ADSORPTION BEHAVIOR OF CU-ZN ALLOY IN ACID ENVIRONMENT USING GREEN INHIBITOR

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ABSTRACT
Adsorption behavior of Cu-30Zn alloy in 1.0N HCl solution in the presence of Lagenaria Siceraria Peel extract was studied by mass loss measurements with various periods of contact and temperature. Inhibition efficiency increased with increase of inhibitor concentration. The inhibitive effect of the Lagenaria Siceraria Peel could be attributed to the presence of some active compound which is adsorbed on the surface of the Cu-30Zn alloy. The LSP was found to conform by various adsorption isotherms viz., Langmuir adsorption, Temkin adsorption, Florry-Huggins adsorption, Frumkin adsorption, Freundlich adsorption and El-Awady adsorption isotherm at different concentration and temperature investigated and inhibitor obeyed Frumkin adsorption isotherm. Thermodynamic parameters also revealed that the adsorption process is spontaneous.

Key words - Cu-Zn alloy, Corrosion inhibition, Lagenaria Siceraria Peel, Adsorption isotherms.

1. INTRODUCTION
Brass is a binary alloy composed of copper and zinc that has been produced for millennia and is valued for its workability, hardness, corrosion resistance and attractive appearance. However, their exhibition in acid media creates problems of corrosion [1-3]. Acid solutions are often used in industry for cleaning, descaling and pickling of metallic structures which are normally accompanied by considerable dissolution of the metal. A useful method to protect metal and alloys in aggressive environments against corrosion is addition of organic and inorganic species to the solution in contact with the surface in order to inhibit the corrosion reaction and hence reduce the corrosion rate. However most of these synthetic chemical inhibitors are toxic to the environments. In an attempt to find corrosion inhibitors which are environmentally safe and easily available, there has been a growing trend in the use of natural products such as leaves or plant extracts as corrosion inhibitors for metals in various environment, because they are inexpensive, readily available, renewable sources of materials and ecologically acceptable [4]. They are rich enough source of active molecules, which have noticeably high inhibition efficiency and hence termed as "Green Inhibitors" [5]. Some investigators namely Ebenso et al. [6], Abiola et al. [7], Bendahou et al. [8], Odiongenyi et al. [9], Eddy et al. [10-12], Deeparani et al. [13-16], Petchiammal et al. [17-19], and A.Sharmila et al. [20], Deivanayagam et al. [21-23], Bright et al. [24,25], have been reported the successful use of naturally occurring substances to inhibit the corrosion of metals in various environment. In continuity of our research work the present study is aimed at investigating the inhibitive and adsorption properties of ethanolic extract of Lagenaria Siceraria Peel for the corrosion of Cu-30Zn alloy in HCl on using mass loss measurements with different time and temperature.

2. MATERIALS AND METHODS
(i). LAGENARIA SICERARIA PEEL [LSP] IS USED AS CORROSION INHIBITOR.
(ii). SPECIMEN PREPARATION
Rectangular specimen of Brass was mechanically pressed cut to form different coupons, each of dimension exactly 20cm^2 (5x2x2cm)with emery wheel of 80 and 120 and degreased with trichloroethylene, washed with distilled water, cleaned and dried, then stored in desicators for our present study.

(iii).MASS LOSS METHOD

In the mass loss measurements on Brass in triplicate were completely immersed in 50ml of the test solution in the presence and absence of the inhibitor. The metal specimens were withdrawn from the test solutions after 24 to 360 hrs at room temperature and also measured 313K to 333K.

3.0 RESULTS AND DISCUSSION

3.1 EFFECT OF TIME VARIATION

Observed results (Table-1) clearly indicates that the percentage of inhibition efficiency and the degree of surface coverage (θ) increased with increase of inhibitor concentration. The maximum of 96.55% inhibition efficiency is achieved even after 120 hrs exposure time. It may be predominantly by the adsorption of the important plant constituents from the inhibitor, on the metal surface by the interaction of π- electrons or lone pair of hetero atoms with the metal ion. The main phytoconstituents like Alkaloids, Tannins, Flavanoids, Terpenoids, and Saponins etc. are found to be a big molecule may capable of covering a large surface area on metal surface. These adsorbed molecules are blocks the active sites in which direct acid attack proceed and protect the metal from dissolution process. From this result, it can be noticed that the inhibition efficiency increased with increase of LSP extract concentration. It is revealed that the LSP extract retards the dealloying process of Cu-30Zn alloy in 1.0 N HCl acid solution.

Table-1: The corrosion parameters of Cu-30Zn alloy in 1.0N HCl containing different concentration (0 to 1000ppm) of LSP extract after 24 to 360 hours exposure time

Conc. of inhibitors (ppm)	24 hrs		72 hrs		120 hrs		240 hrs		360 hrs	
	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E
0	0.9616	-	0.3832	-	0.2424	-	0.1191	-	0.0933	-
10	0.5226	45.65	0.3066	19.98	0.0710	70.70	0.1170	1.76	0.0724	22.40
50	0.5017	47.82	0.2299	40.00	0.0627	74.13	0.1128	5.28	0.0445	52.30
100	0.4180	56.53	0.2020	47.28	0.0418	82.75	0.1107	7.05	0.0334	64.20
500	0.2508	73.91	0.0975	74.55	0.0292	87.95	0.0627	47.35	0.0139	85.10
1000	0.1672	82.61	0.0766	80.00	0.0083	96.55	0.0250	49.26	0.0097	89.60

3.2. EFFECT OF TEMPERATURE

Dissolution behaviour of Cu-Zn alloy in 1.0N HCl containing various concentration of LSP extract at 303to 333K and the observed values are listed out in Table-2. The observed result reveals that the corrosion rate decreased with increase of inhibitor concentrations and increased with rise in Temperature range from 303 to 333K. Maximum of 61.90% inhibition efficiency is only achieved at 333K. However the value of inhibition efficiency is increased with rise in Temperature may suggests and support that the facts that the process of adsorption follows Chemisorption.

Corrosion inhibitor of LSP at various concentrations and temperatures were reflected by Figure-1, in 1.0N HCl with and without of LSP. The corrosion rate (CR) in hydrochloric acid without of the LSP was starting from corrosion rate 43.6494mmpy at 303K and raised to 52.6804mmpy at 333K as increasing sharply. Increasing of LSP concentration lead to reducing the corrosion rate sharply at different temperatures.

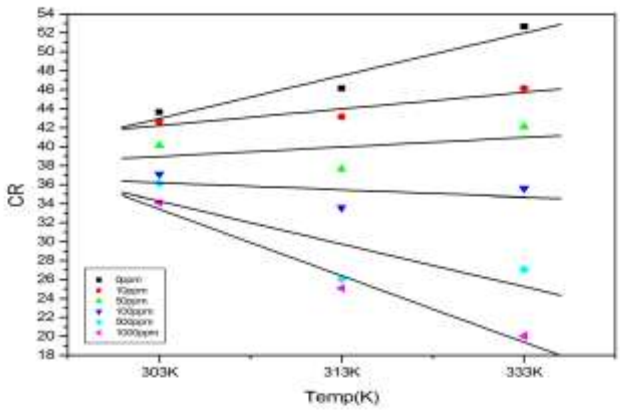

Figure-1. The Corrosion rate of Cu-Zn alloy in 1.0N HCl at different temperature with inhibitor concentration.

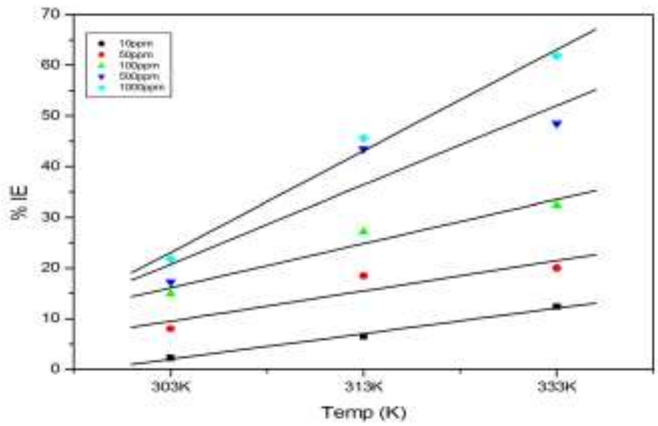

Figure-2. Inhibition efficiency of LSP on Cu-Zn alloy in 1.0N HCl at different temperature with inhibitor concentration.

Percentage of IE increased with increase of inhibitor concentration. The effect of %IE versus Temperature was shown in figure-2 reveals that the %IE increased with increase of temperature and the maximum concentration of 1000ppm and the highest temperature value at 333K. Increasing of IE with raise of LSP concentration is due to the complexity between the metal surface and the active inhibitor molecules via coordination bonds. At highest experimental temperature 333K the %IE was the highest, and this may be due to the naturation of bond formation.

Table-2: Corrosion parameters of Cu-Zn alloy in 1.0N HCl containing different concentration of LSP extract at 303 to 333K after one hour exposure time.

Conc. of inhibitor (ppm)	303 K		313 K		333 K	
	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E	C.R (mmpy)	% I.E
0	43.6494	-	46.1580	-	52.6804	-
10	42.6460	2.29	43.1477	6.52	46.1580	12.38
50	40.1374	8.04	37.6288	18.47	42.1443	20.00
100	37.1271	14.94	33.6151	27.17	35.6219	32.38

500	36.1237	17.24	26.0893	43.47	27.0927	48.57
1000	34.1168	21.83	25.0859	45.65	20.0687	61.90

3.3 ACTIVATION PARAMETERS ON THE INHIBITION PROCESS:

Usually, the temperature plays an important role to understanding the inhibitive mechanism of the corrosion process. To assess the temperature effect, experiments were performed at 303K- 333K in uninhibited and inhibited solutions containing different concentrations of LSP and the corrosion rate was evaluated and the values are presented in Table-3. The relationship b/w the corrosion rate (CR) of mild steel in acidic media and temperature (T) is expressed by the Arrhenius equation,

$$\text{Log CR} = -Ea/2.303RT + \log \lambda \text{ --------- } \rightarrow (1)$$

Where Ea is the apparent effective activation energy, R molar gas constant and λ is the Arrhenius pre-exponential factor.

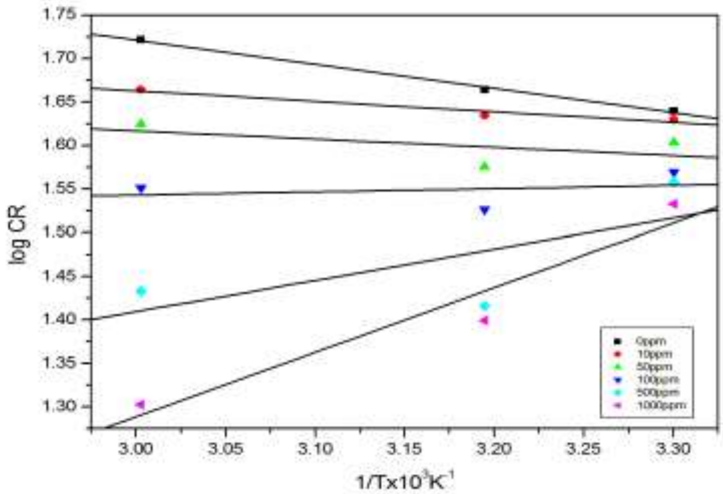

Fig-3. Arrhenius plot for Cu-Zn alloy corrosion 1.0N HCl in the absence and presence of different concentration of LSP.

A plot of log (CR) obtained by weight loss measurement versus 1/T gave straight line with regression co-efficient (R^2) close to unity as shown fig (3). The values of apparent activation energy (Ea) obtained from the slope (-Ea/2.303R) of the lines and the pre-exponential factor (λ) obtained from the intercept (logλ) are given in Table -3. It is evident from the Table that the apparent energy of activation decreased on addition of (LSP) in comparison to the uninhibited solution. These values ranged from 5.3171 to -14.2110 kJ/mol and are lower than the threshold value of 80kJ/mol required for chemical adsorption. This shows that the adsorption of ethanol extract of LSP on Cu-Zn alloy surface is Physical adsorption. Decrease in the activation energy is attributed to appreciable increase in the adsorption of inhibitor on Cu-Zn alloy surface by increase in the temperature. The increase in adsorption leads to decrease in corrosion rate due to the lesser exposed surface area of the Cu-Zn alloy towards 1.0N HCl.

Table:3 Activation parameters of LSP in 1.0N HCl.

Inhibitor conc. (ppm)	E_a kJ/mol	Λ mg/cm	ΔH (kJ/mol)	ΔS (J/mol/k)	Q_{ads} ($KJmol^{-1}$)
Blank	5.3171	$3.58x10^2$	1.1598	77.3098	--
10	2.3014	$1.05\ x10^2$	-0.1488	72.8942	97.0018
50	1.7960	$0.79\ x10^2$	-0.3708	71.8441	29.3845
100	-0.7065	$0.27\ x10^2$	-1.4582	67.9706	28.0515
500	-6.868	$0.02\ x10^2$	4.1312	58.8410	42.2704
1000	-14.211	$0.0011\ x10^2$	7.3221	48.2615	49.2382

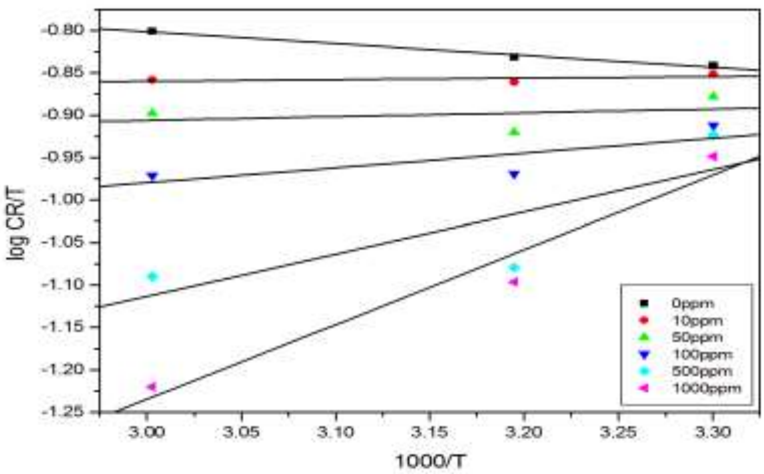

Figure-4 Transition state plot for Cu-Zn alloy corrosion in 1.0N HCl in the absence & presence of different concentration of LSP.

The value of λ is also lower for inhibited solution than for the uninhibited soln. It is clear from equation (1) that corrosion rate is influenced by both Ea & λ. Moreover increase in concentration of (LSP) in leads to an decrease in the value of Ea, indicating that the weak adsorption of the inhibitor molecules on the metal surface.

Experimental corrosion rate values evaluated from the weight loss data for Cu-Zn alloy in 1.0N HCl in the presence and absence of LSP was used to determine the enthalpy of activation (ΔH) and apparent entropy of activation (ΔS) for the formation of the activation complex in the transition state equation (2). An alternative formula for the Arrhenius equation is the transition state equation

$$CR = RT/Nh \exp(\Delta S/R) \exp(-\Delta H/RT) \text{ --------------(2)}$$

A plot of log (CR/T) versus 1/T is shown is fig (4), a straight lines were obtained with slope (-ΔH/2.303R) and intercept of [log (R/Nh)+(ΔS/2.303R)], from which ΔH and ΔS were calculated and listed out in Table -3. The positive value of enthalpy of activation (ΔH) in the presence and absence of various concentration of inhibitor reflects that the endothermic natures of Cu-Zn alloy dissolution process meaning that the dissolution of alloy is difficult. It is evident from the table that the value of ΔH increases in the presence of the inhibitor than the uninhibited solution indicating the higher protection efficiency. This may be attributed to the presence of energy barrier for the reaction; hence the process of adsorption of inhibitor leads to raise in enthalpy of the corrosion process on comparing the values of entropy of activation (ΔS) listed in Table-3. It is clear that the entropy of activation decreased in the presence of the using inhibitor compared to free acid solution. The decrease in the entropy of activation (ΔS) in the presence of inhibitor may decreases in the disordering on going from reactant to activated complex is difficult.

3.4 HEAT OF ADSORPTION: THERMODYNAMIC/ ADSORPTION PARAMETERS:

The heat of adsorption on the surface of various metals in the presence of plant extract in 1.0N HCl environment is calculated by the equation (3).

$$Q_{ads} = 2.303 R [\log (\theta_2/1-\theta_2) - \log (\theta_1/1-\theta_1)] \times (T_2T_1/T_2-T_1) \text{ ------(3)}$$

The calculated Q_{ads} values (Table-3) are ranged from 97.0018 to 49.2382 kJ/mol indicating that the adsorption of ethanol extract of LSP on mild steel surface is endothermic.

3.5 ADSORPTION STUDIES:

Processes of adsorption are very important phenomenon to determine the corrosion rate of reaction mechanism. The most frequently uses of isotherms are viz: Langmuir, Temkin, Frumkin, Flory- Huggins, Freundlich and the El-Awady thermodynamic-kinetic model.

3.5.1. LANGMUIR ISOTHERM:

Langmuir adsorption isotherm is expressed according to equation (4)

$$\text{Log } C/\theta = \log C - \log K \text{ ---------} \rightarrow (4)$$

Plotting log (C/θ) against log C gave a linear relationship as shown in fig.5, and the adsorption parameters are presented in Table- 4. The average regression value (R^2= 0.9761) move close to unity suggest that the adsorption of extract of LSP on surface of mild steel indicated that there is no interaction b/w the adsorbate & adsorbent.

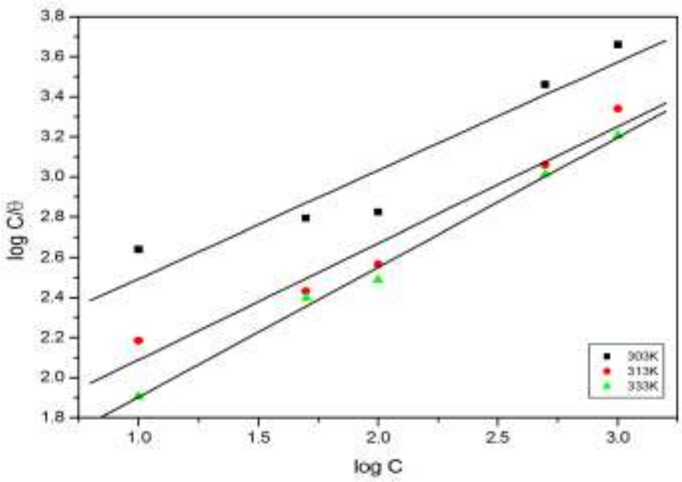

Figure -5. Langmuir isotherm for adsorption of ethanol extract of Lagenaria Siceraria Peel on Cu-Zn alloy surface.

3.5.2. TEMKIN ISOTHERM:

Temkin adsorption isotherm, the degree of surface coverage(θ) is related to the inhibitor concentration (c) according to equation(5),

$$Exp\ (-2a\ \theta) = KC \text{-------------- } (5)$$

K-adsorption of equilibrium constant and a is the attractive parameter, Rearranging & taking logarithm of both sides of equation (E) gives equation(6)

$$\Theta = (-2.303\log k/2a) - (2.303\log C/2a) \text{------------}(6)$$

Plots of θ against log c are presented in fig-6 gave linear relationship, which shows that the adsorption data fitted Temkin Adsorption Isotherm. Adsorption parameters obtained from Temkin adsorption isotherm are recorded in Table-4. The average regression co-efficient value (R^2) is 0.9826 close to unity. The values of attractive parameter (a) are positive in all cases, indicating that the no repulsion exists in the adsorption layer.

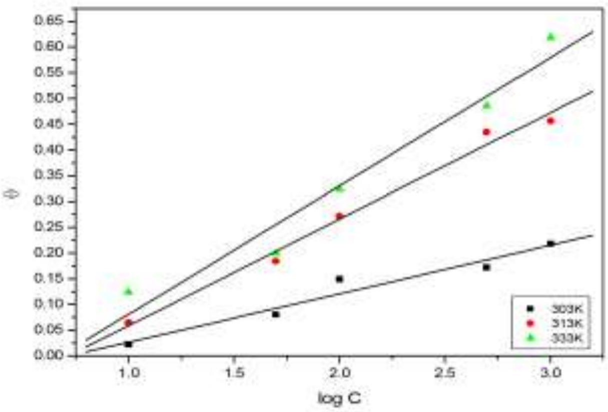

Figure-6. Temkin isotherm for adsorption of ethanol extract of Lagenaria Siceraria Peel on Cu-Zn alloy surface.

3.5.3 FLORRY-HUGGINS ISOTHERM:

Florry- Huggins adsorption isotherm can be expressed according to equation (7)

$$\text{Log}\ (\theta/C) = \log K + x\log (1-\theta) \text{ ---------------- } \rightarrow (7)$$

The plots of log θ/c against log (1- θ) are shown in fig 7, and this data conformed to Florry huggins isotherm with average regression co-efficient (R^2) value 0.9436. It is less than unity. The values of the size parameter x are positive as shown in Table -4. This indicates that the adsorbed species of ethanol extracts of LSP is bulky. Since it could displace more than one water molecule from the Cu-Zn alloy surface.

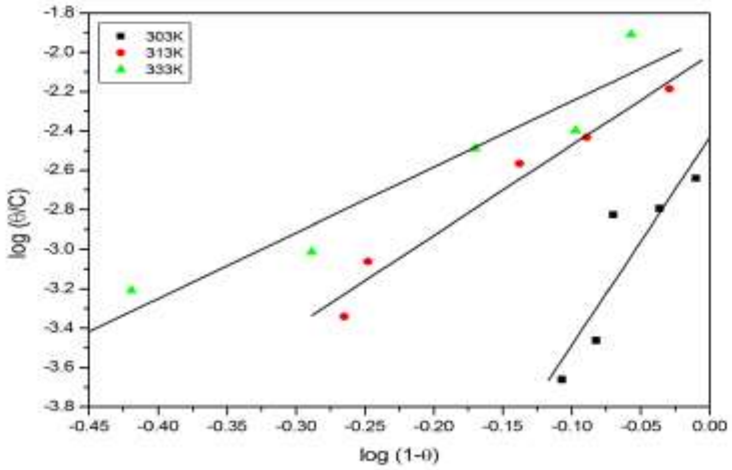

Figure-7. Florry-Huggins isotherm for adsorption of ethanol extract of Lagenaria Siceraria Peel on Cu-Zn alloy surface.

3.5.4. FRUMKIN ISOTHERM:

Frumkin adsorption isotherm is given by equation (8)

$$\log \{ [C]^* (\theta/1-\theta)\} = 2.303 \log K + 2\alpha\theta \text{ ----------} \rightarrow (8)$$

where k is the adsorption –desorption constant and α is the lateral interaction term describing the interaction in adsorbed layer plots of log { [C]* (θ/1- θ)} versus θ as presented were linear which shows the applicability of Frumkin isotherm. The values for Frumkin adsorption parameters were recorded in Table 4. The average regression co-efficient value (R^2=0.9883) is almost close to unity and obeys Frumkin adsorption isotherm. Also shows that values of the adsorption parameters α are positive suggest that the attractive behaviour of the inhibitor on the surface of Cu-Zn alloy.

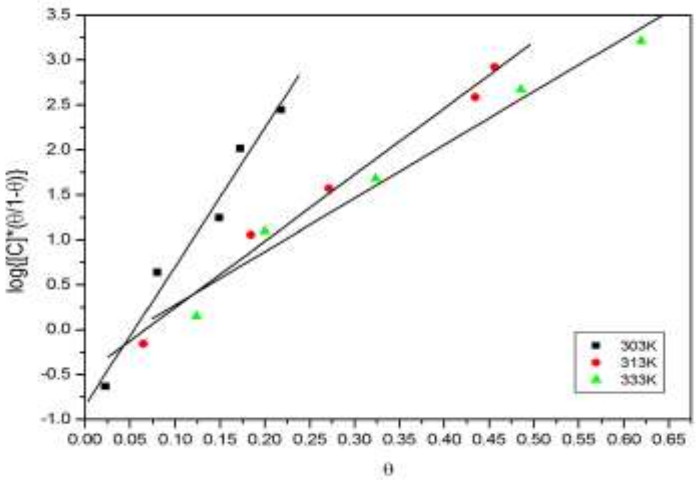

Figure-8. Frumkin isotherm for adsorption of ethanol extract of Lagenaria Siceraria Peel on Cu-Zn alloy surface.

3.5.5 FREUNDLICH ISOTHERM:

The Freundlich adsorption isotherm can be also be applied

$$\Theta = Kc^n \text{ ------------} \rightarrow (9)$$

Freundlich model equation(9) can be rearranged as

$$\text{Log } \theta = \log K + n \log C \text{ --------} \rightarrow (10)$$

This can be plotted as log θ vs log C from the intercept of the values of K can be obtained. Note that the values of the slopes and intercepts were taken from the straight line eqns. The higher values of K indicate that the inhibitor strongly adsorbed on the metal surface.

The magnitude of the exponent n gives an indication on the favourability of adsorption. It is generally stated that values of n in the range 2-10 represent good, 1-2 moderately difficult and less than 1 poor adsorption characteristics. Thus LSP inhibitor adsorbed on the metal surface by physical process.

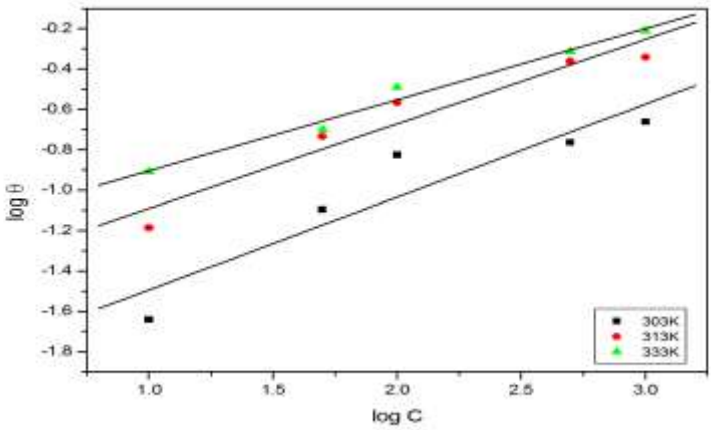

Figure -9. Freundlich isotherm for adsorption of ethanol extract of Lagenaria Siceraria Peel on Cu-Zn alloy surface.

3.5.6. EL AWADY ISOTHERM:

The El-Awady adsorption isotherm is given by

$$\text{Log}\ (\theta/1-\theta) = \log K + y\log C \quad (11)$$

Where C is molar concentration of inhibitor in the bulk solution, θ is the degree of surface coverage, K is the equilibrium const of adsorption process, $k_{ads} = k^{1/y}$ and y represents occupying a given active site. Value of 1/y less than unity implies the formation of multilayer of the inhibitor on the metal surface, while the value of 1/y greater than unity means that a given inhibitor occupy more than one active site [26,27,28]. Curve fitting of the data to the thermodynamic/kinetic model [El-Awady et al.,] is shown in fig(10). The plot gives straight lines which show that the experimental data fits the isotherm. The values of k_{ads} and 1/y calculated from the El-Awady et al isotherm model is listed in table (4).

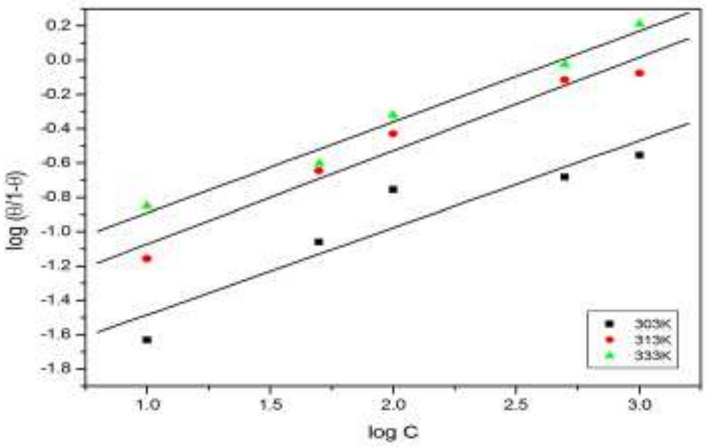

Figure-10. El-Awady isotherm for adsorption of ethanol extract of Lagenaria Siceraria *Peel* on mild steel surface.

3.6. FREE ENERGY OF ADSORPTION

The equilibrium const of adsorption of ethanol extract of (LSP) on the surface of mild steel is related to the free energy of adsorption (ΔG) according to equation (12)

$$\Delta G = -2.303RT \log (55.5K) \quad (12)$$

Where R is gas constant and T is the temperature. The free energy of adsorption was calculated from values of k obtained from Langmuir, Temkin, Flory –Huggins, Frumkin, Freundlich and El-Awady according to equation (12) and is recorded in Table-4. The results show that free energy of adsorption ΔG are negative & less than the threshold value of -40kJ/mol required for chemical adsorption, indicating that adsorption of ethanol extract of LSP on Cu-Zn alloy surface is spontaneous and occurred according to the mechanism of physical adsorption. Since phenomenon is attributed to electrostatic interactions between the charged metal and charged molecules.

Table:4. Adsorption parameters for adsorption of ethanol extract of LSP on Cu-Zn alloy surface.

Isotherm	Temperature	R^2	log K	ΔG_{ads} kJ/mol	Slope value
Langmuir	303K	0.9495	1.9535	-21.4530	
	313K	0.9817	1.5083	-19.4929	
	333K	0.9973	1.2569	-19.1335	
					a
Temkin	303K	0.9748	-0.0676	-9.7273	12.19
	313K	0.9941	-0.1477	-9.5684	5.56
	333K	0.9791	-0.1679	-10.0508	4.62
					x
Florry-Huggins	303K	0.8918	-2.4293	3.9886	10.58
	313K	0.9839	-2.0133	1.6387	4.58
	333K	0.9551	-1.9129	0.0122	3.34
					α
Frumkin	303K	0.9851	-0.8432	-7.9955	7.72
	313K	0.9936	-0.4930	-9.1709	3.69
	333K	0.9863	-0.3175	-10.2429	2.96
					n
Freundlich	303K	0.9324	-1.9535	1.2205	0.46
	313K	0.9656	-1.5083	-1.4122	0.41
	333K	0.9911	-1.2569	-3.1052	0.35
					1/y
El-Awady	303K	0.9400	-1.9896	12.8465	1.9735
	313K	0.9814	-1.6165	7.3494	1.8358
	333K	0.9910	-1.4196	5.9651	1.8864

4. CONCLUSIONS

Using Lagenaria Siceraria Peel (LSP) extract Cu-Zn in 1.0N Hydrochloric acid Lagenaria Siceraria Peel *leaves* have shown excellent inhibition performance for Cu-Zn alloy in 1.0N Hydrochloric acid. The inhibition efficiency increased with the increase of inhibitor concentration (0 to 1000ppm). The maximum percentage of inhibition efficiency was achieved 96.55%. Also, the inhibition efficiency gradually increased with the rise in temperature i.e., to 61.90% for 333K. It follows physical adsorption mechanism. The activation energy (E_a), heat of adsorption (Q_{ads}), Standard free energy adsorption (ΔG_{ads}), enthalpy (ΔH), entropy (ΔS), suggests that, Physisorption, endothermic, spontaneous process respectively. The LSP inhibitor obeys Frumkin adsorption isotherm.

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