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Phytochemical profile and corrosion inhibitive behaviour of *Culcasia scandens* leaf extract as organic inhibitor of mild steel in Trioxonitrate V acid solution

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ABSTRACT

The effect of Culcasia scandens leaf extract on the corrosion of mild steel in 2 M HNO_3 solution was studied using weight loss or gravimetric technique at 303K, 323K and 343K for 30 minutes. The Culcasia scandens leaf extract inhibited the corrosion of mild steel in 2 M HNO_3 solution. The inhibition efficiency increased with the concentration of the extract and temperature rise. The inhibition is attributed to the adsorption of the extract on the surface of the mild steel coupon. The corrosion rate, degree of surface coverage θ increased with increase in the inhibitor concentration and temperature. The increase in the degree of surface coverage with rise in temperature suggests that strong chemical bond exist between the extracts and the adsorbent. The highest degree of surface coverage was 0.9729 at 343 K and 350 g/L concentration of the adsorbate. The adsorption characteristics of the Culcasia scandens leaf extract obey Langmuir isotherm. Negative values were obtained for the free energy of adsorption (G^o_{ads}) from the isotherm parameters indicating that the inhibition is through spontaneous adsorption of inhibitors onto the metal surface supporting physical adsorption mechanism. The heat of adsorption(Q_{ads}) values were all positive implying that the accumulation of the adsorbate on the coupon surface was endothermic. The values of activation energy, E_a ranged from 3.341- 15.71 further supporting physisorption. The preliminary phytochemical screening, FTIR of the Culcasia scandens leaf extract was carried out to determine the phytoconstiuents and the functional groups responsible for the inhibition of mild steel.

Key words: Weight Loss, Adsorption, Langmuir isotherm, Mild steel, Corrosion inhibition

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INTRODUCTION

Plant extracts constitute several organic compounds which have corrosion inhibiting abilities [10].Naturally occurring substances have continued to receive attention as they are good inhibitors of acid cleaning processes and replace the synthetic organic inhibitors which are sometimes toxic to the environment [15, 9]. The growing interest on naturally occurring substances as inhibitors is attributed to the fact that they are cheap, readily available, non-toxic, renewable and ecologically friendly due to more stringent environment quality requirements[1, 5]. Mild steel being the important alloy of iron has found a wide application in industries, constructional materials and machines due to its low cost and excellent mechanical properties despite of its tendency to corrosion in aqueous solution, especially in acidic media [6]. Since corrosion is always a function of the acidic medium and the environmental

conditions, control should be concentrated on preventing contact of the surroundings with the metals. This led to the use of corrosion inhibitors in the control metal corrosion [16]. Corrosion inhibitors are chemical compounds either synthetic or natural usually used in small concentration which, when added to a corrosive media retards the corrosion process and keeps its rate to a minimum. Several heterocyclic organic compounds have been reported as corrosion inhibitors. This inhibition property is attributed to heteroatoms like nitrogen, oxygen, sulphur and phosphorus, π electrons in triple or conjugated double bonds which possess the ability to act as corrosion inhibitor as they are easily adsorbed onto the surface of the metal. The adsorption of the inhibitor onto the metal surface proceeds through charge transfer from the charged inhibitor's molecule to the charged metal physical adsorption or by electron transfer from the inhibitor's molecule to the metal chemical adsorption [7]. Inhibitors, which reduce corrosion on metallic materials, can be divided into three kinds: (i) inorganic inhibitors, (ii) organic inhibitors and (iii) mixed material inhibitors [4]. Corrosion inhibitors generally control corrosion by forming various types of films that modify the environment's corrosivity at the metal surface. Inhibitors form films in several ways: by adsorption, the formation of bulky precipitates, and/or the formation of a passive layer on the metal surface [13]. Inhibition efficiency of these films depends on various factors including but not limited to corrosivity of the environment, concentration of the active inhibitor molecules, any synergetic effects with other molecules present in the environment and/or flow/shear effects [13]. The aim of this study is to investigate the inhibitive effect of *Culcasia scandens* leaf extract as a green inhibitor on mild steel in 2 M trioxonitrate V acid solution.

MATERIALS AND METHODS

Preparation of Plant Extract

The sample was abundantly collected at Uyo, Akwa Ibom state, Nigeria. The leaf were washed thoroughly with running water to remove unwanted materials. Fresh leaf were cut into small pieces, dried and powdered for extraction. The extract was prepared by soaking 20 gm of powdered *Culcasia scandens* leaf in 2M HNO_3acid for 24 hours at room temperature and kept overnight for cooling. The cooled extract was filtered and made up to 500ml with 2M HNO_3acid to get 5%v/v extract of the inhibitor. Different concentrations of the inhibitor were prepared from the filtrate and the corrosive environment in the range 100, 150, 200, 250, 300 and 350 g/L.

Mild Steel Preparation

Materials used for the study were mild steel sheet of composition (wt %); Mn (0.6), P (0.36),C(0.15) and Si (0.03) and the rest Fe. The mild steel of thickness 0.1 cm used for this study was purchase at Port-Harcourt. It was mechanically press-cut into 5 x 3 cm coupons. These coupons were used as supplied, without further polishing. Prior to the experimental work, the already prepared coupons were stored in moisture free desiccators to prevent contamination.

Phytochemical profile

Phytochemical screening was carried out on the extracts of *Culcasia scandens* leaf by the methods described by [12, 14]. The plant extract was screened for saponins, steroid, flavonoid, tannins, glycoside and alkaloid.

Fourier Transformation Infrared (FTIR) spectroscopy

Fourier Transformation Infrared (FTIR) spectroscopy of the extract was also carried out to determine the functional groups which are responsible for the activity of the extract as an inhibitor. FTIR spectra were recorded in a Perkin – Elmer 1600spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made into pellets. The analysis was done by scanning the sample through a wave number range of 400 to 4000 cm^{-1}.

Weight loss or Gravimetric technique

The previously weighed coupons were immersed in 250 ml beaker containing 240 ml of 2.0 M HNO_3 solution of different concentration with and without the inhibitor (0, 100, 150, 200, 250, 300 and 350 g/L) for 30 minutes at temperatures of 303K, 323K and 343K.The temperature was controlled by an aqueous thermostat. The specimens were carefully washed in double-distilled water, dried and then weighed after the immersion test. Duplicate experiments were performed in each set of the test and the mean value of the weight loss is reported. The corrosion rate (ρ) in $gcm^{-2}h^{-1}$ in the absence and presence of extract was determined using the equation (1)

$$CR = \frac{Wi - W_f}{A \times t} \quad (g/cm^2\ hr) \quad \ldots\ldots\ldots\ldots\ldots\ldots 1$$

Where w_i and w_f are the initial and final weight respectively, A is the surface area (cm^2) of the coupon and t is the exposure time (hours). From the corrosion rate, the surface coverage (θ) as a result of adsorption of inhibitor molecules, and percentage inhibition efficiencies of the molecules (η%) were determined using equations (2) and(3), respectively.

$$\theta = \frac{CR_{blank} - CR_{inh}}{CR_{blank}} \quad \text{..... 2}$$

$$\eta\% = \left[\frac{CR_{blank} - CR_{inh}}{CR_{blank}}\right] X \ 100 \quad \text{..... 3}$$

Where CR_{blank} and CR_{inh} are the corrosion rate in the absence and presence of the inhibiting extract respectively

RESULTS AND DISCUSSION

Weight loss measurements

From table 1the weight lose measurement, corrosion rate, surface coverage and inhibition efficiency in 2 M $HNO_3$of *Culcasia scandens* leaf extract was evaluated at various concentrations after 30 minutes of immersion at the temperatures of 303K, 323K and 343K**.** Fig.1indicates the variation in weight loss of the mild steel in the absence and presence of inhibitor. It is evident that the weight loss of mild steel for blank solution is much higher than that obtained for solution containing different concentrations of *Culcasia scandens* extract. Weights lose decreases with increasing concentration of inhibitor. This indicates that the availability of the inhibitor showed significant impact on the corrosion rate of mild steel in 2 M HNO_3.

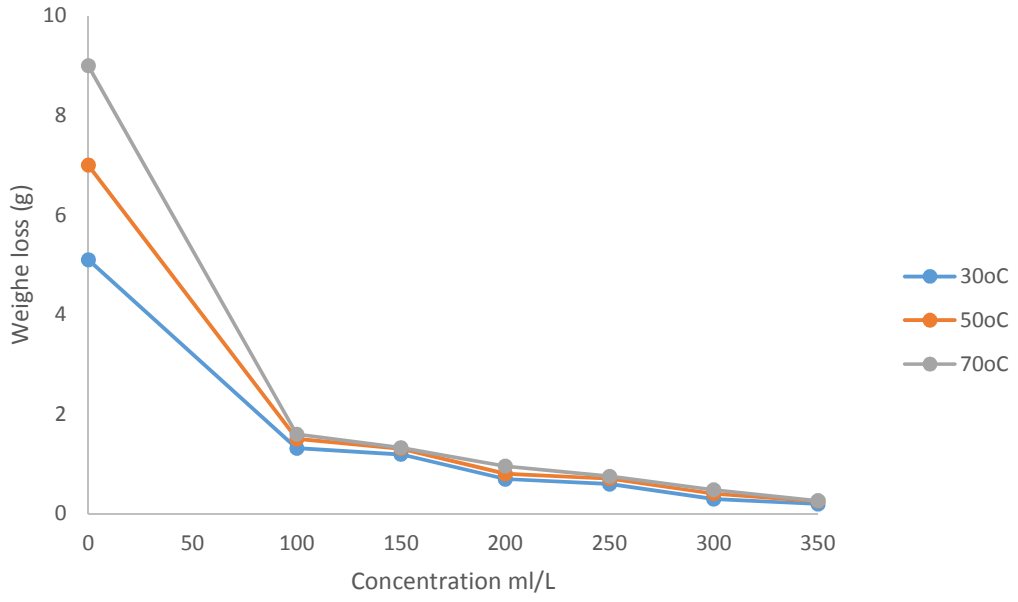

Figure 1. Plot of weight loss against inhibitor concentration for mild steel corrosion in 2 M HNO_3 of *Culcasia scandens* leaf extract at different temperatures

The surface coverage and inhibition efficiency were also evaluated from the weight loss data according to the equations 2 and 3 respectively. Figure 2shows the inhibition efficiency in different concentrations of the *Culcasia scandens* leaf extract. It can be observed that the inhibition efficiency indicates a linear relation with increase in the concentration of extract.

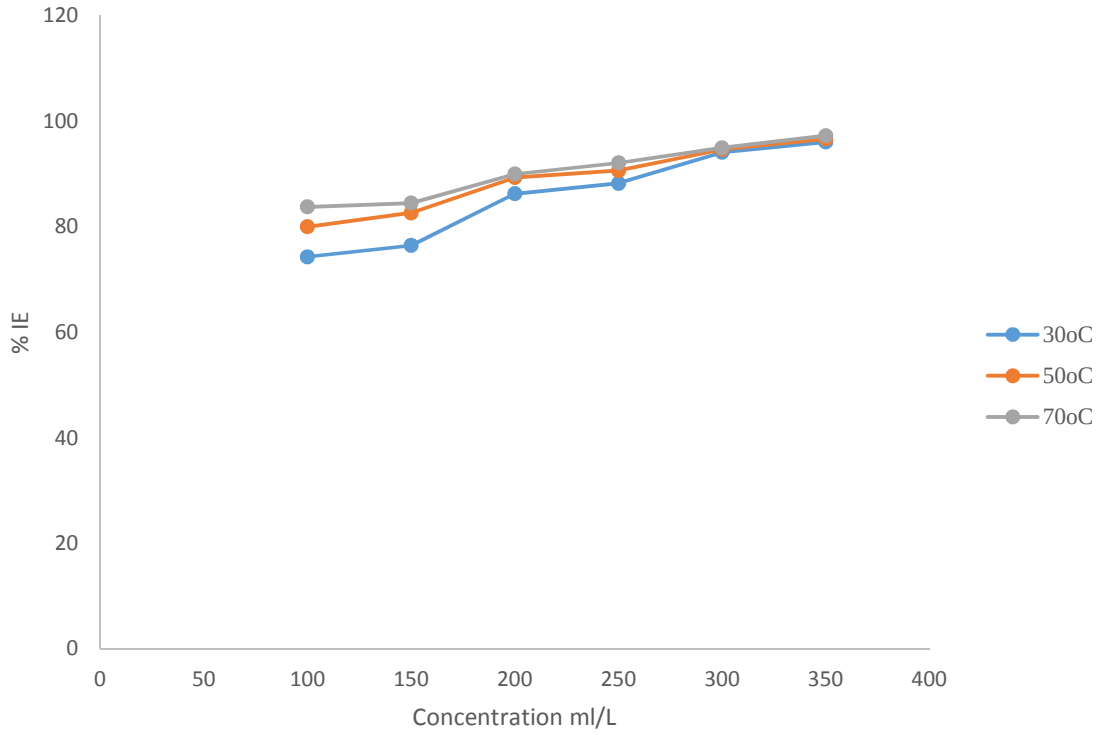

Figure 2. Plot of inhibition efficiency in different concentrations of the *Culcasia scandens* leaf extract at different temperatures

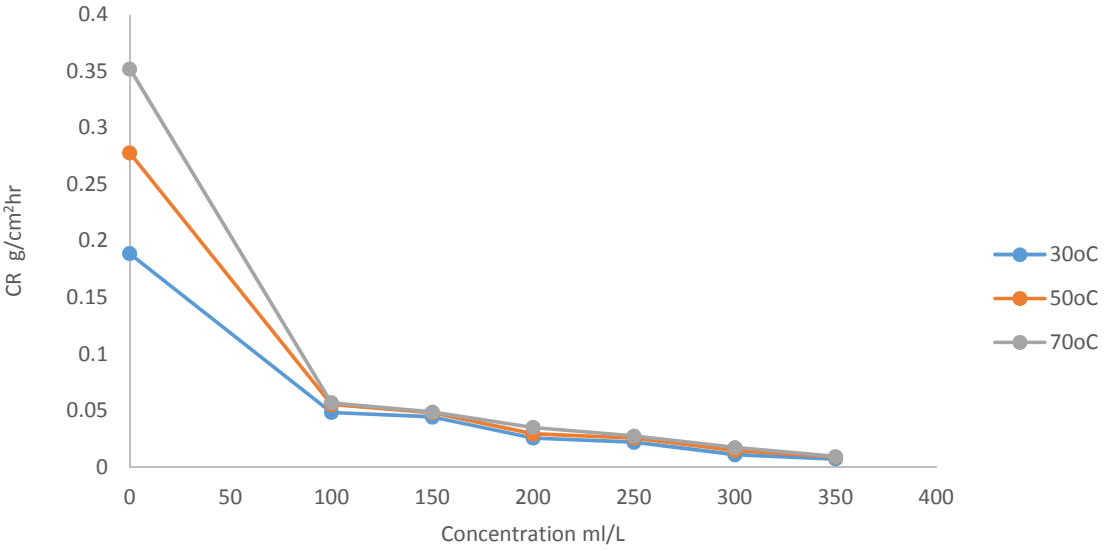

Figure 3. Plot of corrosion rate in different concentrations of the *Culcasia scandens* leaf extract at different temperatures

The corrosion rate decreased as the inhibitor concentration increased. The decrease in corrosion rate was significant when small concentrations 100, 150, 200, 250, 300 and 350 ml/L were introduced. This behavior is attributed to higher adsorption level of active inhibitor molecules from the extract on the metal surface. The maximum value of inhibition efficiency of 96.08%, 96.67% and 97.29% were obtained at 303K, 323K and 343K respectively. The

adsorption of the inhibitor is influenced by the nature and charge of the metal, the chemical structure of the inhibitor and distribution of the charge in the extract.

Table 1. Weight loss, corrosion rates, surface coverage and percentage inhibition efficiency of different concentrations of *Culcasia scandens* leaf extract for corrosion of mild steel in 2 M HNO_3 solution at various temperatures

Temp(K)	Conc. g/L	Weight loss	Corrosion rate	Surface coverage	Inhibition efficiency
303K	2 M HNO_3	5.100	0.1888	-	-
	100	1.310	0.0485	0.7431	74.31
	150	1.190	0.0444	0.7648	76.48
	200	0.690	0.0259	0.8628	86.28
	250	0.590	0.0222	0.8824	88.24
	300	0.290	0.0111	0.9412	94.12
	350	0.190	0.0074	0.9608	96.08
323K	2 M HNO_3	7.00	0.2778	-	-
	100	1.499	0.0555	0.8002	80.02
	150	1.301	0.0482	0.8265	82.65
	200	0.797	0.0296	0.8934	89.34
	250	0.699	0.0259	0.9068	90.68
	300	0.399	0.0148	0.9467	94.67
	350	0.249	0.0092	0.9667	96.67
343K	2 M HNO_3	9.0000	0.3519	-	-
	100	1.5930	0.0570	0.8380	83.80
	150	1.3203	0.0489	0.8450	84.50
	200	0.9504	0.0352	0.9000	90.00
	250	0.7478	0.0277	0.9213	92.13
	300	0.4750	0.0175	0.9500	95.00
	350	0.2565	0.0095	0.9729	97.29

Adsorption isotherm

The nature of inhibitors interaction on the corroding surface during corrosion inhibition of metals has been deduced in terms of adsorption characteristics of the inhibitor. The decrease in the corrosion rate by the addition of 2 M HNO_3extract of *Culcasia scandens* leaf is attributed to either adsorption of the plant components on the metal surface or the formation of a barrier film separating the metal surface from the corrosive medium[2]. This is usually confirmed from the fit of the experimental data to various adsorption isotherms. The adsorption process is influenced by the nature and surface charge of the metal and the chemical structure of the inhibitors[11].Adsorption isotherms provide information about the interaction among adsorbed extract themselves as well as their interactions with the metal surface. The surface coverage values were fitted to Langmuir adsorption isotherm model and best results judged by the correlation coefficient (R^2) was obtained with Langmuir adsorption isotherm. Langmuir isotherm is given by the expression:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad \text{.....4}$$

Where θ is the surface coverage, C is the concentration, K_{ads} is the equilibrium constant of adsorption process.

The plot of C/θ against C shown in Figure 4indicate a linear plots which shows a very good correlation coefficient with Langmuir adsorption isotherm. The R^2values and slope are very close to unity, indicating strong adherence to Langmuir adsorption isotherm. The application of Langmuir isotherm to the adsorption of extract of *Culcasia scandens* leaf on the surface of mild steel indicates that there is no interaction between the adsorbate and adsorbent. The K_{ads} values were obtained from the intercept lines on the C/θ-axis. This is related to the standard free energy of adsorption ($\Delta G°_{ads}$) with the equation (5)

$$\Delta G°_{ads} = -RTln(55.5\ K_{ads}) \text{.....5}$$

Where R is the gas constant and T is the absolute temperature. The constant value of 55.5 is the concentration of water in solution in mol/dm^3. The standard free energy of adsorption, $\Delta G°_{ads}$, which can characterize the interaction of adsorption molecules and metal surface, was calculated using equation 5. The result shows that $\Delta G°_{ads}$ values are negative less than threshold values of -40kJ/mol required for chemisorption. Therefore the adsorption of 2 M

HNO_3extract of *Culcasia scandens* leaf on the surface of mild steel is spontaneous and strongly correlate with the mechanism of physisorption [3, 8].

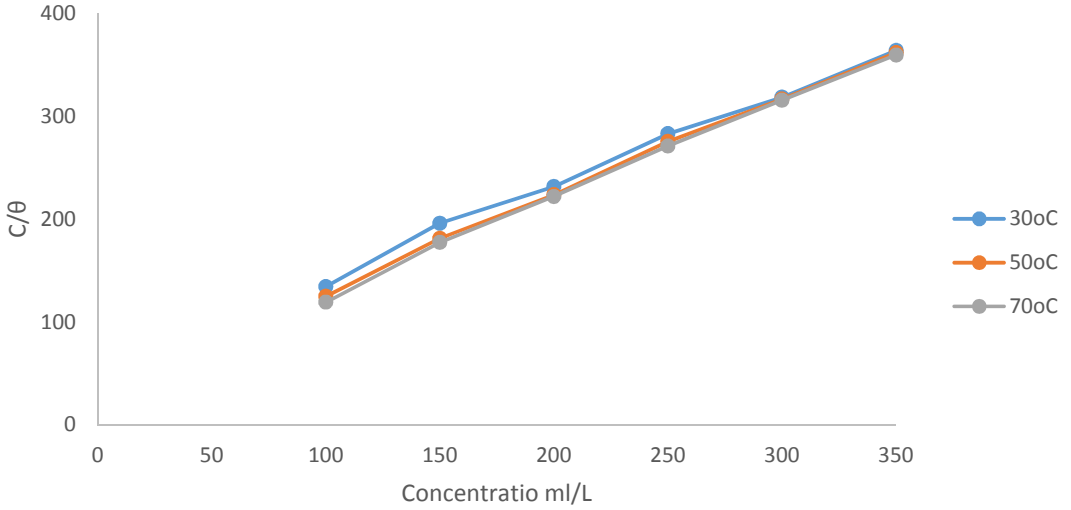

Figure 4. Plot of surface coverage against concentrations of inhibitors in 2.0 M HNO_3 on mild steel surface at different temperatures

Table 2: Correlation coefficient deduce from Langmuir isotherm of mild steel in 2.0 M HNO_3 in the presence of *Culcasia scandens* leaves extract at different temperatures.

Temperature	R^2	Slope	$\Delta G°_{ads}$
303K	0.9944	0.9661	-10.10
323K	0.9980	0.9611	-10.68
343K	0.9979	0.9569	-11.33

The activation energy (E_a) of the corrosion process in the absence and presence of inhibitor were also evaluated using Arrhenius equation for the three temperatures using equation 6 and 7 respectively

$$\text{Log}\ \frac{CR_2}{CR_1} = \frac{Ea}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \quad \text{..... (6)}$$

$$\text{Log}\ \frac{CR_3}{CR_2} = \frac{Ea}{2.303\ R}\left[\frac{1}{T_2} - \frac{1}{T_3}\right] \quad \text{..... (7)}$$

Where CR_1 and $CR_2$are the corrosion rate at temperature T_1(303 K) and T_2 (323 K) while CR_2 and CR_3 are the corrosion rate at temperature T_2 (323 K) and T_3 (343 K) respectively. R is the gas constant. Calculated values of activation energy using equation 6 and 7 are presented in table 3. Since the calculated values of activation energy (E_a) are lower than the threshold values of 80 KJ/mol needed for chemisorption, hence the adsorption of 2 M HNO_3extract of *Culcasia scandens* leaves on the surface of mild steel occur by physisorption mechanism. The heat of adsorption (Q_{ads}) of 2 M HNO_3extract of *Culcasia scandens* leaves on the surface of mild steel were also evaluated using equation 8 and 9

$$Qads = 2.303\ R \left[Log \frac{\theta_2}{1-\theta_2} - Log \frac{\theta_1}{1-\theta_1} \right] x \frac{T_1T_2}{T_2-T_1} \quad .....8$$

$$Qads = 2.303\ R \left[Log \frac{\theta_3}{1-\theta_3} - Log \frac{\theta_2}{1-\theta_2} \right] x \frac{T_2T_3}{T_3-T_2} \quad .....9$$

Where R is the gas constant, θ_1 and θ_2 are the degree of surface coverage of the inhibitor at temperatures T_1(303 K) and T_2 (323 K) while θ_2 and θ_3 are the degree of surface coverage of the inhibitor at temperatures T_2 (323 K) and T_3 (343 K) respectively. Calculated values of Q_{ads} are presented in table 3. The values ranges from 115.779 to 6.88475 and 3.108 to 11.784 for the adsorption of 2 M HNO_3extract of *Culcasia scandens* leaf indicating that the adsorption on the surface of mild steel is endothermic.

Table 3: Thermodynamics parameters of corrosion inhibition of mild steel in 2.0 M HNO_3 in the presence and absence of *Culcasia scandens* leaf extract at different temperatures

Extract conc.	E_a(kJ/mol)	E_a(kJ/mol)	Q_{ads} (kJ/mol)	Q_{ads} (kJ/mol)
Blank	15.71	10.891	-	-
100	5.486	1.228	115.779	8.517
150	3.341	0.664	15.5535	3.108
200	5.434	8.137	10.0545	9.864
250	6.273	3.095	10.6391	11.784
300	11.706	7.719	4.23504	6.215
350	8.859	1.478	6.88475	3.277

FT-IR Technique

The FT-IR spectrum of the acid extract is shown in Figures 5. Inspection of the spectrum shows a broad peak due to hydrogen bonding at 3426.53 cm^{-1}which is attributed to polymeric O-H group. The frequency at 2844.8and 2922.5 cm^{-1}shows a strong correlation with C-H stretching absorption of sp^3 carbon (alkane). The peak at 1642.79 $cm^{-1}$is assigned to C=O, C=C or N-H stretching which may be overlap due to close proximity in their frequency of absorption. The presence of the C-H bending frequency is noted at 1408 cm^{-1}.

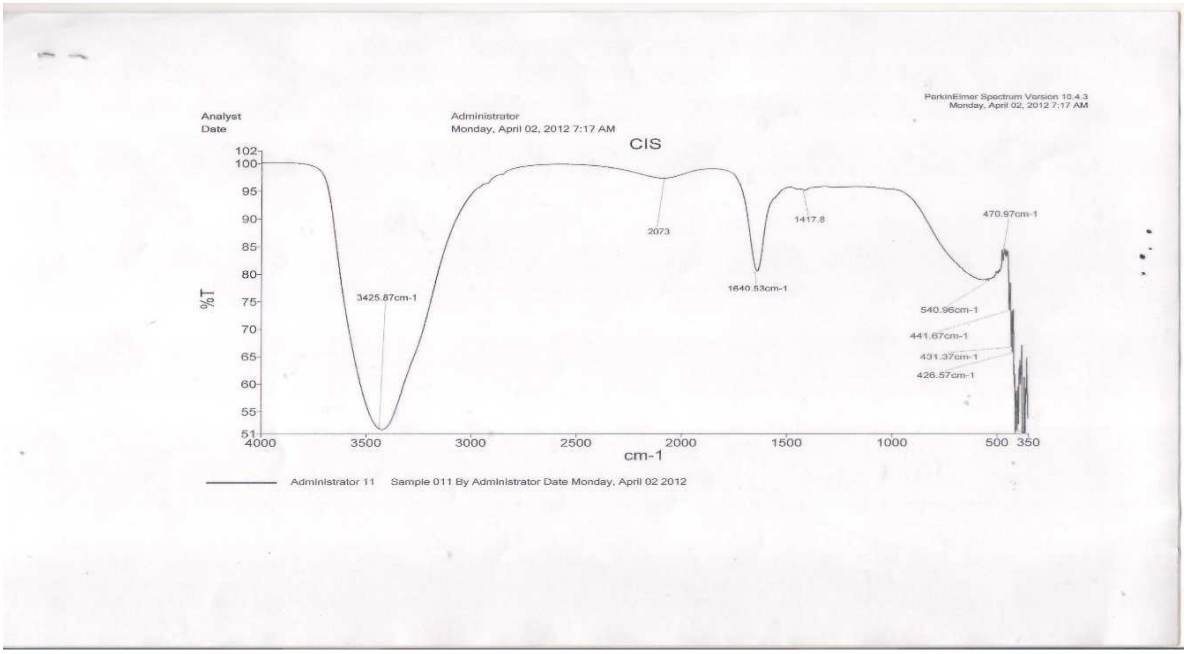

Figure 5: FT-IR spectrum of *Culcasia scandens* leaf extract

The phytochemical constituents of *Culcasia scandens* leaf extract

Plant materials are organic in nature. They contain constituents such as tannins, organic and amino acids, alkaloids and pigments that are known to exhibit inhibiting action [15]. Preliminary phytochemical investigation showed that the adsorption of these extract onto metal surface is responsible for corrosion inhibition effect and hence difficult to assign the inhibitive effect to a particular constituent. Difference in the inhibition efficiency of the inhibitors can be attributed to the variations of these phytochemicals or secondary metabolites among the inhibitors.

Constituents	Value
Saponins	++
Steroid	+++
Flavonoid	+++
Tannins	+++
Glycoside	++
Alkaloid	+
Terpens	+++

Key: +++ Abundantly present
++ Moderately present
+ Present in trace quantity

CONCLUSION

The gravimetric techniques shows that weights loss decreases with increasing concentration of inhibitor, inhibition efficiency indicates a linear relation with increase in the concentration of extract and corrosion rate decreased as the inhibitor concentration increased. Adsorption of inhibitor extract on the mild steel surface indicate a strong relationship with Langmuir adsorption isotherm at all tested temperatures.

Thermodynamic adsorption parameters such as ΔG^{o}_{ads}, E_a and Q_{ads} show that the inhibitors adsorption is spontaneous, endothermic process and strongly correlate with physisorption process. The phytochemical constituents, FTIR spectra clearly reveal the phytochemical constituents and the functional groups are adsorbed on the mild steel surface there by aiding the corrosion inhibition. *Culcasia scandens* leaf are excellent, green, eco–friendly and very cheap corrosion inhibitors for mild steel in 2 M HNO_3 solution. It can be used to replace toxic and highly cost inhibitors.

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