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Thermodynamic, chemical and electrochemical investigation of *pandanus tectorius* extract as corrosion inhibitor for steel in sulfuric acid solutions

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ARTICLE INFORMATION

ABSTRACT

The corrosion inhibition characteristics of *pandanus tectorius* extract on corrosion of steel in 1 M H_2SO_4 were investigated using chemical and electrochemical measurements at various temperatures (30, 40, 50 and 60 °C). The effect of acid concentration on the corrosion rate of steel increases with acid concentration (0.25-2.00 M) showing first order corrosion reaction without changing the reaction mechanism. The results showed that when the concentration of *pandanus tectorius* extract increased from 5% to 15% (v:v), the rate of steel corrosion is decreased, which indicated that *pandanus tectorius* extract are good inhibitor for steel corrosion in 1 M H_2SO_4 at 30 °C and attains 88.02% at 15% (*v:v*) from weight loss method. Electrochemical results showed that the investigated extract was acted as mixed type inhibitor. The free energy of adsorption ΔG_{ads} for *pandanus tectorius*, indicates that the process was spontaneous and physically adsorbed (physisorption) onto the steel surface. Also, scanning electron microscopy (SEM) is used to support the obtained result. The trend of inhibition efficiency with temperature suggests physical adsorption of this extract on the corroding steel surface. Thermodynamic functions ΔE_{app}, ΔH^* and ΔS^* has been calculated and are discussed.

1. Introduction

Corrosion is usually defined as the deterioration of a metal or its properties caused by a reaction with its environment [1]. In many industries, steel is the material of choice in the fabrication of reaction vessels, pipelines for petroleum industries, storage tanks and chemical batteries, etc., those all can be corroded easily in the presence of acids [2,3]. The industrial application of steel is attractive due to some unique properties it exhibits for most engineering requirements. Their applications have been driven by a number of issues, such as its low cost and availability for the manufacturing of reaction vessels; cooling tower reservoirs, pipelines [4]. Among the methods of corrosion control, use of inhibitors is very popular due to the ease of application.

Acids such as HCl and H_2SO_4 are widely used as pickling, descaling, oil well acidizing and cleaning agents in several industries for the removal of undesirable oxide films and corrosion products [5]. Due to their high corrosive nature, acids may cause damage to the system components. Various methods are used to decrease the corrosion rate of metals in acids, among the different methods use of inhibitors is most commonly used [5-8]. These are substances used to stop or slow-down the corrosion process.

Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent unexpected metal dissolution and acid consumption [9-11]. Different organic and inorganic compounds have been studied as inhibitors to protect metals from corrosion attack [12]. The ability of a compound to a serve as inhibitor is dependent on its ability to form a compact barrier film and/or nature of adsorption on metal surface [13-15]. Usually, organic compounds exert a significant influence on the extent of adsorption on the metal surface and therefore can be used as effective corrosion inhibitors. The efficiency of these organic corrosion inhibitors is related to the presence of polar functions with S, O or N atoms in the molecule, heterocyclic compounds and p electrons [16,17]. The polar function is usually regarded as the reaction center for the establishment of the adsorption process [18]. The known hazardous effects of most synthetic organic, inhibitors and restrictive environmental regulations have now made researchers to focus on the need to develop cheap and environmentally benign natural products as corrosion inhibitors. These natural organic compounds are either synthesized or extracted from aromatic herbs, spices and medicinal plants. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost and are biodegradable in nature. This area of research is of much importance because in addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable source of materials [19].

The aim of the present work is to find a naturally occurring, cheap and environmentally safe substance that could be used for inhibition of corrosion of steel in acidic medium. An attempt has been made to ascertain their corrosion inhibition properties. Therefore, in this present work, the aqueous extract of *Pandanus tectorius* in 1 M H_2SO_4 was tested by using chemical (weight loss (*WL*), hydrogen evolution *HE*)) and electrochemical (Potentiodynamic polarization (*P*), electro-chemical impedance (*EI*)) techniques. SEM study was also used to study the surface morphologies.

Pandanus tectorius belongs to the family Pandanaceae, and

grows to a height of 5-8 meters (25 feet) with sharp to blunt spikes along the trunk [20] (Figure 1). According to Walter [21], *P. tectorius* is used as a food and medicine in the Marshalls, Yap, Hawaii, Tonga, and Tahiti. In these cultures, the aerial root is used to relieve several internal diseases including stomachache, food poisoning, and urinary tract problems [22,23]. Whistler [22], and Peungvicha *et al.* [24] reported that *Pandanus tectorius* leave was used for internal ailments, inflammation, sores, relieving stomachaches, and food poisoning.

Figure 1. *Pandanus tectorius* tree.

2. Experimental

2.1. Preparation of steel specimen

Steel sample of size 5.0 cm × 1.0 cm containing the composition of 0.14 %C, 0.35 %Mn, 0.17 %Si, 0.025 %S, 0.03 %P and the remainder Fe was used for chemical methods (weight loss (*WL*) and hydrogen evolution (*HE*)). For electrochemical studies, steel sample of the same composition but with an exposed area of 0.3316 cm^2 were used. Steel samples were polished mechanically with emery papers from 60 to 1200 grades, subsequently degreased with bi-distilled water and finally with acetone. Accurate weight of the samples was taken using electronic balance.

2.2. Preparation of the plant extract

The leaves of the *pandanus tectorius* plant were taken and cut into small pieces, weighed and mixed with bi-distilled water in a bolinder (Electric mixer). The mixture was allowed to stand overnight in a refrigerator at low temperatures and then filtered through ordinary filter paper. From this stock solution, different concentrations of inhibitor solutions ranging from 1% to 15% were prepared.

2.3. Weight loss method

The pretreated specimen initial weight was noted and was immersed in the experimental solution. After one hour, the specimen was taken out, washed thoroughly with distilled water, and dried completely, and their final weight was noted.

The loss in weight was calculated and tabulated, then the corrosion rate (g/cm^2.min), inhibition efficiency (*IE%*), and surface coverage (θ) of plant extract was calculated using formula [25],

$$\text{Corrosion rate } (CR_{WL}) \text{ (g/cm}^2\text{.min)} = \Delta W/At \qquad (1)$$

where *W* is weight loss in *g*, *A* is area in cm^2, *t* is time in min.

$$\text{Inhibition efficiency } (IE_{WL}\%) = CR_B - CR_I / CR_B \times 100 \qquad (2)$$

$$\text{Surface coverage } (\theta) = CR_B - CR_I / CR_B \qquad (3)$$

where CR_B and CR_I are corrosion rates in the absence (blank solution) and presence of the inhibitor.

2.4. Hydrogen evolution method

Hydrogen evolution method measures the volume of H$_2$ gas evolution from the reaction system.

From the volume of hydrogen gas evolved per minute, corrosion rate (mL/cm^2.min), inhibition efficiency (*IE%*) and degree of surface coverage (θ), were calculated using equations,

$$\text{Corrosion rate } (CR_{HE}) \text{ (mL/cm}^2\text{.min)} = (V_H - V_I)/t \qquad (4)$$

where V_I is the volume of hydrogen gas at time t for inhibited solution and V_H is the volume of hydrogen gas evolved at time *t* for uninhibited solution.

$$\text{Inhibition efficiency } (IE_{HE}\%) = CR_B - CR_I / CR_B \times 100 \qquad (5)$$

$$\text{Surface coverage } (\theta) = CR_B - CR_I / CR_B \qquad (6)$$

where CR_B and CR_I are corrosion rates in the absence (blank solution) and presence of the inhibitor.

2.5. Potentiodynamic polarization method

The polarization measurements were made to evaluate the corrosion potential ($E_{corr.}$), corrosion current ($I_{corr.}$), and Tafel slopes (anodic (b_a) and cathodic (b_c)). Experiments were carried out in a conventional three-electrode cell assembly with working electrode as steel specimen of 0.3316 cm^2 area, a rectangular Pt foil as the counter electrode, and the reference electrode as standard calomel electrode (SCE).

A time interval of 10-15 minutes was given for each experiment to attain the steady state open-circuit potential. The polarization was carried from a cathodic potential of -800 mV (versus SCE) to an anodic potential of -200 mV (versus SCE) at a sweep rate of 1 mV per second. The inhibition efficiency was calculated using the formula,

$$\text{Inhibition efficiency } (IE_P\%) = I_{corr} - I'_{corr} / I_{corr} \times 100 \qquad (7)$$

where I_{corr} and I'_{corr} are corrosion current in the absence and presence of inhibitor.

2.6. Electrochemical impedance method

The electrochemical AC-impedance measurements were also performed using electrode cell assembly as that used for potentiodynamic polarization studies.

A sine wave with amplitude of 10 mV was superimposed on the steady open circuit potential. The real part (*Z*`) and the imaginary part (*Z*``) were measured at various frequencies in the range of 100 KHz to 10 MHz. A plot of *Z*` versus *Z*`` was made. From the plot, the charge transfer resistance (R_{ct}) was calculated, and the double layer capacitance was then calculated using

$$C_{dl} = 1/ 2\pi f\max R_{ct} \qquad (8)$$

where R_{ct} is charge transfer resistance, and C_{dl} is double layer capacitance. The experiments were carried out in the absence and presence of different concentrations of inhibitors. The percentage of inhibition efficiency was calculated using

$$\text{Inhibition efficiency } (IE_{Rct}\%) = R^*_{ct} - R_{ct} / R^*_{ct} \times 100 \qquad (9)$$

where R^*_{ct} and R_{ct} are the charge transfer resistance in the presence and absence of inhibitor.

2.7. Surface examination studies

Surface examination of steel specimen in the absence and presence of the optimum concentration of the extract immersed for 1 h at 30 ℃ was studied using Digi scope II V2.

3. Results and discussion

3.1 Effect of sulfuric acid concentration on steel corrosion at 30 ℃

The influence of H_2SO_4 concentrations (0.25, 0.50, 1.00, 1.50 and 2.00 M) on steel corrosion at 30 ℃ is shown in Figure 2. It is clear that as the concentration of the H_2SO_4 solution increases, the slop of the straight lines also increases, indicating an increase in the dissolution of steel and increased of corrosion rate. The ideality of the straight lines in Figure 2 indicates the absence of any insoluble formed layer on the surface of the metal through the process of corrosion. The presence of induction period in the beginning of the interaction indicates the dissolution of the oxide layer formed on the surface of steel. The decrease of induction period in the beginning of the interaction with increasing acid concentration is detected. The rates of corrosion from ML and HE methods ($CR`$ & CR) are recorded in Table 1, it is found that the rates of corrosion increases with increasing acid concentration, this indicates that steel corrosion in H_2SO_4 is concentration dependent.
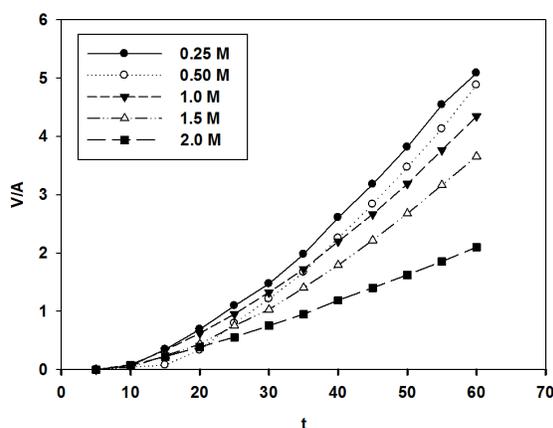

Figure 2. Volume of hydrogen evolution/time curves for the corrosion of steel in different concentrations of H_2SO_4 at 30 °C. (As the concentration of the H_2SO_4 solution increases, the dissolution of steel and the corrosion rate are increased).

The relation between corrosion rate and acid concentration can be illustrated by the kinetic equation as:

$$\log CR = \log A + n \log C \qquad (10)$$

where A represents corrosion rate constant which represents the rate of metal dissolution (corrosion), n reaction order and C

molar concentration of H_2SO_4 acid. The relationship log CR and /or log CR' vs. log C gave a straight lines as in Figure 3.

The slopes of these lines represent the reaction order (n) and the intercept is Log A. It was found that the value of n is equal to unity indicating that corrosion of steel in H_2SO_4 solution is the first order reaction and depends on the concentration of H_2SO_4 acid.

Table 1. Corrosion rates for steel in different concentrations of H_2SO_4 at 30 °C.

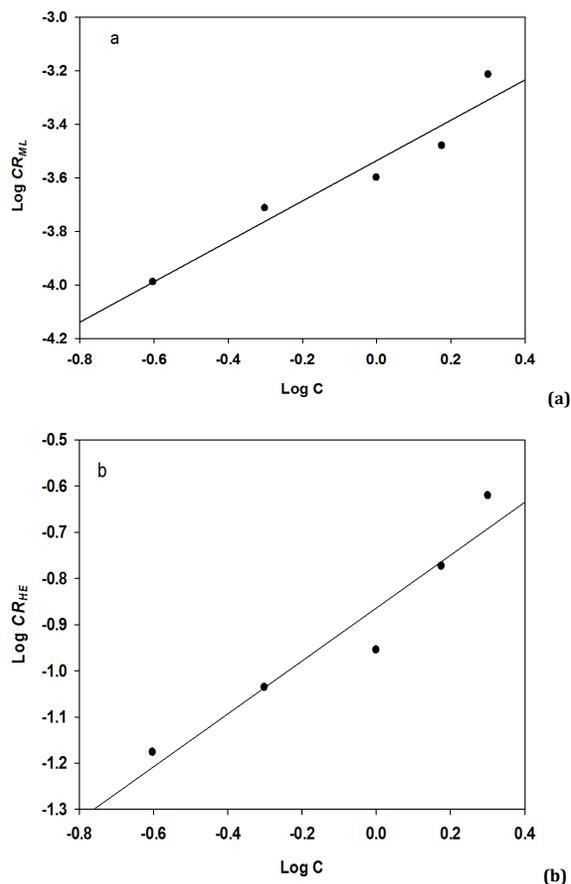| Concentration of H_2SO_4 (M)	Corrosion rate	
	$CR'_{WL} \times 10^4$ (g/cm².min)	CR_{HE} (mL/cm².min)
0.25	1.0236	0.0665
0.50	1.9314	0.0920
1.00	2.5123	0.1108
1.50	3.3064	0.1684
2.00	6.3931	0.2392

(a)

(b)

Figure 3. The relation between (a) log CR_{ML} and/or (b) log $CR_{HE}`$ for steel and log C of H_2SO_4. (The corrosion of steel in H_2SO_4 solution is the first order reaction and depends on the concentration of H_2SO_4 acid)

3.2 Effect of extract concentration on steel corrosion in 1 M H_2SO_4 at 30 ℃

3.2.1. Weight loss studies

The various corrosion parameters such as corrosion rate (CR), inhibition efficiency (IE), and surface coverage (θ) were obtained from weight loss method in 1M sulphuric acid in the absence and presence of different concentrations of the *pandanus tectorius* leaves extract ranging from 1% to 15% (*v*:*v*) and listed in Table 2. It was found that the maximum inhibition efficiency is 88.02% at 15% (*v*:*v*) and 1 hour of immersion. This

result indicates that the *pandanus tectorius* extract could acts as corrosion inhibitor.

Table 2. Corrosion rates and inhibition efficiencies for steel in 1 M H_2SO_4 in the presence of different concentrations of *pandanus tectorius* leaves extract at 30 °C.

C_{inh} (% $v{:}v$)	Corrosion rate		Inhibition efficiency	
	$CR'_{WL} \times 10^4$ (g/cm².min)	CR_{HE} (mL/cm².min)	$IE_{WL}\%$	$IE_{HE}\%$
0.0	2.5123	0.1108	-	-
1.0	1.6180	0.0713	35.59	35.64
5.0	1.0473	0.0470	58.31	57.58
10.0	0.3529	0.0189	85.95	82.94
15.0	0.3010	0.0139	88.02	87.46

3.2.2. Hydrogen evolution studies

The corrosion rates of steel in the absence and presence of different concentrations of *pandanus tectorius* leaves extract was monitored from the volume of hydrogen gas evolved at fixed time intervals. Figure 4 shows representative plots of the volume of hydrogen gas evolved as a function of reaction time at 30 °C for steel in 1 M H_2SO_4 without and with different concentrations of *pandanus tectorius* extract. It is observed from the figure that the volume of hydrogen gas evolved varies linearly with time and it is was less in the presence of plant extract compared to the blank solution.
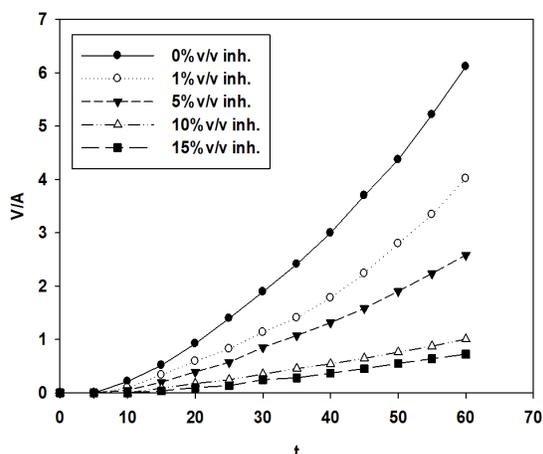

Figure 4. Volume of hydrogen evolution/time curves for the corrosion of steel in 1 M H_2SO_4 in the presence of different concentrations of aqueous extract of *pandanas tictorius* leaves at 30 °C. (The corrosion rate of steel is less in the presence of plant extract compared to the blank solution).

Table 2 presents the computed values of the hydrogen evolution rates and the inhibition efficiency of the various concentrations of *pandanus tectorius* leaves extract. Results in the table reveal that the rates of hydrogen evolution were reduced on the introduction of the *pandanus tectorius* leaves extract to the uninhibited solution. The increase of the rate of hydrogen evolution in the uninhibited solution can be rationalized on the basis that sulphuric acid reacts with iron and forms metal sulphates that are soluble in aqueous media [26]. There are two reactions occurring, namely the anodic reaction and cathodic reaction. The equations 11 and 12 represent iron reaction in acidic solutions [26,27].

Anodic reaction (oxidation reaction):

$$Fe \rightarrow Fe^{+2} + 2e^-$$ (11)

Cathodic (reduction reaction or hydrogen evolution reaction):

$$2H^+ + 2e^- \rightarrow H_2$$ (12)

This suggests that the components of the *pandanus tectorius* leaves extract are adsorbed onto the metal surface and block the electrochemical reaction efficiently by decreasing the available surface area. The values of inhibition efficiency are also listed in Table 2 can be seen to follow the trend reported for weight loss measurements.

3.2.3. Potentiodynamic polarization studies

Electrochemical corrosion kinetic parameters such as E_{corr}, I_{corr}, b_a, b_c, and IE_p for the corrosion of steel in 1 M H_2SO_4 at 30 °C in the absence and presence of different concentrations (5% and 15% ($v{:}v$)) of the *pandanus tectorius* extract are given in Table 3, and its corresponding polarization curves are shown in Figure 5. Potentiodynamic polarization studies revealed that the corrosion current density (I_{corr}) markedly decreased with the addition of the inhibitor and the corrosion potential ($E_{corr.}$) shifts to more negative values upon addition of the plant extract. Moreover, the values of anodic and cathodic Tafel slopes (b_a and b_c) are slightly changed indicating that this behavior reflects the plant extracts ability to inhibit the corrosion of steel in 1 M H_2SO_4 solution via the adsorption of its molecules on both anodic and cathodic sites, and, consequently, the extract acts through mixed mode of inhibition [28,29]. It was observed that with increase in concentration of the *pandanus tectorius* extract from 5% to 15%, the maximum inhibition efficiency varied from 59.44% to 87.01%.
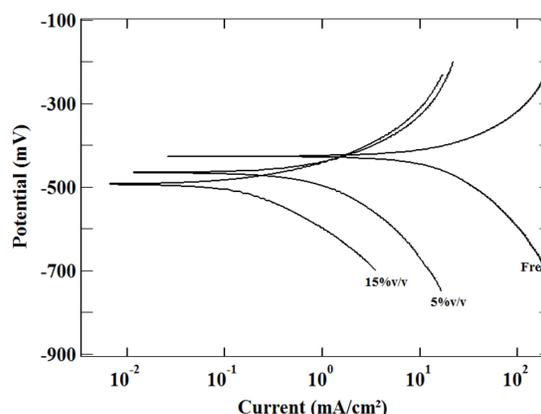

Figure 5. Potentiodynamic polarization curves for steel in 1 M H_2SO_4 solution in the absence and presence of 5% ($v{:}v$) and 15% ($v{:}v$) of the *pandanus tectorius* extract at 30 °C. (The extract acts as mixed type of inhibitor, with increase in concentration of the *pandanus tectorius* extract from 5% to 15%, the maximum inhibition efficiency varied from 59.44% to 87.01%).

3.2.4. Electrochemical impedance studies

Impedance measurements were studied to evaluate the charge-transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}), and through these parameters the inhibition efficiency was calculated. Figure 6 shows the impedance diagrams for steel in 1 M H_2SO_4 with 5% and/or 15% ($v{:}v$) of the *pandanus tectorius* leaves extract, and the impedance parameters derived from these investigations are given in Table 3. From Figure 6, the obtained impedance diagrams are almost in a semicircular appearance, indicating that the charge-transfer process mainly controls the corrosion of steel. Deviations of perfect circular shape are often referred to the frequency dispersion of interfacial impedance. This anomalous phenomenon may be attributed to the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena. In fact, in the presence of the plant extract, the values of R_{ct} have enhanced and the values of C_{dl} are also brought down to the maximum extent.

Table 3. Potentiodynamic polarization and impedance parameters for the corrosion of steel in 1 M H_2SO_4 in the absence and presence of 5% (*v:v*) and 15% (*v:v*) of the *pandanus tectorius* extract at 30 °C.

Concentration of extract (% *v:v*)	Polarization					Impedance		
	$-E_{corr.}$ (mV)	$I_{corr.}$ (mA/cm²)	b_a	b_c	$IE_p\%$	R_{ct} (Ω.cm²)	C_{dl} (F/cm²)	$IE_{Rct}\%$
Blank	426.98	3.859	141.14	214.84	-	43.53	2.15x10⁻⁴	-
5	462.44	1.565	107.55	164.94	59.44	105.30	5.52x10⁻⁵	58.66
15	488.23	0.5011	59.026	131.46	87.01	282.53	1.99x10⁻⁵	84.60

The decrease in C_{dl} shows that the adsorption of the inhibitor takes place on the metal surface in acidic solution. The inhibition efficiency obtained as 58.66% at 5% (*v:v*) and 84.60% at 15% (*v:v*).

A good agreement is observed between the results of chemical methods (weight loss and hydrogen evolution) and electrochemical methods (potentiodynamic polarization and impedance).
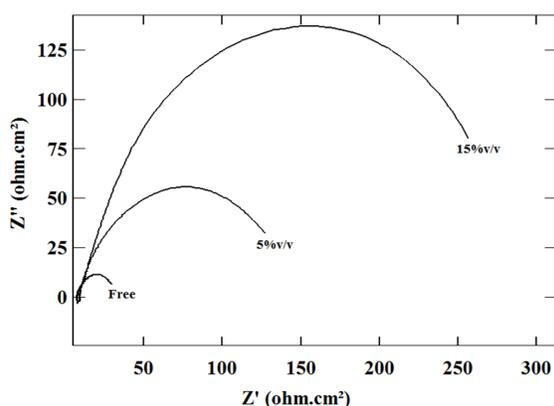

Figure 6. Impedance diagrams for steel in 1 M H_2SO_4 solution in the absence and presence of 5% (*v:v*) and 15% (*v:v*) of the *pandanus tectorius* extract at 30 °C. (The inhibition efficiency obtained as 58.66% at 5% (*v:v*) and 84.60% at 15% (*v:v*)).

3.3. Kinetics and mechanism of corrosion inhibition

Figure 7 shows the relation between *IE%* and inhibitor concentration C_{inh} for the investigated extract from Hydrogen evolution (Gasometric) and weight loss (Gravimetric) methods. As can be readily seen, the plots have the form of *S*-shaped adsorption. This indicates that the aqueous extract of *pandanus tectorius* plant inhibit the acid dissolution for steel by adsorption of the molecules of the *pandanus tectorius* plant at metal acid solution interface, also the obtained figure indicated one step of adsorption.

Inspection of the chemical structures of the phytochemical constituents reveals that the compounds in this plant are isopentenyl and dimethylallyl acetates and cinnamates in large amounts in an essential oil obtained from the leaves of *Pandanus tectorius* [30] and they are oxygen compounds with OH group which easily hydrolysable and can adsorb on the metal surface via the lone pair of electrons present on their oxygen atoms and make a barrier for charge and mass transfer leading to decreasing the interaction of the metal with the corrosive environment. As a result, the corrosion rate of the metal was decreased. The formation of film layer essentially blocks discharge of H⁺ and dissolution of metal ions. Due to electrostatic interaction, the protonated constituent's molecules are adsorbed (physisorption) and high inhibition is expected. Acid pickling inhibitors containing organic N, S, and OH groups behave similarly to inhibit corrosion [31].

The inhibition of the corrosion of steel in 1 M H_2SO_4 medium with addition of different concentrations of the extract can be explained by the adsorption of the components of the plant extract on the metal surface. Inhibition efficiency (*IE*) is directly proportional to the fraction of the surface covered (*θ*) by the adsorbed molecules. Therefore, (*θ*) with the extract concentration specifies the adsorption isotherm that describes the system and gives the relationship between the coverage of an interface with the adsorbed species and the concentration of species in solution. The values of the degree of surface coverage (*θ*) were evaluated at different concentrations of the inhibitors in 1 M H_2SO_4 solution from WL and HE methods. Attempts were made to fit *θ* values to various adsorption isotherms.
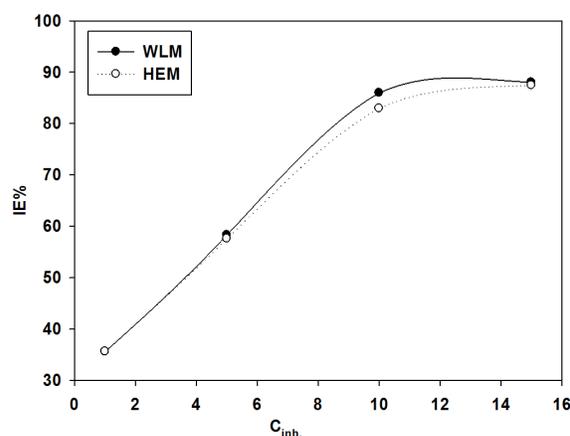

Figure 7. The variation of inhibition efficiency (*IE*%) against log C_{inh} for steel in 1 M H_2SO_4 in the absence and presence of *pandanas tictorius* leaves extract at 30 °C. (The aqueous extract of *pandanus tectorius* plant inhibit the acid dissolution for steel by adsorption of the molecules of the *pandanus tectorius* plant at metal acid solution interface and the adsorption was done in one step).

On examining, the adsorption of different concentrations of *pandanus tectorius* extract on the surface of steel in 1M sulphuric acid was found to obey Langmuir adsorption isotherm.

Langmuir adsorption isotherm equation [31].

$$\theta/C = 1/K + C \tag{12}$$

where C is the concentration of aqueous extract of *pandanus tectorius* plant, *K* is adsorption constant and *θ* is degree of coverage.

The Langmuir adsorption isotherm plot for the adsorption of various concentrations of the plant extract is shown in Figure 8.

The standard free energy of adsorption $\Delta G°_{ads}$ which can characterize the interaction of adsorption molecules and metal surface was calculated

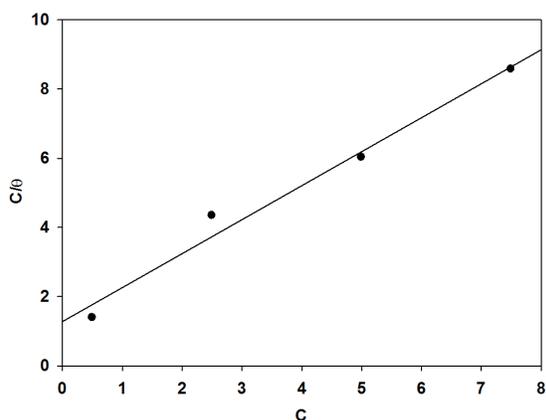$$\text{Ln } K = \ln 1/55.5 - \Delta G°_{ads}/RT \tag{13}$$

where one molecule of water is replaced by one molecule of inhibitor and the numerical value (1/55.5) in the equation stands for the molarity of water. The value of *K* can be calculated using

$$K = \theta/(1-\theta)C \tag{14}$$

Table 4. Corrosion rates for steel in 1 M H₂SO₄ with different concentration of aqueous extract of *pandanus tectorius* at different temperature.

Temperature (t)	Corrosion rate				Inhibition efficiency	
	$CR_{WL} \times 10^4$ (g/cm².min)		$CR_{HE n}$ (mL/cm².min)		IE_{WL} %	IE_{HE} %
	0% (*v:v*)	5% (*v:v*)	0% (*v:v*)	5% (*v:v*)		
30	2.5123	1.0473	0.1108	0.0470	58.31	57.09
40	6.2469	2.7995	0.2582	0.1196	55.18	53.68
50	12.7250	9.3975	0.5202	0.3997	26.15	23.16
60	22.615	19.606	0.9305	0.8361	13.31	10.15

The values of $\Delta G°_{ads}$ around -20 kJ/mol or lower are consistent with the electrostatic interaction between organic charged molecules and the charged metal (physisorption) and those around -40 kJ/mol or higher involved charge sharing or transfer from the organic molecules to the metal surface to format coordinate type of bond (chemisorption) as discussed by Moretti *et al.* [32]. In this case, the negative sign of free energy of adsorption for the plant extract indicates that the adsorption of the plant extract on steel surface was a spontaneous process and the adsorption could be physisorption, where $\Delta G°_{ads}$ is equal -10.60 kJ/mol. Studies of El-Etre [33] and Li *et al.* [34] reported similar kind of results. .

Figure 8. The relation between C/θ against C$_{inh.}$ of aqueous extract of *pandanus tectorius* for steel corrosion in 1 M H₂SO₄ at 30 °C (Langmiur isotherm).
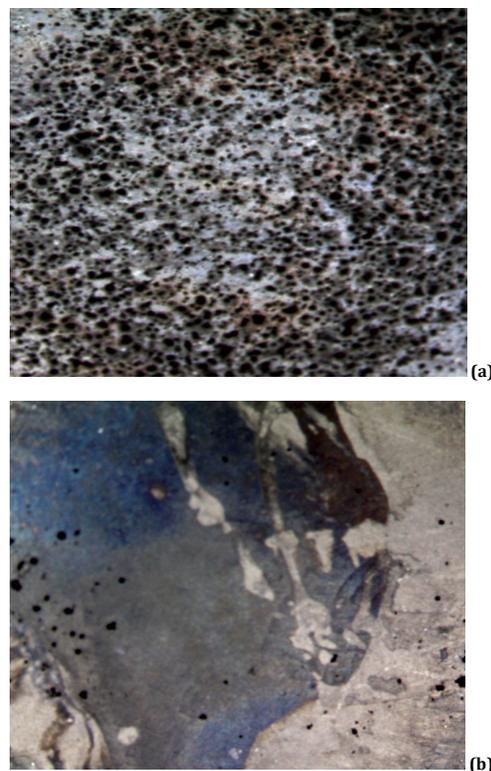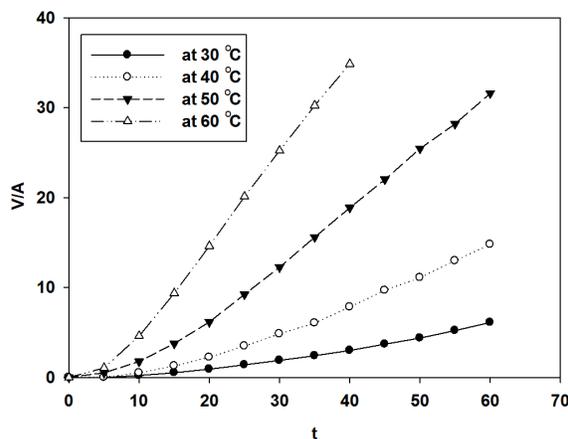
3.4. Surface examination studies

Surface examination of the steel specimen was made using Digi scope II V2. The steel specimen after immersion in 1M H₂SO₄ solution for one hour at 30 ℃ in the absence and presence of 15% (*v:v*) of the plant extract were taken out, dried, and kept in a dessicator. The protective film formed on the surface of the steel was confirmed by SEM studies (Figure 9a and b). It was found that more grains were found in SEM image of steel immersed in 1 M H₂SO₄ solution in the absence of the inhibitor (Figure 9a), whereas no grains were found in the SEM image of steel immersed in 1 M H₂SO₄ solution in the presence of 15% (*v:v*) of the extract (Figure 9b), which shows the presence of a protective film over the surface of the steel in the presence of the inhibitor.

The SEM morphology of the adsorbed protective film on the steel surface has confirmed the high performance of inhibitive effect of the plant extract.

3.5. Effect of temperature

Temperature can modify the interaction between the steel electrode and the acidic medium in the absence and the presence 5% (*v:v*) (which give an average value of inhibition efficiency) of inhibitor (*pandanus tectorius)* extract. To assess the influence of temperature on corrosion and corrosion

inhibition processes, the weight loss and hydrogen evolution measurements were carried out at 30-60 °C temperature range and given in Figures 10 and 11 and Table 4.

Figure 9. SEM of the steel surface in (a) 1 M H₂SO₄ and (b) 1 M H₂SO₄ +15% (*v:v*) of plant extract at 30 °C. (Grains were found in the absence of the inhibitor and the presence of a protective film over the surface of the steel in the presence of the inhibitor).

Figure 10. Volume of hydrogen evolution/time curves for steel corrosion in 1 M H₂SO₄ at different temperatures.
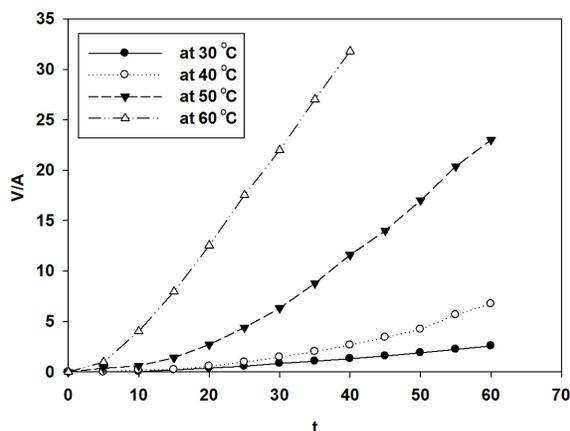
Figure 11. Volume of hydrogen evolution/time curves for steel corrosion in 1 M H_2SO_4 in the presence of 5% (*v:v*) of aqueous extract of *pandanas tictorius* leaves at different temperatures. (Corrosion rates increase with rise of temperature both in uninhibited and inhibited solutions).

The results obtained indicated that corrosion rates increase with rise of temperature both in uninhibited and inhibited solutions. Figure 12 shows the relation between IE% against temperature (t) from both WL and HE methods. The decrease in inhibition efficiency with increasing temperature may be attributed to a possible shift of the adsorption-desorption equilibrium towards desorption of some adsorbed inhibitor molecules from the steel surface due to increased solution agitation resulting from higher rates of H_2 gas evolution at higher temperatures. This shows a weak adsorption interaction between steel surface and the inhibitor [35,36].
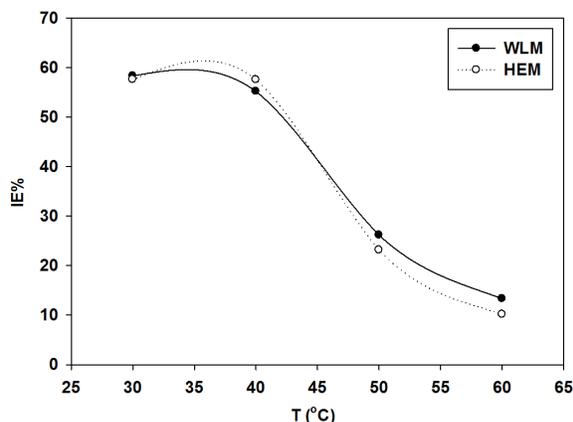

Figure 12. Plots of *IE% vs.* temperature (t) for steel in 1 M H_2SO_4 in the presence of 5% (*v:v*) *pandanus tectorius* extract. (The inhibition efficiency decrease with increasing temperature).

The dependence of corrosion rate on the temperature can be regarded as an Arrhenius-type process, the rate of which is given by [37]:

$$\log CR = \log A - E_a /2.303RT \qquad (15)$$

where *CR* is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant, *T* is the absolute temperature and A is the frequency factor.

The Arrhenius plot is shown in Figure 13 for steel in free acid solution and inhibited solution containing 5% (*v:v*) aqueous extract of *pandanas tectorius* plant from weight loss method. Linear plots were obtained from the slope

(E_a/2.303.R), activation energy (E_a) values are deduced and listed in Table 5.

Table 5. Activation parameters for steel corrosion in 1 M H_2SO_4 in the absence and presence of 5% (*v:v*) *Pandanus tectorius* extract from weight loss method.

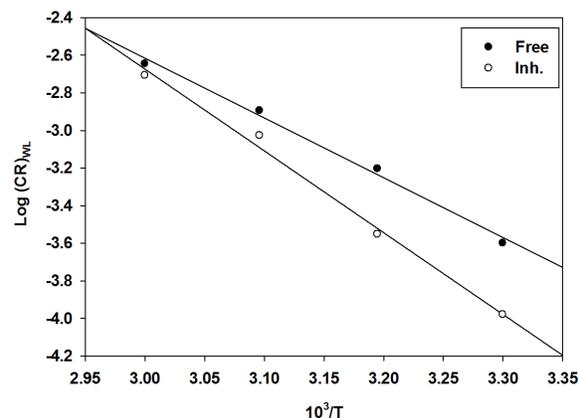| Concentration	E_a (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (J/mol.K)
Blank	19.54	18.71	-76.38
5% (*v:v*)	25.04	27.94	-8.95

Figure 13. Arrhenius plot for steel in 1 M H_2SO_4 without and with 5% (*v:v*) *pandanus tectorius* extract.

The temperature dependence of the inhibiting effect and the comparison of the values of the apparent activation energy of the corrosion process in the absence and presence of inhibitor can provide further evidence [38] concerning the mechanism of the inhibiting action. The decrease of the inhibitor efficiency with temperature rise, which refers to a higher value of E_a, when compared to that in an acid with no inhibitor, is interpreted as an indication for an electrostatic character of the inhibitor adsorption. The lower value of E_a in an inhibited solution when compared to that of an uninhibited one shows that strong chemisorption bond between the inhibitor and the metal is highly probable [39]. Activation energy, Ea values in the table are higher for inhibited solution (for the studied extract) than the uninhibited one, indicating a strong inhibitive action of the additive by increasing energy barrier for the corrosion process, emphasizing the electrostatic character of the inhibitor adsorption on the steel surface (physisorption). Experimental corrosion rate values obtained from weight loss measurement for steel in 1 M H_2SO_4 in the absence and presence of extract was used to further gain insight on the change of enthalpy (ΔH^*) and the entropy (ΔS^*) of activation complex in the transition state using transition state equation [40].

$$\text{Log } CR/T = [(\text{Log } (R/N.h))+\Delta S^*/2.303.R)-\Delta H^*/2.303.R.T \qquad (16)$$

where *CR* is the corrosion rate, h is the plank's constant, N is the Avogadro's number, R is the universal gas constant and T is the absolute temperature. Figure 14 shows the plot of log (*CR*/T) *vs.* 1/T for steel corrosion in 1 M H_2SO_4 for the extract studied. Straight lines were obtained with slope of (-ΔH^*/2.303.R) and intercept of [Log(R/N.h) + (ΔS/2.303.R)] from which the values of ΔH^* and ΔS^*, respectively, were calculated and listed in Table 5. The positive values of ΔH both in the absence and presence additive reflect the endothermic nature of the steel dissolution process and it indicates that the dissolution of steel is difficult [41]. Large and negative values of ΔS^* in the uninhibited and inhibited systems imply that the activation complex in the rate determining steps represents association rather than dissociation step, meaning that a

decrease in disordering takes place on going from reactants to the activated complex. Similar observations have been reported in the literature for steel dissolution in the absence and presence of inhibitors in H_2SO_4 solution [42].
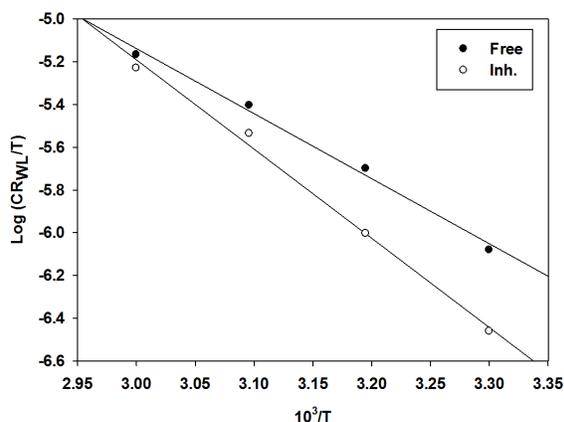

Figure 14. Transition state plot for steel in 1 M H_2SO_4 without and with 5% (*v:v*) *pandanus tectorius* extract.

4. Conclusion

The corrosion rate of steel increases with increasing H_2SO_4 acid concentration 0.25-2.00 M showing first order corrosion reaction without changing the reaction mechanism. The results indicate that the extract of *pandanus tectorius* leaves acts as good and efficient inhibitor for corrosion of steel in 1M sulphuric acid and it was found that the maximum inhibition efficiency is 88.02% at 15% (*v:v*) and 1 hour of immersion. Potentiodynamic polarization studies revealed that the extract acts through mixed mode of inhibition. The impedance method revealed that charge-transfer process mainly controls the corrosion of steel. The adsorption of different concentrations of the plant extracts on the surface of steel in 1 M sulphuric acid followed Langmuir adsorption isotherm. The negative sign of free energy of adsorption indicates that the adsorption of the inhibitor on steel surface was a spontaneous process and the adsorption was found to be physisorption. The SEM morphology of the adsorbed protective film on the steel surface has confirmed the high performance of inhibitive effect of *pandanus tectorius* leaves extract. The phenomenon of physical adsorption is proposed from a decrease in inhibition efficiency with an increase in temperature. The value of activation energy *Ea* revealed that the adsorbed organic matter provided a physical barrier to charge and mass transfer, leading to reduction in corrosion rate. The positive value of enthalpy of adsorption (ΔH^*) suggests that the reaction was endothermic and the adsorption of the inhibitors on the metal surface takes place. Large and negative values of ΔS^* in the uninhibited and inhibited systems imply that the activation complex in the rate determining steps represents association rather than dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex.

Acknowledgements

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