

Anticorrosion properties of *Vitex doniana* on Mild steel in HCl solution

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Abstract— The retarding potentials of bark (BK), leaves (LV) and roots (RT) extracts of *Vitex doniana* for mitigating corrosion of mild steel specimens subjected to 2.5% and 5.5% HCl respectively was assessed by combined experimental (weight loss and gas evolution) methods at 30-70°C. The existence of core phytochemicals in the bark (BK), leaves (LV) and roots (RT) extracts was explored by phytochemical analyses. Based on the results, 1.0g/l of (BK), (LV) and (RT) extracts gave inhibition capacities of 86, 88 and 90% respectively. Furthermore, Inhibition was observed to increase with increase in concentrations of the extracts and decrease with increasing temperature and time in order RT > BK > LV. The inhibition behaviour of the phytochemical constituents of the extracts displays physical adsorption mechanism. The experimental data fitted into Temkin adsorption isotherm model.

Keywords— Acid corrosion; corrosion inhibition; photochemical; retarding potentials;

I. INTRODUCTION

The development of modern society and industry has led to a stronger demand for specialized knowledge in corrosion. There are a number of reasons for this: The application of new material requires new corrosion knowledge. Industrial production has led to pollution, acidification and increased corrosivity of water and the atmosphere. Stronger materials, thinner cross-sections and more accurate calculation of dimensions make it relatively more expensive to add corrosion allowance to the thickness. The development of industrial sectors like nuclear power production and offshore oil and gas extraction has required stricter rules and corrosion control. Considering the future, it should be noticed that most methods for alternative energy production will involve corrosion problems. Mild steels are solid substances obtained from the

mother earth. These substances are general purpose construction materials mostly used as a result of their natural properties like rigidity, ductility, tensile strength conduct of heat and electricity etc [1]. Mild steel has numerous industrial applications and is mainly used for the corrosion protection of steel [2]. They are also widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries because of their advantages [3]. According to [4] mild steel and its alloys are low cost and remarkable materials in industrial technology because of their durability as well as high resistance to corrosion in a wide variety of corrosion environments. Generally, corrosion resistance of metals such as steel, in corrosive environment, may be attributed to the formation of a protective tightly adhered invisible oxide film on the metal surface [5].

The search for effective and proficient eco-friendly alternatives provided opportunity into the study of inhibiting potentials of plant extract. Plant extracts comprise of compounds with functional groups containing hetero-atoms (P, N, O, S) and π -bonds, that displays good inhibitive properties by providing electrons to interact with the metal surface [6]. The activities of these inhibitors are associated to factors like the electronic charge in the molecules, type and number of adsorption sites, molecule's functional groups etc [6]. The current study aims at retarding of mild steel corrosion in aerated 2.5% and 5.5% HCl respectively using BK, LV and RT extracts of *Vitex doniana* using weight loss and gasometric methods.

2. EXPERIMENTAL PROCEDURE

2.1 Materials

The materials including mild steel sheet and *Vitex doniana* plant extracts used in this study were locally obtained in Awka. The mild steel sheet were mechanically cut into (5cm x 4cm x 0.1cm) coupons and each coupon composed of P (0.02%), Mn (0.11%), Si (0.02%), S (0.02%), Cu (0.01%), C (0.23%), Ni (0.02), Cr (0.01%) and Fe (99.56 %). The coupons were further cleaned as previous discussed in [7] stored for further use. Analytical grade

chemicals and reagents were used throughout the study. The blank corrodent of 2.5% HCl and stock solutions of the plant extracts including LV, BK and RT of *Vitex doniana* were prepared as discussed in [8].

2.2 Phytochemical screening

Phytochemical examination was performed on BK, LV and RT extracts from ethanolic extracts of VD plant using chemical tests described by [7, 8]. The plant extracts were analyzed for alkaloids, cardiac glycosides, flavonoids, polyphenols, saponins, tannins.

2.3 Weight loss (Gravimetric) measurements

These measurements were carried out on the mild steel specimens following procedures previously described [8]. BK, LV and RT were tested as inhibitors for mild steel in 2.5% HCl. The samples were polished, degreased, and dried as discussed before in [7, 8]. Specimens were immersed into solution leaving a constant surface area of 0.26cm^2 to contact the solution. The electrolyte solution was 2.5% HCl. The concentrations of the inhibitors were in the range of 0.1 to 1.2g/L. For weight loss measurements mild steel sheets having dimensions of $5\text{cm} \times 4\text{cm}$ with exposed total area of 2.42cm^2 were used. The samples were weighed (m_1) and immersed in the corrosive medium (2.5% HCl) containing different concentrations of inhibitor for 8hrs, cleaned and washed with acetone and reweighed (m_2). Corrosion rate and inhibition efficiencies were calculated from the following equations (1) and (2) [9]:

$$CR = \frac{m_1 - m_2}{At} \quad (1)$$

$$\eta\% = \frac{CR_{\text{blank}} - CR_{\text{inh}}}{CR_{\text{blank}}} \times 100 \quad (2)$$

Where m_1 is the weight loss in g, A is the total surface area in cm^2 , T is the time of exposure in hrs, CR_{blank} and CR are the corrosion rates in $(\text{mgcm}^{-2}\text{hr}^{-1})$ without and with different concentrations of the plant extracts, respectively. The inhibition efficiency depends on the degree of coverage of mild steel surface by molecules of the inhibitor.

2.4 Hydrogen gas evolution (gasometric) measurements

Hydrogen gas was produced from cathode during corrosion reaction of mild steel in aqueous 5.5% HCl. It was found out that the volume of hydrogen evolved was directly proportional to corrosion rate [10]. Temperature measurements were studied within $30 - 70^\circ\text{C} \pm 1^\circ\text{C}$ in test solution 5.5% HCl as blank and inhibited concentrations of LV, BK and RT extracts. Volume of hydrogen given out from the reaction was checked every 1minute by noting the height of the paraffin oil in the burette. Hence, the rate at which hydrogen gas evolved RV_H , was evaluated from the

slope of the graph of volume of gas evolved against immersion time (min). The volume of gas evolved at time T , inhibitor surface coverage (θ) and inhibition efficiency ($\eta\%$), was calculated using the mathematical expression [9, 10]

$$RV_H = \frac{V_1 - V_2}{T_1 - T_2} \quad (3)$$

Where V_1 and V_2 are volumes of hydrogen gas evolved at times, T_1 and T_2 respectively.

$$\theta = \frac{RV_{H0} - RV_{Hinh}}{RV_{H0}} \quad (4)$$

$$\eta\% = \frac{RV_{H0} - RV_{Hinh}}{RV_{H0}} \times 100 \quad (5)$$

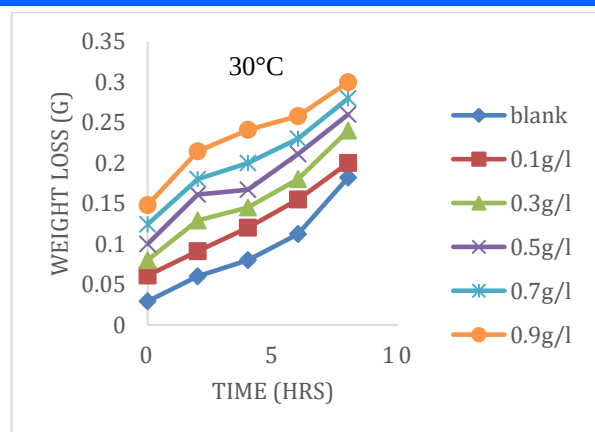
where RV_{H0} and RV_{Hinh} are the rates of hydrogen evolution in the absence and presence of the inhibitor molecules respectively. Weight loss and hydrogen evolution tests were run more than twice and the data showed good reproducibility. The data presented are therefore an average of at least two measurements.

3. RESULTS AND DISCUSSIONS

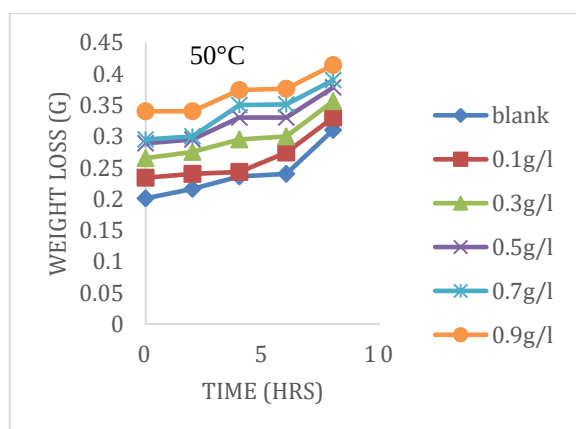
3.1 Weight loss (Gravimetric) results

This study were carried out at 30°C to 70°C but only three results (30 , 50 and 70°C) were presented.

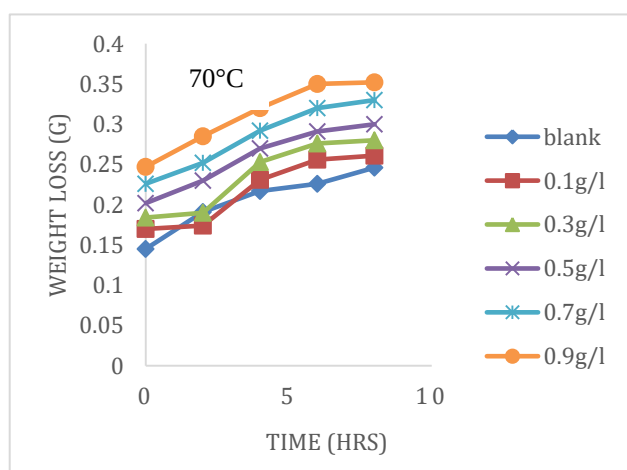
The result of Weight loss measurements for mild steel in 2.5% HCl with and without different concentrations of plant extracts (VD extracts) were presented in Figure 1 and 2 respectively. The results obtained showed that increase in the length of immersion (time) leads to increase in weight loss and high loss of weight at high temperatures. The graph of weight loss against time using LV, BK and RT exhibit similar trend but only the results of leaves and bark were shown in Figure 1 and 2. Table 1 presents corrosion rates for mild steel in 2.5% HCl containing different concentrations of BK, LV and RT extracts at different temperatures studied. Examination of Table 1 indicates that corrosion rates decrease as concentrations of plant extracts increase. This implies that the three extracts suppressed the corrosion of mild steel in aggressive 2.5% HCl solutions. It was observed from Table 1 that the values of corrosion rates of mild steel containing barks, leaves and roots extracts were lower than values in blank solutions. Furthermore, corrosion rates from roots extract were higher than that of bark and leaves. This is in agreement with [10, 11]. It can also be inferred that the magnitude of suppression depends on the quantity of plant extracts. The inhibition efficiency were obtained using Equation 2 and present in Table 1. Close observation of Table 1 reveals that inhibition efficiencies increase with increase in concentration of VD plant extracts.



(a)



(b)

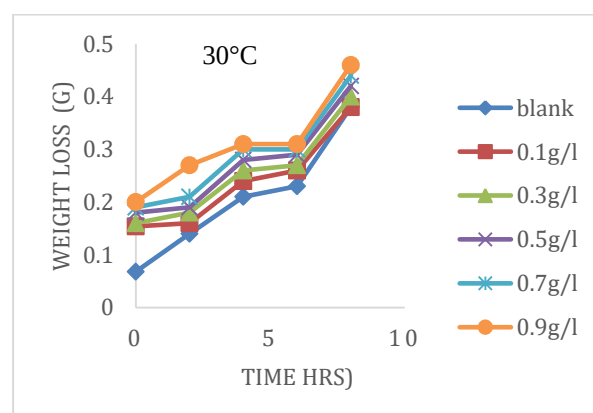


(c)

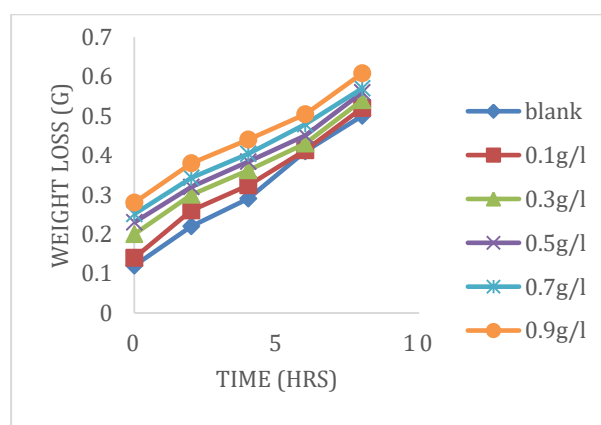
Figure 1. Variation of weight loss against time for mild steel coupons in 2.5% HCl with and without **leaves (LV)**, **extracts** from *Vitex doniana* using weight loss technique at 30, 50 and 70°C

The inhibitive capability of the plant extracts reached maximum 90.19% for root extracts (RT) concentration of 0.9g/l. Fig 3 shows the correlation between the inhibition efficiency and plant extracts for mild steel in 2.5% HCl solutions consisting of different parts of VD

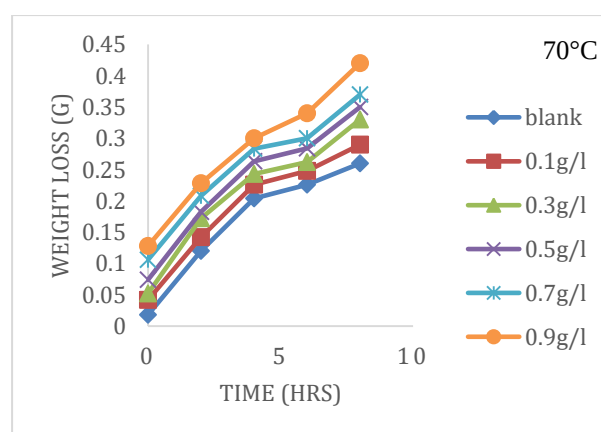
extracts. The plots reveals that the inhibition efficiencies increase with increase in VD extracts concentrations. Comparing the inhibition efficiencies of the three extracts, it was seen that the style of the curves followed RT > BK > LV.



(a)



(b)



(c)

Figure 2. Variation of weight loss against time for mild steel coupons in 2.5% HCl with and without **bark (BK)**, **extracts** from *Vitex doniana* using weight loss technique at 30, 50 and 70°C.

Table 1: Calculated values of the corrosion rate and inhibition efficiency for mild steel coupons in 2.5% HCl solutions containing extracts from *Vitex doniana* (using the weight loss technique).

Plant part	Inh. conc g/l	Corrosion rates (mg cm ⁻² h ⁻¹)			Inhibition Efficiency (%)		
		30°C	50°C	70°C	30°C	50°C	70°C
	Blank	3.72	3.97	4.32	-	--	-
LV	0.1	2.80	2.43	2.77	40.54	38.79	37.21
	0.3	2.60	2.05	2.20	51.35	49.62	48.84
	0.5	1.80	1.10	1.44	78.23	72.81	67.44
	0.7	0.81	1.00	1.31	84.54	77.33	72.09
	0.9	0.51	0.32	1.20	86.10	80.21	75.32
RT	0.1	2.93	3.00	3.23	50.00	45.11	39.03
	0.3	2.54	2.73	2.87	60.03	50.05	42.43
	0.5	2.05	2.38	2.10	56.54	60.03	57.14
	0.7	1.74	1.69	0.79	68.20	60.10	59.02
	0.9	0.08	0.29	0.31	88.23	87.05	90.19
BK	0.1	2.33	2.74	3.01	33.41	30.00	28.50
	0.3	1.64	2.12	2.58	58.35	53.16	48.32
	0.5	1.53	1.72	1.68	70.53	68.25	50.12
	0.7	1.34	1.45	0.12	80.61	70.26	68.22
	0.9	0.62	0.86	0.04	85.75	80.18	77.04

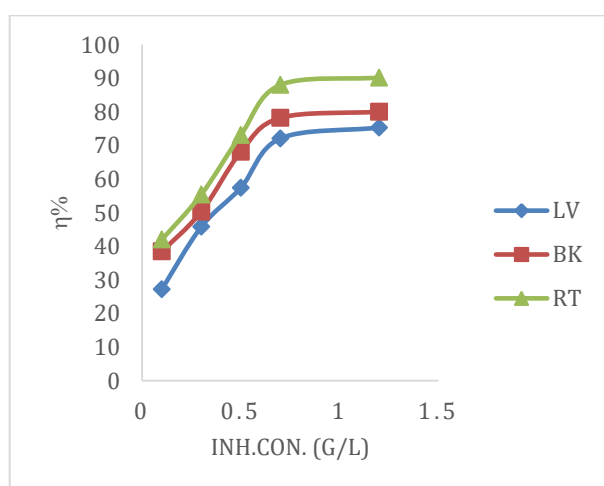
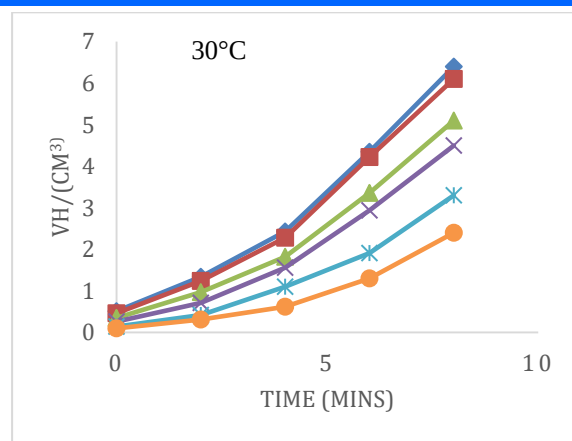


Figure 3: The relationship between inhibition efficiency and plant extract concentration for mild steel in 2.5% HCl solutions using weight loss approach.

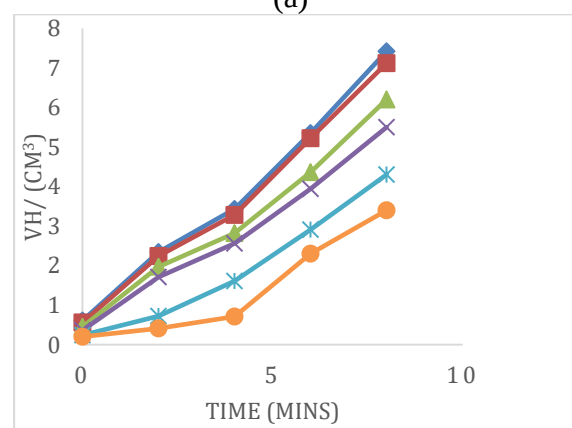
3.2 Hydrogen evolution

Corrosion reaction processes at low concentrations are best monitored using weight loss method whereas high corrodent concentrations require evolution of gases [12]. Therefore, this study utilized the hydrogen evolution approach to assess the corrosion of mild steel

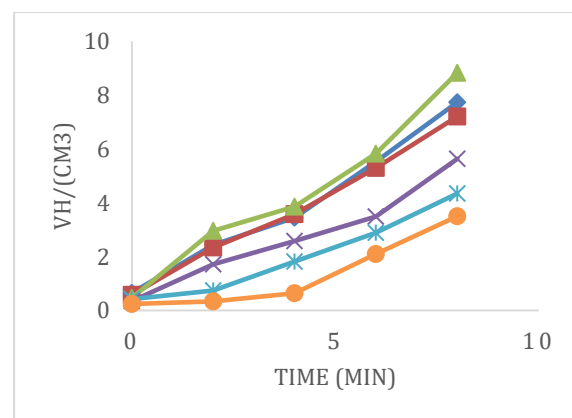
in 5.5% HCl using different extracts from *Vitex doniana* plant various temperatures. Figures 4 and 5 depicts the volume of hydrogen evolved.



(a)

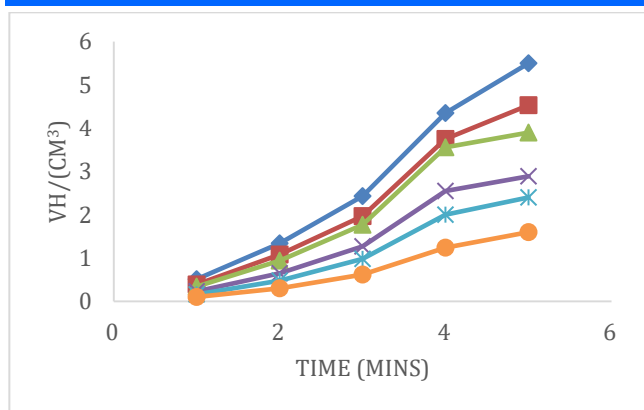


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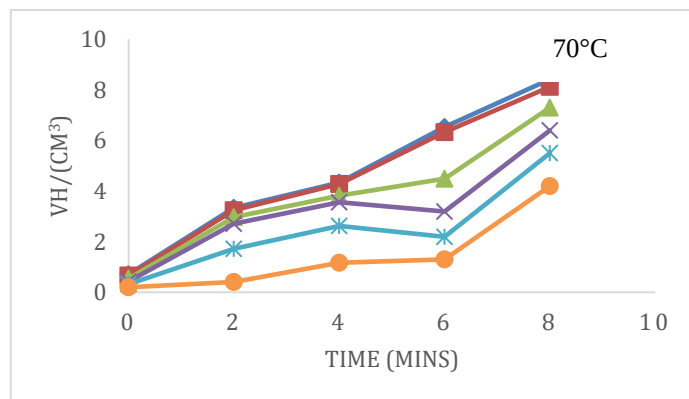


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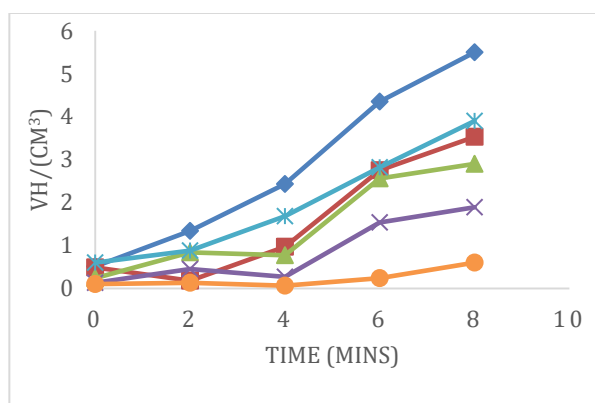
Figure 4. Variation of volume of hydrogen evolved (V_H) with extract concentration for mild steel coupons in 5.5 % HCl solutions containing extracts from **leaves (LV)** using hydrogen evolution technique at (a) 30°C, (b) 50°C and (c) 70°C.



(a)



(c)



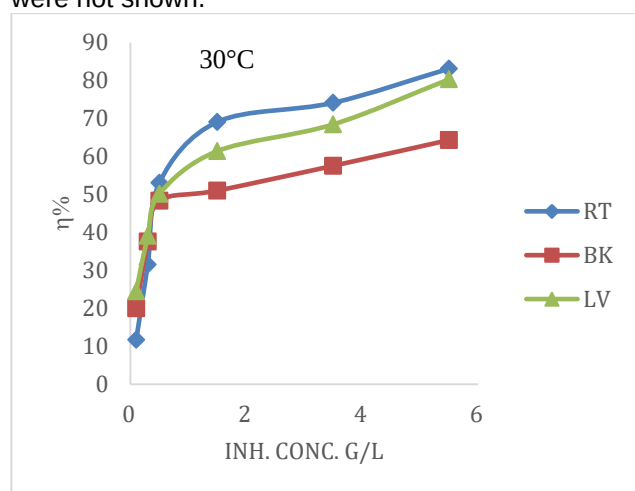
(b)

Figure 5. Variation of volume of hydrogen evolved (V_H) with extract concentration for mild steel coupons in 5.5 % HCl solutions containing **extracts from bark (BK)** using hydrogen evolution technique at (a) 30°C (b) 50°C and 70°C.

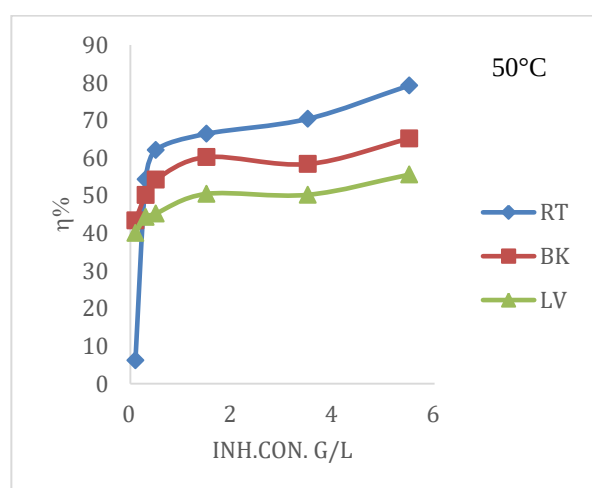
Table 2. Calculated values of the rate of hydrogen evolution, inhibition efficiency, activation energy, change in enthalpy and change in entropy for mild steel coupons in 5.5% HCl solutions containing extracts from *Vitex doniana* (using hydrogen evolution technique).

Plant part	Inh. Conc. g/l	Weight loss (g/cm)			Rate of Hydrogen evolution (cm ³ /min)			Ea (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol/K)
		30°C	50°C	70°C	30°C	50°C	70°C			
RT	Blank	0.51	3.24	5.04	-	-	-	60.62	50.51	-62.24
	0.1	0.48	3.40	4.42	11.71	6.21	4.02	63.14	59.01	-58.07
	0.3	0.31	2.16	3.47	31.52	54.32	35.09	64.23	60.53	-55.71
	0.5	0.27	1.22	2.81	53.05	62.1	44.06	70.45	60.63	-41.15
	1.5	0.20	1.18	2.23	69.12	76.41	55.31	74.44	69.20	-32.53
	3.5	0.16	0.29	1.14	74.14	58.38	70.03	71.17	66.41	-31.36
BK	5.5	0.09	0.10	1.10	83.12	79.25	75.31	72.32	65.10	-33.18
	0.1	0.40	2.56	4.68	20.02	43.39	3.31	62.56	54.54	-56.13
	0.3	0.36	2.01	3.41	37.62	50.13	24.46	65.71	60.23	-54.65
	0.5	0.28	1.88	2.55	48.34	54.21	35.11	66.10	58.14	-46.73
	1.5	0.21	1.39	2.21	51.01	70.23	50.34	72.03	58.02	-56.34
	3.5	0.17	0.72	1.49	57.54	54.37	54.25	69.40	62.41	-65.05
LV	5.5	0.12	0.31	1.19	64.33	51.15	69.38	71.32	56.31	-57.18
	0.1	0.38	2.66	4.12	24.51	40.05	3.23	61.21	63.06	-45.76
	0.3	0.30	2.11	3.51	39.11	44.30	21.34	65.06	57.23	-56.21
	0.5	0.26	1.73	2.43	50.14	50.22	30.25	73.43	60.17	-35.33
	1.5	0.21	1.23	1.64	61.41	69.45	45.35	74.10	64.54	-35.54
	3.5	0.14	0.84	1.29	68.45	48.23	51.60	75.23	55.66	-56.24
	5.5	0.11	0.24	1.01	80.32	39.56	60.10	64.08	61.41	-57.17

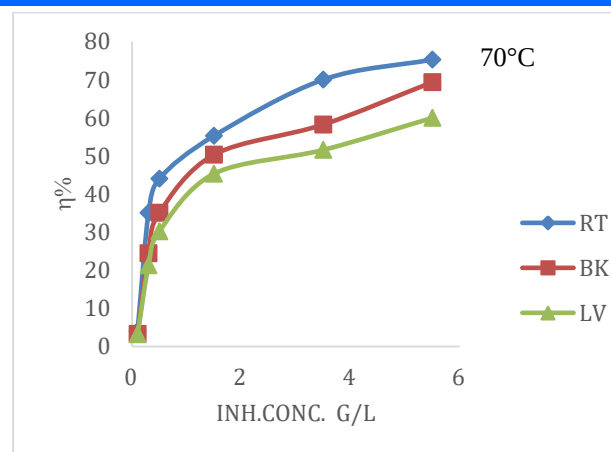
The rate of hydrogen evolution presented in Table 2 followed the style; RT > BK > LV. Inhibition efficiency at different temperatures was calculated from rate of hydrogen evolution using Equation (5) and displayed in Figure 6a-c. Close examination of Figure 6a-c show that the inhibition efficiencies rise as the concentration of different parts of plant extracts rise at all temperatures studied. The increase in inhibition efficiency can be attributed to the adsorption of photochemical species on mild steel interface [9]. Comparism of inhibition performance of three different plant parts investigated and presented on Figure 7 revealed that highest inhibition efficiency was achieved at 83.12% using roots extracts of 5.5g/l HCl solutions employing hydrogen evolution method at various temperatures [9, 11-13]. The order shows RT > BK > LV and similarly this particular trend was equally obtained using 50°C and 70°C respectively but were not shown.



(a)



(b)



(c)

Figure 6. Relationship between inhibition efficiency with plant extracts for mild steel in 5.5% HCl solutions containing different parts of VD extracts at (a) 30°C (b) 50°C and (c) 70°C.

3.3 Activation parameters studied

The activation energy for the dissolution of mild steel coupons 5.5% HCl solutions in the absence and presence of VD extracts were estimated from the Arrhenius Equation (6) and the transition state Equation (7):

$$K = A \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

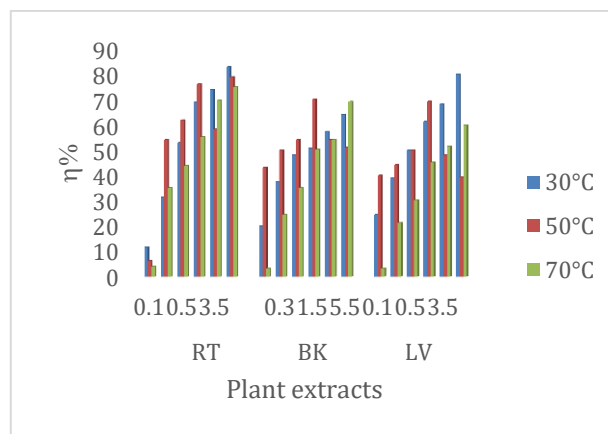


Figure 7. Highest inhibition efficiency of hydrogen for mild steel in 5.5% HCl containing different parts of *Vitex doniana* plant extracts at different temperatures.

$$K = \frac{RT}{Nh} \exp\left(\frac{\Delta S^\circ}{R}\right) \exp\left(-\frac{\Delta H^\circ}{RT}\right) \quad (7)$$

where R is the universal gas constant, N is the Avogadro's number ($6.02252 \times 10^{23} \text{ mol}^{-1}$), h is the Plank's constant ($6.626176 \times 10^{-34} \text{ Js}$), E_a is the

activation energy, T is the absolute temperature, and ΔH° and ΔS° are the standard enthalpy and entropy of activation, respectively. The values of k were taken to be equal to the rate of hydrogen evolution [10, 12, 14-15]. A plot of $\log k$ versus $1/T$, for mild steel in 5.5% HCl containing VD extracts (Figure. 8 for root extracts) gave straight lines. Similarly, the same shape of plots were obtained using LV and BK extracts at different temperatures but were not presented. The computed activation energies obtained from the slopes of the plots are listed in Table 2.

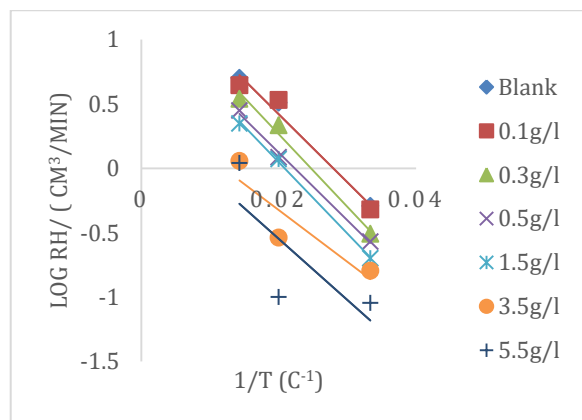


Figure. 8: Arrhenius plot for mild steel coupons in 5.5% M HCl solutions containing extracts from the root of VD extracts using hydrogen evolution technique at 30°C.

The result obtained is in accordance with physical adsorption process because E_a values increased in the presence of the VD extracts compared to the blank system [12, 16]. The average activation energy obtained were 69.13 kJ/mol (for RT extract), 67.85 kJ/mol (for BK extract) and 60.08 kJ/mol (for LV extract). The inhibition of steel corrosion was furthermore, confirmed using physical adsorption mechanism which is in agreement with those of [17, 18]. Author [10] reported that activation energy for physical adsorption mechanism should be less than 80 kJ/mol. The higher E_a values in the presence of inhibitor compared to the blank solution indicates that the inhibitor will be effective at low temperatures, but efficiencies will be diminished at higher temperatures. The entropy and the enthalpy of activation values for the dissolution of mild steel in 5.5% HCl solutions obtained from linear square fit of $\log(k/T)$ data versus $1/T$ (Figure. 9 for bark extract) are also presented in Table 2. The higher values for ΔH° in the presence of the plant extracts implies greater protection efficiency within for the system [10, 17, 18]. Usually, negative values of ΔH° show an exothermic adsorption process and this exothermic adsorption process suggests either chemical or physical adsorption whereas endothermic adsorption process is associated with chemisorption. In an exothermic process, physical adsorption is differs from chemisorption by considering the absolute value of

adsorption enthalpy. Naturally, enthalpy processes lower than 80 kJ/mol is attributed to physical adsorption whereas enthalpy processes close to 100 kJ/mol are associated with chemisorption [19]. Therefore, the enthalpy results gotten from the present study reveals that the VD extracts were physically adsorbed on the metal surface. Although, data for ΔS° in blank and inhibited solutions of VD extracts are all negative indicating that decrease in disordering takes place on going from reactants to the activated complex hence the activation complex is the rate determining step representing association rather than dissociation step [19, 20]

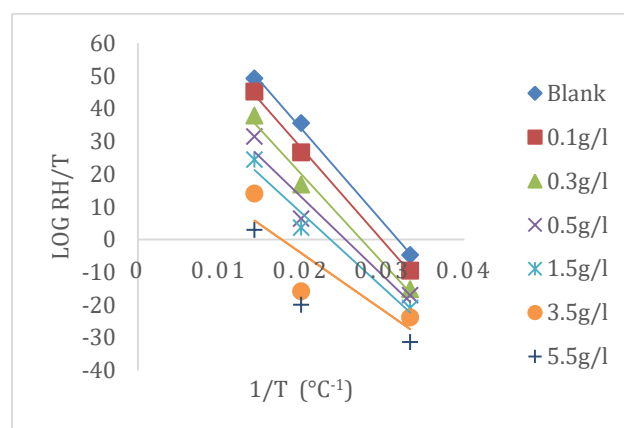


Figure 9. Transition state plot for mild steel coupons in 5.5% HCl solutions containing extracts from leaves of VD using hydrogen evolution technique at 30°C.

3.4 Adsorption considerations

Adsorption process was performed by fitting different adsorption isotherms including Frumkin, Langmuir, Flory-Huggins, Temkin etc into the surface coverage data to determine the best that will be used in calculating thermodynamic parameters relating to inhibitor adsorption. Different adsorption isotherms were found to describe the adsorption of the inhibitors on steel. The isotherms are generally expressed as [21];

$$f(\theta, x) \exp(-2\alpha\theta) = kc \quad (8)$$

Where $f(\theta, x)$ is the configurational factor, which depends on the physical mode and assumptions underlying the derivation of the isotherm, θ is the degree of surface coverage, c is the concentration of the adsorbate in the bulk solution, x is the size ratio factor, ' a ' is the molecular interaction parameter and k is the equilibrium constant of the adsorption process. However, the graph of surface coverage against logarithms of VD extracts concentration (Temkin adsorption isotherm model) gives a linear plot with $R^2 > 0.96$ for all the extracts as presented in Figure10 [21-23]. The linearity of the plot implies that the experimental results conform to Temkin adsorption isotherm model. The values of ' a ' molecular

interaction property were all negative (both weight loss and

Hydrogen evolution methods) as pointed out in Table 3. The positive values of 'a' implies that attraction forces occur between adsorbed molecules whereas negative values suggest repulsion forces between the adsorption layers [7, 24]. Table 3 showed clearly that all values of 'a' were negative implying that repulsive force exist in the adsorption molecules. Normally, K values signifies the strength and better interaction between the adsorbate and adsorbent [24, 25]. K values from this study decrease as the temperature increases hence, high K values portrays weak adsorption. Therefore, the statistical data of K present inhibition efficiency in the order of RT > BK > LV.

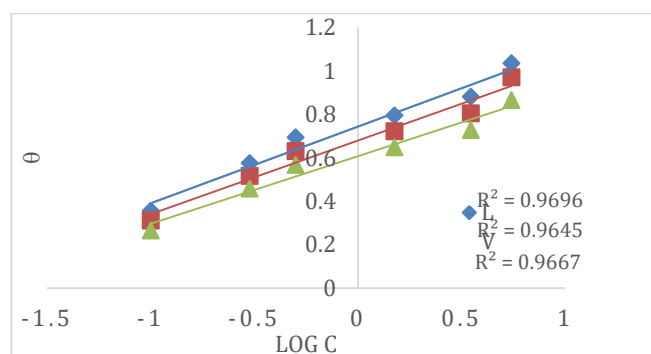


Figure 10: Temkin adsorption plots of steel in 5.5% HCl containing various concentrations of VD extracts at 30°C

Table 3. Temkin adsorption parameters for mild steel in 5.5% HCL solutions containing various VD extracts

Plant part	Temp (°C)	ΔG°_{ads} (kJ/mol)	Hydrogen evolution technique		Weight Loss technique	
			K	a	K	a
LV	30	-2.556	0.051	-1.904		
	50	-2.675	0.051	-2.141	0.561	-1.519
	70	-2.474	0.042	-2.390		
BK	30	-4.76	0.193	-2.454		
	50	-6.897	0.145	-2.507	0.635	-1.122
	70	-5.342	0.137	-1.096		
RT	30	-6.541	1.527	-1.324		
	50	-7.332	1.434	-1.672	0.812	-3.211
	70	-6.436	1.313	-2.031		

3.5 Inhibition mechanism

The mechanism of corrosion inhibition and their activities vary depending on the structure of the inhibitor, metal and medium. The adsorption of the inhibitor, which obstructs the steel surface thereby preventing corrosion process from occurring can be a potential mechanism [26]. The corrosion inhibition of mild steel in 5.5% HCL solutions with increase in VD extract concentrations can be explained by adsorption of the molecules of the VD extracts on steel surface [27]. The VD extracts consist of several natural occurring organic compounds. The inhibitive potential of leaves, bark and roots extracts of VD against the acid corrosion of steel can be associated with the

adsorption of VD extracts on the steel surface. The nonbonded electrons of heteroatoms are protonated and as a result get adsorbed on the negatively charged steel surface. The protonated molecule are adsorbed electrostatically (physisorption) leading to high inhibition efficiency.

The VD extracts can adsorb on the steel surface based on donor-acceptor interaction between the π -electrons of aromatic ring and vacant d-orbitals of Fe. Also when these protonated VD extracts adsorbed on the steel surface, coordinate bond can be formed due transfer of electrons from polar atoms to the metal surface. Hence, in the current study, the adsorption of the Molecules on the surface of the metal were presumed to be accountable for the inhibition of the corrosion reaction. Although, the common effects of the phytochemical constituents (Table 4) of VD plant may also contribute to the inhibition performance.

Table 4: Phytochemical screening of aqueous extracts from (RT), (LV) and (BK) of VD.

Chemical constituent Screening	Root	Bark	Leaves
Alkaloids	+	+	-
Saponins	-	-	-
Flavonoids	+	+	+
Tannins	-	-	+
phenols	+	+	+
Glycosides	+	+	+

NB: +; present in the extracts, -; absent in the extract

4. Conclusion

Extracts from the root, leaves and bark of VD were found to inhibit the corrosion of mild steel in 5.5% HCL solutions. The inhibition efficiency increases with increase in concentration of the extracts and with decrease in temperature suggesting physical adsorption.

The inhibition is as a result of the adsorption of phytochemicals in the extracts on the surface of the metal, thereby hindering the energetic corrosion sites. The presence of alkaloids in the root and leaves extracts is presumed to be responsible for the observed inhibition style RT > BK > LV. The experimental results obey the Temkin adsorption isotherm Model.

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