Adsorption behavior of Mimusops Elengi leaves on Carbon Steel in 1.0N HCl Acid

[1]I.Malar vizhi, [2]S. Selvaraj

[1]Research Scholar, Reg.No:12419, [2]Associate Professor & Head,

Postgraduate and Research Department of Chemistry, Sri Paramakalyani College, Alwarkurichi,

Affiliated to Manonmaniam Sundaranar University, Abishekapatti, Tirunelveli, Tamil Nadu, India.

ABSTRACT - Adsorption behavior of Carbon steel in 1.0N HCl solution in the presence of mimusops elengi leaves (MEL) 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 mimusops elengi leaves could be attributed to the presence of some active compound which is adsorbed on the surface of the Carbon steel. The MEL was tried 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 but among these the inhibitor obeyed Frumkin adsorption isotherm. Thermodynamic parameters also revealed that the adsorption process is spontaneous, Physisorption.

Key words – Carbon Steel, 1.0N HCl, Corrosion inhibition, Mimusops Elengi Leaves, Adsorption isotherms.

I. INTRODUCTION

Corrosion of Carbon steel is one of the most common forms of corrosion in acidic medium. The practical importance of such corrosion is in acid pickling of iron, chemical cleaning of scales of boilers, oil and petrochemical industries. Hydrochloric acids and Carbon steel are most commonly used in the industries. So this leads to researchers studying the effect of corrosion inhibitors on Carbon steel in hydrochloric acid environment [1-5]. The inhibition of steel in acid solutions by different type of organic compounds has been extensively studied [6]. Pure synthetic chemicals are costly, but some of them are easily biodegradable and their disposal creates pollution problems. Plant extracts are environmentally friendly, bio-degradable, non-toxic, plenty and potentially low cost. Recently, a few investigators studied the plant extracts and the derived organic species become more important as an environmentally benign, readily available, renewable and acceptable source for a wide range of inhibitors. Several efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors. The plant extract are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as “Green Inhibitors”. These inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Recent years, several green inhibitors have been used for the prevention of corrosion by most of the investigators. Few examples are *Cnidoscolus chayamans*, *Solanum Torvum*, *Pisonia Grandis*, *mimusops elengi*, *Sauropus Androgynus*, *Kingiodendron pinnatum*, *Wrightia Tinctoria*, Lagenaria Siceraria Peel, Tephrosia Purpurea, *Alangium Salvifolium* Leaves *[7-16]*. In continuous of our research work, our present investigation is the corrosion inhibitive efficacy of *Mimusops elengi leaves* on Carbon steel in 1.0N Hydrochloric acid have been studied with various periods of contact and temperature using the mass loss measurements.

II. MATERIALS AND METHODS

2.1 MIMUSOPS ELENGI LEAVES USED AS A CORROSION INHIBITOR

2.2 STOCK SOLUTION OF MIMUSOPS ELENGI LEAVES EXTRACT:

Mimusops elengi leaves (MEL) was collected from the source and dried under shadow for about 10 days, grained well, then soaked in a solution of ethyl alcohol for about 48 hrs, Then it is filtered followed by evaporation in order to remove the alcohol solvent completely and the pure plant extract was collected. From this extract, different concentration of 10 to 1000ppm stock solution was prepared using double distilled water and used throughout our present investigation.

2.3 SPECIMEN PREPARATION

Rectangular specimen of Carbon steel was mechanically pressed cut to form different coupons, each of dimension exactly 20cm^2 (5x4.9x1.9cm)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.

 DOI : 10.18231/2454-9150.2019.0096

III. RESULTS AND DISCUSSION

3.1 EFFECT OF TIME VARIATION

Dissolution behavior of Carbon steel in 1.0N HCl containing the presence and absence of MEL extract with different exposure time (from 24hrs to 360 hrs) are shown in Table-1. The observed values are clearly indicates that the presence of MEL extract, the corrosion rate considerably decreased from 1.4414 to 0.9299 mmpy for 24 hrs and 0.1162 to 0.0304 mmpy after 360 hrs with increase of inhibitor concentration (0 to 1000 ppm) the maximum of 73.33 % of inhibition efficiency is achieved even after 360 hrs exposure time, suggests that the adsorption process occurs mainly due to the film formation by the presence of active phytochemical constituents present in the inhibitor molecule especially oxygen containing species and the ion from the surface of the Carbon steel.

Table- 1 The corrosion parameters of Carbon steel in 1.0N Hydrochloric acid containing various concentration of MEL inhibitor at different 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	1.4414	-	0.5192	-	0.3208	-	0.1673	-	0.1162	-
10	1.3949	3.22	0.4649	10.45	0.2836	11.59	0.1115	33.35	0.0805	30.72
50	1.2554	12.90	0.4262	17.91	0.2603	18.85	0.1022	38.91	0.0666	42.68
100	1.1159	22.58	0.3719	28.37	0.2417	24.65	0.0743	55.58	0.0557	52.06
500	1.0461	27.42	0.3099	40.31	0.1999	37.68	0.0511	69.45	0.0340	70.66
1000	0.9299	35.48	0.2944	43.29	0.1720	46.38	0.0464	72.26	0.0304	73.33

3.2. EFFECT OF TEMPERATURE

Dissolution behavior of Carbon Steel in 1.0N HCl containing various concentration of MEL extract at 303to 333K and the observed values are listed in Table-2. Observed results reveals that the corrosion rate decreased with increase of inhibitor concentrations and also increased with rise in Temperature from 303 to 333K. The maximum of 75.51% inhibition efficiency is achieved at 333K. However the value of inhibition efficiency is increased with rise in Temperature may suggests and support the facts that the process of adsorption follows **chemisorption**.

Table- 2. The corrosion parameters of Carbon steel in 1.0N Hydrochloric acid containing various concentration of MEL inhibitor at different temperature after one hours 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	30.6878	-	32.3617	-	27.3401	-
10	27.3401	10.90	30.6878	5.17	25.1082	8.16
50	24.5503	19.99	24.5503	24.13	22.3184	18.36
100	22.3184	27.27	21.2025	34.48	19.5286	28.57
500	21.7605	29.09	16.7388	48.27	12.2751	55.10
1000	21.2025	30.90	14.5070	55.17	6.6955	75.51

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 the range of 303K- 333K in uninhibited and inhibited solutions containing different concentrations of MEL and the corrosion rate was evaluated and the values are presented in Table-3. The relationship b/w the corrosion rate (CR) of Carbon steel in acidic media and temperature (T) is expressed by the Arrhenius equation,

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

 DOI : 10.18231/2454-9150.2019.0096

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

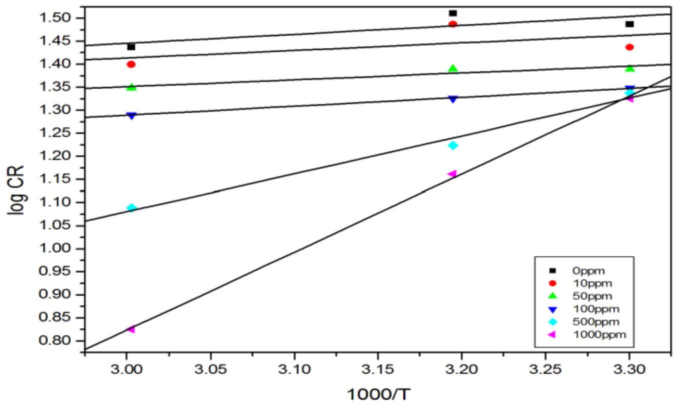

Fig-1. Arrhenius plot for Carbon steel corrosion 1.0N HCl in the absence and presence of different concentration of MEL.

A plot of log (CR) obtained by weight loss measurement versus 1/T gave straight line with average regression co-efficient (R^2) value close to unity as shown fig (1). 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-3 that the apparent energy of activation decreased on addition of MEL in comparison to the uninhibited solution. These values ranged from -3.7279 to -32.3950 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 MEL extract on Carbon Steel surface is Physical adsorption. Decrease in the activation energy is attributed to appreciable increase in the adsorption of inhibitor on Carbon Steel 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 Carbon steel towards 1.0N HCl.

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

Inhibitor conc. (ppm)	E_a kJ/mol	Λ mg/cm	ΔH (kJ/mol)	ΔS (J/mol/k)
Blank	-3.7279	7.26	-6.3721	145.6245
10	-3.1477	8.32	-5.7958	146.7484
50	-2.8433	8.05	-51.0807	330.8367
100	-3.7145	5.10	29.5306	259.6457
500	-15.6987	$4.17x10^{-2}$	-30.4765	63.1846
1000	-32.3950	$5.59x10^{-5}$	-67.8555	-59.2268

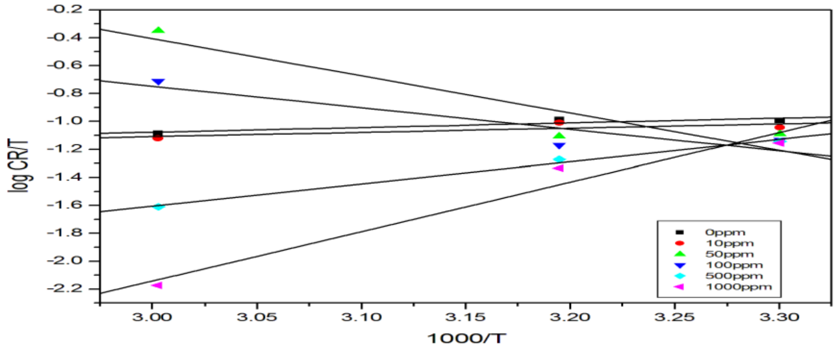

Figure-2 Transition state plot for Carbon steel corrosion in 1.0N HCl in the absence and presence of different concentration of MEL.

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 and λ. Moreover increase in concentration of (MEL) in leads to an decrease in the value of Ea, indicating that the weak adsorption of the inhibitor molecules on the metal surface.

 DOI : 10.18231/2454-9150.2019.0096

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

CR = RT/Nh exp(ΔS/R) exp(-ΔH/RT) --------------(2)

A plot of log (CR/T) versus 1/T is shown is fig -2, 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 negative value of enthalpy of activation (ΔH) in the presence and absence of various concentration of inhibitor reflects that the exothermic natures of Carbon steel. 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 when 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 Adsorption studies:

Process of adsorption are very important surface phenomenon to determine the corrosion rate of reaction mechanism. The most frequently use of isotherms are viz: Langmuir, Temkin, Frumkin, Flory- Huggins, Freund lich, Bockris-Swinkles, Hill-de Boer, Parson's and the El-Amady, thermodynamic-kinetic model.

3.4.1. LANGMUIR ISOTHERM:

Langmuir adsorption isotherm is expressed according to equation -3,

Log C/θ = log C – log K --------- →(3)

Plotting log (C/θ) against log C gave a linear relationship as shown in fig.3, and the adsorption parameters are presented in Table- 4. The average regression value (R^2= 0.9758) far away unity suggest that the adsorption of extract of MEL on surface of Carbon steel indicated that there is no interaction b/w the adsorbate and adsorbent.

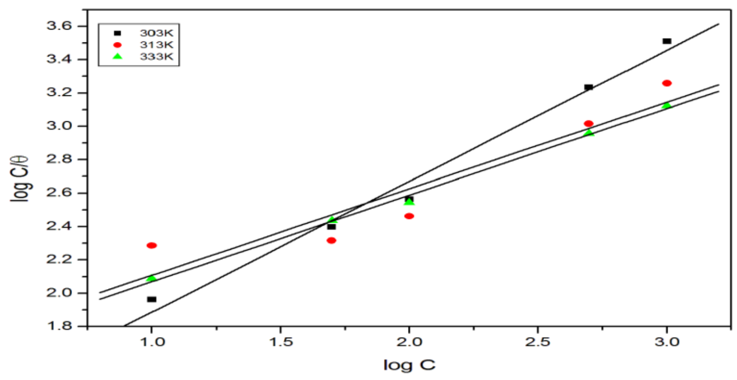

Figure -3. Langmuir isotherm for adsorption of ethanol extract of *Mimusops elengi leaves* on Carbon steel surface.

3.4.2. TEMKIN ISOTHERM:

Temkin adsorption isotherm, the degree of surface coverage(θ) is related to the inhibitor concentration (c) according to equation - 4,

Exp (-2a θ) =KC-------------- (4)

K-adsorption of equilibrium constant and a is the attractive parameter, Rearranging and taking logarithm of both sides of equation (4) gives equation - 5

Θ = (-2.303logk/2a)- (2.303log C/2a)------------(5)

Plots of θ against log c are presented in fig-4 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 0.9708 far away the unity. However values of attractive parameter (a) are positive in all cases, indicating that the no repulsion exists in the adsorption layer.

 DOI : 10.18231/2454-9150.2019.0096

ISSN : 2454-9150 Vol-04, Issue-12, Mar 2019

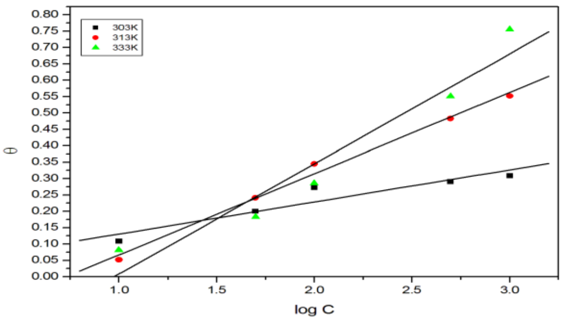

Figure-4. Temkin isotherm for adsorption of ethanol extract of *Mimusops elengi leaves* on Carbon steel surface.

3.4.3 FLORRY-HUGGINS ISOTHERM:

Florry- Huggins adsorption isotherm can be expressed according to equation (6)

$$\text{Log}\,(\theta/C) = \log K + x\log(1-\theta) \text{ ---------------- } \rightarrow (6)$$

The plots of log θ/c against log (1- θ) are shown in fig 5, and this data conformed to Florry huggins isotherm with average regression co-efficient (R^2) value 0.9203. It is very far away the 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 MEL is bulky. Since it could displace more than one water molecule from the Carbon steel surface.

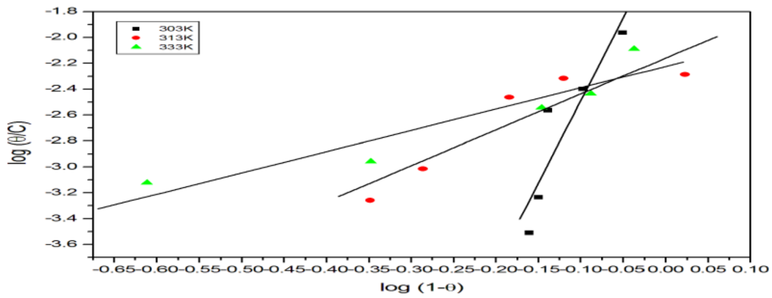

Figure-5. Florry-Huggins isotherm for adsorption of ethanol extract of *Mimusops elengi leaves* on Carbon steel surface.

3.4.4. FRUMKIN ISOTHERM:

Frumkin adsorption isotherm is given by equation (7)

$$\log\{[C]^*(\theta/1-\theta)\} = 2.303 \log K + 2\alpha\theta \text{ ----------} \rightarrow (7)$$

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 that the applicability of Frumkin isotherm. The values for Frumkin adsorption parameters were recorded in Table 4. Average regression co-efficient value (R^2=0.9856) 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 Carbon Steel.

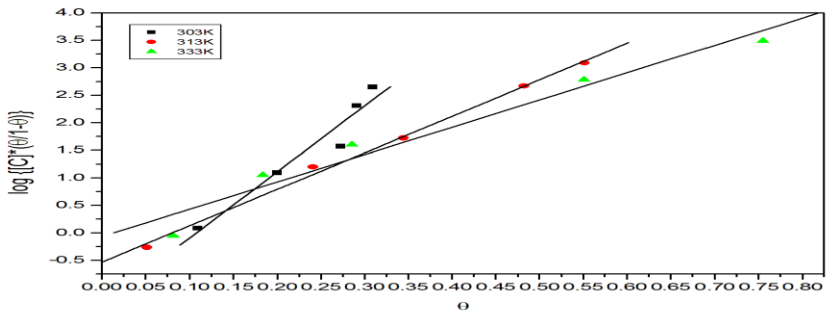

Figure-6. Frumkin isotherm for adsorption of ethanol extract of *Mimusops elengi leaves* on Carbon steel surface.

DOI : 10.18231/2454-9150.2019.0096

ISSN : 2454-9150 Vol-04, Issue-12, Mar 2019

3.4.5 FREUNDLICH ISOTHERM:

The Freundlich adsorption isotherm can be also be applied using equation - 8,

$$\Theta = Kc^{n} \text{ ------------} \rightarrow (8)$$

Freundlich model equation(8) can be rearranged as (9),

$$\text{Log } \theta = \log K + n\log C \text{ --------} \rightarrow (9)$$

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 equations. 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 MEL inhibitor adsorbed on the metal surface by physical process.

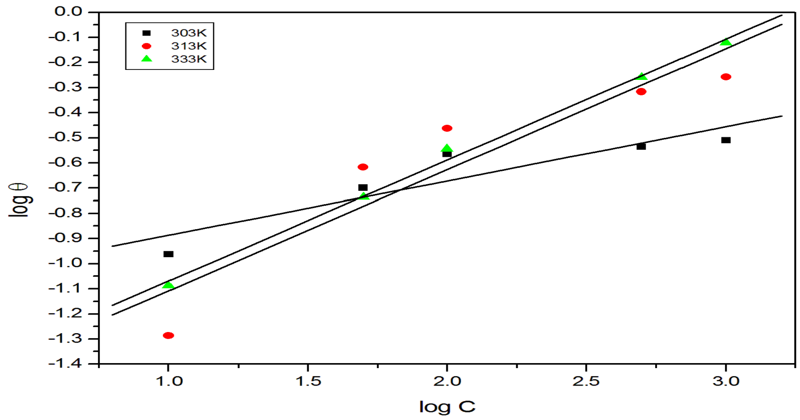

Figure -7. Freundlich isotherm for adsorption of ethanol extract of *Mimusops Elengi* Leaves on Carbon steel surface.

3.4.6. EL AWADY ISOTHERM:

The El-Awady adsorption isotherm is given by

$$\text{Log } (\theta/1-\theta) = \log K + y\log C \text{-------------} (10)$$

Where C is molar concentration of inhibitor in the bulk solution, 'θ' is the degree of surface coverage, K is the equilibrium constant 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 [17,18,19]. Curve fitting of the data to the thermodynamic/kinetic model [El-Awady et al.,] is shown in fig - 8. 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.

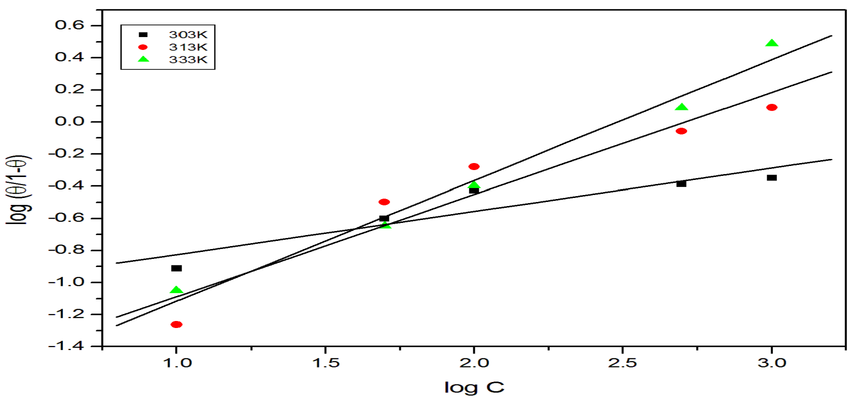

Figure-8. El-Awady isotherm for adsorption of ethanol extract of

 DOI : 10.18231/2454-9150.2019.0096

***Mimusops Elengi* Leaves on Carbon steel surface.**

3.5. FREE ENERGY OF ADSORPTION

The Equilibrium constant of adsorption of ethanol extract of (MEL) on the surface of Carbon steel is related to the free energy of adsorption (ΔG) according to equation (11)

$$\Delta G = -2.303RT \log (55.5K) \text{ -------------- } (11)$$

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, Florry –Huggins, Frumkin, Freundlich and El-Awady according to equation - 11 and is recorded in Table-4. The results show that free energy of adsorption ΔG are negative and less than the threshold value of -40kJ/mol required for chemical adsorption, indicating that the adsorption of ethanol extract of MEL on Carbon Steel surface is spontaneous and the mechanism of physical process. Since phenomenon is attributed to electrostatic interactions between the charged metal and the inhibitor molecules.

Table:4. Adsorption parameters for adsorption of ethanol extract of MEL on Carbon steel surface.

Isotherm	Temperature	R^2	K	ΔG_{ads} kJ/mol	
	303K	0.9931	12.6531	-16.5141	
Langmuir	313K	0.9364	38.8955	-19.9819	
	333K	0.9981	35.5222	-21.0075	a
					11.7860
Temkin	303K	0.9477	0.0016	-5.9723	4.6450
	313K	0.9959	4.6450	-14.4509	3.4291
	333K	0.9689	-0.0048	-3.6627	
					x
					12.7011
Florry- Huggins	303K	0.9144	0.0598	-3.0225	2.7728
	313K	0.9120	0.0069	2.4926	1.6448
	333K	0.9346	0.0059	3.0638	
					α
Frumkin					5.9943
	303K	0.9707	0.2756	-6.8723	3.3166
	313K	0.9981	0.5858	-9.0617	2.4824
	333K	0.9801	0.9340	-10.9325	
Freundlich					n
					0.2153
	303K	0.9190	0.0790	-3.7241	0.4817
	313K	0.9274	0.0257	0.9242	0.4812
	333K	0.9978	0.0281	-1.2356	
El-Awady					1/y
					3.7091
	303K	0.9276	0.0001	13.4669	1.5701
	313K	0.9576	0.0019	5.7886	1.3280
	333K	0.9917	0.0032	4.7121	

IV. CONCLUSIONS

Using *Mimusops Elengi* Leaves (MEL) extract on Carbon steel shown excellent inhibition performance in 1.0N Hydrochloric acid environment. The inhibition efficiency increased with the increase of inhibitor concentration the maximum efficiency was achieved 73.33%. Also, the inhibition efficiency gradually increased with the rise in temperature i.e., to 75.51% for 333K. It follows physical adsorption process. Thermodynamic parameter viz., activation energy (E_a), Standard free energy adsorption (ΔG_{ads}), enthalpy (ΔH), entropy (ΔS), suggests that Physisorption, exothermic, spontaneous process respectively. The MEL inhibitor obeys Frumkin adsorption isotherm.

REFERENCES

[1] G. E. Badr, Corros. Sci 51 (2009) 2529.

[2] Y. Ren, Y. Luo, K. Zhang, G. Zhu, X. Tan, Corros. Sci. 50 (2008) 3147.

[3] A. El – Maksoud, A.S. Fouda, Mater. Chem. Phys. 93 (2003) 84.

[4] M. A. Quraishi, S.K. Shukla, Mater. Chem. Phys. 113 (2009) 685.

[5] I. B. Ibot, N. O. Obi-Egbedi, S.A. Umoren, E.E. Ebenso, Int. J. Electrochem. Sci. 5(2010) 978.

 DOI : 10.18231/2454-9150.2019.0096

[6] S. K. Shukla, M. A. Quraishi, R. Prakash, Corros. Sci. 50 (2008) 2867.

[7] Bright A, Michlin Ruphina Maragatham S, Malar vizhi I, Dr. Kalirajan K, Dr. Selvaraj S.Corrosion Effect of Cu- 30Zn Alloy Using Cnidoscolus Chayamansa Leaves Extract In Acid Media International Journal of Innovative Research in Science, Engineering and Technology 2015:4(10):10181-10191.

[8] Bright A, Michlin Ruphina Maragatham S, Malar Vizhi I, Kalirajan K, Selvaraj S. Solanum Torvum Fruits Extract as an Eco- Friendly Inhibitor on Copper in Acid Medium, Research Journal of Chemical Sciences, 2015; 5(11):31-39..

[9]Bright A, Michlin Ruphina Maragatham S, Malar Vizhi I, Kalirajan K, Selvaraj S. Corrosion inhibition of pure Copper using Pisonia Grandis Leaves extract in acid environment, International Journal of Current Research. 2015; 7(9):20566-20573.

[10] Deivanayagam P, Malarvizhi I, Selvaraj S, Deeparani P. Corrosion inhibition efficacy of ethanolic extract of mimusops elengi leaves (MEL) on copper in 1.0N Hydrochloric acid, International Journal of multidisciplinary research and development. 2015; 2(4):100-107.

[11] Deivanayagam P, malarvizhi I, Selvaraj S, Deeparani P. Corrosion behavior of Sauropus androgynus leaves (SAL) on mild steel in Natural Sea Water, International Journal of Advances in pharmacy, biology and Chemistry. 2015; 4(3):574-583.

[12] Deivanayagam P, Malarvizhi I, Selvaraj S, Rufus DP. Effect of kingiodendron pinnatum leaves on zinc in Natural Sea Water, International Journal of engineering research and general science. 2015; 3(6):52-61.

[13] Deivanayagam P, Malarvizhi I, Selvaraj S. Inhibitive effect of Wrightia Tinctoria leaves as green inhibitor for mild steel in acid medium, International Journal of engineering Science and research technology. 2016; 5(4):93-101.

[14] I. Malarvizhi, S.Selvaraj, adsorption behavior of cu-zn alloy in Acid environment using green Inhibitor, Journal of Emerging Technologies and Innovative Research (JETIR), 2018, 5(7), 158-168.

[15] Malar vizhi. I, Selvaraj. S, Kalirajan. K, Corrosion Behavior Of Mild Steel In Nattural Sea Water With Tephrosia Purpurea– A Green Approach, International Journal of Research and Analytical Reviews (IJRAR), 2018, 5(4), 164-174.

[16] I.Malar vizhi, Dr.S.Selvaraj, Dr.K.Kalirajan, Electro Chemical Behaviour of Alangium Salvifolium Leaves For Mild Steel in 1.0N HCl, International Journal of Scientific Development and Research (IJSDR), 2019, 4(1), 162-165.

[17] Singh A K, Shukla S K, Singh M, Quraishi M A. 2011. Mater.chemphys Doi: 10.1016/j.mat chem phys.03.054.

[18] Ibot I B, Obi-egbedi N O, Umoren S A.. 2009. Int. J. Electro chem. Sci. 4,863.

[19] Singh A K, Quraishi M A. 2011. Corros.Sci, 53,1288.

 DOI : 10.18231/2454-9150.2019.0096