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Inhibitive and kinetic properties of Eco friendly corrosion inhibitor (Cucurbita maxima peel) for mild steel in acidic medium

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Abstract
Natural products of plant origin are used as green corrosion inhibitors, because plant extracts are ecologically acceptable, nontoxic, environmentally friendly, readily available and renewable sources of materials. The corrosion inhibition efficiency of peel of *Cucurbita maxima* (PCM) on mild steel in 1N H_2SO_4 was studied using weight loss measurement and Gas Chromatography-Mass Spectrometry (GC-MS) analysis. The inhibition efficiency value reaches 95% at 3% v/v concentration of PCM. Totally ten active constituents in plant extract were identified by GC-MS analysis. Adsorption, kinetic and thermodynamics properties of the plant extract also discussed.

Keywords: *Cucurbita maxima*, mild steel, corrosion rate, inhibition efficiency

1. Introduction
Corrosion can be defined as a deteriorative loss of a metal as a result of dissolution due to environmental reactions. It is electrochemical and ordinarily begins at the surface [1]. Mild steel is a familiar material employed widely in a variety of industries. But the main problem of using mild steel is its dissolution in acidic solutions. In various industrial processes, acid solutions are commonly used for removal of rust and scale. Use of inhibitors in these processes to prevent metal dissolution is very common [2]. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulfur, oxygen, heterocyclic compounds with a polar functional group and conjugated double bond. These compounds are adsorbed on the metallic surface and block the active corrosion sites [3, 4]. Most of the synthetic chemicals are costly, toxic to both human being and environment. To solve the above defects, it is necessary to develop cheap, non – toxic and environmentally friendly natural products as corrosion inhibitors [5]. These natural organic compounds are extracted from aromatic herbs, spices and medicinal plants. Plant extracts are an incredibly rich source of phytochemicals that can be extracted by simple procedures with low cost and are biodegradable in nature *Garcinia mangostana* [6] *Allamanda blanchetii* [7], *Salvia aucherimesatlantica* [8], rubber leaf extract [9], Elephant grass [10], *Sesamum indicum*[11], *Pachylobus edulis* [12], *Cucumeropsis mannii* [13], *Sida acuta* [14] Extracts of naturally occurring plants products contain mixture of compounds and are biodegradable in nature and they are used as a good corrosions inhibitor [15]. The safety and environmental issues of corrosion inhibitors arisen have always been a global concern. *Cucurbita maxima* belongs to the family cucurbitaceae widely distributed in India. In the Present work an attempt has been made to study the corrosion inhibition properties of the acid extract of the peel of *Cucurbita maxima* on mild steel by weight loss method.

2. Experimental
2.1 Materials
The mild steel sheet was 2 mm in thickness and was mechanically press – cut into 5 cm ⨯ 2 cm coupons. The 1N H_2SO_4 Solution, prepared from AR grade H_2SO_4 was employed as the corrodent for the study. The extract was prepared by refluxing 25g of powdered dry peel of *Cucurbita maxima* in 500 ml of 1N H_2SO_4 for 3 h and kept overnight. Then it was filtered and this was taken as a stock solution. From the respective stock solution, inhibitor test solutions were prepared in the concentration range from 0.05% v/v to 3% v/v.

Fig 1: Fresh peel of *Cucurbita maxima*

Fig 2: Dried peel of Cucurbita maxima

2.2 Methods

2.2.1 GC-MS analysis

The presence of chemical constituents in the peel of *Cucurbita maxima* was investigated using GC-MS study. The GC-MS analysis of the PCM sample was tested at the South India Textile Research Association (SITRA), Coimbatore. The sample was analysed using a Shimadzu GCMS-QP2010 gas chromatograph-mass spectrometer interfaced with a Turbo Mass quadrupole mass spectrometer, fitted with an Rtx-5 fused silica capillary column (30 X0.25 mm, with 1 Cm film thickness). The oven temperature was programmed from 100^0C to 320^0C at100^0C/min and a hold for 10 min. Helium was used as carrier gas at flow 1.0 mL/min. The injector temperature was 250^0C, injection size1 µL neat, with split ratio 1:10. The interface and MS ion source were maintained at 320^0C and 200^0C, respectively, the mass spectra were taken at 70eV with a mass scan range of 40-700 amu. Data handling was done using GCMS solution software. The identification of compounds was based on comparison of their mass spectra with those of WILEY and NIST Libraries.

2.2.2 Weight loss measurements

The weight loss measurements carried out at different temperature range (303K, 313K, 323K, 333K & 343K) at 1h. Mild steel specimens were immersed in blank and various concentrations of inhibitor solutions. The weight of the specimens before and after immersion was determined using a digital balance. The rate of corrosion of the metal (CR) and the inhibition efficiency (IE %) of the plant extract were calculated from the following equations [16].

$$CR\ (mpy) = 534W / D\ A\ t \quad (1)$$

Where W is the weight loss in mg, D is the density of mild steel (7.8/cm^3), A is the area of metal specimen and t is the time if immersion.

$$IE\ \% = [\ W_o - W_i / W_o] * 100 \quad (2)$$

Where W_o and W_i are the weight loss values in absence and in presence of inhibitor.

2.2.3 Kinetic study

Weight loss studies at different temperatures enable the determination of activation energy in the absence and presence of inhibitor. The value of apparent activation energy (E_a), was calculated using the Arrhenius equation [17].

$CR = A \exp^{-Ea/RT}$

Where CR is the corrosion rate of mild steel, A is Arrhenius constant or pre-exponential factor, R is the gas constant and T is absolute temperature. The enthalpy of activation, ΔH*, and entropy of activation, ΔS*, values were obtained through the transition-state theory equation [18] given as;

$\log (CR/T) = \log (R/Nh) + \Delta S^*/R - \Delta H^*/RT$

Where h is Planck's constant and N is Avogadro's number. A plot of Log (CR/T) versus 1/T (Eyring plot) gives a straight line. From the slope and intercept, the values of ΔH* and ΔS* were calculated.

3. Results and discussion

3.1 GC-MS analysis

GC-MS chromatogram of the PCM showed 10peaks (Figure.1) and have been identified after comparison of the mass spectra with WILEY and NIST libraries. The active principle Molecular Weight (MW), Probability, Concentration (%), Molecular Formula (MF) and Retention Time (RT) is presented in Table 1. Totally ten compounds were identified in the PCM. The prevailing compounds were 2-Methyl-1-nonen-3-ol, 1-Tetradecanol, 1-Hexadecanol,1,5-anhydro-arabino– furanose, Methyl 10-trans,12-cis-octadecadienoate, Hentriacontane, Docosane, 2-(6'-Methoxy-7'-methyl-',2',3',4' tetrahydronaphthalen-1'-yl) ethyl-4, 7,7 trimethyl 3oxo2oxabicyclo [2.2.1] heptane-1 carboxylateand 9,10bis (trifluoromethylthio) anthracene. The Structure of the phyto constituent in PCM is given in Table 2. All the identified compounds from peel of *Cucurbita maxima* contained oxygen, sulphur and/or π electrons in their molecules. Hence, the corrosion inhibition of metal surface through this plant extract may be attributed to the adsorption of the phytochemicals containing O, S or π electrons in their molecules as these atoms are regarded as centers of adsorption onto the metal surface [19-21].

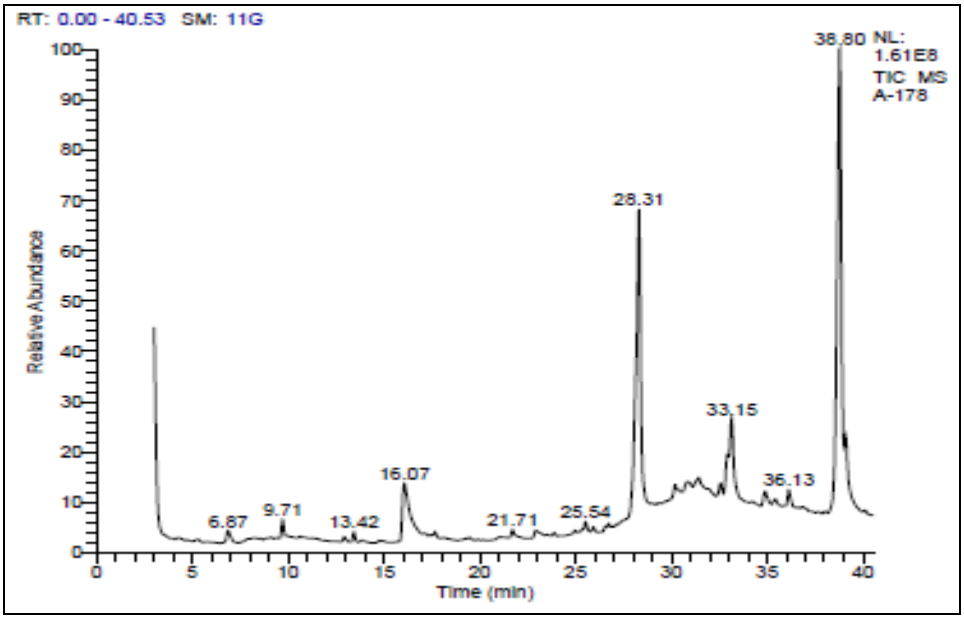
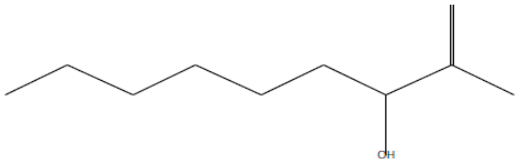
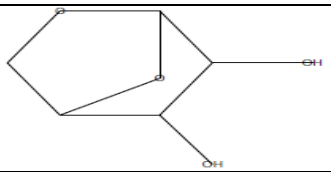


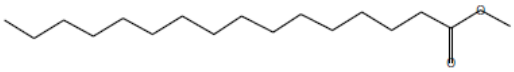
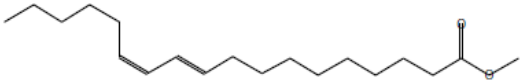
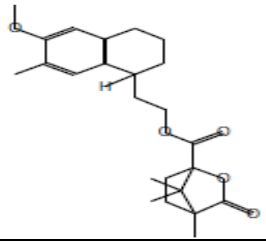
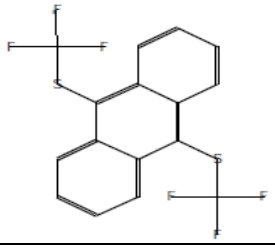
Fig 1: GC-MS spectrum of PCM

Table 1: Components identified in PCM (GC MS study)

RT	Phyto constituents	Probability	Molecular Formula	Peak Area %
6.87	2-Methyl-1-nonen-3-ol	48.97	$C_{10}H_{20}O$	1.09
9.71	1-Tetradecanol	7.99	$C_{14}H_{30}O$	1.37
13.42	1-Hexadecanol	5.47	$C_{16}H_{34}O$	0.55
16.07	1,5 - anhydro - arabino - furanose	49.69	$C_5H_8O_4$	6.34
21.71	Hexadecanoic acid, methyl ester	48.25	$C_{17}H_{34}O_2$	0.67
25.54	Methyl 10-trans,12-cis-octadecadienoate	8.98	$C_{19}H_{34}O_2$	1.01
28.31	Hentriacontane	85.39	$C_{31}H_{64}$	27.17
33.15	Docosane	12.65	$C_{22}H_{46}$	8.82
36.13	2-(6'-Methoxy-7'-methyl-1',2',3',4'-tetrahydronaphthalen-1'-yl)ethyl -4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate	54.77	$C_{24}H_{32}O_5$	1.28
38.80	9,10-bis(trifluoromethylthio)anthracene	20.98	$C_{16}H_8F_6S_2$	39.64

Table 2: Structure of the phyto constituents in PCM

S. No	Phyto constituents	Structure
1	2-Methyl-1-nonen-3-ol	
2	1-Tetradecanol	
3	1-Hexadecanol	
4	1,5 - anhydro - arabino - furanose	

5	Hexadecanoic acid, methyl ester	
6	Methyl 10-trans,12-cis-octadecadienoate	
7	Hentriacontane	
8	Docosane	
9	2-(6'-Methoxy-7'-methyl-1',2',3',4'-tetrahydronaphthalen-1'-yl)ethyl -4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1 -carboxylate	
10	9,10-bis(trifluoromethylthio)anthracene	

3.2 Weight loss method

3.2.1 Effect of temperature on corrosion rate of mild steel and IE of PCM

The CR and IE values for mild steel corrosion in 1N H_2SO_4 with different PCM concentration at different temperatures are listed in Table 3. Fig 2 shows the corrosion rate of mild steel in 1N H_2SO_4 for different PCM concentration at various temperatures. Inhibition efficiency PCM at different temperatures for mild steel corrosion in 1N H_2SO_4 is shown in Fig 3. The result shows that the inhibition efficiency increased and corrosion rate decreased with increase in the inhibitor concentration at various temperatures. This may be due to adsorption of the inhibitor molecules on the metal surface [22]. At 343K the decrease in corrosion rate observed from 6227 mpy to 283 mpy at increased PCM concentration from 0.01% to 3% v/v. The maximum IE of 78% obtained at 303K and 95% at 343K for 3% v/v inhibitor concentration. IE% of PCM in sulphuric acid medium shows slight decrease for low concentration of inhibitor but at higher concentration IE% is not much varied. Inhibition efficiency values show the metal corrosion protection ability of the PCM extract in 1N H_2SO_4 medium.

Table 3: Corrosion rate of mild steel and inhibition efficiency of PCM in 1N H_2SO_4 at different temperatures

Conc. of PCM (%v/v)	303K		313K		323K		333K		343K	
	CR mpy	IE%	CR mpy	IE%	CR mpy	IE%	CR mpy	IE%	CR mpy	IE%
Blank	1334	-	1138	-	2446	-	3174	-	6227	-
0.01	414	69	375	67	741	69	937	70	2006	67
0.05	340	75	353	69	501	79	641	79	1857	70
0.1	231	83	309	73	475	80	553	83	1343	78
0.5	122	91	139	88	252	89	392	87	684	89
1	113	92	117	89	178	92	244	92	470	92
1.5	104	92	113	90	161	93	222	93	453	93
2	91	93	109	90	143	94	191	94	375	94
2.5	91	93	95	92	139	94	183	94	331	95
3	78	94	78	93	130	95	152	95	283	95

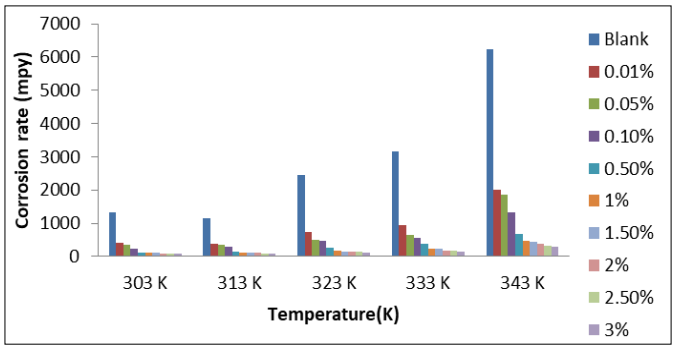


Fig 2: Corrosion rate of mild steel in 1N H_2SO_4 for different PCM concentration at various temperatures.

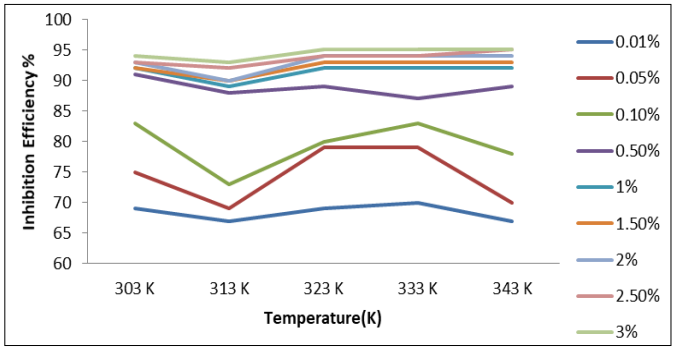


Fig 3: Inhibition efficiency PCM at different temperatures for mild steel corrosion in 1N H_2SO_4.

3.3 Kinetic study

3.3.1 Activation parameters for PCM in 1N H_2SO_4 on mild steel corrosion

The activation parameters for mild steel corrosion in 1N H_2SO_4in the presence of PCM extract is listed in Table 4. The corresponding Arrhenius and Eyring plots are shown in Fig 4 and Fig 5. From Table 4, the E_a values found to vary from 35.13kJ/mol to 27.76 kJ/mol with increasing PCM concentration. The ΔH* values decreased from 35.8kJ/mol at 0.5% v/v concentration to 25.1kJ/mol at 3% v/v concentration and the ΔS*values range from -337.7 J/mol to -384.8J/mol. A decrease in E_a from blank to inhibitor solution is attributed to chemisorptions [23-25]. The positive value of ΔH* indicates the endothermic nature of the corrosion process. The negative values of ΔS* implies the association of the inhibitor molecules on mild steel surface.

Table 4: Activation parameters for mild steel corrosion in 1N H_2SO_4 in the presence of PCM extract

Concentration % v/v	E_a kJ/mol	ΔH* kJ/mol	ΔS* J/mol
Blank	35.13	32.4	-337.7
0.01	34.80	32.1	-348.4
0.05	33.94	31.2	-352.9
0.1	35.17	32.5	-350.8
0.5	38.52	35.8	-345.6
1	30.65	27.9	-372.4
1.5	30.90	28.2	-372.2
2	29.02	26.3	-379.1
2.5	27.68	25.0	-383.8
3	27.76	25.1	-384.8

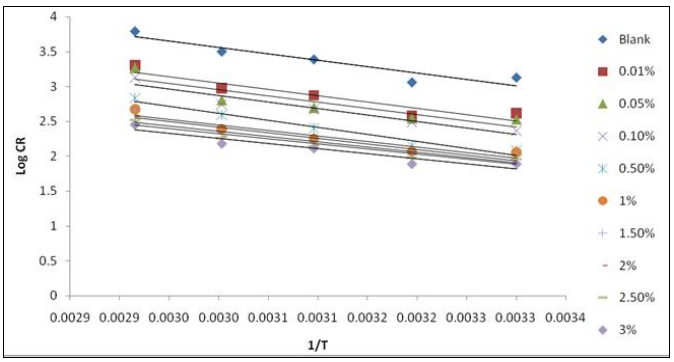


Fig 4: Arrhenius plot for PCM in 1N H_2SO_4 on mild steel corrosion

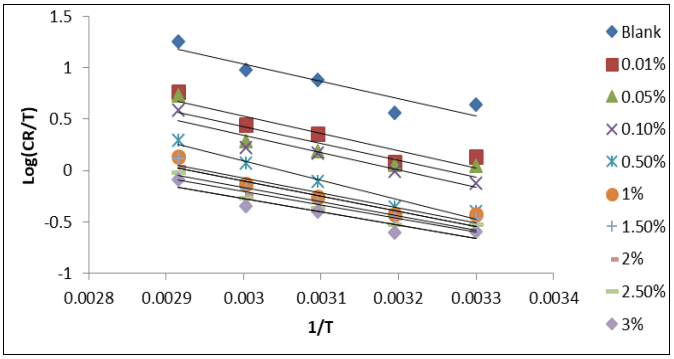


Fig 5: Eyring plot for PCM in 1N H_2SO_4 on mild steel corrosion

4. Conclusions

The following conclusions can be made on the basis of the results obtained.

1. The inhibitor (PCM) shows good inhibition performance for the corrosion of mild steel in 1N H_2SO_4 solution.The inhibition effect increases with increasing concentartions of inhibitor.
2. The results of weight loss measurements for different temperatures showed the maximum inhibition efficiency of 95% for 3% v/v PCM at 343K.
3. GC-MS analysis of peel shows the presence of various active components which are found to be responsible for inhibition. The peel of *Cucurbita maxima* reveals the presence of phytoconstituents belonging to the type, esters, alcohols, ethers, *etc.*
4. The changes in E_a values could be attributed to the fact that the energy barrier for the corrosion process increased after the addition of inhibitor to the aggressive solution, which lead to the inhibition of corrosion.
5. Positive values of ΔH* implies that corrosion process is endothermic. ΔS* values are negative in presence of the additives, indicating that the corrosion process is controlled by activation complex.
6. The experimental data shows that the LCM is a low cost and ecofrindly anticorrosive inhibitor for mild steel in acid medium.

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