

## Research Article

# *Baphia nitida* Leaves Extract as a Green Corrosion Inhibitor for the Corrosion of Mild Steel in Acidic Media

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The inhibiting effect of *Baphia nitida* (BN) leaves extract on the corrosion of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl was studied at different temperatures using gasometric and weight loss techniques. The results showed that the leaves extract is a good inhibitor for mild steel corrosion in both acid media and better performances were obtained in 2 M HCl solutions. Inhibition efficiency was found to increase with increasing inhibitor concentration and decreasing temperature. The addition of halides to the extract enhanced the inhibition efficiency due to synergistic effect which improved adsorption of cationic species present in the extract and was in the order KCl < KBr < KI suggesting possible role of radii of the halide ions. Thermodynamic parameters determined showed that the adsorption of BN on the metal surface is an exothermic and spontaneous process and that the adsorption was via a physisorption mechanism.

## 1. Introduction

One of the most practical methods of preventing electrochemical corrosion is to isolate the metal surface from corrosive agents [1]. Of the many methods available, the use of corrosion inhibitors is usually the most appropriate method to achieve this objective [2–9]. These inhibitors could be in the form of organic, inorganic, precipitating, passivating, or volatile species. Generally, corrosion inhibitors may be divided into three broad classes, namely, oxidizing, precipitating, and adsorption inhibitors [10]. Adsorption inhibitors are usually organic substances containing heteroatoms with high electron density such as nitrogen, sulfur, and oxygen [11, 12] and the presence of unsaturated bonds or aromatic rings in the molecular structure of the inhibitor favors adsorption on corroding metal surface [13]. The adsorption is influenced by the nature and the surface charge of the metal, the type of corrosion media, and the molecular structure of the inhibitor [4]. Some corrosion inhibitors used in different media and for different metals and alloys decrease considerably the oxidation states of the corroding metals. In acid corrosion, inhibitor adsorption may lead to structural changes in the

double layer, which could reduce the rates of either the anodic metal dissolution and the cathodic hydrogen ion reduction or both.

It is known that some corrosion inhibitors and their derivatives are toxic and pollute the environment [14]. There is therefore the need to explore new nontoxic, environmental friendly, ecologically acceptable and inexpensive corrosion inhibitor substitutes. Among the alternative corrosion inhibitors, natural products of plant origin have been shown to be quite efficient as corrosion inhibitors [15–19].

In this work, the inhibitory properties of leaf extracts of *Baphia nitida* on mild steel corrosion in 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl have been studied using gasometric and weight loss techniques. The plant popularly called camwood and also known as African sandalwood belongs to the family of *Leguminosae* and its wood is commonly used to make a red dye. Phytochemical analysis of the leaves detected tannins, flavonoids, and saponin glycosides [20]. The actions of the leaf extract as inhibitor in both acid media over a range of inhibitor concentration and solution temperature, as well as synergistic effects of halides, have been studied.

## 2. Experimental

### 2.1. Materials Preparation

**2.1.1. Metal Specimen.** Mild steel strips of compositions 0.05% C, 0.6% Mn, 0.36% P, and 0.03% Si remainder iron and dimensions 3 cm × 1.5 cm × 0.14 cm were used for gasometric and weight loss studies. The specimens were washed with distilled water, degreased by soaking in absolute ethanol, dried in acetone, and stored in moisture-free desiccators prior to use.

**2.1.2. Reagents.** Analytical grade reagents were utilized to prepare 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl using distilled water.

**2.1.3. Plant Extracts.** The *Baphia nitida* leaves used were obtained locally and were dried to a constant weight in an oven at a temperature of 110°C, and then ground to fine powder. The *Baphia nitida* (BN) extract was prepared by adding 10 g of the powder into 250 mL of 1 M H<sub>2</sub>SO<sub>4</sub> in a round bottom flask. The same was repeated for 2 M HCl. The resulting solutions were heated under reflux for 2 h and left to cool overnight, and then filtration was carried out using filter paper. From the respective stock solutions, inhibitor test solutions were prepared in the concentration range 5–100 mg/L.

### 2.2. Methods

**2.2.1. Gasometric Experiments.** The gasometric setup is essentially an apparatus that measures the volume of gas evolved from a reaction system as described by Onuchukwu [21]. The reaction vessel was connected to a burette via a delivery tube, which was in turn connected to a reservoir of paraffin oil. Fifty milliliters of the test solutions were introduced, respectively, into the reaction vessel for blank determinations and the initial volumes of air in the burette, taken against that of the paraffin oil, were recorded. Thereafter, two mild steel coupons were introduced into the reaction vessel and the flask quickly closed. The volume of hydrogen gas evolved by the corrosion reaction was monitored by the drop in the volume of the paraffin oil level in the gasometric gauge. The progress of the corrosion reaction was monitored by careful volumetric measurement of the evolved hydrogen gas at fixed time intervals. The temperature of the experiment was controlled at 30 ± 1 and 60 ± 1°C. The experiments were performed separately employing 20 and 100 mg/L inhibitor concentrations in 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl. The effects of halide ions on the inhibitive action of the BN extract were studied by adding KCl, KBr, and KI separately to 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl with and without 100 mg/L BN extract solutions to yield 0.5 mM concentrations of the halides in each case.

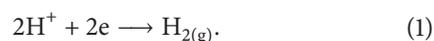
**2.2.2. Weight Loss Experiments.** The prepared and weighed mild steel coupons were immersed in beakers containing 200 mL of the test solutions with and without the addition of BN extract of concentrations ranging from 5 to 100 mg/L inhibitor concentrations in 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl at 30, 40, 50, and 60°C. The metal strips were suspended in the

beakers using glass rods and hooks. After 3 h, the specimens were removed from the solutions, washed appropriately, dried, and reweighed. The weight loss was taken to be the difference between the weight of the coupons after the 3 h period of immersion in the solutions and the initial weight of the coupons. Gravimetric experiments were performed in triplicate and the results showed good reproducibility. The average values were taken and used in subsequent calculations.

## 3. Results and Discussion

### 3.1. Gasometric Measurements

**3.1.1. Effect of Immersion Time on Corrosion Rate.** The spontaneous dissolution of mild steel in acidic media is accompanied by the cathodic reduction of hydrogen ions as shown in (1)



The corrosion of iron and steel in acidic solutions is controlled by the hydrogen evolution reaction [22]. Thus, the corrosion rates of the test coupons in absence and presence of inhibitor were assessed using hydrogen evolution measurements. Previous workers have demonstrated the effectiveness of the gas-volumetric technique in monitoring any modifications in the double layer resulting from the action of an adsorbed inhibitor in a metal/corrosion system [23–25]. Results obtained by this technique are corroborated by other well established methods including weight loss and thermometry, potentiostatic polarization, and impedance spectroscopy [24, 26–28].

Gasometric measurements of mild steel subjected to the effect of acidic media in the absence and presence of BN extract were made at various time intervals. Figures 1(a) and 1(b) present plots of evolved hydrogen gas as a function of time for mild steel corrosion in 1 M H<sub>2</sub>SO<sub>4</sub>, in absence and presence of 20 and 100 mg/L BN extract concentrations at 30 and 60°C, respectively. Similar plots are shown in Figures 2(a) and 2(b) for 2 M HCl at 30 and 60°C. The plots in Figures 1 and 2 show a remarkable decrease in hydrogen evolution with the introduction of the inhibitor indicating that BN extract inhibits corrosion of mild steel in acidic environments. The rates of hydrogen evolution were observed to decrease with increasing inhibitor concentration, suggesting that the inhibiting effectiveness of the BN extract depends on the inhibitor concentration. This dependence was almost linear throughout the time interval studied in the absence and presence of BN extract indicating that the inhibitor acts rapidly and does not lose its inhibitory properties with time. However, the kinetic parameters indicate satisfactory inhibitor efficiencies even at low concentration of BN extract.

In all the cases, the dissolution of steel was characterized by a linear increase in the evolution of hydrogen with time. The reaction rate was characterized by differentiating the volume of hydrogen evolved with time and was obtained from the slope of the linear portions of Figures 1(a) and 1(b). Table 1 shows the values of corrosion rates obtained for the different

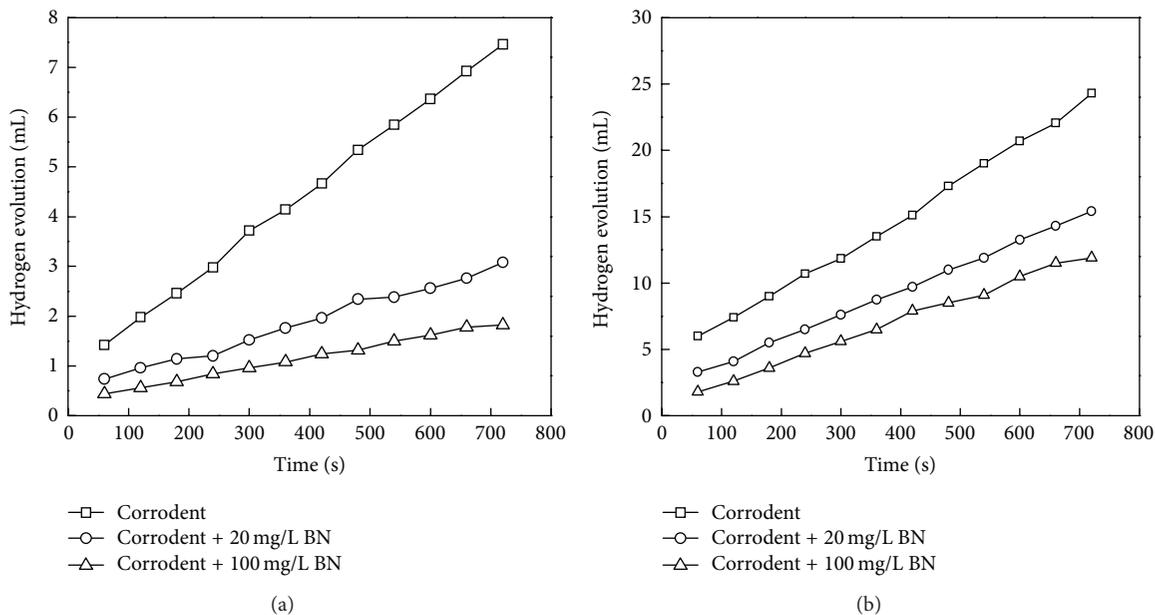


FIGURE 1: Hydrogen evolution during mild steel corrosion in 1 M H<sub>2</sub>SO<sub>4</sub> in absence and presence of *Baphia nitida* extract at (a) 30°C and (b) 60°C.

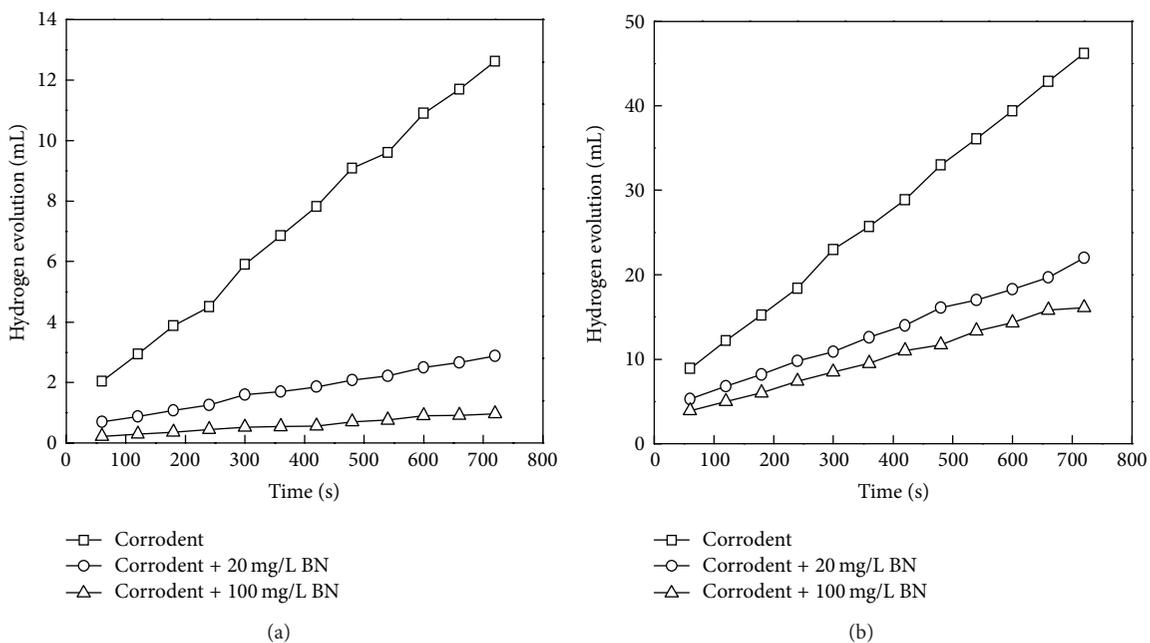


FIGURE 2: Hydrogen evolution during mild steel corrosion in 2 M HCl in absence and presence of BN extract at (a) 30°C and (b) 60°C.

test solutions. The results show that corrosion rate reduced in the presence of the inhibitor and was found to decrease with increasing BN extract concentration in both corrodents. Also, mild steel was observed to exhibit higher corrosion susceptibility in 2 M HCl than in 1 M H<sub>2</sub>SO<sub>4</sub>.

3.1.2. *Inhibition Efficiency.* For the gasometric experiments, the degree of surface coverage ( $\theta$ ) and the inhibition

efficiency (IE, %) of BN extract on mild steel in acidic media was evaluated from (2). Consider

$$\theta = 1 - \frac{v_{inh}}{v_{free}},$$

$$IE = 100 \times \left( 1 - \frac{v_{inh}}{v_{free}} \right), \tag{2}$$

TABLE 1: Corrosion rates of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl in absence and presence of BN extract obtained from gasometric method.

System	Corrosion rate ( $\times 10^{-3}$ H <sub>2</sub> gas vol. mL s <sup>-1</sup> )	
	30°C	60°C
1 M H <sub>2</sub> SO <sub>4</sub>		
Corrodent alone	9.20	27.65
Corrodent + 20 mg/L inhibitor	3.52	18.49
Corrodent + 100 mg/L inhibitor	2.17	15.83
2 M HCl		
Corrodent alone	16.34	56.96
Corrodent + 20 mg/L inhibitor	3.28	24.68
Corrodent + 100 mg/L inhibitor	1.14	19.25

TABLE 2: Degree of surface coverage and inhibition efficiencies of different concentrations of BN extract during mild steel corrosion in 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl obtained from gasometric method.

Concentration (mg/L)	Surface coverage, $\theta$		Inhibition efficiency, IE (%)	
	30°C	60°C	30°C	60°C
1 M H <sub>2</sub> SO <sub>4</sub>				
Blank	—	—	—	—
20	0.62	0.33	61.7	33.1
100	0.76	0.43	76.4	42.8
2 M HCl				
Blank	—	—	—	—
20	0.80	0.57	79.9	56.7
100	0.93	0.66	93.0	66.2

where  $v_{\text{free}}$  and  $v_{\text{inh}}$  are the corrosion rates in the absence and presence, respectively, of a given concentration of BN extract. Table 2 shows values of the degree of surface coverage ( $\theta$ ) and the inhibition efficiency (IE, %) obtained for different concentrations of BN extract in both corrodents using the gasometric technique. The result shows that the extract retarded acid corrosion of the mild steel and surface coverage and hence inhibition efficiencies increased with increasing inhibitor concentration at both temperatures.

Phytochemical analysis of leaves of BN detected tannins, flavonoids, and saponin glycosides and these are known to possess corrosion inhibitory properties [20]. The inhibitive effect could be attributed to the net adsorption of the organic matter on the steel/acid solution interface thereby reducing the surface area available for corrosion reaction and the degree of protection increases with increasing inhibitor concentration. It can be clearly noticed that the inhibition efficiency of BN extract was higher in 2 M HCl than in 1 M H<sub>2</sub>SO<sub>4</sub> over the concentration range studied, suggesting that the nature of the acid anion influences metal-inhibitor interactions. In the presence of strong acids, some inhibitor species become protonated. The surface charge on iron in acidic solution is positive at the corrosion potential and specific adsorption of chloride ions of HCl renders the metal surface more negative and susceptible to adsorption

of protonated inhibitor species compared to H<sub>2</sub>SO<sub>4</sub> [29, 30]. Thus, the adsorption of the protonated inhibitor species on the metal surface will be enhanced in HCl, leading to higher inhibition efficiencies.

3.2. *Weight Loss Measurements.* The inhibition efficiency (IE, %) for the weight loss measurements was calculated using (3) as follows:

$$\text{IE} = \frac{(W_2 - W_1)}{W_1} \times 100, \quad (3)$$

where  $W_1$  (mg) is the weight loss of steel in uninhibited solutions and  $W_2$  (mg) the weight loss of steel in inhibited solutions. IE (%) and  $\theta$  for mild steel exposed to 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl at various temperatures as a function of BN concentration are shown in Tables 3 and 4. It is observed that at all temperatures inhibition efficiency increased on increasing BN concentration. This observation is in support of results obtained with the gasometric experiments.

The effect of temperature on the corrosion behavior of mild steel in the absence and presence of BN extract was investigated by performing weight loss experiments at 30, 40, 50, and 60°C. The results as shown in Tables 3 and 4 demonstrate that the weight loss increased and the inhibition efficiency decreased with increase in temperature. The decrease in inhibition efficiency with increasing temperature suggests weak adsorption interaction between the metal and the extract organic matter. Such behavior corresponds to physical adsorption, such that at higher temperatures, there is a possible shift of the adsorption-desorption equilibrium towards desorption of adsorbed inhibitor [31]. The increase in solution agitation resulting from higher rates of H<sub>2</sub> gas evolution as well as the agitation of the interface and roughening of the metal surface as a result of enhanced corrosion all contribute to the reduced stability of the adsorbed inhibitor at higher temperature [15, 32].

3.3. *Adsorption Isotherm Behaviour.* Experimental and theoretical studies have shown that the protective action of organic substances during metal corrosion is based on the adsorption ability of their molecules, where the resulting adsorption film isolates the metal surface from the corrosive medium [4–16]. Therefore, Langmuir adsorption isotherm expression (4), which relates the surface coverage  $\theta$  defined by IE/100 and the inhibitor concentration ( $C$ ), could be applied to determine adsorption equilibrium constant,  $K$ , at the different temperatures. Consider

$$\frac{C}{\theta} = \frac{1}{K} + C. \quad (4)$$

The plots of  $C/\theta$  versus  $C$  for 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl are shown in Figures 3(a) and 3(b), respectively, and the values of  $K$  subsequently calculated from the intercept are shown in Table 5. The adjusted correlation coefficient ( $R^2$ ) values which were all above 0.990 shows a good fit of the experimental data and suggests that the adsorption of BN extract on metal surface followed the Langmuir adsorption

TABLE 3: Corrosion parameters obtained from weight loss of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> containing various concentrations of BN extract at different temperatures.

Concentration of BN (mg/L)	Temperature											
	30°C			40°C			50°C			60°C		
	W (mg/cm <sup>2</sup> )	IE (%)	θ	W (mg/cm <sup>2</sup> )	IE (%)	θ	W (mg/cm <sup>2</sup> )	IE (%)	θ	W (mg/cm <sup>2</sup> )	IE (%)	θ
0	5.82	—	—	7.47	—	—	14.57	—	—	23.87	—	—
5	2.56	56.01	0.5601	3.96	46.99	0.4699	9.19	36.93	0.3693	16.81	29.58	0.2958
10	2.39	58.93	0.5893	3.86	48.33	0.4833	8.96	38.5	0.3850	16.48	30.96	0.3096
20	2.21	62.03	0.6203	3.7	50.47	0.5047	8.58	41.11	0.4111	16.02	32.89	0.3289
40	1.93	66.84	0.6684	3.45	53.82	0.5382	8.21	43.65	0.4365	15.35	35.69	0.3569
60	1.69	70.96	0.7096	3.19	57.3	0.5730	7.69	47.22	0.4722	14.98	37.24	0.3724
80	1.54	73.54	0.7354	2.95	60.51	0.6051	7.19	50.65	0.5065	14.24	40.34	0.4034
100	1.41	75.77	0.7577	2.75	63.19	0.6319	6.98	52.09	0.5209	13.55	43.23	0.4323

TABLE 4: Corrosion parameters obtained from weight loss of mild steel in 2 M HCl containing various concentrations of BN extract at different temperatures.

Concentration of BN (mg/L)	Temperature											
	30°C			40°C			50°C			60°C		
	W (mg/cm <sup>2</sup> )	IE (%)	$\theta$	W (mg/cm <sup>2</sup> )	IE (%)	$\theta$	W (mg/cm <sup>2</sup> )	IE (%)	$\theta$	W (mg/cm <sup>2</sup> )	IE (%)	$\theta$
0	4.44	—	—	5.43	—	—	9.38	—	—	13.66	—	—
5	1.18	73.42	0.7342	1.92	64.64	0.6464	4.00	57.36	0.5736	6.60	51.68	0.5168
10	1.07	75.9	0.7590	1.83	66.3	0.6630	3.82	59.28	0.5928	6.27	54.1	0.5410
20	0.88	80.18	0.8018	1.68	69.06	0.6906	3.58	61.83	0.6183	5.86	57.1	0.5710
40	0.65	85.36	0.8536	1.48	72.74	0.7274	3.24	65.46	0.6546	5.43	60.25	0.6025
60	0.52	88.29	0.8829	1.31	75.87	0.7587	2.90	69.08	0.6908	5.01	63.32	0.6332
80	0.41	90.77	0.9077	1.13	79.19	0.7919	2.70	71.26	0.7126	4.77	65.08	0.6508
100	0.29	93.47	0.9347	0.97	82.14	0.8214	2.53	73.03	0.7303	4.59	66.4	0.6640

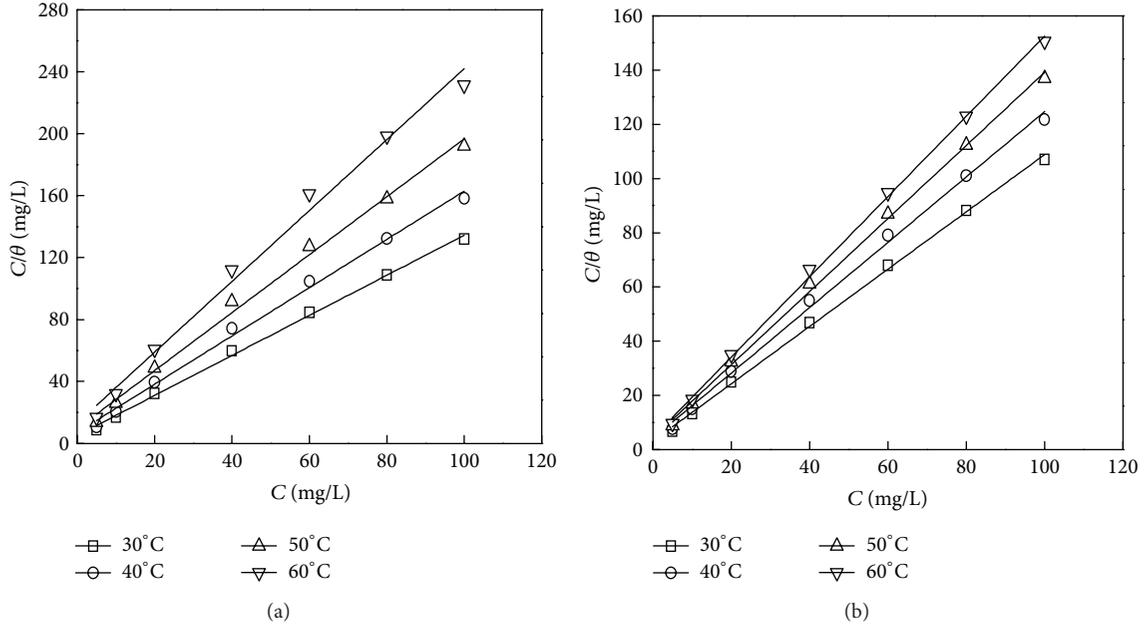


FIGURE 3: Langmuir adsorption plots for mild steel corrosion with BN extract as inhibitor at different temperatures in (a) 1 M  $H_2SO_4$  and (b) in 2 M HCl.

TABLE 5: Thermodynamic parameters for the adsorption of BN extract in 1 M  $H_2SO_4$  and 2 M HCl on the mild steel at different temperatures.

Temperature	$K$ (L/mg)	$R^2$	$\Delta G$ (kJ/mol)	$\Delta H$ (kJ/mol)	$\Delta S$ (J/mol K)
1 M $H_2SO_4$					
30	0.194	0.997	-1.028	-26.21	-83.11
40	0.141	0.995	-1.270	-26.21	-79.68
50	0.103	0.994	-1.517	-26.21	-76.45
60	0.076	0.990	-1.772	-26.21	-73.39
2 M HCl					
30	0.316	0.999	-0.723	-9.61	-29.33
40	0.241	0.997	-0.921	-9.61	-27.76
50	0.228	0.998	-0.988	-9.61	-26.69
60	0.221	0.999	-1.041	-9.61	-25.73

isotherm. The results show that the adsorption equilibrium constant ( $K$ ) decreased with increasing temperature, indicating better adsorption of BN extract onto the steel surface at lower temperatures. However, at higher temperatures, the equilibrium tends towards desorption.

**3.4. Thermodynamic Parameters.** The thermodynamic parameters, the standard free energy of adsorption ( $\Delta G^\circ$ ), the standard heat of adsorption ( $\Delta H^\circ$ ), and the standard entropy of adsorption ( $\Delta S^\circ$ ) give an insight into the mechanism of the corrosion inhibition process. From the van't Hoff equation (5),  $\Delta H^\circ$  was determined by a linear regression between  $\ln K$  and  $1/T$  [33]. Consider

$$\ln K = \frac{-\Delta H}{RT} + C. \quad (5)$$

The values of  $\Delta G^\circ$  were evaluated from (6) [34]

$$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G^\circ}{RT}\right). \quad (6)$$

The  $\Delta S^\circ$  values were then obtained from the basic thermodynamic equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ. \quad (7)$$

The thermodynamic parameters obtained are listed in Table 5. The negative values of  $\Delta H^\circ$  show that the adsorption of BN on the metal surface is an exothermic process, supporting the previous observation that IE decreases with increase in temperature. Exothermic process signifies either physisorption or chemisorption while endothermic process is indicative solely of chemisorptions [35]. For an exothermic process, the absolute value of  $\Delta H^\circ$  of the process is used

to distinguish physisorption from chemisorptions. If  $\Delta H^\circ$  is lower than 41.86 kJ/mol, physisorption is involved, while if  $\Delta H^\circ$  approaches 100 kJ/mol, it is a chemisorption process [36]. The absolute value of  $\Delta H^\circ$  in the present study is lower than 41.86 kJ/mol, confirming the physisorption mechanism proposed involving electrostatic interactions between charged BN molecules and charged metal. The negative values of  $\Delta G^\circ$  indicate the stability of the adsorbed layer on the steel surface and that the adsorption of BN molecules onto the steel surface is spontaneous. The negative values of  $\Delta S^\circ$  show that the adsorption process is accompanied by a decrease in entropy. The explanation is that the adsorption of BN molecules onto the steel surface reduces the level of chaos on the steel surface leading to a decrease in entropy.

**3.5. Apparent Activation Energy ( $E_a$ ).** It has been reported that for the acid corrosion of mild steel, the natural logarithm of the corrosion rate is a linear function of  $1/T$ . Therefore, the apparent activation energy of the corrosion inhibition process could be obtained by the application of the Arrhenius-type equation (8) [1]. Consider

$$\ln \nu = \ln A - \frac{E_a}{RT}, \quad (8)$$

where  $\nu$  (mg/cm<sup>2</sup> h) is the corrosion rate,  $E_a$  (J/mol) is the apparent activation energy,  $R$  (8.314 J/mol K) is the universal gas constant,  $T$  (K) is the absolute temperature, and  $A$  (mg/cm<sup>2</sup> h) is the pre-exponential factor. The corrosion rate,  $\nu$ , was obtained from the relation

$$\nu = \frac{W}{t}, \quad (9)$$

where  $W$  (mg/cm<sup>2</sup>) is the weight loss per area and  $t$  is the immersion (corrosion) time (3 h). From the slope and intercept of the linear regression of  $\ln \nu$  versus  $1/T$  (Figure not shown), the values of  $E_a$  and  $A$  for mild steel corrosion in different concentrations of BN in both 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl were calculated, respectively, as shown in Table 6. The results show that the value of  $E_a$  increased with the addition of BN extract. Increase in  $E_a$  with increasing concentration of inhibitor indicates physisorption mechanism [21]. Similar results have been reported in some previous studies [9, 37].

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 [22]. The results for both acid media show higher activation energy values in the presence of the extract compared to the blank acids, suggesting physical adsorption [30–32, 38].

TABLE 6: Calculated values of apparent activation energy ( $E_a$ ) and preexponential factor ( $A$ ) for mild steel corrosion in 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl with BN extract as inhibitor.

C (mg/L)	$E_a$ (kJ/mol)	$A$ (mg/cm <sup>2</sup> h)	$R^2$
1 M H <sub>2</sub> SO <sub>4</sub>			
0	40.97	$2.02 \times 10^7$	0.950
5	54.30	$1.79 \times 10^9$	0.974
10	55.55	$2.78 \times 10^9$	0.980
20	56.81	$4.26 \times 10^9$	0.984
40	59.40	$1.05 \times 10^{10}$	0.989
60	62.24	$2.87 \times 10^{10}$	0.992
80	63.39	$4.13 \times 10^{10}$	0.992
100	64.72	$6.44 \times 10^{10}$	0.992
2 M HCl			
0	32.75	$6.06 \times 10^5$	0.951
5	49.44	$1.26 \times 10^8$	0.988
10	50.66	$1.87 \times 10^8$	0.992
20	54.11	$6.24 \times 10^8$	0.994
40	60.12	$5.22 \times 10^9$	0.992
60	63.84	$1.87 \times 10^{10}$	0.989
80	69.26	$1.28 \times 10^{11}$	0.987
100	77.82	$2.82 \times 10^{12}$	0.979

TABLE 7: Effect of halide ions on the mild steel corrosion in 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl in the absence and presence of BN extract.

System	Inhibition efficiency, $E$ (%)			
	1 M H <sub>2</sub> SO <sub>4</sub>		2 M HCl	
	30°C	60°C	30°C	60°C
100 mg/L BN	76.4	42.8	93.0	66.2
0.5 mM KCl	32.7	26.2	26.4	20.9
0.5 mM KBr	52.9	45.7	52.4	40.3
0.5 mM KI	69.6	60.0	65.0	54.8
100 mg/L BN + 0.5 mM KCl	79.2	44.8	94.4	67.3
100 mg/L BN + 0.5 mM KBr	81.7	47.0	95.8	68.4
100 mg/L BN + 0.5 mM KI	89.5	54.5	97.8	69.8

**3.6. Synergism Considerations.** The influence of halide ions on the inhibitive action of BN extract was assessed. Table 7 illustrates the effects of 0.5 mM KCl, KBr, and KI without or with 100 mg/L BN extract on the corrosion of mild steel in 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl. The inhibition efficiency of BN extract was significantly improved in the presence of halide ions in both acid media and at both temperatures studied. This suggests that adsorption of protonated species in the BN extract is enhanced through ion pair interactions, with the halide ions forming an intermediate bridge between the positively charged metal surface and the inhibitor [22, 39]. From the inhibition efficiencies, corrosion inhibition efficiencies of the halide alone as well as in combination with BN extract increased in the order KCl < KBr < KI. This is in accordance with the findings of other researchers [15, 39–42]. This observation could be explained on the basis of the

TABLE 8: Synergism parameter ( $S_I$ ) for the various halides at 30 and 60°C.

Halides	Synergism parameter ( $S_I$ )			
	1 M H <sub>2</sub> SO <sub>4</sub>		2 M HCl	
	30°C	60°C	30°C	60°C
KCl	1.38	1.55	1.27	1.29
KBr	1.59	1.82	1.52	1.57
KI	1.64	1.90	1.62	1.74

halide ion radii, which increases in the order  $\text{Cl}^-$  (0.09 nm) <  $\text{Br}^-$  (0.114 nm) <  $\text{I}^-$  (0.135 nm), with the highest ionic radius being more predisposed to adsorption.

The data in Table 7 also shows that inhibition efficiencies in the presence of halides were better improved in 1 M H<sub>2</sub>SO<sub>4</sub> than in 2 M HCl which implies that more halide ions are adsorbed on the metal surface in 1 M H<sub>2</sub>SO<sub>4</sub>. This could be attributed to comparatively more positive charge on the steel surface in 1 M H<sub>2</sub>SO<sub>4</sub> [43].

At 60°C, all the halides in combination with BN extract exhibited reduced inhibition efficiencies, indicating that the synergistic effect of BN extract and halide ions is diminished at higher temperatures. The decrease in inhibition efficiency of the BN extract and halide complex with rise in temperature as shown in Table 7 still supports the physisorption mechanism for BN extract on the mild steel surface which is in line with the observation in the absence of halides.

The synergism parameters,  $S_I$ , were calculated using the relationship (10) given by Aramaki and Hackermann [44]:

$$S_I = \frac{1 - I_{1+2}}{1 - I'_{1+2}}, \quad (10)$$

where  $I_{1+2} = (I_1 + I_2)$ ;  $I_1$  is the inhibition efficiency of the halide;  $I_2$  is the inhibition efficiency of BN extract;  $I'_{1+2}$  is the inhibition efficiency of BN extract in combination with halide. The calculated values are presented in Table 8 for the different halides at 30 and 60°C. From Table 8, it could be seen that all values of  $S_I$  are greater than unity, clearly showing that the corrosion inhibition brought about by the complex of BN extract and halide is due mainly to synergistic effect [41, 45].

#### 4. Conclusion

*B. nitida* leaf extract inhibited mild steel corrosion in 1 M H<sub>2</sub>SO<sub>4</sub> and 2 M HCl at the temperatures studied. Inhibition efficiency increased with increase in BN extract concentration and synergistically increased in the presence of halide ions. Temperature studies revealed a decrease in inhibition efficiency with rise in temperature and corrosion activation energies being higher in the presence of the plant extract. Comparative analyses of the results from both acid solutions suggest that protonated species in the extract play a predominant role in inhibitive behavior observed, with the predominant effect being the physical adsorption of protonated species.

#### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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