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Chemistry

EFFECT OF ADSORPTION ON API – 5L – GRADE – X60 STEEL IN CRUDE OIL WITH 50% FREE WATER USING CRL EXTRACT

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ABSTRACT Adsorption effect of *Canjera Rheedi* leaves extract on API – 5L – Grade – X60 Steel in Crude oil with 50% Free water has been investigated using various concentrations of inhibitor and temperature by mass loss measurements. Observed result reveals that the percentage of inhibition efficiency increased with increase of inhibitor concentration as well as temperature. Various thermodynamic parameters Ea, Q_{ads}, ΔG_{ads}, ΔH_{ads} and ΔS may also suggests that the adsorption of CRL extract is endothermic, spontaneous and Chemisorptions process. We attempt various adsorption isotherms in this present studies but only the Frumkin Adsorption isotherm obeys with this inhibitor.

KEYWORDS : API – 5L – Grade – X60 Steel, Mass Loss, CRL, Crude oil with 50%, Free water, Adsorption studies.

1. INTRODUCTION

Protection of various metals against corrosion is a major industrial problem in the world wide(1-2). Since the scientist attempted for their research work in this corrosion field area. The heavy loss of metal whenever it contact with acid and other corrosive environment can be minimized to a great extent by the use of corrosion inhibitors(3). Several efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors(4). The plant extract are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as "Green Inhibitors"(5). These inhibitors are biodegradable and do not contain heavy metals or other toxic compounds(6-7). Recent studies using plants containing heteroatom such as oxygen, nitrogen and sulphur like Tamarind tea leaves, Beet root1-2, Saponin3, Terminalia bellerica4, Oxandra asbeckii5,Argemone mexicana6, Betanin7, Henna8, Wheat9, Ginger10,Marraya koeningii11, Garlic extract12, Ananas sativum13, Artemisia Mesatlantica essential oil14, spirogyraalgae15, Tragacanth gum16, Prunus Persic17, Lemon Gross18, Secang heartwood extract (Caesalpinia sappan I)19, Dried marjoram leaves20. In continuous of our research work, the present investigation is the *Canjera Rheedi* leaves extract used as corrosion inhibitor on API – 5L – Grade – X60 Steel on Crude oil with 50%, Free water have been investigated with various periods of contact and temperature using the mass loss measurements(8-12).

2. MATERIALS AND METHODS

(I). CANJERA RHEEDI LEAVES [CRL] IS USED AS CORROSION INHIBITOR.

(ii). SPECIMEN PREPARATION

Rectangular specimen of API – 5L – Grade – X60 Steel was mechanically pressed cut to form different coupons, each of dimension exactly **40.092 cm^2 (5.1x2.5x0.96cm)** 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 investigations.

(iii).MASS LOSS METHOD

Mass loss measurements on API – 5L – Grade – X60 Steel in triplicate were immersed in 50ml of the test solution in the presence and absence of the inhibitor. After the immersion process over, the metal specimens were withdrawn from the test solutions after 24 to 360 hrs at room temperature and also measured in the temperature range of 303K to 333K.

3.0 RESULTS AND DISCUSSION

3.1 EFFECT OF TIME VARIATION

Observed results clearly indicates that the percentage of inhibition efficiency and the degree of surface coverage (θ) increased with increase of inhibitor concentration (Table-01). The maximum of 99.17% inhibition efficiency is achieved after 24hrs exposure time. It is due to the adsorption of the important plant constituents presents in the inhibitor,on the metal surface by the interaction of π- electrons and lone pair of hetero atom of Sulphur with the metal ion. The main phytoconstituents like Alkaloids, Tannins, Flavanoids, Terpenoids, and Saponins and amino acids are found to be a big molecule may capable of covering a large surface area on the metal surface(12-18). These adsorbed molecules are blocks the active sites in which direct attack of free water proceed and protect the metal from dissolution process(19). From this result, it can be noticed that the inhibition efficiency increased with increase of CRL extract concentration and Suggests that the CRL extract retards the dissolution process of API – 5L – Grade – X60 Steel in Crude oil with 50% Free water solution.

Table-1: Corrosion parameters of API – 5L – Grade – X60 Steel in Crude oil with 50% free water containing CRL extract after 24 to 360 hrs 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	1.4035	-	0.0662	-	0.1403	-	0.0655	-	0.0561	-
10	0.1286	90.84	0.0350	47.12	0.0280	80.05	0.0269	58.93	0.0171	69.51
50	0.0701	95.00	0.0350	47.12	0.0187	86.67	0.0245	62.59	0.0163	70.94
100	0.0233	98.33	0.03119	52.88	0.0140	90.00	0.0198	69.77	0.0163	70.94
500	0.0116	99.17	0.0233	64.80	0.0023	98.36	0.0187	71.45	0.0124	77.89
1000	0.0116	99.17	0.0233	64.80	0.0023	98.36	0.0105	83.96	0.0093	83.42

3.2. EFFECT OF TEMPERATURE

Dissolution behaviour of API – 5L – Grade – X60 Steel in Crude oil with 50% Free water containing various concentration of CRL extract at 303K to 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 75% 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 Chemisorptions.

Corrosion inhibitor of CRL at various concentrations and temperatures were showed in Figure-1, Crude oil with 50%, Free water in presence and absence of CRL extract. The corrosion rate (CR) in the Crude oil with 50%, Free water in the absence of the CRL extract was starting from the corrosion rate 1.9650 mmpy at 303K and raised to 2.2457 mmpy at 333K as increasing sharply. Increasing of CRL extract concentration leads to reducing the corrosion rate sharply at different temperatures.

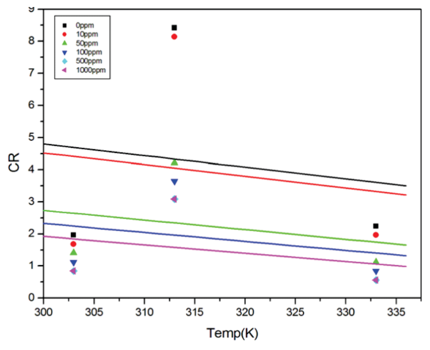

Figure-1. The Corrosion rate of API – 5L – Grade – X60 Steel in Crude oil with 50% Free water at different temperature with different inhibitor concentration.

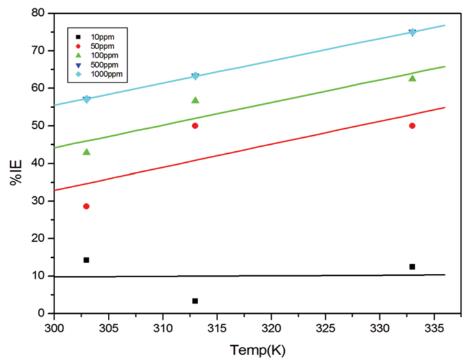

Figure-2. Inhibition efficiency of CRL on API – 5L – Grade – X60 Steel in Crude oil with 50% Free water at different temperature with inhibitor concentration.

Thus the percentage of IE increased with increase of inhibitor concentration. The effect of %IE versus Temperature was shown in figure-2 reveals that the efficiency increased with increase of concentration and the temperature. Increasing of IE with raise of CRL concentration is due to the complexity between the metal surface and the active inhibitor molecules through the coordination bonds. Even at highest experimental temperature (333K) the %IE was also be increased due to the naturation of bond formation.

Table-2: Corrosion parameters of API – 5L – Grade – X60 Steel in Crude oil with 50% Free water containing different concentration of CRL 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	1.9650	-	8.4212	-	2.2457	-
10	1.6843	14.28	8.1409	3.32	1.9650	12.49
50	1.4036	28.56	4.2108	49.99	1.1228	50.00
100	1.1228	42.86	3.6493	56.66	0.8421	62.50
500	0.8421	57.14	3.0879	63.33	0.5614	75.00
1000	0.8421	57.14	3.0879	63.33	0.5614	75.00

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 from 303K- 333K in inhibited and un-inhibited solutions containing different concentrations of CRL and the corrosion rate was evaluated and the values are presented in Table-3. The relationship b/w the Corrosion rate (CR) of API – 5L – Grade – X60 Steel in acidic media and Temperature (T) is expressed by the Arrhenius equation,

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

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

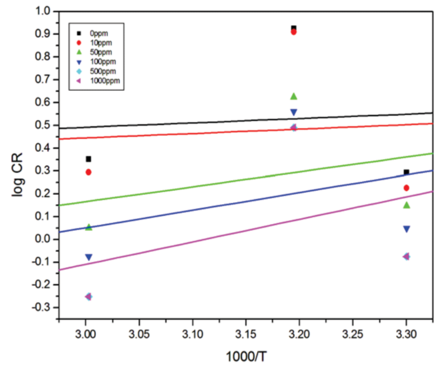

Fig-3. Arrhenius plot for API – 5L – Grade – X60 Steel corrosion Crude oil with 50%, Free water in the absence and presence of different concentration of CRL.

A plot of log (CR) obtained by mass loss versus 1/T gave straight line with regression co-efficient (R2) close to unity (0.99) 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 (log λ) are given in Table -3. It is evident that the apparent energy of activation decreased on addition of (CRL) in comparison to the uninhibited solution. These values ranged from -3.6762 to -18.9384kJ/mol and are lower than the threshold value of 80kJ/mol as required for chemical adsorption. This shows that the adsorption of ethanol extract of CRL on API – 5L – Grade – X60 Steel surface is Physical adsorption. Decrease in the activation energy is attributed to appreciable increase in the adsorption of inhibitor on API – 5L – Grade – X60 Steel surface by increase in the temperature. The increase in adsorption may leads to decrease in corrosion rate due to the lesser exposed surface area of the API – 5L – Grade – X60 Steel Crude oil with 50%, Free water .

Table:3 Activation parameters of CRL in Crude oil with 50% Free water .

Inhibitor conc. (ppm)	E_a kJ/mol	Λ mg/cm	ΔH (kJ/mol)	ΔS (J/mol/k)	Q_{ads} ($KJmol^{-1}$)
Blank	-3.6762	0.8230	-2.7452	55.3666	--
10	-3.6973	0.7333	-0.8081	60.8913	-4.3210
50	-12.4398	0.0164	-4.1703	48.5109	25.6366
100	-14.7854	0.0054	-7.5690	37.232	32.1858
500	-18.9384	0.0008	-9.3723	30.4878	22.6872
1000	-18.9384	0.0008	-9.3723	30.4878	22.6872

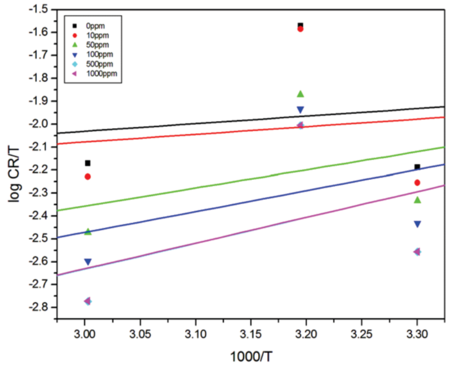

Figure-4 Transition state plot for API – 5 L – Grade – X60 Steel corrosion in Crude oil with 50%, Free water in the absence & presence of different concentration of CRL.

Value of λ is also lower for inhibited solution than for the uninhibited solution. It is clear from equation (1) that corrosion rate is influenced by both the Ea & λ. Moreover increase in concentration of CRL 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 are evaluated from the mass loss data for API – 5L – Grade – X60 Steel in Crude oil with 50% free water in the presence and absence of CRL 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(ΔS/R) exp(-ΔH/RT) --------------(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 generated 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 nature of process is exothermic. It is evident from the table that the value of ΔH decreased in the presence of the inhibitor than the uninhibited solution suggests that the lesser protection efficiency. This may be attributed to the presence of energy barrier for the reaction and 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 out in Table-3. It is clear that the entropy of activation decreased in the presence of the using inhibitor compared to crude oil with free water 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:

Heat of adsorption on the surface of various metals in the presence of plant extract in Crude oil with 50%, Free water environment is calculated by the equation (3).

Q ads =2.303 R [log (θ2/1- θ2)-log (θ1 /1- θ1)] x (T2T1/T2-T1) ------(3)

The calculated Q ads values (Table-3) are ranged from -4.3210 to 22.6872 kJ/mol indicating that the adsorption of ethanol extract of CRL on API – 5L – Grade – X60 Steel surface is endothermic process.

3.5 ADSORPTION STUDIES:

Processes of adsorption are very important phenomenon to determine the corrosion rate of reaction mechanism. The 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)

Log C/q = log C – log K --------- à(4)

Plotting log (C/q) 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 (R2= 0.8904) suggests that the adsorption of extract of CRL on surface of API – 5L – Grade – X60 Steel indicated that there is no interaction b/w the adsorbate & adsorbent.

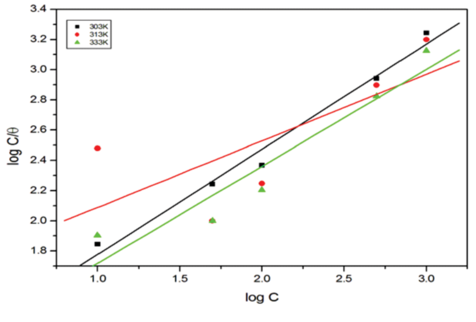

Figure -5. Langmuir isotherm for adsorption of ethanol extract of Canjera Rheedi Leaves on API – 5L – Grade – X60 Steel surface.

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 θ) =KC-------------- (5)

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

Θ = (-2.303logk/2a)- (2.303log C/2a)------------(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 (R2) is 0.9083 close to unity. The values of attractive parameter (a) are negative in all cases, indicating that the strong repulsion exists in the adsorption layer.

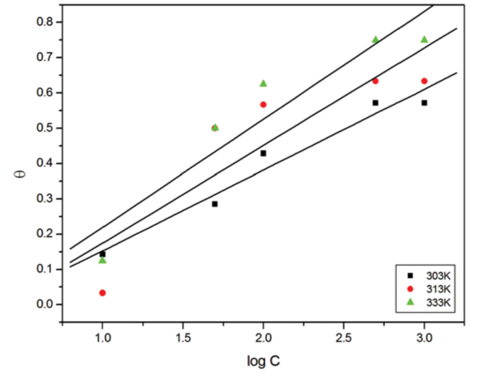

Figure-6. Temkin isotherm for adsorption of ethanol extract of Canjera Rheedi Leaves on API – 5L – Grade – X60 Steel surface.

3.5.3 FLORRY-HUGGINS ISOTHERM:

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

Log (θ/C) = log K + xlog (1- θ) ---------------- →(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 (R2) value 0.7512. 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 CRL is bulky. Since it could displace more than one water molecule from the API – 5L – Grade – X60 Steel surface.

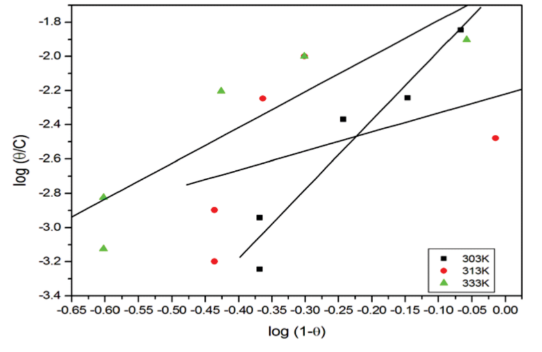

Figure-7. Florry-Huggins isotherm for adsorption of ethanol extract of *Canjera Rheedi* Leaves on API – 5L – Grade – X60 Steel surface.

3.5.4. FRUMKIN ISOTHERM:

Frumkin adsorption isotherm is given by equation (8)

log { [C]* (θ/1- θ)} = 2.303 log K +2αθ ----------→(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 (R2=0.9823) 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 API – 5L – Grade – X60 Steel.

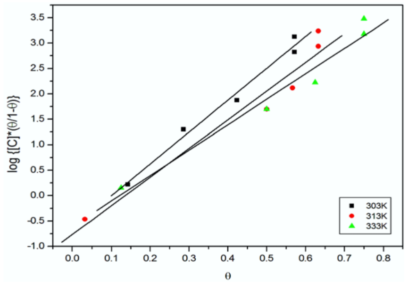

Figure-8. Frumkin isotherm for adsorption of ethanol extract of *Canjera Rheedi* Leaves on API – 5L – Grade – X60 Steel surface.

3.5.5 FREUNDLICH ISOTHERM:

The Freundlich adsorption isotherm can be also be applied

Θ = Kcn ------------→(9)

Freundlich model equation(9) can be rearranged as

Log θ = logK + nlog C -------- →(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 lower values of 'K' indicate that the inhibitor weakly 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 CRL inhibitor adsorbed on the metal surface by physical process.

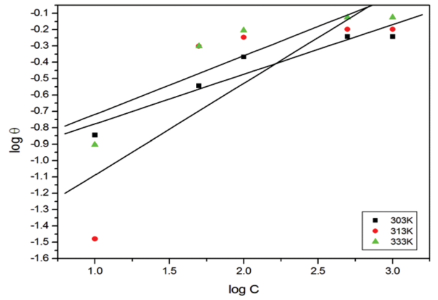

Figure -9. Freundlich isotherm for adsorption of ethanol extract of *Canjera Rheedi* Leaves on API – 5L – Grade – X60 Steel surface.

3.5.6. ELAWADY ISOTHERM:

The El-Awady adsorption isotherm is given by

Log (θ/1-θ) = log K +ylogC------------- (11)

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, kads = k1/y and y represents occupying a given active site. Value of 1/y less than unity implies that 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 [23,24,25]. Curve fitting of the data to the thermodynamic/kinetic model [El-Awady et al.,] is shown in fig(10). The average regression coefficient value (R2) is 0.9136,suggests that it moves to unity.The plot gives straight lines which show that the experimental data fits the isotherm. The values of kads and 1/y calculated from the El-Awady et al isotherm model is listed in table (4).

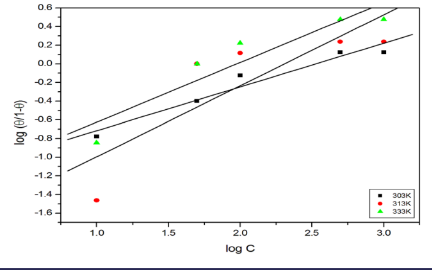

Figure-10. El-Awady isotherm for adsorption of ethanol extract of *Canjera Rheedi* Leaves on API – 5L – Grade – X60 Steel surface.

3.6. FREE ENERGY OF ADSORPTION

The equilibrium const of adsorption of ethanol extract of (CRL) on the surface of API – 5L – Grade – X60 Steel is related to the free energy of adsorption (ΔG) according to equation (12)

ΔG= -2.303RT log (55.5K) -------------- (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, Florry –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 on 40kJ/mol required for chemical adsorption, indicating that adsorption of ethanol extract of CRL on API – 5L – Grade – X60 Steel surface is spontaneous and occurred according to the mechanism of physisorption. Since this phenomenon is attributed to electrostatic interactions between the charged metal ions and charged molecules.

Table:4. Adsorption parameters for adsorption of ethanol extract of CRL on API – 5L – Grade – X60 Steel surface.

Isotherm	Temperature	R^2	log K	ΔG_{ads} kJ/mol	Slope value
Langmuir	303K	0.9912	1.0810	-16.3911	a
	313K	0.7253	1.6481	-20.3307	-5.03
	333K	0.9547	1.0776	-17.9923	-4.16
Temkin					-3.76
	303K	0.9801	1.1906	6.0141	
	313K	0.8745	0.7919	5.9483	x
	333K	0.9424	0.8190	7.0432	1.10
					4.03
Florry-					2.08
Huggins	303K	0.3991	-2.2204	-1.0376	
	313K	0.9640	-1.5654	2.8620	α
	333K	0.8905	-1.5806	-1.0367	3.13
					2.82
Frumkin					2.50
	303K	0.9917	-0.2733	-8.5333	
	313K	0.9738	-0.3324	-8.8149	n
	333K	0.9815	-0.2647	-9.4332	0.30
					0.55
Freundlich					0.35
	303K	0.9565	-1.0810	-3.8455	
	313K	0.8011	-1.6481	-0.5665	1/y
	333K	0.8734	-1.0775	-4.2495	2.1340
					1.3154
El-Awady					1.5632
	303K	0.9739	-1.1848	4.5525	
	313K	0.8339	-1.7555	3.3997	
	333K	0.9331	-1.2641	1.4952	

4. CONCLUSIONS

Using *Canjera Rheedi* leaves (CRL) extract on API – 5L – Grade – X60 Steel with Crude oil in the presence of 50% Free water Canjera Rheedi leaves extract have shown excellent inhibition performance for API – 5L – Grade – X60 Steel Crude oil with 50%, Free water . The inhibition efficiency increased with the increase of inhibitor concentration. The maximum percentage of inhibition efficiency was achieved 99.17%. Also, the inhibition efficiency gradually increased with the rise in temperature i.e., to 75% for 333K. It follows physical adsorption mechanism and it moves to chemisorption. The activation energy (Ea), heat of adsorption (Qads), Standard free energy adsorption (ΔGads), enthalpy (ΔH), entropy (ΔS) also suggests that, Physisorption, endothermic, spontaneous process respectively. The CRL inhibitor obeys Frumkin adsorption isotherm.

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