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INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY
GREWIA TILIAEFOLIA BARK EXTRACT AS GREEN INHIBITOR OF MILD STEEL CORROSION IN SULPHURIC ACID MEDIUM

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ABSTRACT
This paper presents the inhibitory properties of *Grewia tiliaefolia* bark extract on the corrosion of mild steel in sulphuric acid medium. The corrosion rates and inhibition efficiencies were evaluated   by weight loss measurements. The adsorption of inhibitor obeyed Langmuir isotherm and the negative values of Gibbs energy indicate the nature of interactions between inhibitor molecules and metal surface. Further, the inhibition effect was proved by FTIR spectroscopy, scanning electron microscopy and energy dispersive X-ray analysis.

KEYWORDS: Mild steel, corrosion, inhibition,adsorption,kinetics, *Grewia tiliaefolia*.

INTRODUCTION

The importance of mild steel corrosion mechanism in sulphuric acid media is interesting to researchers because this phenomenon is in particular for all industries. Most industries used sulphuric acid as a reagent for acid pickling, acid cleaning, and acid descaling. To remove unwanted scale such as rust or mill scale formed during manufacture/at different environmental conditions, ferrous materials are immersed in acidic solutions. In order to decrease the dissolution rate of metallic materials, usually inhibitors are used. A vast category of organic corrosion inhibitors is used for iron and ferrous alloys in sulphuric acid solutions [1-3].

The compounds containing nitrogen, oxygen and/or sulphur have been considered as corrosion inhibitors and have shown outstanding performance [4-6]. However, the environmental impact of these inhibitors has been studied in the recent decades due to their toxic effects on aquatic and possibly animal life [7]. At present, research is focusing on producing and testing environmentally welcoming corrosion inhibitors [8]. Few studies report the use of natural products as corrosion inhibitors [9, 10].

Grewia tiliaefolia **Vahl** is belonging to the family of tileaceae. It is a moderate sized tree; its barks are greyish black or brown thick. The pharmacological

was 0.25 to 0.5 volume % and for adsorption studyused 0.05 to 0.5 % extract.The experiments were carried out by MS with the following composition (in weight percentage)   C=0.091;

properties of *Grewia tiliaefolia* were well documented [11-13]. Its bark is used externally to remove the irritation from cow-itch and to treat throat complaints, biliousness, cough and diseases of the blood. It is an antidote to opium poison [11]. Researchers isolated three triterpenoids from this plant [14-16]. In the present work, the practicability of using extract of *Grewia tiliaefolia* bark (GTB) , as a non-toxic inhibitor for the inhibition of the corrosion of mild steel (MS) in 0.5M H_2SO_4 was examined.

MATERIALS AND METHODS
MATERIALS PREPARATION: The aggressive solution of 0.5 M H_2SO_4 was made up using concentrated H_2SO_4 (MERCK) and distilled water. Bark of *Grewia tiliaefolia* were collected from a moist deciduous forest of *Anangan malai,* which is a part of Western Ghats, in the northern end of Palakkad district, Kerala, India, cut in to small pieces, air dried and powered. The extracts was prepared by refluxing 25 g of powdered bark in 0.5 M H_2SO_4 for 3 h and kept overnight for cooling. The cooled extract was filtered and made up to 500ml to get 5 % v/v concentration. The desired concentrations of the inhibitor were prepared by diluting the above stock solution with distilled water. The concentration range of GTB used for weight loss and kinetic study

Si=0.016; Mn=0.195; S=0.013; P=0.020; Ni=0.018; Mo=0.020; Cr=0.027 and Fe=99.6. The specimens were mechanically polished; their edges were abraded with fine grade emery papers (NO 400),

degreased, rinsed with acetone, stored in desiccator and used for all studies. Mild steel coupons were weighed in a SHIMADZU Digital balance with an accuracy of 0.00001 g and then exposed to the selected aggressive media.

WEIGHT LOSS TEST: Mild steel specimens were sheared from commercially available cold rolled MS sheet into 5 x 1 cm^2 coupons for immersion studies. In each experiment, samples were immersed in 100 ml of solution (with and without inhibitor) for a predetermined time period viz., ½ h, 1 h, 3 h, 6 h, 12 h and 24 h. The specimens were taken out, neutralized with saturated sodium bicarbonate solution, washed with distilled water, dried and reweighed. The resulted weight loss of the triplicates were averaged and used for further calculations.

The experiments were also performed with different concentrations of inhibitor for predetermined time periods and at various temperatures. The higher temperature studies were performed for the temperature range 303 – 353 K, after half an hour exposure. The data obtained in the higher temperature studies were used to evaluate activation parameters of metal corrosion in the absence and presence of inhibitor and the adsorptive nature of inhibitor on metal surface.

FTIR SPECTRA ANALYSIS: Fourier Transform Infrared (FTIR) spectra were recorded using Perkin Elmer FTIR spectrophotometer. To verify the adsorption of corrosion inhibitor on the mild steel surface, the film formed on the metal surface after 3 h was carefully removed, dried and mixed thoroughly with potassium bromide. The mixture was ground in to disks using a hydraulic press. The pellets were subjected to FTIR analysis to determine the protective film formed on the surface of the metal coupons which extended from 4000 and 400 cm^{-1}. In addition, the spectra of crude extract of GTB also characterized by FTIR.

SURFACE ANALYSIS: To monitor the surface morphology of the sample, Scanning Electron Microscopic and Energy Dispersive X-ray Spectroscopic methods were carried out. The images of samples in the presence and absence of inhibitor were recorded. The specimen size of 1x1 cm^2 were exposed in 0.5 M H_2SO_4 containing 0.5% of GTB for 3 h at 25 °C and washed with distilled water. After washing, specimens were dried and examined using JEOL Model JED-2300 dispersive spectrometer and JEOL JSM-6390LV energy electron microscope.

RESULTS AND DISCUSSION

WEIGHT LOSS TECHNIQUE: Weight loss method is the simplest, reliable well established and widely used technique to estimate corrosion losses. This method was adopted following the ASTM G 31 procedure to determine the inhibition efficiency of GTB extract. The corrosion rate (CR) and inhibition efficiency (IE) were obtained using the following equations:

$$CR(mpy) = 534\, W/DAT \qquad (1)$$
$$IE(\%) = \left(\frac{w_0 - w}{w_0}\right) x\, 100 \qquad (2)$$

where, w is the weight loss in g, D is the density of mild steel in gm / cm^2 (7.9 gm / cm^2), A is the area of the specimen in cm^2, T is the exposure time in hours, W_0 is the weight loss without inhibitor and W is the weight loss with inhibitor respectively.

Effect of Concentration of GTB on MS Corrosion in 0.5 M H_2SO_4: The effect of different concentrations of GTB extract on corrosion rates in acid solution up to 24 h exposure were given in Table 1. The plant extract was seen to reduce the corrosion rate at all studied concentrations indicating inhibition of the corrosion reaction. The effect becomes more pronounced with increasing extract concentration which suggested that the corrosion process was sensitive to the amount of extract added.

The effectiveness of the extract was expressed in terms of inhibition efficiency (IE). Table 1 illustrates the variation of IE with extract concentration at 0.5 M H_2SO_4 at 303 K and it clearly showed that IE increases with increase in concentration of the extract. Maximum IE of 70.26 % was achieved at 0.5 % concentration at 3 h of immersion. The adsorption of phyto constituents [13-15] present in *Grewia tiliaefolia* on the metal surface makes a barrier for metal dissolution. This leads to a protection of the metal surface from the attack of the acid. The increase in IE with increase in extract concentration was due to the adsorption of the components present in the extract over the mild steel surface, blocking the active sites, in which direct acid attack proceeds and protected the metal from corrosion.

Table 1: Role of immersion time on CR and IE of GTB extract

Conc. (v/v %)	1/2 h		1 h		3 h		6 h		12 h		24 h	
	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
0	2981		3200		3308		3575		2859		1974	
0.25	1886	36.75	1435	55.20	1392	57.91	1783	50.12	1625	43.15	1193	39.54
0.3	1870	37.27	1421	55.60	1352	59.12	1700	52.46	1518	46.91	1119	43.33
0.35	1537	48.43	1248	61.00	1269	61.64	1640	54.12	1517	46.94	1058	46.39
0.4	1351	54.67	1119	65.00	1206	63.56	1527	57.28	1449	49.33	1073	45.63
0.45	1302	56.34	1111	65.30	1039	68.60	1466	59.00	1374	51.93	1020	48.32
0.5	1148	61.49	1043	67.40	984	70.26	1400	60.85	1358	52.52	977	50.50

Effect of Immersion Time on MS Corrosion in 0.5 M H_2SO_4: The results of immersion study at various intervals obtained were presented in Figure 1. It observed from the plot that corrosion rate decreased with an increase in the immersion time up to 3 h and had a hike at 6 h, then continuously decreased till 24 h.
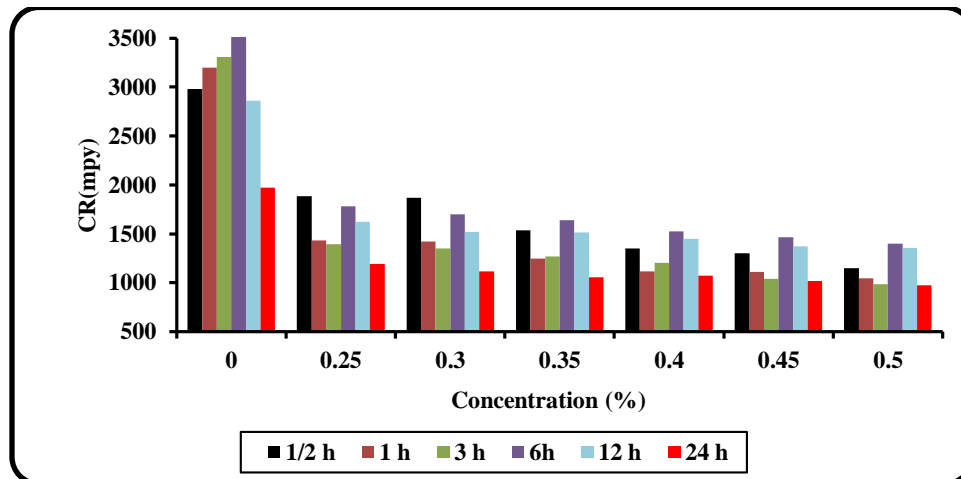

Figure 1: Variation of corrosion rate with exposure time for MS corrosion with varying concentrations of GTB

Effect of Temperature on MS Corrosion Inhibition: To evaluate the stability of adsorbed layer / film of inhibitor on MS surface as well as activation parameters of the corrosion process of steel in acidic medium, weight loss measurements were carried out in the absence and presence of different concentrations of the extract at 1/2 h immersion time. Table 2 showed that the rates of MS corrosion in free and inhibited solutions, increased with increasing temperature. The corrosion rate in inhibited solution was more affected than that in free acid solution.

Consequently the IE of the extract decreased with increasing temperature. This was due to increased rate of dissolution process of mild steel and partial desorption of the inhibitor from the metal surface with temperature. The decrease in inhibition efficiency with temperature rise was suggestive of electrostatic interaction (physical adsorption) of the phytoconstituents of the extract on mild steel surface[17].

Table 2: Outcome of weight loss measurements for MS corrosion in 0.5 M H₂SO₄ in the absence and presence of different concentrations of GTB extract

Conc. (v/v %)	303 K		313 K		323 K		333 K		343 K		353 K	
	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)	CR (mpy)	IE (%)
0.00	2981	-	8178	-	11995	-	23488	-	32054	-	45694	-
0.25	1886	36.75	5272	35.53	8511	29.05	16818	28.40	23681	26.12	33012	27.75
0.30	1870	37.27	4707	42.43	7993	33.36	15993	31.91	23207	27.60	31891	30.21
0.35	1537	48.43	4550	44.36	7334	38.86	14852	36.77	21249	33.71	29460	35.53
0.40	1351	54.67	4386	46.37	6889	42.57	13864	40.97	20725	35.34	27331	40.19
0.45	1302	56.34	3050	51.23	6493	45.87	13524	42.42	19459	39.29	26490	42.03
0.50	1148	61.49	2701	56.82	5995	50.02	13269	43.51	18602	41.97	25530	44.13

Oguzie *et al.*, reported that the physisorption process may hindered by the enhanced rate of hydrogen gas evolution of higher temperatures which increasingly agitates the interface and also promotes dispersal of the adsorbed inhibitor [18]. Accordingly an increase in the temperature was accompanied by the desorption of GTB constituents that are physisorbed on the metal surface due to the decrease in the strength of the adsorption process at higher temperature that leads the reduction of surface coverage and hence lower inhibition efficiency[19].

Kinetic Parameters of Corrosion: The activation energies of corrosion process in free and extract containing acid at various temperature was determined by Arrhenious plots, log CR vs 1/T .

$$log(CR) = logA - \frac{Ea}{2.303RT} \qquad (3)$$

where A is the frequency factor, E_a is the activation energy of corrosion process, R is molar gas constant and T is the temperature. From the slope of the plot, the activation energy (E_a) was calculated by using the following formula,

 Ea =- 2.303 x R x slope of the plot   (4)

Arrhenious plots of the logaritham of corrosion rate vs 1/T for H_2SO_4 in the presence and in the absence of GTB extract was presented in Figure 2. The E_a values were determined from slopes of curve and was reported in Table 3. The calculated activation energies were 47.14 KJmol^{-1} and 49.93 to 56.56 KJmol^{-1} in the absence and presence of inhibitor in sulphuric acid medium. The higher value of E_a for inhibited solution than that of uninhibited solution suggested that dissolution of MS was slow in the presence of inhibitor.
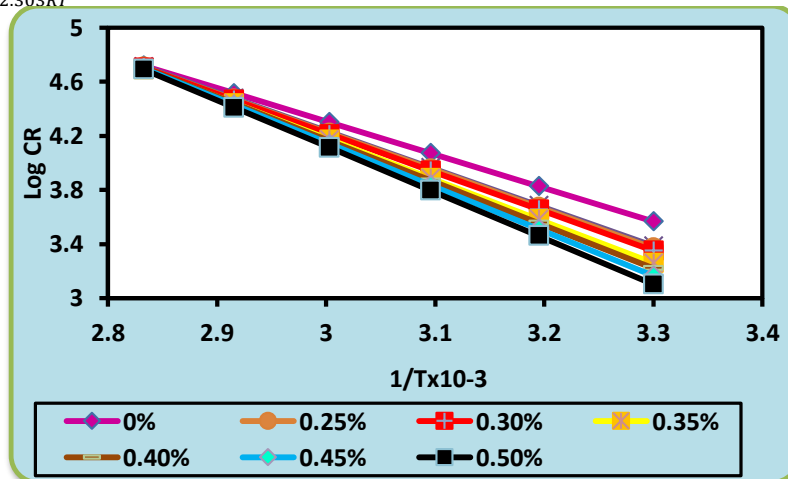

Figure 2: Arrhenious plot for the MS corrosion in 0.5 M H₂SO₄ at various concentrations of GTB

The higher activation energy in the presence of GTB in sulphuric acid media may be interpreted as physical adsorption that occurs in the first stage [20].

The value of activation energy around 40-80 kJ mol^{-1} suggested the physical adsorption mechanism [21]. Moreover the activation energy increased with

inhibitor concentration, indicating energy barrier for corrosion process increased. The increase in activation energy with inhibitor concentration is often interpreted by physical adsorption with the formation of adsorptive film of an electrostatic character [22].

Thermodynamic Parameters of Corrosion Process:
Transition state equation was used to evaluate the corrosion activation parameters, namely the enthalpyof activation (ΔH) and entropy of activation (ΔS) and was given by the expression

$$CR = \frac{RT}{Nh} exp^{\left(\frac{\Delta S^{\circ}}{R}\right)} exp^{\left(-\frac{\Delta H^{\circ}}{RT}\right)} \qquad (5)$$

where CR is the corrosion rate, h is the Plank's constant N is the Avogadro number, R is the gas constant and T is the absolute temperature. Linear plots were obtained with the slope of (-ΔH/2.303R) and an intercept of log (R/Nh+ΔS/2.303R).
The plots of log (CR/T) against (1/T), for mild steel corrosion in 0.5 M H₂SO₄ in the absence and presence of different concentrations of GTB are presented in Figure3.It was clear from the Table 3

that Eₐ and ΔH values vary in the same way. The values of ΔH were lower than that of Eₐ. The lower ΔH values compared to Eₐ had been noticed by Noor , indicate that the corrosion process must involve a gaseous reaction, simply hydrogen evolution reaction associated with decrease in total reaction volume [23]. This results permit to verify the known thermodynamic relation between Eₐ and ΔH as shown in Table 3.

$$E_a\text{-}\Delta H = RT \qquad (6)$$

It was found that for all the system the difference is 2.72 in H₂SO₄ medium. This is very close to the approximate value estimated for RT (2.69 kJmol⁻¹) where, T is the range of experimental temperatures.
Positive enthalpies reflected the endothermic nature of the steel dissolution process and means that dissolution of steel was difficult [24]. The values of entropy of activation (ΔS) in the absence and presence of extract were positive. The increase ΔS values revealed that an increase in disordering takes place on going from reactants to the activated complex [25, 26].

Table 3: Thermodynamic constraints for MS corrosion in presence of GTB in 0.5 M H₂SO₄

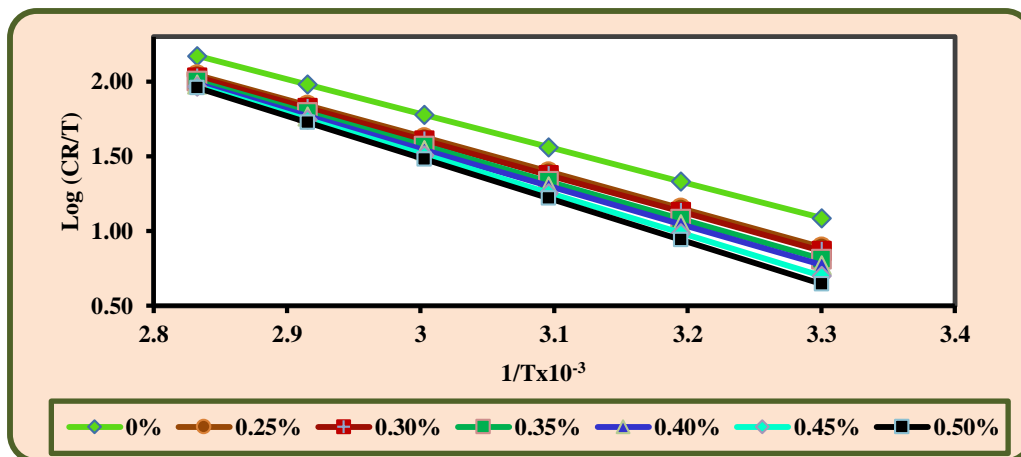| Concentration (v/v %)	0	0.25	0.3	0.35	0.4	0.45	0.5
Ea (KJmol⁻¹)	47.14	49.93	50.3	51.46	52.27	54.67	56.56
ΔH (KJmol⁻¹)	44.42	47.22	47.58	48.75	49.55	51.95	53.84
ΔS (Jmol⁻¹)	237.91	243.4	244.12	246.91	248.82	255.36	260.54
Ea-ΔH	2.72						

Figure 3: Transition state plots for MS corrosion in 0.5 M H₂SO₄ at various concentrations of GTB

Adsorption Isotherm: In acid corrosion generally, it is assumed that inhibitors are get adsorbed on the metal surface. The adsorbed molecules interact with

the active sites of the metal surface and may hinder the reactivity of the metal in the process of dissociation. If the adsorption is followed by

reactions like hydration, reduction or polymerization of inhibitor molecules, it will lead to a layer formation. Basic information on the interaction between the inhibitor and MS surface can be provided by the adsorption isotherm. The knowledge of the adsorption behavior of the plant extracts is important for the definition of its action mechanism. For this reason, the dependence of surface coverage on the inhibitor concentration is studied through adsorption isotherm.

Under the assumptions that the corrosion of the covered parts of the surface is equal to zero and that corrosion takes place only on the uncovered parts of the surface, the degree of surface coverage θ had been estimated as

$$\theta = IE/100 \qquad (7)$$

An adsorption isotherm gives the relation between the amount adsorbed and the concentration of the species in solution. The type of adsorption isotherm provides information about the interaction among the adsorbed molecules themselves and also their interactions with the electrode surface. The best fitting results were obtained by the Langmuir adsorption isotherm which is hinged on three basic assumptions, (a) that the surface of the adsorbant (in this case the mild steel test coupon) is in contact with a solution containing an adsorbate that is strongly attracted to the surface (monolayer adsorption),(b) that the surface has a fixed number of possible adsorption sites where solute molecules can be adsorbed, which are equivalent, and (c) that the ability of a molecule to be adsorbed is independent of the occupation of neighbouring sites (no interactions between adsorbed molecules) [27].
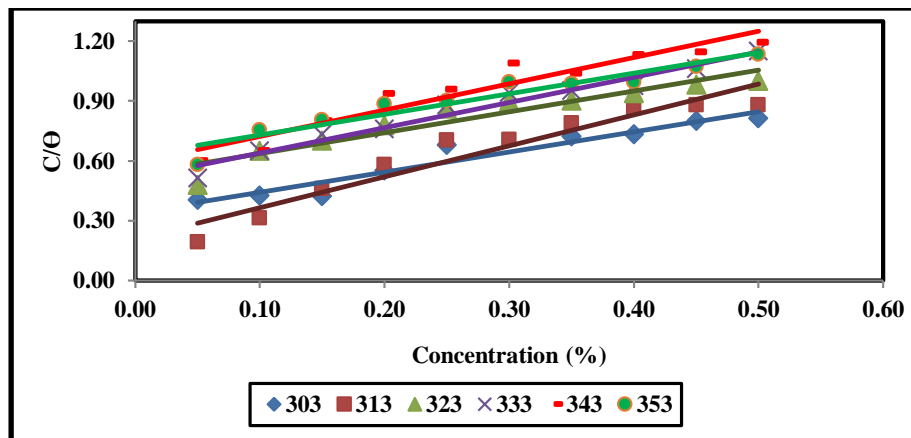

Figure 4: Langmuir adsorption plots for MS corrosion in 0.5 M H₂SO₄ having different concentrations of GTB extract

Assumptions of Langmuir relates to the concentrations of the adsorbate in the bulk of the electrolyte to the degree of surface coverage according to the equation

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (8)$$

where c is the concentration of the extract, θ is the surface coverage and K_{ads} is the adsorptive equilibrium constant. A plot of C/θ vs concentration from the weight loss data obtained for GTB extract yielded straight line as shown in Figure 4.

Due to the complex composition of the extract, the different components can be adsorbed on the cathodic and anodic sites of the metal surface, and such adsorbed species may interact by mutual repulsion or attraction. It is therefore, pertinent to say that the adsorption of the extract on the mild steel surface at all temperatures studied can be more appropriately represented by a modified Langmuir equation suggested by Villamil *et al*., taking into consideration

the interactions between adsorbate species as well as changes in heat of adsorption with changing surface coverage as follows [28]:

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \qquad (9)$$

Here n is the correction factor, which characterizes the interactions between the adsorbed molecules and the degree of uniformity of the adsorbent [29]. From the intercept of the straight lines C/θ axis, the K_{ads} values were calculated and are given in Table 4. A large value of K_{ads} corresponds to better inhibition efficiency of a given inhibitor [30].The values of K_{ads} were found to decrease after 313 K in test media because of the weakening of the interactions between the adsorbed molecules and the metal surface. Then the inhibitor molecules become easily removable. This explains the decrease in protective efficiency with increasing temperature [31].

Table 4: Langmuir adsorption isotherm parameters for GTB in 0.5 M H₂SO₄

Temperature (K)	R^2	Slope	K_{ads}	ΔG (KJmol⁻¹)	Basic thermodynamic equation		Vant'hoff equation	
					ΔH (KJmol⁻¹)	ΔS (Jmol⁻¹)	ΔH (KJmol⁻¹)	ΔS (Jmol⁻¹)
303	0.93	1.01	2.95	-12.84				
313	0.92	1.55	7.37	-15.65				
323	0.9	1.04	1.95	-12.59	-14.5	-0.0025	-14.3	-0.0019
333	0.96	1.27	2.47	-13.63				
343	0.92	1.32	2.23	-13.75				
353	0.92	1.04	1.85	-13.28				

The constant of adsorption K_{ads} was related to the standard free energy of adsorption $\Delta G°_{ads}$ by the expression

$$K_{ads} = \frac{1}{55.5} exp\left(\frac{-\Delta G°_{ads}}{RT}\right) \qquad (10)$$

Generally, values of $(\Delta G°_{ads})$ up to -20 kJmol⁻¹ are consistent with electrostatic interactions between the charged molecules and the charged metal (physisorption) while those around -40 kJmol⁻¹ or higher are associated with chemisorptions as a result of sharing or transfer of electrons from adsorbed molecules to the metal surface to form co-ordinate type of bond (chemisorptions) [32,33].

The calculated $\Delta G°_{ads}$ values for all the extracts were ranging from -12.84 to -15.65 KJmol⁻¹ indicating, therefore, that the adsorption mechanism of the extract molecules was typical physisorption which is consistent with the electrostatic interaction between charged molecules and a charged metal [34].The negative value of $\Delta G°_{ads}$ revealed the spontaneity of the adsorption process and the stability of the adsorbed layer on the MS [35].

The values of enthalpy and entropy of the inhibition process have no distinct changes in the temperature range studied; the thermodynamic parameters $\Delta H°_{ads}$ and $\Delta S°_{ads}$ for the adsorption of extract molecules on mild steel was calculated from the following equation:

$$\Delta G°_{ads} = \Delta H°_{ads} - T\Delta S°_{ads} \qquad (11)$$

where $\Delta H°_{ads}$ and $\Delta S°_{ads}$ were the vertiction of enthalpy and entropy of adsorption process respectively. The calculated values were depicted in Table 4. The negative sign of $\Delta H°_{ads}$ indicated the adsorption of inhibitor molecules was an exothermic process, which means lower IE at higher temperature. This indicated the gradual desorption of inhibitor from the surface of mild steel [30].

$$R_L = \frac{1}{1 + K_{ads}C} \qquad (13)$$

In this study the R_L value were less than unities

In the present study, the $\Delta H°_{ads}$ values were less than 40 kJ mol⁻¹, emphasizing the physical adsorption. $\Delta H°_{ads}$ can also be deduced from the integrated version of the van't Hoff equation expressed as equation;
$$ln(K_{ads}) = \frac{-\Delta H°_{ads}}{RT} + constant \qquad (12)$$

The plot of ln K_{ads} versus 1/T gives a straight line with slope of $\frac{-\Delta H°_{ads}}{R}$ and the intercept is (ΔS_{ads} / R + ln 1/55.5) .The calculated $\Delta H°_{ads}$ using van't Hoff equation is – 14.3 kJmol⁻¹ confirmed the exothermic behavior of adsorption of these inhibitors on mild steel surface, which also proved the physisorption process. Values of $\Delta H°_{ads}$ obtained by both method were in good agreement. Moreover the observed $\Delta S°_{ads}$ value of the inhibitor was -0.002 Jmol⁻¹ .The negative $\Delta S°_{ads}$ values ensure that the inhibitor molecules move freely in the bulk solution before adsorption, while as adsorption progresses, the inhibitor molecule adsorbed onto the mild steel surface became more orderly, resulting in decrease in entropy[36].When the adsorption is an exothermic process, it must be accompanied by a decrease (becomes more negative) in the entropy change which means that an ordered layer is formed onto the steel surface [37].This order may probably be explained by the possibility of formation of iron-inhibitor complex [38].

The essential characteristics of Langmuir can be expressed in terms of a dimentionless separation factor R_L,which was reported by Khadem *et al*.,as: if R_L >1, unfavorable; R_L=1, linear; 0< R_L <1, favorable;and if R_L=0, irreversible [39].In order to find out the adsorptive nature of GTB on MS surface as a protective layer,RL was calculated using the following equation :

(Table 5) confirmed the adsorption processes was favorable in this situation [40].

Table 5: Dimentionless separation factor (R_L) for GTB at various concentrations

Concentration (%)	Temperature (K)					
	303	313	323	333	343	353
0.05	0.87	0.73	0.91	0.89	0.90	0.92
0.10	0.77	0.58	0.84	0.80	0.82	0.86
0.15	0.69	0.48	0.77	0.73	0.75	0.80
0.20	0.63	0.40	0.72	0.67	0.69	0.75
0.25	0.58	0.35	0.67	0.62	0.64	0.71
0.3	0.53	0.31	0.63	0.57	0.60	0.67
0.35	0.49	0.28	0.59	0.54	0.56	0.63
0.40	0.46	0.25	0.56	0.50	0.53	0.60
0.45	0.43	0.23	0.53	0.47	0.50	0.57
0.5	0.40	0.21	0.51	0.45	0.47	0.55

FOURIER TRANSFORM INFRARED SPECTROSCOPY:

FTIR spectra were used to support the adsorption of inhibitor molecules on the mild steel surface. Since extracts contained different types of organic compounds and these organic compounds were adsorbed on the metal surface providing protection against corrosion, and this analyses can be useful for confirming the formation of protective film on MS surface.

Spectra of extract and subsequent protective film formed over the MS were monitored and shown in Figure 5.The broad peak at 3341 cm^{-1} indicated the presence of hydroxyl group overlapped by the strong stretching mode of N-H bond[41,42]. A peak at 1736 cm^{-1} furnished the presence of –CHO group in extract and the appearance of a peak at 1157 cm^{-1} corresponds to the existence of ring oxygen atom in extract.A peak at 1042 cm^{-1} attributed to the presence of –OH group[43].The peak at 887 cm^{-1} indicated the presence of stretching vibration of ether linkage in corresponding extracts. This showed that this plant extract contained a mixture of compounds with functional groups of O−H, N−H and C−O linkages.

By comparing both spectra, it was noticed that the O-H / N-H stretch at 3341 cm-1 was shifted to 3387 cm-1 and the C=O stretching in aldehyde 1736 cm-1 was shifted to 1759 cm-1 indicating that there was an interaction between the inhibitor and mild steel surface (44). Further , the prominent bands at 602 and 412 cm-1 were characterize of iron oxide which was absent in the pure GTB extract. Other functional groups were missing suggesting that the adsorption of the inhibitor on the surface of mild steel might have occurred through the missing bonds (45).The shift in vibrational frequencies noted on comparison of the spectra clearly indicated the interaction of the lone pair of electrons of hetero atom and the π electron of C=C, C=O with the metal leading to the formation of a protective layer of GTB on the metal surface.

S E M- EDAX ANALYSIS:

The surface morphology of the mild steel samples was investigated after corrosive attack by the media during 3 h immersion time in the absence and presence of the inhibitor was shown in Figure 6. Figure showed the SEM images recorded for the surface of the polished mild steel sample (a). In the absence of inhibitor the image revealed clear pits and cavities with roughness due to metal dissolution under corrosive attack by the media (b). For 0.5% concentration of inhibitor there were fewer corrosion marks observed on sample (c), suggesting that the mild steel surface was protected by compounds present in GTB extract. The surface was relatively smooth due to the formation of protective film on the surface. The surface analysis results suggest higher adsorption of extract components on the surface which support weight loss analysis.
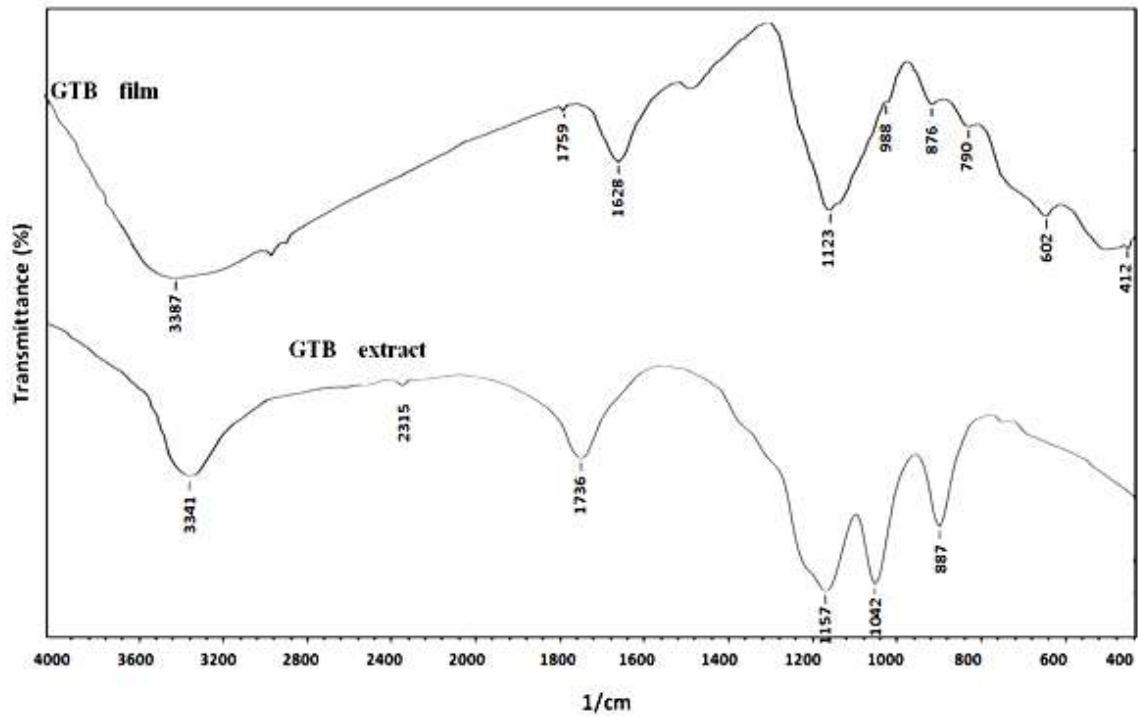
Figure 5: FTIR spectra of GTB extract and film formed on MS surface

The EDAX analysis of mild steel samples were taken at different spots. The EDAX spectra of polished surface (a), in absence of extract (b) and in the presence of extract(c) were shown in Figure7. Some additional lines of oxygen, carbon and sulphur were seen in Figure 7c. These may be due to the adsorption of phytoconstituents on metal surface. The variation of weight percentage of these elements on the surface can be used quantitatively to explain the adsorption of extract.
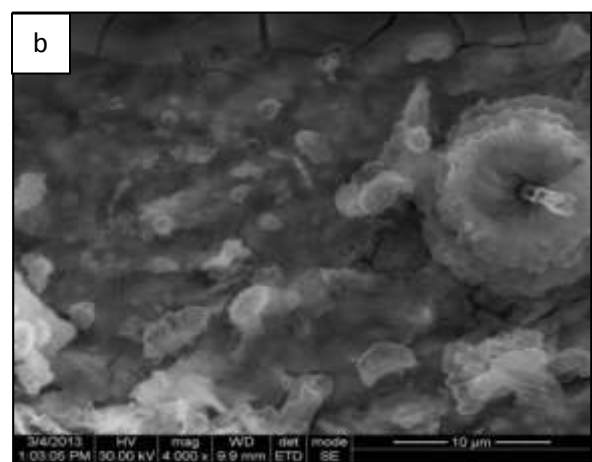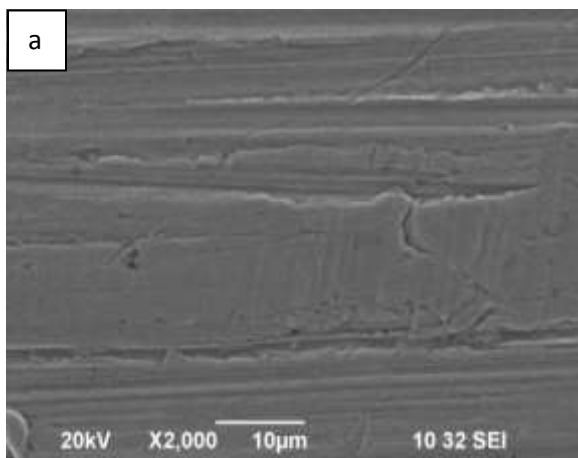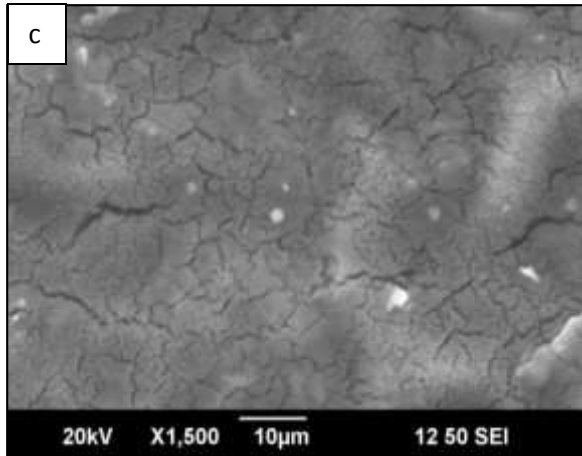
Figure 6. SEM images of MS for polished surface (a); after 3 h immersion in the blank solution (b); and after 3h immersion in the test solution with 0.5% GTB (c).
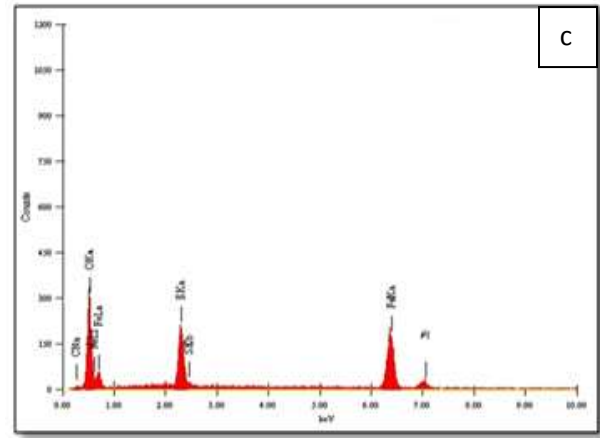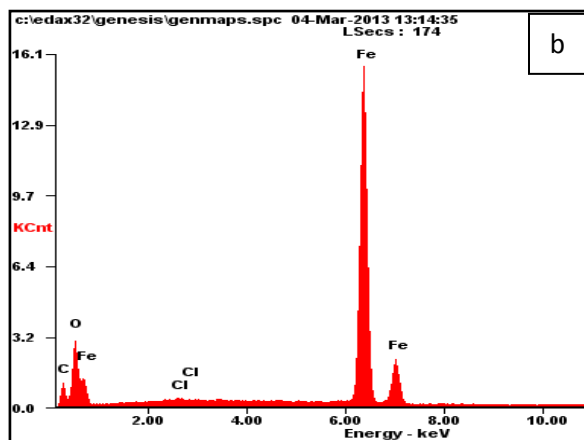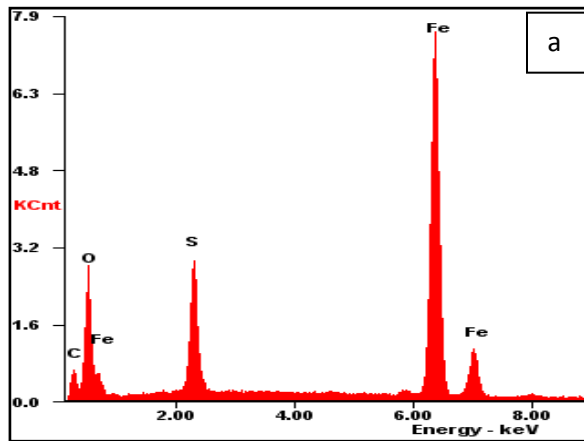

Figure 7: EDAX spectrum of (a)Polished MS (b) MS in H_2SO_4(c) MS in GTB extract

CONCLUSION

GTB is a safe corrosion inhibitor for mild steel in acid solutions that acts both over the cathodic process of hydrogen evolution and the anodic process of metal dissolution. Inhibition efficiency was determined by weight loss method and it increased with the amount of inhibitor and the maximum value was 70.26% for 0.5% GTB extract. The corrosion resistance with increase in immersion time was due to the formation and maintenance of complex layer on the mild steel surface. A decrease in inhibition efficiency with rise in temperature, with analogues increase in corrosion activation energy in the presence of the extracts compared to its absence was interpreted as the physical nature of adsorption. The adsorption of main constituents of the extracts can be attributed to the presence of hetero atoms, π electrons and aromatic / heterocyclic rings.The adsorption of extract on metal surface obeyed Langmuir isotherm, and the value of Gibbs free energy revealed the electrostatic interactions between the charged molecules and the charged mild steel. Generally, values of the free energy less negative than -40 kJ mol^{-1} were associated with processes that occur by physical adsorption of the inhibitor on metal surface. This mode of adsorption can be visualized as follows.

The steel surface bears positive charge in the acid solution [46]. Sulphate ions get adsorbed on the surface and these ions should bring excess of negative charges in the vicinity of metal / solution interface and far or adsorption of the positively charged inhibitor molecules. In aqueous acidic solution main constituents exist either as natural molecules or as protonated (cation) molecules. Synergism between SO_4^{2-} ions and protonated

inhibitor molecules showed that the inhibitor adsorbed on the metal surface through electrostatic interaction.

The surface analysis showed that the extract suppressed the corrosion process by forming a protective film over the metal surface which prevents

penetration of the corrosive media. The good inhibition efficiencies of GTB in sulphuric acid solution make it a suitable alternative as environmentally friendly corrosion inhibitor. The advantages of this inhibitor consist in biodegradability and zero impact on the environment.

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