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# Corrosion Inhibition of Mild Steel in Sulphuric Acid (H<sub>2</sub>SO<sub>4</sub>) Medium of the Stem Extract of *Tetrapleura Tetraptera*

Rita Oghenyerhovwo Ididama, Vincent Ishmael Egbulefu Ajiwe,  
Chingbudun Nduadim Emeruwa

Department of Pure and Industrial Chemistry, Nnamdi Azikiwe University, Awka, Nigeria

## Email address:

emerite9@gmail.com (R. O. Ididama), vie.ajiwe@unizik.edu.n.s (V. I. E. Ajiwe),

emeruwa\_chigbundu@yahoo.com (C. N. Emeruwa)

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**Abstract:** The inhibitive action of stem extracts of *Tetrapleura tetraptera* on mild steel corrosion in 1.0M & 5.0M H<sub>2</sub>SO<sub>4</sub> solutions was studied. The stem were dried under room temperature and mechanically ground into powder form. 100g of the stem powder were extracted with a mixture of methanol/water in the ratio of 4:1 using a Soxhlet extractor for 24 hours. The extracts were distilled at 60°C in a water bath until almost the entire methanol evaporated. 4.0g of the methanol extracts were digested in 1000ml of 1M H<sub>2</sub>SO<sub>4</sub> and 5M H<sub>2</sub>SO<sub>4</sub> and left to cool for 24 hours and the resulting solution was filtered and stored in a 1.0L volumetric flask. The stem extracts test solutions were prepared from the stock solution by dissolving 0.5g/L, 1.0g/L, 2.0g/L and 4.0g/L of the extracts in 1L solution of 1M H<sub>2</sub>SO<sub>4</sub> and 5M H<sub>2</sub>SO<sub>4</sub>. Phytochemical analysis was carried out and the result showed the presence of some secondary metabolites such as alkaloids, flavonoids, steroids, saponins and tannins. Weight loss (gravimetric) and gasometric techniques were used to determine the inhibition action of the stem of *Tetrapleura tetraptera*. The results showed that stem of *Tetrapleura tetraptera* can function as good corrosion inhibitor in acid medium. Inhibition efficiencies (%I) of the stem of *Tetrapleura tetraptera* extracts was found to reach 73.69% & 50.39% for 1.0M H<sub>2</sub>SO<sub>4</sub> while for 5.0M was 83.31% & 79.54% for gravimetric and gasometric analyses respectively. The corrosion inhibition efficiency increased with increase in the concentration of the extracts and decreased with the increase in time and temperature. The corrosion inhibition efficiency exhibited by the *Tetrapleura tetraptera* stem extracts is attributed to the stronger adsorption of the phytochemicals present in the plant extracts onto the mild steel. The mechanism of adsorption proposed for the *Tetrapleura tetraptera* stem extracts is physical adsorption. The corrosion inhibition of the stem of *Tetrapleura tetraptera* extracts followed Langmuir, Tempkin and Freundlich adsorption isotherm for both 1.0M & 5.0M H<sub>2</sub>SO<sub>4</sub>.

**Keywords:** Mild Steel, Corrosion, Sulphuric Acid, *Tetrapleura Tetraptera* Stem Extract, Gravimetric, Gasometric

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## 1. Introduction

Corrosion control of metals and alloys is an expensive process and industries spend huge amount to control this problem. Mild steel also known as plain carbon steel is now the most common form of steel because its price is relatively low, while it provides material properties that are acceptable for many applications [1]. However the challenge is that it has low corrosion resistance especially in acidic environments [2]. Industrial processes such acid cleaning, pickling, descaling and drilling operations in oil and gas

exploration use acidic solutions extensively and as such iron and steel vessels or surfaces used in these environments are prone to corrosion [3]. The use of many inorganic inhibitors, particularly those containing phosphate, chromate and other heavy metals is now being gradually restricted or banned by various environmental regulations because of their toxicity and difficulties faced in their disposal especially in the marine industry where aquatic life is at threat [4]. Synthetic organic inhibitors have also been extensively applied but their use is being marred by their toxicity and high cost of manufacturing. This has prompted researchers to explore other areas to produce eco-friendly, cheap and biodegradable

green corrosion inhibitors to replace inorganic and synthetic organic inhibitors. Natural products such as plant extract, amino acids, proteins and biopolymers have been reported to be efficient corrosion inhibitors. [5]. Plant extracts are viewed as rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost [6]. These natural extracts are analogous to the synthetic organic inhibitors and are being proven to work as much as their synthetic counterparts. This gives an overview of recent work on the inhibitive effect of various plant extracts particularly for mild steel in acidic medium so as to provide industrialists with vital comparative literature for possible large scale use of natural inhibitors in their operations.

As a contribution to the current interest on environmentally friendly, green, corrosion inhibitors which are readily available and renewable, the present study investigates the use of extracts from the stems of *Tetrapleura tetraptera* as corrosion inhibitor for mild steel in H<sub>2</sub>SO<sub>4</sub> medium using weight loss and gasometric techniques which has not been reported anywhere in literature to the best of our knowledge. *Tetrapleura tetraptera* (commonly known as Aridian) is called overen in Urhobo and ihikiri in Igbo. So many works ranging from phytochemistry, nutritional traits and antimicrobial has been carried out on the plant which confirmed its nutritional and medicinal properties [7-8]. However, the stems of *Tetrapleura tetraptera* plant has not been reported anywhere in literature to the best of our knowledge for corrosion inhibition of metals and alloys.

## 2. Materials and Method

### 2.1. Material Collection and Preparation

The mild steel coupons used in this work were obtained from Urata market, Aba in Abia State, Nigeria. The mild steel sheets used were mechanically cut into 5.0cm x 1.5cm coupons. The surfaces of the mild steel coupons were mechanically polished with series of emery paper (sand paper) of variable grades. These polished mild steel coupons were then washed with distilled water, respectively degreased with methanol and acetone, air-dried and weighed using a digital weighing balance. The weights were recorded and the weighed coupons were used for corrosion study.

### 2.2. Preparation of Plant Extracts

The stems of *Tetrapleura tetraptera* were collected from Oha, Okpe L. G. A., Delta State, Nigeria. They were dried under room temperature away from direct sun light. A mechanical grinder was used to grind the dried stems into powder form. 100 g of the stem powder was extracted with 4:1 methanol:water (80% methanol) using a soxhlet extractor for 24 hours. The extract was distilled at 60°C in a water bath until almost the entire methanol evaporated. The methanol extract (4.0 g) was digested in 1000 mL of 1.0M H<sub>2</sub>SO<sub>4</sub> & 5.0M H<sub>2</sub>SO<sub>4</sub> and left to cool for 24 hours. The resultant solutions were filtered and stored in a 1.0 L volumetric flask

as the stock solution. The stem extract test solutions of concentration of 0.5 g/L, 1.0 g/L, 2.0 g/L, and 4.0g/L were prepared from the stock solution. These solutions were used for the corrosion inhibition test.

### 2.3. Weight Loss Technique

The weighed polished mild steel coupons were suspended in beakers containing 100mL of the acidic test solutions (1.0M H<sub>2</sub>SO<sub>4</sub> & 5.0M H<sub>2</sub>SO<sub>4</sub>) at room temperature. The mild steel coupons were completely immersed in the test solutions and retrieved every hour for 1-5hours. The retrieved coupons were washed, scrubbed with bristle brush under fast flowing water, rinsed in methanol, dried using acetone, and re-weighed. The weight loss of the mild steel was evaluated as the difference in the initial and final weight of the coupons. The experiment was carried out for stem of *Tetrapleura tetraptera* extract using concentrations of 0.5g/L, 1.0g/L, 2.0g/L and 4.0g/L at ambient temperature and in triplicates respectively. From the weight loss data, the corrosion rates (CR) were calculated using equation (1):

$$CR = \frac{WL}{A.t} \quad (1)$$

Where WL is weight loss in mg, A is the metal surface area and t, the time of immersion in hours. From corrosion rate, the percentage inhibition efficiencies of the stem extracts (I%) were determined using equation (2):

$$I\% = \left[ \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \right] \times 100 \quad (2)$$

Where CR<sub>blank</sub> and CR<sub>inh</sub> are the corrosion rates in the absence and presence of the stem extracts respectively.

The order of reaction for corrosion of mild steel in 1.0M and 5.0M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of the various plant extracts were calculated using the equations 3, 4 and 5.

$$W_f = W_o - kt \quad (3)$$

$$\text{Log} \left( \frac{W_o}{W_f} \right) = kt \quad (4)$$

$$1/W_f = 1/W_o + 2kt \quad (5)$$

Where W<sub>o</sub> and W<sub>f</sub> are weight in grammes before and after post treatment of mild steel coupons respectively, k is the rate constant obtained from the slope of the graph and t is the time in hours.

From the rate constant values, the half-life values t<sub>1/2</sub> of the extracts in the test solutions were calculated using the equation 6.

$$T_{1/2} = \frac{0.693}{K} \quad (6)$$

### 2.4. Gasometric Technique

The gasometric technique was conducted using a gasometric assembly consisting of a reaction chamber, connected to burette that contained paraffin oil through a reservoir. In determining the rate of hydrogen evolution per

surface area, the contribution of other gases, including water vapour at higher temperature is assumed to be insignificant. In the gasometric measurements the volume of hydrogen evolved was determined following procedures previously described [9-10]. 100 mL of the corrodant (acidic test solution) was introduced into the reaction chamber, connected to a burette through a delivery tube. A mild steel coupon was dropped into the acidic test solution in the chamber and the reaction vessel was quickly closed to avoid any escape of hydrogen gas. The volume of the hydrogen gas evolved from the reaction was monitored by the depression (in mL) in the level of paraffin oil. This depression in the paraffin oil level was recorded every minute for a maximum of 15 minutes at 313K. The same experiment was repeated in the presence of the inhibitor, stem of *Tetrapleura tetraptera* extract, with concentrations of 0.5g/L, 1.0 g/L, 2.0 g/L, 4.0g/L. The same procedure was repeated at elevated temperature of 323 ± 2 K. The rate of evolution of the hydrogen gas (Rh) was determined from the slope of the graph of volume of the hydrogen gas evolved (VHE) against time (t) and the inhibitors efficiencies (I%) determined using equation (7).

$$I\% = \left[ \frac{Rh_{blank} - Rh_{inh}}{Rh_{blank}} \right] \times 100 \quad (7)$$

In examining the effect of temperature on the corrosion process, the activation (Ea) was calculated using the condensed Arrhenius equation (equation 8):

$$Ea = 2.303R \left[ \text{Log} \left[ \frac{R_2}{R_1} \right] \times \frac{T_1 T_2}{T_2 - T_1} \right] \quad (8)$$

Where R<sub>1</sub> and R<sub>2</sub> are the corrosion rates at temperatures T<sub>1</sub> and T<sub>2</sub> respectively, and R is the molar gas constant. An estimate of the heat of adsorption was obtained from the trend of surface coverage (θ) (% I = 100 × θ) with temperature as follows:

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

Where θ<sub>1</sub> and θ<sub>2</sub> are the degrees of surface coverage at temperature T<sub>1</sub> and T<sub>2</sub> respectively. Langmuir, Tempkin and Freundlich adsorption isotherms are given by the expression in equation 8.9 and 10 respectively.

**Table 2.** Corrosion Rate (mg/cm<sup>2</sup>/hr<sup>-1</sup>) and Inhibition Efficiency (%) of mild steel in the Absence and Presence of Plant Stem Extract in 1.0M H<sub>2</sub>SO<sub>4</sub> & 5.0M H<sub>2</sub>SO<sub>4</sub>.

	Corrosion Rate (mg/cm <sup>2</sup> /hr <sup>-1</sup> )					Inhibition Efficiency (%)				
	Blank	0.5g/L	1.0g/L	2.0g/L	4.0g/L	Blank	0.5g/L	1.0g/L	2.0g/L	4.0g/L
1.0M H <sub>2</sub> SO <sub>4</sub>										
STEMS										
1hr	11.85	4.57	4.16	3.33	3.12	61.41854	64.92594	71.94075	73.69446	
2hrs	11.22	5.51	4.68	4.05	3.74	50.91742	58.32611	63.88263	66.66089	
3hrs	11.85	7.27	7.07	5.75	5.06	38.6204	40.3741	51.48089	57.32656	
4hrs	15.27	10.7	8.57	7.53	6.86	29.91218	43.86169	50.66634	55.08936	
5hrs	12.72	9.48	8.81	7.36	5.69	25.5007	30.72873	42.16503	55.23508	
5.0M H <sub>2</sub> SO <sub>4</sub>										

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (10)$$

$$\text{Log } \theta = \text{log } K + n \text{ log } C \quad (11)$$

$$\theta = RT \text{ log } C + b \quad (12)$$

Where θ is the surface coverage, C is the concentration and K<sub>ads</sub> is the equilibrium constant of the adsorption process.

The Gibbs free energy was calculated using equation (13):

$$\Delta G^\circ_{ads} = -2.303RT \text{Log} (55.5K_{ads}) \quad (13)$$

The entropy of adsorption, (ΔS<sub>ads</sub>) was calculated using equation (12):

$$\Delta G^\circ_{ads} = \Delta H^\circ_{ads} - T \Delta S^\circ_{ads} \quad (14)$$

### 2.5. Phytochemical Screening

Phytochemical screening was carried out on the stem by testing for alkaloids, saponins, flavonoids, tannin and steroids as described by some workers [11-13].

## 3. Results

### 3.1. Result Of Phytochemical Screening

The results from the phytochemical screening of the stem extracts are shown in Table 1.

**Table 1.** Phytochemical screening result.

Phytochemical	Stems
Alkaloids	+
Flavonoids	+
Steroids	+
Saponins	+
Tannins	+

+ = present.

### 3.2. Weight Loss (Gravimetric) Analysis

Different concentrations of the inhibitor were used to test the corrosion behaviour of mild steel. The Corrosion rates (mg/cm<sup>2</sup>/hr<sup>-1</sup>) and inhibition efficiencies (%) for weight loss of mild steel in 1.0M H<sub>2</sub>SO<sub>4</sub> & 5.0M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of different concentrations of the plant extracts are shown in Table 2.

	Corrosion Rate (mg/cm <sup>2</sup> /hr <sup>-1</sup> )					Inhibition Efficiency (%)				
	Blank	0.5g/L	1.0g/L	2.0g/L	4.0g/L	Blank	0.5g/L	1.0g/L	2.0g/L	4.0g/L
STEMS										
1hr	26.39	18.14	16.46	15.15	13.09	31.26184	37.62789	42.59189	50.39788	
2hrs	29.51	20.89	19.64	18.39	16.24	29.21044	33.44629	37.68214	44.96781	
3hrs	26.95	20.16	19.53	18.31	17.08	25.19481	27.53247	32.05937	36.62338	
4hrs	25.82	20.11	19.17	18.24	17.14	22.11464	25.75523	29.35709	33.61735	
5hrs	27.1	21.7	21.07	20.07	19.94	19.9262	22.25092	25.94096	26.42066	

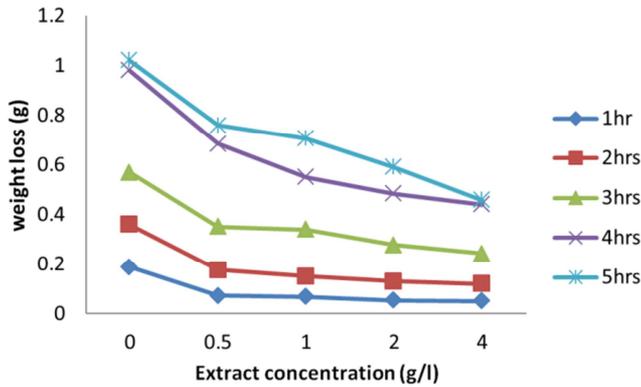


Figure 1. Variation of weight loss against extract for the corrosion of mild steel in 1.0 M H<sub>2</sub>SO<sub>4</sub> solution in the absence and presence of different concentrations of the stem extract of *Tetraptera tetrpleura*.

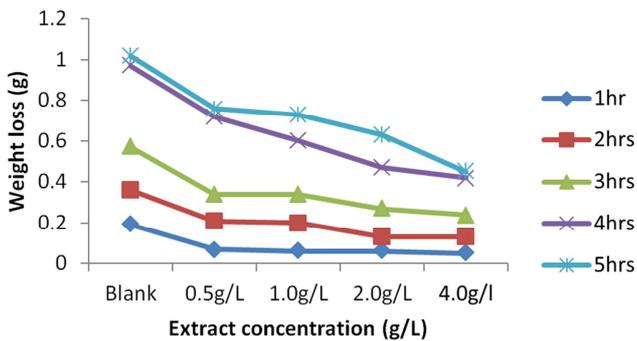


Figure 2. Variation of weight loss against extract for the corrosion of mild steel in 5.0 M H<sub>2</sub>SO<sub>4</sub> solution in the absence and presence of different concentrations of the stem extract of *Tetraptera tetrpleura*.

The order of reaction for corrosion of mild steel in 1.0M H<sub>2</sub>SO<sub>4</sub> & 5.0M H<sub>2</sub>SO<sub>4</sub> in the absence and presence of the plant stem extracts were calculated using equation 3.

The plots of w<sub>f</sub> against time, Log (W<sub>o</sub>/W<sub>f</sub>) against time and 1/w<sub>f</sub> against time are showed in figures 3-8.

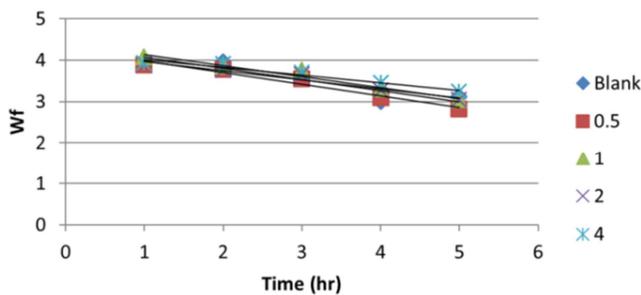


Figure 3. Plot of W<sub>f</sub> against Time for Stem in 1M H<sub>2</sub>SO<sub>4</sub>.

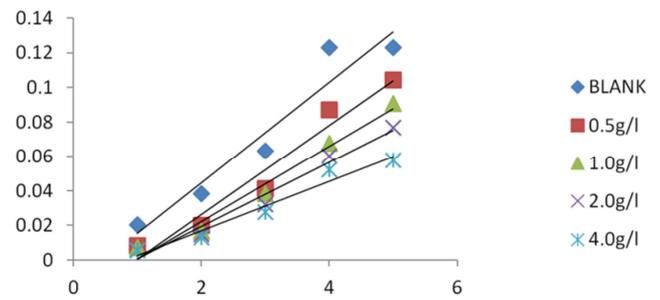


Figure 4. Plot of Log (W<sub>o</sub>/W<sub>f</sub>) against time for stem extract in 1.0M H<sub>2</sub>SO<sub>4</sub>.

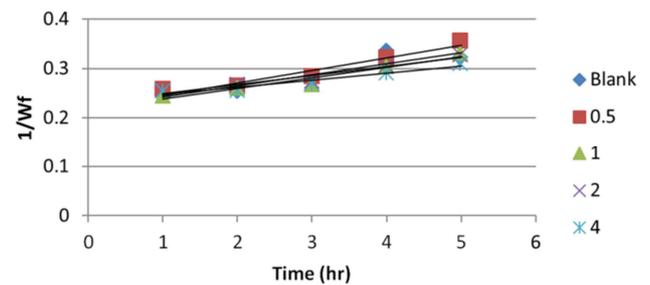


Figure 5. Plot of 1/W<sub>f</sub> against time for stem extract in 1.0M H<sub>2</sub>SO<sub>4</sub>.

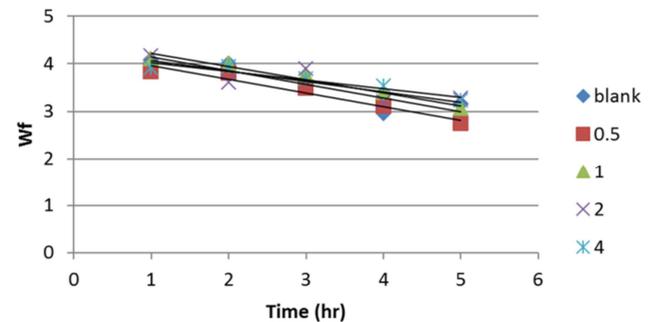


Figure 6. Plot of W<sub>f</sub> against Time for stem extract in 5.0M H<sub>2</sub>SO<sub>4</sub>.

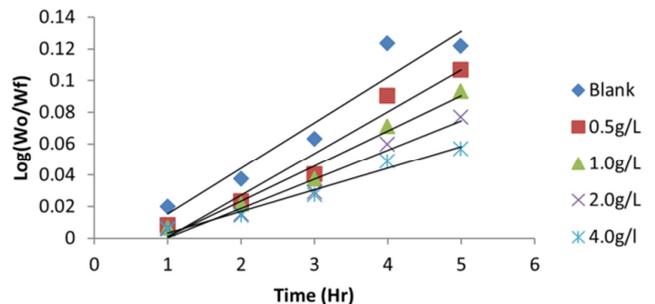


Figure 7. Plot of Log(W<sub>o</sub>/W<sub>f</sub>) against time for stem extracts in 5.0M H<sub>2</sub>SO<sub>4</sub>.

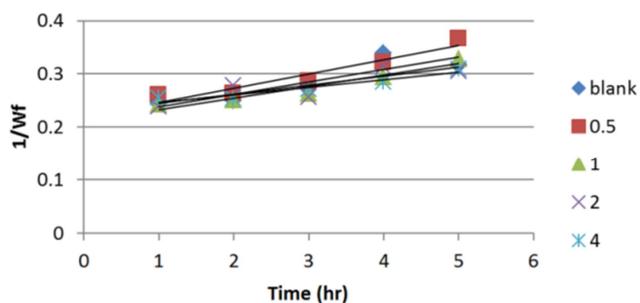


Figure 8. Plot of  $1/W_f$  against Time for stem Extract in  $5.0M H_2SO_4$ .

Table 3. Values of  $R^2$  from zero, first and second order reaction in  $5.0M H_2SO_4$ .

Stems	Zero order	First order	Second order
Blank	0.833	0.921	0.786
0.5	0.945	0.975	0.914
1.0	0.962	0.977	0.934
2.0	0.709	0.962	0.711
4.0	0.923	0.975	0.908

The values of the rate constant  $K$ , where obtained from the slope of the graph of first order reaction kinetics. From the

Table 5. Rate of Hydrogen Evolution (mL/min) and Inhibition Efficiency (%) for Mild Steel Corrosion in  $1.0M H_2SO_4$  and  $5.0M H_2SO_4$ .

Rate of Hydrogen Evolution (mL/ min)	Inhibition Efficiency (%)							
	Blank	0.5g/L	1.0g/L	4.0g/L	0.5g/L	1.0g/L	2.0g/L	4.0g/L
STEM ( $1.0M H_2SO_4$ )								
40C	2.307	1.526	1.201	0.385	33.85348938	47.94104898	78.24013871	83.31166016
50C	4.101	2.472	2.123	1.806	39.72201902	48.2321385	48.98805169	55.9619605
STEM ( $1.0M H_2SO_4$ )								
40C	3.9	1.985	1.432	0.798	49.1025641	63.28205128	71.23076923	79.53846154
50C	5.675	3.489	2.952	1.946	38.51982379	47.98237885	57.37444934	65.7092511

### 3.4. Effect of Temperature

Table 6. Calculated Values of Activation Energy ( $E_a$ ) and Heat of adsorption ( $Q_{ads}$ ) for mild steel in  $1.0M H_2SO_4$  and  $5.0M H_2SO_4$ .

	$E_a$				$Q_{ad}$				
	Blank	0.5g/L	1.0g/L	2.0g/L	4.0g/L	0.5g/L	1.0g/L	2.0g/L	4.0g/L
STEM ( $1.0M H_2SO_4$ )	48.3634	40.5529	47.8920	119.9894	129.9390	13.4395	0.5089	-39.3616	-33.4524
STEM ( $5.0M H_2SO_4$ )	31.5337	47.4145	60.8163	64.5852	74.9409	-20.4067	-23.2676	-18.1863	-16.0572

### 3.5. Thermodynamic and Adsorption Consideration

The experimental data were subjected to Langmuir Tempkin and Freundlich adsorption isotherm equations. The Langmuir Tempkin and Freundlich plots for the stem of *Tetrapleura tetraptera* in  $1.0M H_2SO_4$  and  $5.0M H_2SO_4$  are shown in Figures 9, 10, 11, 12, 13 and 14 respectively. The adsorption parameters,  $K_{ads}$ ,  $K$  and  $R^2$  are presented in Table 6.

rate constant values, the half life values  $t_{1/2}$  of the metal in the test solution were calculated using the equation (6) and all the values are shown in Table 4.

Table 4. Calculated Values of Rate constant  $K$  and Half life  $t_{1/2}$ .

	STEM ( $1.0M H_2SO_4$ )		STEM ( $5.0M H_2SO_4$ )	
	$K$	$t_{1/2}$	$K$	$t_{1/2}$
Blank	0.029	23.897	0.028	24.75
0.5g/L	0.025	27.72	0.026	26.654
1.0g/L	0.021	33	0.022	31.5
2.0g/L	0.018	38.5	0.018	38.5
4.0g/L	0.014	49.5	0.013	53.307

### 3.3. Gasometric Analysis

The volume of hydrogen evolved,  $V_H$ , during the corrosion of mild steel in  $1.0M H_2SO_4$  and  $5.0M H_2SO_4$  solutions in the absence and presence of the stem of *Tetrapleura tetrapleura* plant extracts at  $40^\circ C$  and  $50^\circ C$  was measured as a function of time.

The values of the rate of hydrogen evolution and inhibition efficiency obtained are presented in Table 5.

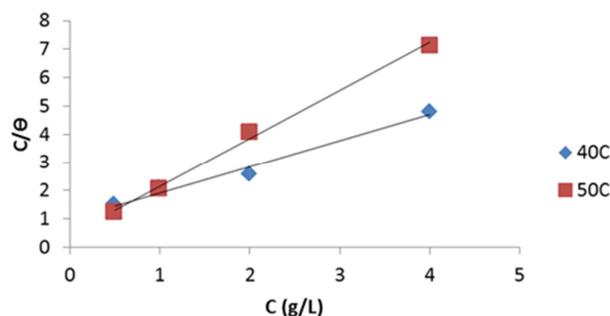


Figure 9. Langmuir plot of  $C/\Theta$  against  $C$  for stem extract in  $1M H_2SO_4$ .

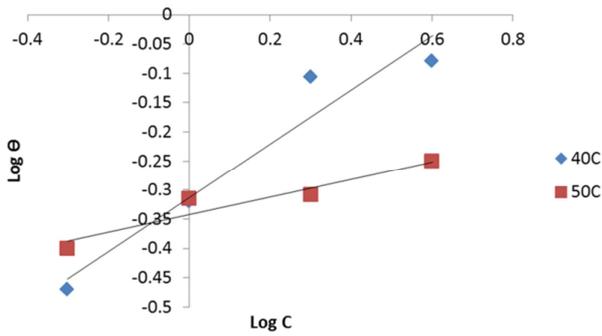


Figure 10. Freundlich Plot of  $\text{Log}\Theta$  against  $\text{Log } C$  for stem extract in  $1M \text{H}_2\text{SO}_4$ .

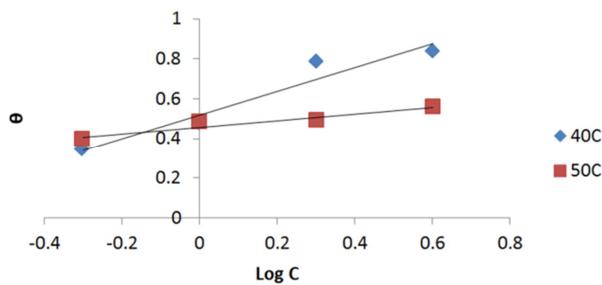


Figure 11. Temkin Plot of  $\theta$  against  $\text{Log } C$  for stems extract in  $1M \text{H}_2\text{SO}_4$ .

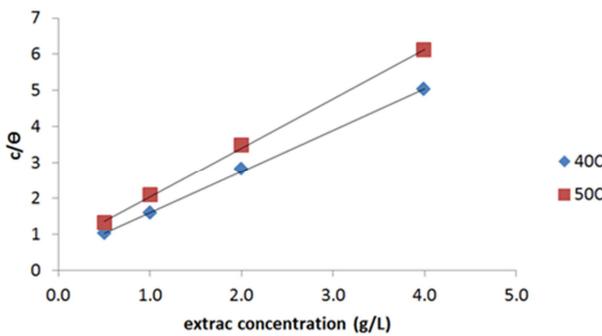


Figure 12. Langmuir plot of  $C/\Theta$  against  $C$  for stem extract in  $5M \text{H}_2\text{SO}_4$ .

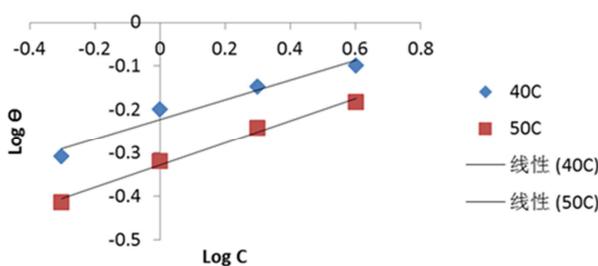


Figure 13. Freundlich plot of  $\text{Log}\Theta$  against  $\text{Log } C$  for stem extract in  $5M \text{H}_2\text{SO}_4$ .

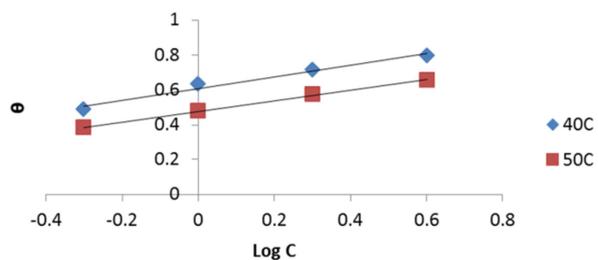


Figure 14. Temkin plot of  $\theta$  against  $\text{Log } C$  for stem extract in  $5M \text{H}_2\text{SO}_4$ .

Table 7. Langmuir, Freundlich and Tempkin Adsorption parameters for Stem Extracts for mild steel in  $1.0M \text{H}_2\text{SO}_4$  and  $5.0M \text{H}_2\text{SO}_4$ .

	STEM ( $1.0M \text{H}_2\text{SO}_4$ )		STEM ( $5.0M \text{H}_2\text{SO}_4$ )	
	Kads	R <sup>2</sup>	Kads	R <sup>2</sup>
Langmuir				
40C	1.00898	0.9806	2.197802	0.999
50C	2.12811	0.9965	1.445087	0.999
Freundlich				
40C	0.48618	0.9331	0.598963	0.954
50C	0.45436	0.9111	0.470002	0.989
Tempkin				
40C	3.303695	0.9376	4.055085	0.9786
50C	2.864178	0.9220	3.006076	0.9991

Values of adsorption equilibrium constant determined from the slope of Langmuir adsorption isotherm were used to calculate the free energies of adsorption of methanol extracts of the stem of *Tetratpleura tetraptera* in mild steel surface using the equation 13. The values are recorded in Table 8.

Table 8. Calculated values of  $\Delta G^{\circ}_{ads}$  and  $\Delta S_{ads}$  for the Stem in  $1.0M \text{H}_2\text{SO}_4$  &  $5.0M \text{H}_2\text{SO}_4$ .

	STEM ( $1.0M \text{H}_2\text{SO}_4$ )		STEM ( $5.0M \text{H}_2\text{SO}_4$ )	
	40°C	50°C	40°C	50°C
$\Delta S_{ads}$				
0.5g/L	0.075722	0.042938	-0.02607	-0.02949
1.0g/L	0.040488	0.001626	-0.03521	-0.03863
2.0g/L	-0.08689	-0.12576	-0.01898	-0.02239
4.0g/L	-0.06801	-0.10688	0.01218	-0.01559
$\Delta G$				
4.0g/L	-10.2614	-12.1639	-12.246	-11.1772

### 4. Discussion

The result in Table 1 revealed that the stem extracts contained appreciable quantities of phytochemicals (alkaloids, flavonoid, steroids, saponins, and tannins). These pyto compounds had the following functional groups: N-H, C-N, C=O, C-O, and O-H. The presence of these functional groups could be the reason for the inhibition effects and increased inhibitions efficiencies of the plant extracts.

Table 2 revealed that the corrosion rates of the mild steel decreased with increased in the concentration of the stem extracts, where the corrosion rate was 5.69 for  $1.0M \text{H}_2\text{SO}_4$  and 19.94 for  $5.0M \text{H}_2\text{SO}_4$  at the concentration of 4.0g/L. However, there was an increase in corrosion rate of the stem extract of the plant over time. Comparing the corrosion rate of the stem extracts for both concentrations of the acidic medium, it was observed that the stem extracts had the least corrosion rate of 5.69 at 5hrs for  $1.0M \text{H}_2\text{SO}_4$ , and a higher corrosion rate of 19.94 at 5hrs for  $5.0M \text{H}_2\text{SO}_4$ . These showed that the stem extracts inhibited the corrosion of the mild steel in both concentrations (1.0M and 5.0M) of  $\text{H}_2\text{SO}_4$  solutions. The stem extracts showed significant inhibition efficiency on mild steel in  $1.0M \text{H}_2\text{SO}_4$  &  $5.0M \text{H}_2\text{SO}_4$  solutions. Inhibition efficiency reached up to 79.69% for  $1.0M \text{H}_2\text{SO}_4$  and 50.39% for  $5.0M \text{H}_2\text{SO}_4$  extract concentration at 4.0g/L. From Figure 1 & 2, it is seen that

weight loss of mild steel decreased with increase in concentration of the plant extracts. The decrease is due to the inhibitive effects of the plant extracts and these effects increased with increase in the plant extracts concentration. The plots from the stem extracts revealed a linear variation, which confirmed a zero order, first order and second order reaction kinetics with respect to mild steel in 1.0M and 5.0M H<sub>2</sub>SO<sub>4</sub> solutions. However, the first order reaction gave a better correlation coefficient (R<sup>2</sup>) of the kinetics due to its values that are closer to unity as shown in Table 3. From Table 4, it was revealed that the rate constant decreased with increase in the stem extracts concentration of *Tetrapleura tetrapleura* plant for both acid concentrations. The half life in both acid concentrations medium increased with increased in concentration of the plant stem extracts. This indicated decrease in the dissolution rate of the metal in the solution with increase in the plant extracts concentration.

It was observed from table 5 that the presence of the plant stem extracts decreased the volume of hydrogen evolved as well as the rate of hydrogen evolution, and consequently, the corrosion rate of the mild steel in 1.0M H<sub>2</sub>SO<sub>4</sub> and 5.0M H<sub>2</sub>SO<sub>4</sub> solutions compared to the blank. The decrease was also dependent on the concentration of the plant stem extracts and temperature. This suggested that the phytochemical components of the plant extracts were adsorbed on the mild steel solution interface thereby reducing the surface area available for corrosion, thus inhibiting the rate of the metal dissolution process [14]. The trend in the temperature in which the inhibition efficiency decreased with increase in temperature proved that the process is efficient at a room temperature or low temperature [15]. From the rate of hydrogen evolution, the inhibition efficiencies were determined and are also presented in Table 5. It was observed that the inhibition efficiency increased relatively with increase in the concentration of the plant stems extracts and decreased relatively with increase in temperature. The maximum inhibition efficiency observed was 83.32% for 1.0M H<sub>2</sub>SO<sub>4</sub> and 79.54% for 5.0M H<sub>2</sub>SO<sub>4</sub>. These observations are indication that the stem extract inhibited corrosion of mild steel in both concentration of H<sub>2</sub>SO<sub>4</sub>, however it was more efficient at the lower concentration of 1.0M H<sub>2</sub>SO<sub>4</sub>.

The effect of temperature on the corrosion of mild steel in the absence and presence of methanol extract of the stem of *Tetrapleura tetrapleura* in 1.0M H<sub>2</sub>SO<sub>4</sub> and 5.0M H<sub>2</sub>SO<sub>4</sub> was studied using the condensed Arrhenius equation (equation 9). The values of activation energy (E<sub>a</sub>) that was calculated are recorded in Table 6. Calculated values showed there was an increase in E<sub>a</sub> with an increase in concentration of methanol extracts of the stem for both concentration of H<sub>2</sub>SO<sub>4</sub> except at 0.5g/L and 1.0g/L stem extracts concentration of 1.0M H<sub>2</sub>SO<sub>4</sub>. Analysis of the temperature dependence on inhibition efficiency as well as comparison of corrosion activation energies in the absence and presence of inhibitor gives insight into the possible mechanism of inhibition adsorption. An increase in inhibition efficiency with rise in temperature,

with analogous decrease in corrosion activation energy in the presence of inhibitor compared to its absence, is frequently interpreted as being suggestive to formation of chemically adsorption film, while a decrease in inhibition efficiency with rise in temperature, with corresponding increase in corrosion activation energy in the presence of inhibitor compared to its absence, is ascribed to physical adsorption mechanism [16]. The trend in inhibition efficiency with temperature obtained in this study therefore suggested a physical adsorption on the surface of the mild steel which was also confirmed in the activation energies, E<sub>a</sub>, that was calculated.

An estimate of the heat of adsorption (Q<sub>ads</sub>) of methanol extracts of the stem of *Tetrapleura tetrapleura* on mild steel in 1.0M H<sub>2</sub>SO<sub>4</sub> and 5.0M H<sub>2</sub>SO<sub>4</sub> was obtained from the trend of surface coverage (% I = 100 × θ) with temperature using equation 10. The values were all negative for both 1.0M H<sub>2</sub>SO<sub>4</sub> and 5.0M H<sub>2</sub>SO<sub>4</sub> indicating that the adsorption of methanol extracts of the stem of *Tetrapleura tetrapleura* plant are exothermic except also at 0.5g/L and 1.0g/L of stem extracts concentration in 1.0M H<sub>2</sub>SO<sub>4</sub> where it is endothermic (positive values). These values are approximately the enthalpy of adsorption (ΔH<sub>ads</sub>) because the reactions were carried out at constant pressure. The results are shown in Table 6.

Figures 9 – 14 showed Linear plots, indicating the adsorption of methanol extracts of the stems of *Tetrapleura tetrapleura* plant obeyed Langmuir, Freundlich and Tempkin adsorption isotherms with good correlation coefficients (R<sup>2</sup>). The results indicated that the values of ΔG<sup>o</sup><sub>ads</sub> are negative and this implied that the adsorption of methanol extracts of the stem of *Tetrapleura tetrapleura* plant in 1.0M H<sub>2</sub>SO<sub>4</sub> and 5.0M H<sub>2</sub>SO<sub>4</sub> was spontaneous suggesting a physical adsorption mechanism [17]. With ΔG<sup>o</sup><sub>ads</sub> known, the entropy of adsorption (ΔS<sub>ads</sub>) was calculated using (equation 14). The results are also presented in Table 8.

## 5. Conclusion

Methanol extracts of the stem of *Tetrapleura tetrapleura* were found to inhibit the corrosion of mild steel in 1.0M H<sub>2</sub>SO<sub>4</sub> and 5.0M H<sub>2</sub>SO<sub>4</sub> solutions. However, the inhibition in 1.0M H<sub>2</sub>SO<sub>4</sub> was more efficient than the inhibition in 5.0M H<sub>2</sub>SO<sub>4</sub>. *Tetrapleura tetrapleura* stem extracts followed the zero, first and second order reaction but first order reaction gave a better correlation coefficient (R<sup>2</sup>). The mechanism of adsorption proposed for the extracts is physical adsorption as it was evidenced from the activation parameters that the E<sub>a</sub> of the blank is lower than the E<sub>a</sub> in the presence of the stem extracts except at 0.5g/L and 1.0g/L extract concentration of 1.0M H<sub>2</sub>SO<sub>4</sub>. This was also an indication that the process was spontaneous and exothermic in both concentration of H<sub>2</sub>SO<sub>4</sub> except at 0.5g/L and 1.0g/L extract concentration of 1.0M H<sub>2</sub>SO<sub>4</sub> where it was endothermic and this may be due to experimental errors. The corrosion inhibition of the stem extracts followed Langmuir, Tempkin and Freundlich isotherm because the inhibitor acted by being adsorbed on the surface of mild steel.

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