	0.11	70.09	72.37	51.22	-2.72
1 MHCl +10.0g/l SMLE	0.01	0.09	74.16	74.10	53.50	-

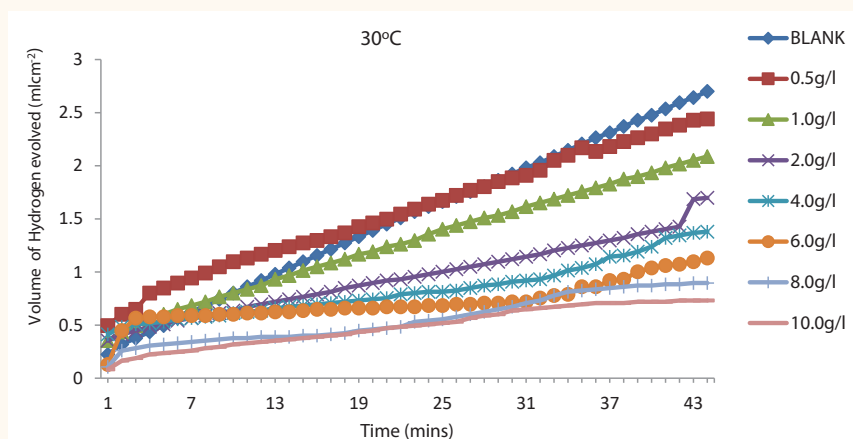


Figure 3 Variation of volume of H₂ evolved with time for mild steel corrosion in 1M HCl in the absence and presence of different concentrations of extract at 30 °C

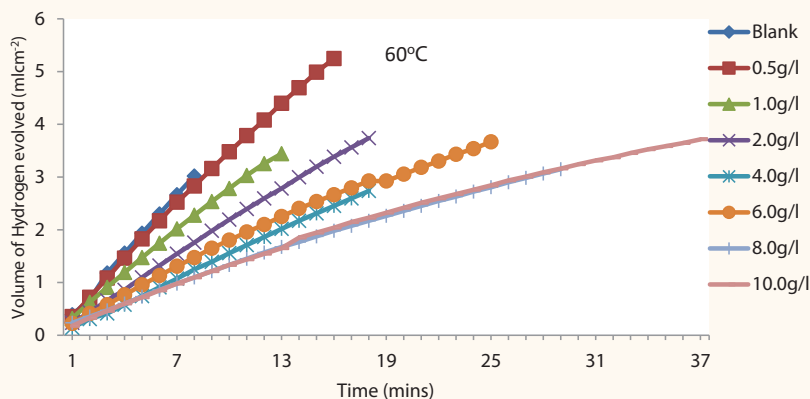


Figure 4 Variation of volume of H₂ evolved with time for mild steel corrosion in 1M HCl in the absence and presence of different concentrations of extract at 60 °C

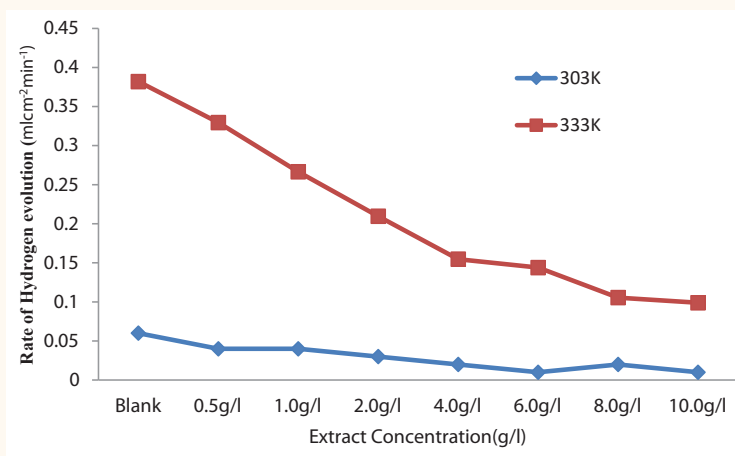


Figure 5 The relationship between corrosion rate ($mlcm^{-2} min^{-1}$) and extract concentration in the absence and presence of different concentrations of SMLE at 30 and 60°C

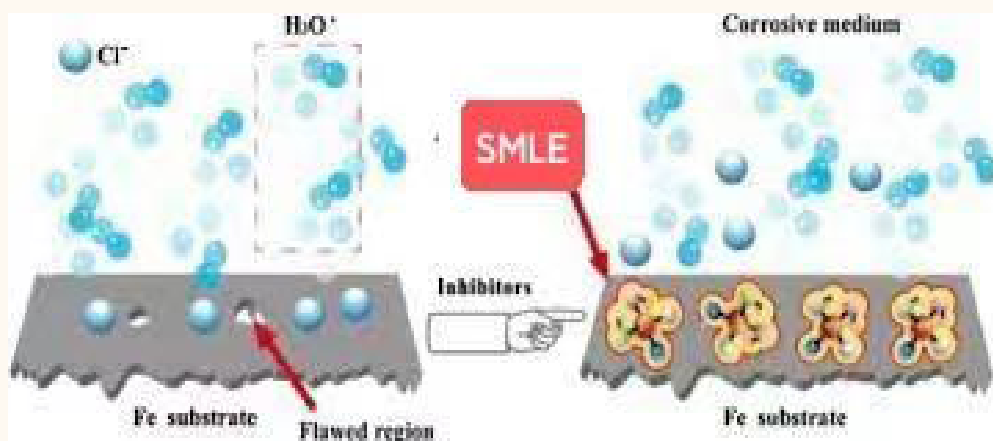


Figure 6 Schematic diagram showing the mechanistic interaction of SMLE on mild steel surface.

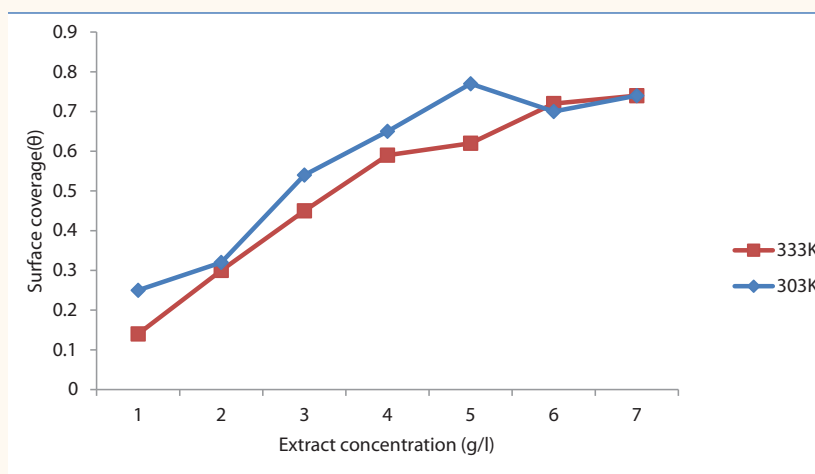


Figure 7 Adsorption curve for *Stachytarpheta mutabilis* extract on mild steel in 1M HCl from

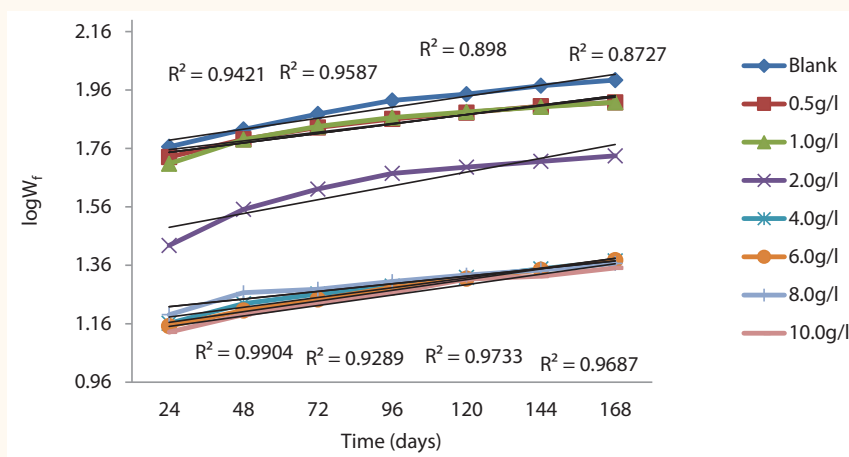


Figure 8 Plot of log Wf against time for mild steel coupons in 1M HCl with and without SMLE

the corrosion rates increase with rise in temperature and were decrease in the presence of SMLE compared to the blank solution. Inspection of Table 2 revealed that the percentage inhibition efficiency for the different test solutions increased with analogous increase in SMLE concentration but decreases with rise in temperature. This behaviour may be attributed to the high dissolution rate of MS coupon at elevated temperature and the desorption of the phytochemical constituent of the SMLE as a result of increased solution agitation resulting from elevated rates of hydrogen gas evolution which may retard the adsorption of the inhibitor on the metal surface [56]. The decrease in percentage inhibition with rise in temperature is suggestive of physical adsorption of the *S. mutabilis* crude extract constituents onto the MS surface. The percentage inhibition efficiency obtained from the two independent investigations (weight loss and hydrogen evolution) is in good agreement with each other (Table 3). On comparing the percentage inhibition of SMLE with previously documented inhibition efficiencies of different plant extracts in acidic media, it was found that the present SMLE under this investigation could serve as an effective green corrosion inhibitor for mild steel in acidic media. The inhibition efficiency obtained from SMLE compared well with other plants extract reported in the literature (Tables 4-8).

Effect of temperature and inhibition mechanism

Temperature affects the rate of coatings of metallic surfaces in electrochemical corrosion. In case of corrosion of MS coupons in a neutral solution (oxygen depolarization), increase in temperature has a positive effect on the overpotential of oxygen depolarization and the rate of oxygen permeation but retards oxygen solubility. On the other hand, in corrosion of MS coupons in acidic medium (hydrogen depolarization), the corrosion rates increase exponentially with temperature rise due to decrease in hydrogen evolution overpotential [57]. Thus, in investigating the effect of temperature on the corrosion of MS coupons in 1M HCl in the presence and absence of inhibitor, the apparent activation energies (ϵ_a) were estimated from the condensed Arrhenius equation [58]

$$\log \frac{\rho_2}{\rho_1} = \frac{\epsilon_a}{2.303} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \tag{4}$$

Where ρ_2 and ρ_1 are the corrosion rates at absolute temperature T_2 and T_1 respectively, and R is the molar gas constant ($8.314 JK^{-1} mol^{-1}$). An estimate of the heat of adsorption (Q_{ads}) was obtained from the trend of surface coverage with temperature. The calculate values for both variables in the presence and absence of inhibitor in 1M HCl are presented in Table 2.

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

Analysis of the temperature dependence of inhibition efficiency and comparison of corrosion activation energies profile in inhibited and uninhibited acid solution gives an insight

Table 4: R^2 Values for the various adsorption isotherms considered

	Langmuir	Tempkin	Freundlich	Flory-Huggins	EL-Awady	Frumkim
Temp (K)	R^2					
303	0.991	0.947	0.931	0.988	0.947	0.920
333	0.992	0.993	0.923	0.952	0.980	0.944

Table 5: The values of dimensionless separation factor, K_L at various concentrations of SMLE at 30 °C and 60 °C

System/Concentration	K_L	
	30 °C	60 °C
1 MHCl +0.5g/l SMLE	0.746	0.835
1 MHCl +1.0g/l SMLE	0.595	0.717
1 MHCl +2.0g/l SMLE	0.424	0.559
1 MHCl +4.0g/l SMLE	0.269	0.388
1 MHCl +6.0g/l SMLE	0.197	0.297
1 MHCl +8.0g/l SMLE	0.155	0.240
1 MHCl +10.0g/l SMLE	0.128	0.202
Mean value	0.357	0.464

Table 6: The thermodynamic parameters for SMLE in 1 MHCl on mild steel corrosion at 30 and 60 °C.

T °C	Slope	($K_{ads} M^{-1}$)	$\Delta G_{ads} (KJmol^{-1})$	$\Delta H_{ads} (KJmol^{-1})$	$\Delta S_{ads} (Jmol^{-1} K^{-1})$
30	1.47	0.68	-9.15	-15.18	-19.0
60	2.53	0.39	-8.55		

Table 7: Qualitative analysis of phytochemical compounds of *Stachytarpheta mutabilis*

S.No	Phytochemical components	Aqueous extract
1.	Alkaloids	+
2.	Saponins	-
3.	Flavonoides	+
4.	Polyphenols	++
5.	Phlobatins	-
6.	Antranoids	+
7.	Anthraquinones	-
8.	Cardiac glycoside	+
9.	Tannins	-
10.	Reducing sugar	+

Note: +ve=present, -ve = absent, ++ve = present in large amount

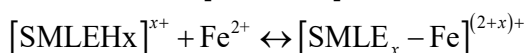
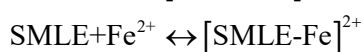
Table 8: Comparison of Inhibition efficiency of SMLE with other natural inhibitors on MS

Natural products	Percentage Inhibition	References
Pectin from citrus peels	94.20%	Fiori-Bimbi et al. (2015)
Punica granatum peel extract	92.40%	Behpour et al. (2012)
Murraya Koenigii extract	84.60%	Sharmila et al. (2010)
Justicia gendarussa extract	93.00%	Satpathy et al. (2009)
Griffonia simplicifolia extract	91.73%	Ituen et al. (2017)
Water Melon rind extract	83.35%	Odewunmi et al. (2015)
Longan seed and peel extracts	92.93%	Liao et al. (2017)
Sodium Nitrite	61.8%	Rizvi et al. (2021)
SMLE	82.69%	

into the inhibitor mechanism of adsorption. It has been reported elsewhere [58] that a decrease in inhibition efficiency with rise in temperature with corresponding increase in apparent activation energy in the presence of an inhibitor compared to its absence is suggestive of physical adsorption while the reverse process;

increase in percentage inhibition with analogous increase in temperature with a decrease in \mathcal{E}_a in the presence and absence of inhibitor in 1M HCl corresponds to a chemisorption mechanism. The trend for SMLE suggests that physisorption process governs the inhibition process. Thus, it can be inferred that the increase in apparent activation energies was due to the corrosion reaction mechanism in which charge transfer was blocked (geometric blocking effect) by the adsorption of phytochemical constituents of SMLE on the MS surface; [59,60]. It also implies that the sorption process was controlled by the surface reaction, since the activation energies of the corrosion process in the inhibited and uninhibited solution was higher than 20 KJmol^{-1} [61]. The \mathcal{E}_a as shown in Table 2, is greater for the inhibited process than for an uninhibited process due to the increased energy barrier. These observations also suggest the formation of a complex compound between the SMLE and MS- solution surface [62]. The negative Q_{ads} values imply that the degree of surface coverage decreased with rise in temperature, supporting the earlier proposed physisorption mechanism [63].

Due to the complex chemical composition of the crude extract of SMLE, it is difficult to identify the active constituent that is responsible for the inhibiting effect of SMLE in 1M HCl. In aqueous acidic solutions, SMLE exists either as neutral molecules or in the form of cations (protonated SMLE) depending on the nature of chemical interactions occurring to the inhibitor. In acidic solution, adsorption of Cl^- ions onto the MS surface renders its surface negatively charged and susceptible to physical adsorption of cationic moieties of the crude extract. The SMLE molecules can be adsorbed also on the metal surface through donor- acceptor reaction between the π - electrons of the crude extract of the phytochemical constituents and the vacant d- orbitals of iron. The combined adsorption of anion with cation gives a positive synergistic effect which is responsible for the observed increase in %I with analogous rise in extract concentration. Thus, the metal complexes of Fe^{2+} and SMLE or protonated SMLE can be explained further as follows:
 $SMLE+xH^+ \leftrightarrow [SMLExH]^{x+}$



From the observed mechanism, it can be inferred, that the insoluble **Fe-Inhibitor** complex could act as catalyst by promoting or inhibiting metal dissolution depending on its solubility. Consequent upon this, the **Fe-Inhibitor** complex might be adsorbed on the MS surface via Vander Waals force to form a protective film that prevents the corrosion of MS surface. Similar observation has been documented elsewhere [64,65].

Adsorption isotherm and thermodynamics

In general, the adsorption isotherm gives an insight on the adsorption of inhibitor on metal surface. Figure 8,7 profiles the variation of the degree of surface coverage with concentration of SMLE obtained from hydrogen evolution measurements technique for the corrosion medium-SMLE systems at 30 and

$60^\circ C$. Assuming a direct relationship between the inhibitor efficiency and surface coverage (θ), the plot in Figure 7, describes an S-shaped curve [66]. This suggests that SMLE acts as an inhibitor by formation of a thin coat which acts as a protective barrier film that blocks the corrosive agents from accessing the MS surface –solution interface. The degree of surface coverage was estimated from the expression [67].

$$\theta = \frac{\%I}{100} \quad (6)$$

Sorption isotherm models were utilized for fitting data in order to estimate the relationship between the amount in the aqueous concentration at equilibrium and the amount sorbed by SMLE onto the MS surface. Adsorption isotherm equations were used to characterize the corrosion inhibition mechanism.

Customarily, adsorption isotherms are expressed in the form of Eq. (7) [68].

$$f(\theta, x) \exp(-2\alpha\theta) = K_{ads}C \quad (7)$$

where $f(\theta, x)$; denotes the configurational factor which depends on the physical mode and the assumptions underlying the derivation of the isotherm, θ is the degree of surface coverage, C the inhibitor concentration, x is the size factor ratio, α is the molecular interaction parameter and K_{ads} is the adsorption-desorption equilibrium constant of the sorption process. The adsorption isotherm model that best describes the adsorption of *S. mutabilis* leave extract on mild steel in 1M HCl medium was obtained by fitting the concentration of the extract and the degree of surface coverage of the inhibitor, θ into the various adsorption isotherms models (Langmuir, Tempkin, Freundlich, Frumkim, El Awady, and Flory-Huggins adsorption isotherm) to examine the equilibrium between SMLE concentration in 1M HCl and the amount sorbed on the MS surface. In the current study, correlation coefficient (R^2) was used to determine the best fit isotherm.

Freundlich adsorption isotherm [69,70]

$$\log \theta = \log K_{ads} + n \log C \quad (8)$$

Tempkin adsorption isotherm model [71-73]

$$\theta = InC + K_{ads} \quad (9)$$

Frumkim adsorption isotherm model [69]

$$\log \left[C \left(\frac{\theta}{1-\theta} \right) \right] = 2\alpha\theta + 2.303 \log K_{ads} \quad (10)$$

El -Awady thermodynamic /kinetic adsorption isotherm model [74]

$$\log \left(\frac{\theta}{1-\theta} \right) = y \log C + \log K \quad (11)$$

$$K_{ads} = K^{1/y} \quad (12)$$

Flory-Huggins adsorption isotherm model [70]

$$\log \frac{\theta}{C} = b \log(1 - \theta) + \log K_{ads} \quad (13)$$

Langmuir adsorption Isotherm model [75]

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (14)$$

Table 4. (Supporting document) profiles the various adsorption isotherm models considered in this study. The R^2 values for each isotherm model presented in Table 4 were used to determine the most suitable model. The experimental data fitted into all the isotherms under this investigation but the Langmuir isotherm model gave the best fit. Langmuir isotherm with R^2 values of 0.992 which is close to unity compared with others tested adsorption isotherms in this study, best describes the adsorption mechanism of *S. mutabilis* extract on mild steel in 1M HCl. Therefore, Langmuir adsorption isotherm is most appropriate for evaluating the equilibrium adsorption-desorption constant, K_{ads} at the studied temperature. Moreover, the dimensionless separation factor, K_L which describe the type of isotherm is related to the equilibrium adsorption- desorption constant, K_{ads} by the following equation [76].

$$K_L = \frac{1}{1 + K_{ads}C} \quad (15)$$

If K_L is >1 unfavourable, $K_L = 1$ linear, $0 < K_L < 1$ favourable, $K_L = 1$ irreversible. Table 5 gives the calculated values of K_L for SMLE at different concentration at 30 and 60 °C. Inspection of Table 5 revealed that all K_L values are less than unity confirming that the adsorption process is favourable. However, further inspection of the Table shows that the mean value of K_L at 30 °C is lower than K_L at 60 °C indicating that the inhibitory action of SMLE is more favourable at lower temperature. Table 6 indicates that the adsorption equilibrium constant K_{ads} values decrease with analogous increase in temperature. Large values of K_{ads} implies better inhibition efficiency of the inhibitor and the adsorbing inhibitor molecules. On the other hand, small values of K_{ads} revealed that such interactions between adsorbing inhibitor molecules and the metal surface are weaker, confirming that the inhibitor molecules are easily ejectable by the solvent molecules from the metal interface [77]. These results confirm that SMLE is physically adsorbed on the metal surface and that the strength of the adsorption decreases with temperature.

The free energy of adsorption ΔG_{ads}^o of the inhibitors on MS surface can be estimated using the following relation [78]

$$\Delta G_{ads}^o = -RT \ln(K_{ads} \times 55.5) \quad (16)$$

Where ΔG_{ads}^o is the standard free energy of adsorption, K_{ads} is the equilibrium constant of adsorption, the value of 55.5 is the concentration of water in solution (molL^{-1}), R is the molar gas constant ($\text{kJmol}^{-1}\text{K}^{-1}$) and T is the temperature (K). The

calculated ΔG_{ads}^o and K_{ads} results are also summarised in Table 6. The negative values of ΔG_{ads}^o indicate the spontaneous adsorption of these molecules from HCl solution to the metal surface. Values of ΔG_{ads}^o around -20 kJmol^{-1} or lower are compatible with electrostatic interaction between charged organic molecules and the charged metal surface (physisorption); those around -40 kJmol^{-1} or higher are in accordant with charge sharing or transfer from the organic molecules to the metal surface to form a co-ordinate type of bond (chemisorptions) [50]. In this present study, the values of ΔG_{ads}^o for SMLE being less than $-40 \text{ kJmol}^{-1}\text{K}^{-1}$ indicate physical adsorption. Thus, the inhibition efficiency decreased with the increase in temperature as a result of desorption of SMLE from the MS surface.

The thermodynamic parameters: enthalpy of adsorption ΔH_{ads}^o and entropy of adsorption ΔS_{ads}^o can be estimated from integrated version of the Van't Hoff equation expressed by (Ramesh and Adhikari, 2008).

$$\ln K_{ads} = \frac{-\Delta H_{ads}^o}{RT} + \frac{\Delta S_{ads}^o}{R} + \ln \frac{1}{55.5} \quad (17)$$

The above equation shows that the plot of $\ln K_{ads}$ versus $1/T$ which gives straight lines with slope of $(-\Delta H_{ads}^o/R)$ and intercepts of $(\frac{\Delta S_{ads}^o}{R} + \ln \frac{1}{55.5})$. Estimated value of ΔH_{ads}^o and

ΔS_{ads}^o using the Van't Hoff equation are $-15.18 \text{ kJmol}^{-1}$ and $-19.94 \text{ Jmol}^{-1}\text{K}^{-1}$, respectively. The enthalpy and entropy for the adsorption of SMLE on mild steel were also deduced from the thermodynamic basic equation [79].

$$\Delta G_{ads}^o = \Delta H_{ads}^o - T \Delta S_{ads}^o \quad (18)$$

Where ΔH_{ads}^o and ΔS_{ads}^o are the enthalpy and entropy changes of adsorption process, respectively. A plot of ΔG_{ads}^o versus T was linear with the slope equal to $(-\Delta S_{ads}^o)$ and intercept of (ΔH_{ads}^o) . The enthalpy of adsorption, ΔH_{ads}^o and the entropy of adsorption ΔS_{ads}^o obtained are $-15.18 \text{ kJmol}^{-1}$ and $-19.0 \text{ Jmol}^{-1}\text{K}^{-1}$ respectively. The negative sign of ΔH_{ads}^o showed that the adsorption of SMLE molecules is an exothermic process. For an exothermic process, physisorption is differentiated from chemisorption by considering the absolute value of ΔH_{ads}^o . For physisorption process, the enthalpy of adsorption is less than 40 kJmol^{-1} while that for chemisorption approaches 100 kJmol^{-1} [80]. In the present investigation, ΔH_{ads}^o is lower than 40 kJmol^{-1} clearly indicating that physical adsorption is involved. Values of ΔH_{ads}^o and ΔS_{ads}^o obtained by the two methods are in accord with each other. The entropy of adsorption obtained from Eqs. (17) and (18) are negative because inhibitor molecule freely moving in the bulk

solution (inhibitor molecule were disordered), were adsorbed in an orderly fashion onto the mild steel, thereby retarding the entropy [81].

Kinetics of mild steel corrosion in 1M HCl with and without SMLE

The study of kinetics modeling-based studies gives an insight into the reaction and mechanism of the MS- solution interaction and helps to explain several process variables for monitoring and evaluating system performance and optimization. The kinetics of MS corrosion in inhibited and uninhibited 1M HCl solution containing different SMLE concentration was studied at 30 °C by fitting the corrosion data into different rate laws. Correlation coefficients R^2 were used to determine the most suitable law for the corrosion process. The rate laws examined [82]

$$\text{Zero-order: } W_t = kt \quad (19)$$

$$\text{First-order: } \ln W_t = -Kt + \ln W_o \quad (20)$$

$$\text{Second-order: } 1/W_t = Kt + 1/W_o \quad (21)$$

Where W_o the initial weight of mild steel, W_t is the weight loss of mild steel at time t and K is the rate constant. On fitting of the experimental data to the different rate laws, the first -order kinetics gave the best R^2 value. The plot of $W_f(g)$ against time (t) is portrayed in Figure 8 and calculated values obtained are summarized in Table 1. Observation from the plot showed that the rate constant decreased with increase in SMLE concentration. The one-dimensionality of the plot in the inhibited and uninhibited acid solution suggests that its presence does not alter the corrosion process. Similar observations for other inhibitors have been made documented by others researcher [83].

The half-life ($t_{1/2}$) value was estimated using the equation [84]

$$t_{1/2} = \frac{0.693}{K} \quad (22)$$

Where K is the rate constant, the values of the rate constant and half-life periods obtained are summarized in Table 1 and were observed to increase with increase in concentration of SMLE the results further affirmed that the corrosion rate is higher in the uninhibited solution than in the inhibited MS sample solution. These suggest that the presence of SMLE decreases the dissolution rate of MS corrosion. The results corroborated findings by [85].

Phytochemical studies

The results obtained from the crude extract of SMLE are displayed in Table 7. The results revealed that SMLE contains considerable amount of phytochemicals which are good corrosion inhibitors that have been well documented in literature

to exhibit good inhibitive properties [86, 87] making it possible to attribute the inhibiting action of *Stachytarpheta mutabilis* to the much presence of polyphenol [88]. These compounds have been reported by several investigators to possess high anticorrosion activity as a result of the lone pairs of electron on their heteroatom [89].

CONCLUSION

The capacity of SMLE as a green corrosion inhibitor has been assessed in this research by using the weight loss and hydrogen evolution technique. SMLE acts as an inhibitor for the corrosion of mild steel in 1 M HCl. Inhibition efficiency values increase with the inhibitor concentration but decrease with rise in temperature suggesting physical adsorption mechanism. The adsorption of extract film was found to obey Langmuir isotherm and first-order kinetics. The values of the activation energy, enthalpy, Gibbs free energy and parameters estimated from the isotherm models suggested that the adsorption mechanism of SMLE on the MS is spontaneous, exothermic and accompanied with a decrease in entropy of the system from thermodynamic point of view. The results obtained from weight loss and hydrogen evolution measurements are in good agreement. However, further investigation to assess the corrosion morphology and to isolate and validate the active phytochemical constituent in the extract of SMLE that is responsible for the inhibition of mild steel in acidic media is required.

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