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Thermodynamic characterisation of mild steel corrosion and inhibition adsorption of *Uncaria gambir* and catechin in 1 M HCl

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ABSTRACT

Uncaria gambir, a native Southeast Asia herbal plant has been widely used as an astringent medicine for treatment of spongy gums, tooth acne, diarrheas and sore throat. Previous studies have shown that more than 80 % of gambir extract consist mostly flavan monomer, which is catechin and epicatechin. The anti-oxidant properties exhibit in catechin attracts people to study further of its applications. The effect of both *Uncaria gambir* and catechin as corrosion inhibitors for mild steel in acidic solution was done using weight loss measurement at various temperatures. The free energy of adsorption ΔG_{ads} for both *Uncaria gambir* and catechin, indicates that the process was spontaneous and physically adsorbed (physiosorption) onto the mild steel surface. The comparison of inhibition efficiency revealed that *Uncaria gambir* performed more significant than catechin.

Keywords: Uncaria gambir, catechin, corrosion inhibitor, adsorption.

INTRODUCTION

Uncaria gambir, a native of Southeast Asia herbal plant, can be found mostly in countries such as Malaysia, Singapore and Indonesia. Some might call it as Gambir, Gou Teng, Asen'yaku, Cat's Claw, Una de Gato, and Pale Catechu [1-3]. Gambir plant can grow about eight feet high and has oval shape of leave around 8 to 14 cm in length with 4 to 5 pairs or nerves [4]. The flowers also originate at the base of the leaves with each pair of leaves may have a pair of globular inflorescences. According to Hadad *et al.*, (2009), gambir plant can be grown only at certain condition, which is the plant must be grown at 200 to 800 meter above sea level with rainfall around ±3.3 mm per year and humidity around 70 to 85 %. Any types of soil can be used for gambir plantation with the pH range from 4.8 to 5.5 [5].

Quantitative analysis of gambir done by Taniguchi *et al.* (2007a), has shown that the total flavan content by using the vanillin-acid estimation method ranged from 24 to 79 % while analysis using RP-HPLC techniques reveal that catechin content is around 76 %, epicatechin content is 1.5 %, and 1 % each for the content of gambiriin B1, B3 and A1 . The analysis indicated that catechin was the most abundant constituent in gambir [1]. Besides RP-HPLC, Hayani (2003) has studied the catechin content in three different extraction method using spectrophotometer. From the study, she conclude that the extraction of gambir using a hot plate shows higher percentage of catechin content with the range around 81 to 88 % [6].

Catechin (Figure 1) is polyphenolic antioxidant plant metabolites. They belong to the family of flavonoids (C6-C3-C6 skeletal) and to be more specific, flavan-3-ols [7-8]. These compounds are abundant in teas [7, 9], sea buckthorn [10] and other vegetable and plant. Figure 1.13 shows the chemical structure of (+)-catechin. Catechin compounds present in various natural foods are known to show some health-enhancing effects such as carcinogenesis reduction in the external and internal organs [11-13] and reduction in atherosclerotic plaques [14]. Green tea catechins have also shown to possess antibiotic properties due to their role in disrupting a specific stage of the bacterial DNA replication process [15].

Corrosion affects most of industrial sector and may cost billions of dollars each year for preventing and replacement of maintenance [16]. Thus, modern world today made an investigation to overcome this problem by doing enrichment study of corrosion inhibitors. Corrosion inhibitors will reduce the rate of either anodic oxidation or cathodic reduction or both. This will give us anodic, cathodic or mixed type of inhibition. Most of the potential corrosion inhibitor posses an active functional group such a nitro (-NO_2) and hydroxyl (-OH) [17-18]. Despite all these, none of previous studies done to test the performance of *Uncaria gambir* or catechin as corrosion inhibitor. Thus, the aim of this study is to determine the anticorrosive performance of *Uncaria gambir* extract and catechin standard using various techniques.

EXPERIMENTAL

Raw materials of gambir cube were purchased from Medan Province, Indonesia were ground into fine powder and sieved through a 50 μm mesh. The ground gambir were kept in closed container at room temperature prior for extraction. All chemicals and solvents used in this study were analytical reagent (AR) grade and have been used without purification. Standard catechin hydrate were supplied from Sigma Aldrich.

2.1. Preparation of gambir extract

Parts from the ground gambir (5.0 g) were dissolved in 100 mL of distilled water (~90 °C). The aqueous extract of gambir was shaken with the rotational speed of 200 rpm for 1 hour. Then it was transferred to a centrifuge tube and centrifuged for 5 minutes to separate the undissolve gambir and the mother liquors. The mother liquors were then treated with 50 mL of n-Hexane three times in separation funnel to remove lipid and oil from the extracts. The aqueous-phase (lower phase) of from this separation were collected and kept in a refrigerator for further freeze-drying purposes. These to ensure that the aqueous extract can be last for a long time as it will polymerized in liquid form. The resulting aqueous extract powder (1.0 g) was then dissolved in 50 mL of ethyl acetate. Then, the ethyl acetate extract was concentrated at 50 °C under reduced pressure in a rotary evaporator, and dried in an oven at 50 °C.

2.2 Preparation of specimens

Mild steel coupons having chemical composition (wt %) of 0.17 C, 0.20 Si, 0.37 Mn, 0.03 S, 0.01 P and remaining Fe were used. The specimens were polished successively using 400, 600 and 800 gritted emery paper, degreased with methanol and washed with distilled water before experiment.

2.3 Electrolyte

The solutions used were made of AR grade hydrochloric acid. Appropriate concentrations of acids (1 M HCl) were prepared by using distilled water. The concentration range of inhibitor (gambir extract and catechin) employed was varied from 250 ppm to 1000 ppm in non-deaerated solution.

2.4 Weight loss method

Weight loss of rectangular mild steel specimens of dimension 1 mm x 3 cm x 4 cm were immersed in 100 mL of electrolyte with and without the addition of different concentrations of gambir extract and catechin at different temperature (303, 313, 323, 333 K) was determined after 24 hr. The percentage inhibition efficiency (IE) was calculated from:

$$IE\% = \frac{Wo - Wi}{Wo} \; x\ 100 \qquad (1)$$

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

RESULTS AND DISCUSSION

3.1 Effect of temperature

In an attempt to get more information about the performance of the inhibitor (gambir and catechin), and the nature of adsorption isotherm which can be used to explain the adsorption and activation processes, the effect of temperature is therefore been studied. Hence, the weight loss measurements are used in the range of temperature 303-333 K, in the absence and presence of inhibitor at various concentrations during 24 h of immersion. The degree of surface coverage θ for different concentrations of gambir extract has been evaluated using the equation:

$$\theta = \frac{W - W^{\circ}}{W - Wm} \tag{2}$$

where Wm is the smallest corrosion rate.The respective data are shown in Table 1 and 2. Here, as the temperature increases the corrosion rate of acid and inhibitor are also increases. As gambir extract and catechin has been added into the solution, the degree of surface coverage values decreases slightly with increasing temperature in which it could be caused by the desorption of inhibitor from the mild steel surface. In order to calculate activation thermodynamic parameters of the corrosion reaction such as activation energy E_a, activated entropy ΔS and enthalpy ΔH, the Arrhenius equation and its alternative formulation called transition state equation were employed [19]:

$$W = K\, exp\left\{-\frac{Ea}{RT}\right\} \tag{3}$$

$$W = \frac{RT}{Nh}\, exp\left(\frac{\Delta S}{R}\right) exp\left(-\frac{\Delta H}{RT}\right) \tag{4}$$

T is the absolute temperature, *K* is a constant and *R* is the universal gas constant, *h* is Plank's constant, *N* is Avogadro's number. Plotting the natural logarithm of corrosion rate versus $1/T$, the activation energy can be calculated from the slope ($-Ea/R$) (Figure 2 and 3). Plot of log (W/T) versus 1/T give a straight line with a slope of $\Delta H^*/R$ and an intercept of log (R/Nh) + $\Delta S^*/R$ as shown in Figure 4 and 5. The value of ΔH^* and ΔS^* can be calculated from this relation (Table 3 and 4). The activation energies in the presence of gambir extract and catechin were observed higher than those in absence of gambir extract and catechin. This explains that the energy barrier of corrosion reaction increases with the concentration of gambir extract and catechin. Physiosorption is often related with this phenomenon, where an adsorptive film of electrostatic character is formed on the mild steel surface [20]. Thermodynamic parameters (ΔH^* and ΔS^*) of the dissolution reaction of mild steel in the presence of inhibitor are higher than those of the non-inhibited solution. Positive value of activated enthalpy, ΔH^* means that the process is an exothermic process and it needs more energy to achieve the activated state or equilibrium state [19, 21]. Also, the positive of activated entropy, ΔS^* of solution containing gambir extract and catechin indicates that the system passes from less orderly to a more random arrangement [22].

3.2 Adsorption Isotherm

In Langmuir adsorption isotherm, the surface of adsorbent is uniform that is all the adsorption sites are equivalent. It was revealed that Langmuir adsorption isotherm explain about the monolayer formation on the metal surface [21, 23]. According to Morad and Kamal

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El-Dean (2006), Langmuir adsorption isotherm is attributing to physisorption and chemisorption phenomenon [22]. Langmuir is given by:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{5}$$

where C is the concentration inhibitor, θ is the surface coverage and K_{ads} is the adsorption equilibrium constant. The free energy of adsorption ΔG_{ads}, also can be calculated using the following equation:

$$\Delta G_{ads} = -RT \ln(K_{ads} \times 55.5) \tag{6}$$

where 55.5 is the water concentration, R is the universal gas constant and T is the temperature in K. Figure 6 and 7 shows the Langmuir adsorption isotherm plots for gambir extract and catechin at 303 K.

The calculated value of free energy of adsorption for gambir was found to be ΔG_{ads} = -21.9570 kJ mol^{-1} whereas for catechin was found to be ΔG_{ads} = -13.457 kJ mol^{-1}, where adsorption-desorption equilibrium constant K value was obtained from the linear regression of Langmuir isotherm (109.89 M^{-1} for gambir and 3.7651 M^{-1} for catechin). The negative value of ΔG_{ads} indicates that the inhibitor, in this case gambir extract and catechin is spontaneously adsorbed onto the mild steel surface. It is well known that values of ΔG_{ads} around -20 kJ mol^{-1} or lower are associated with the physiosorption phenomenon where the electrostatic interaction assemble between the charged molecule and the charged metal, while those around -40 kJ mol^{-1} or higher are associated with the chemiosorption phenomenon where the sharing or transfer of organic molecules charge with the metal surface occurs [24, 25]. Hence, it is clear that gambir extract and catechin is physically adsorbed onto the mild steel surface.

Moreover, the decrease of inhibition efficiency with the increased in temperature may supports that the adsorption of gambir extract and catechin on the mild steel surface is physical in nature. As the temperature increases, the number of adsorbed molecules decreases, leading to a decrease in the inhibition efficiency. The adsorption is enhanced by the presence of electron donor atom of O, with lone pair electron and delocalized π electrons in the catechin molecules that create electrostatic adsortion with the mild steel surface. As a result, insoluble stable films formed on the mild steel surface thus decrease the metal dissolution.

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CONCLUSION

- Gambir extract and catechin exhibit corrosion inhibition properties with the maximum inhibition at 1000 ppm.
- Temperature study shows that as the temperature becoming high the inhibition efficiency of gambir extract and catechin is decreases.
- Both gambir extract and catechin follows the Langmuir adsorption isotherm. The negative value of free energy of adsorption ΔG_{ads}, indicates that the process was spontaneous and physically adsorbed (physiosorption) onto the mild steel surface.
- The above results show that gambir extract performed more significant than standard catechin.

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FIGURES AND TABLES

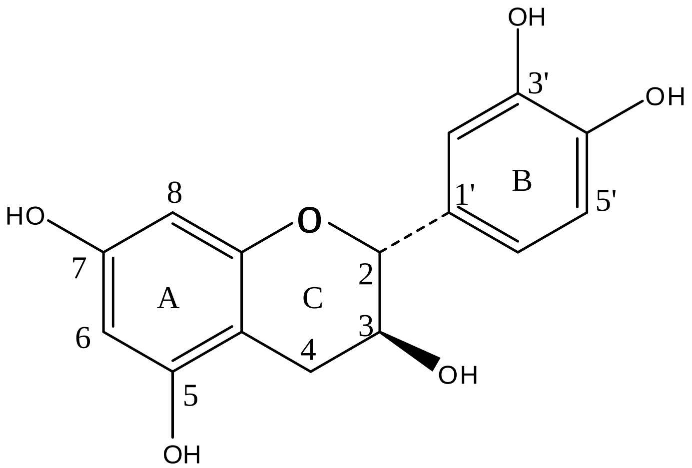

Figure 1: The chemical structure of (+)-catechin.

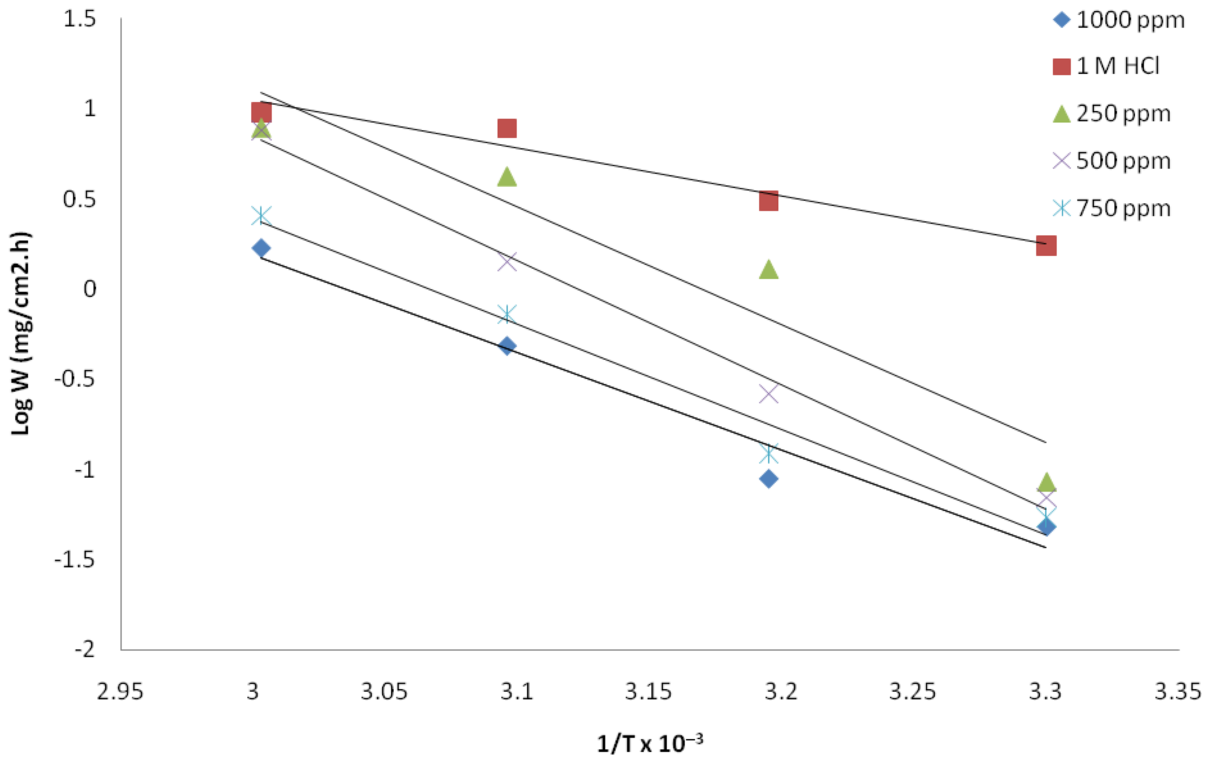

Figure 2: Arrhenius plots for mild steel in 1 M HCl at different concentration of gambir extract.

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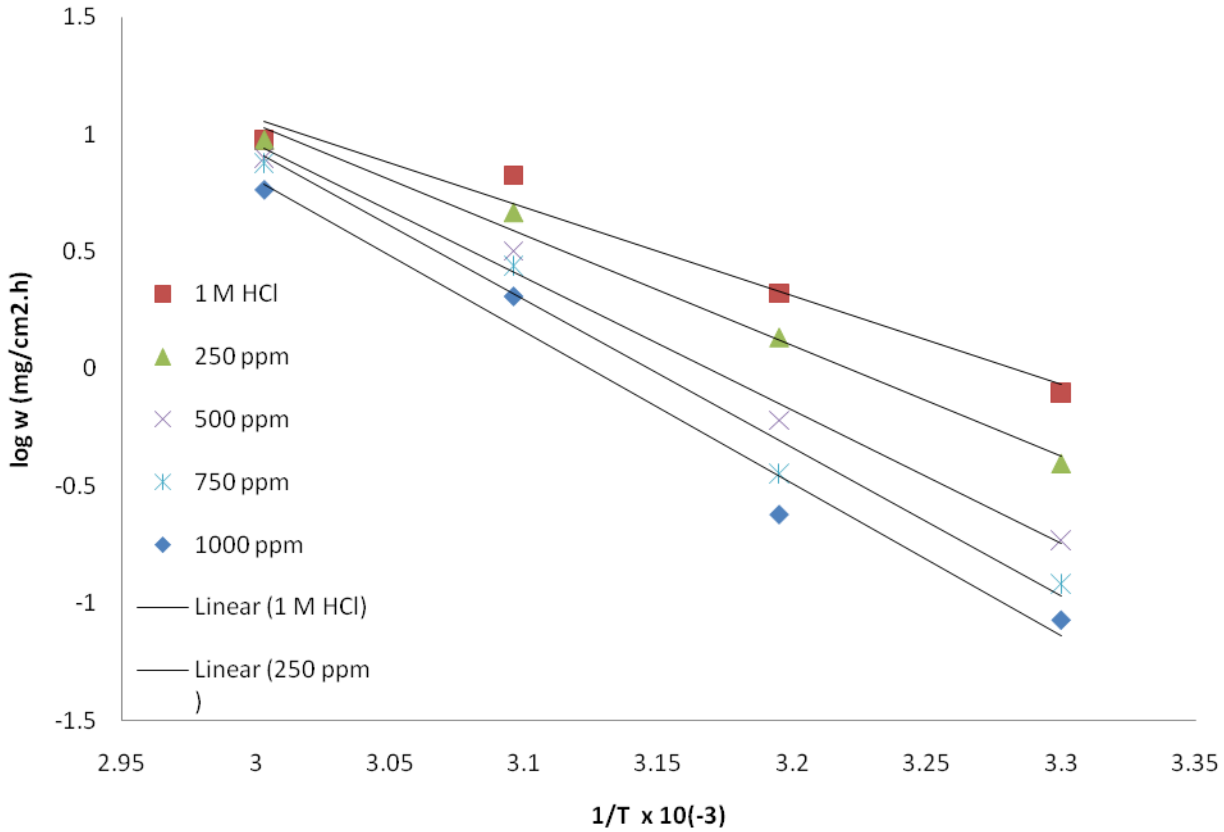

Figure 3: Arrhenius plots for mild steel in 1 M HCl at different concentration of catechin.

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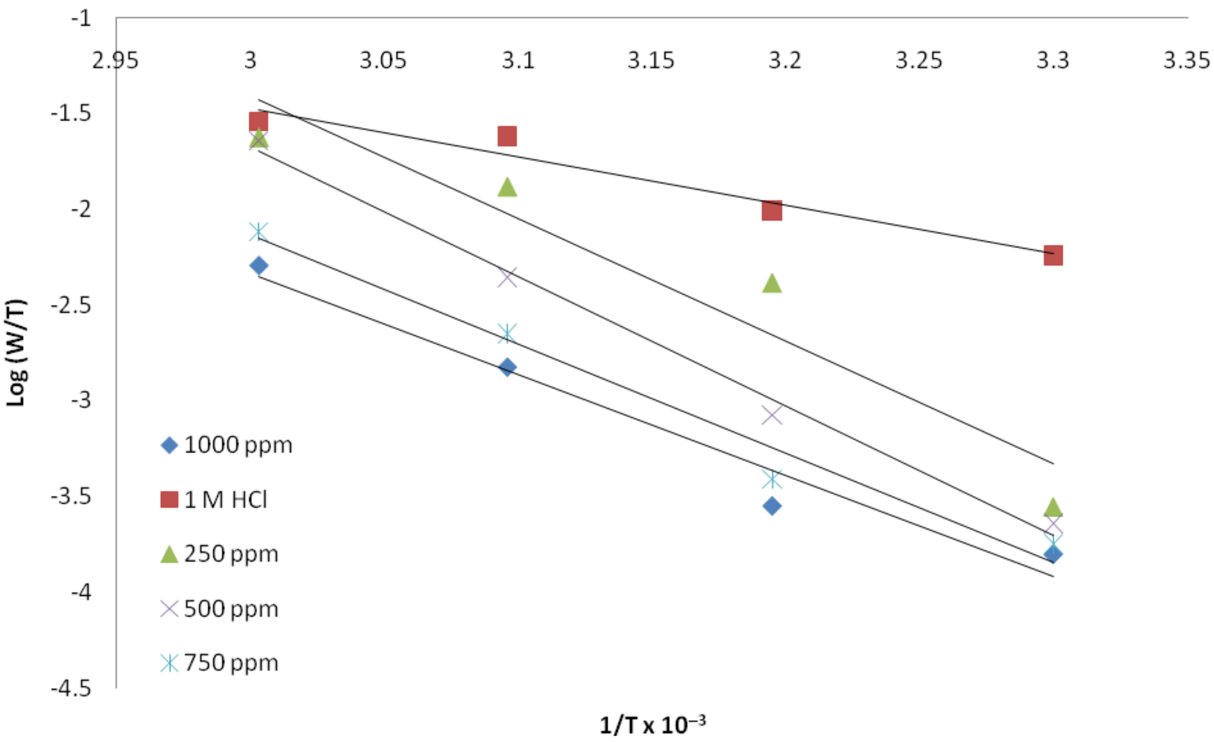

Figure 4: The relation between log (W/T) vs. 1/T for mild steel at different concentration of gambir extract.

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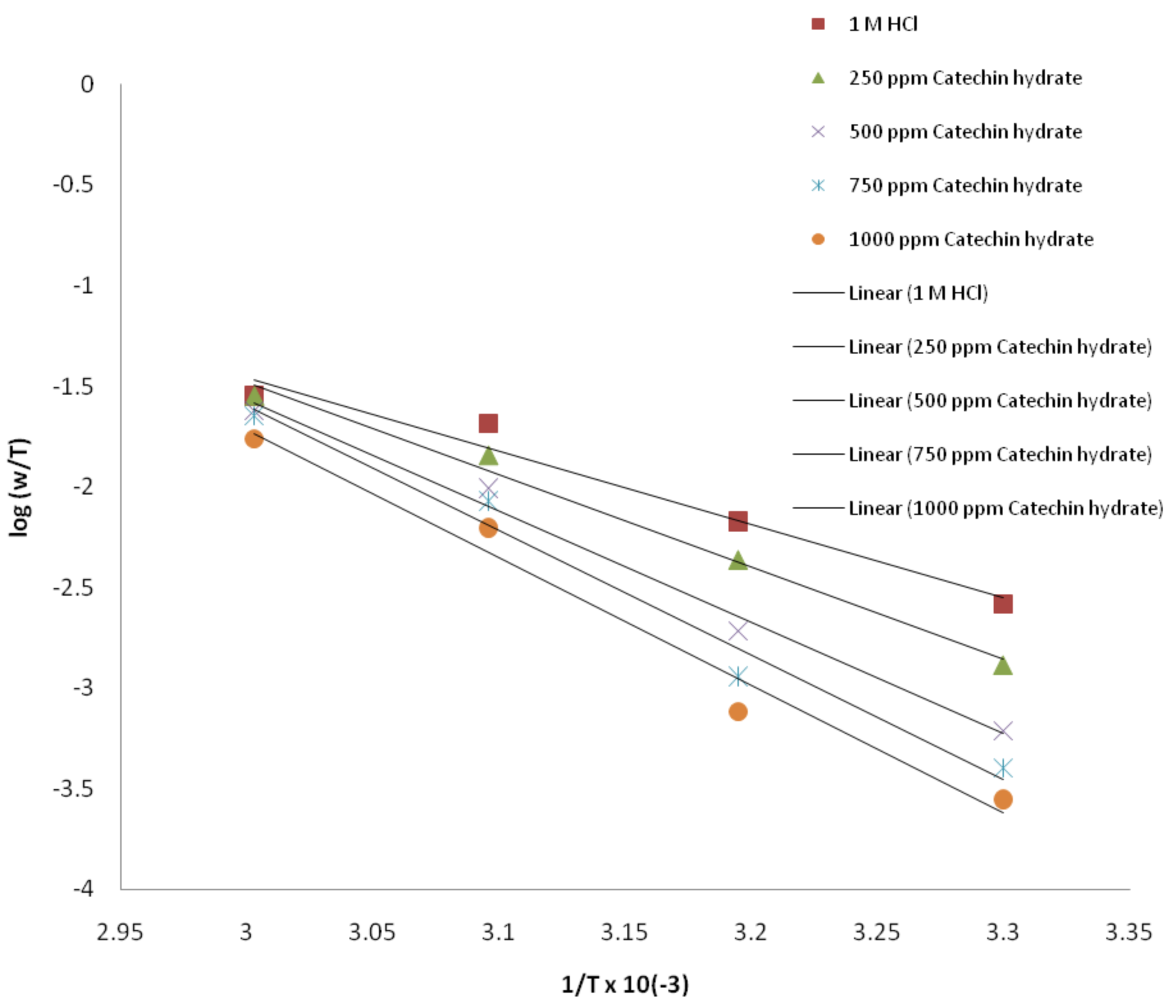

Figure 5: The relation between log (W/T) vs. 1/T for mild steel at different concentration of catechin.

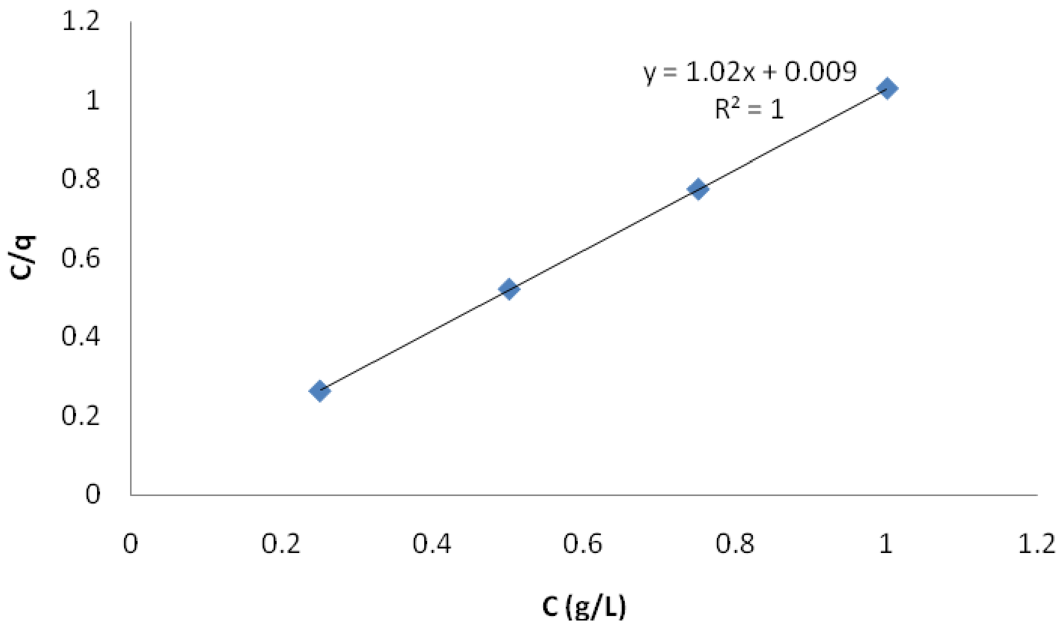

Figure 6: Langmuir adsorption isotherm model for gambir extract in 1 M HCl at 303K.

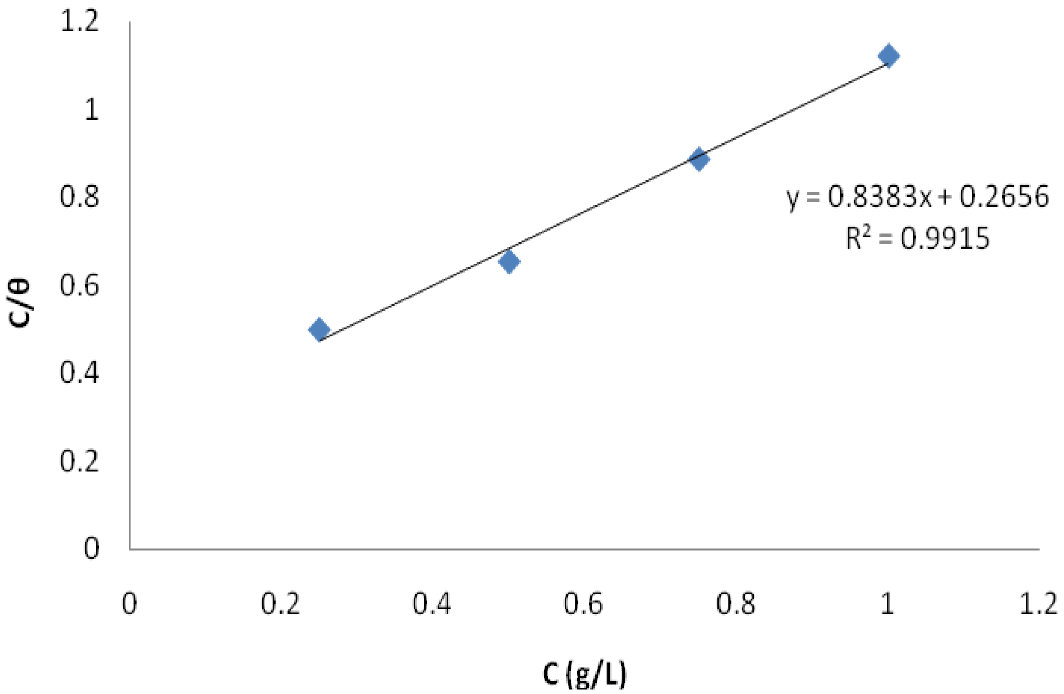

Figure 7: Langmuir adsorption isotherm model for catechin in 1 M HCl at 303K.

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Table 1: Effect of temperature on the corrosion rate of mild steel in 1 M HCl at different concentrations of gambir extract with its efficiency.

Temperature (K)	Concentration (ppm)	W_L	W (mg/cm^2 h)	Ewt (%)	θ	θ/1-θ
303	1 M HCl	0.5013	1.7406	-	-	-
	250	0.0244	0.0847	95.13	0.9513	19.5338
	500	0.0200	0.0694	96.00	0.9600	24
	750	0.0156	0.0542	96.88	0.9688	31.0512
	1000	0.0138	0.0479	97.25	0.9725	35.3636
313	1 M HCl	0.8873	3.0809	-	-	-
	250	0.3713	1.2892	58.15	0.5815	1.3894
	500	0.0757	0.2628	91.46	0.9146	10.7096
	750	0.0352	0.1222	96.03	0.9603	24.1889
	1000	0.0255	0.0885	97.12	0.9712	33.7222
323	1 M HCl	2.2417	7.7837	-	-	-
	250	1.2171	4.2260	45.71	0.4571	0.8419
	500	0.4086	1.4188	81.77	0.8177	4.4867
	750	0.2087	0.7247	90.69	0.9069	9.7411
	1000	0.1392	0.4833	93.79	0.9379	15.103
333	1 M HCl	2.7561	9.5697	-	-	-
	250	2.267	7.8715	17.75	0.1775	0.2158
	500	2.1893	7.6017	55.72	0.5572	1.2588
	750	0.7331	2.5455	73.40	0.7340	2.7593
	1000	0.4858	1.6868	82.37	0.8237	4.6721

Table 2: Effect of temperature on the corrosion rate of mild steel in 1 M HCl at different concentrations of catechin with its efficiency.

Temperature (K)	Concentration (ppm)	W_L	W (mg/cm2 h)	Ewt (%)	θ	θ/1-θ
303	1 M HCl	0.2279	0.7913	-	-	-
	250	0.1137	0.3948	50.11	0.5011	1.0044
	500	0.0535	0.1858	76.52	0.7652	3.2589
	750	0.0349	0.1212	84.69	0.8469	5.5317
	1000	0.0244	0.0847	89.28	0.8928	8.3284
313	1 M HCl	0.6053	2.1017	-	-	-
	250	0.3912	1.3583	35.37	0.3537	0.5473
	500	0.1738	0.6035	71.29	0.7129	2.4831
	750	0.1027	0.3566	83.03	0.8303	4.8928
	1000	0.0687	0.2385	88.64	0.8864	7.8028
323	1 M HCl	1.925	6.6840	-	-	-
	250	1.3338	4.6313	30.71	0.3071	0.4432
	500	0.9137	3.1726	52.54	0.5254	1.1070

	750	0.791	2.7465	58.91	0.5891	1.4337
	1000	0.5842	2.0285	69.65	0.6965	2.2948
333	1 M HCl	2.7169	9.4337	-	-	-
	250	2.7147	9.4260	0.809	0.0008	0.0008
	500	2.2873	7.9420	15.81	0.1581	0.1878
	750	2.1681	7.5281	20.19	0.2019	0.2529
	1000	1.6614	5.7688	38.85	0.3885	0.6353

Table 3: Activation parameters of the dissolution reaction of mild steel in 1 M HCl in the absence and presence of gambir extract.

Conc. (ppm)	*Ea* (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (kJ/mol.K)
1 M HCl	22.0902	20.9429	-35.24
250	54.3403	53.2013	62.03
500	57.4082	56.2608	69.02
750	48.4706	47.3233	38.42
1000	44.9787	43.8314	26.28

Table 4: Activation parameters of the dissolution reaction of mild steel in 1 M HCl in the absence and presence of catechin.

Conc. (ppm)	*Ea* (kJ/mol)	ΔH^* (kJ/mol)	ΔS^* (kJ/mol.K)
1 M HCl	31.4569	30.3062	-6.9754
250	39.2769	38.1313	16.3062
500	47.1612	46.0172	39.2279
750	52.5994	51.4537	55.3072
1000	53.9495	52.8030	58.3501