IJIRR

International Journal of Information Research and Review
Vol. 2, Issue, 01, pp. 261-266 January, 2015

Full Length Research Article

THERMODYNAMIC AND ADSORPTION STUDIES FOR CORROSION INHIBITION OF MILD STEEL USING *MILLINGTONIA HORTENSIS*

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ARTICLE INFO

Article History:
Received 24th October, 2014
Received in revised form
04th November, 2014
Accepted 30th December, 2014
Published online 31st January, 2015

Keywords:

Millingtonia Hortensis,
Mild Steel,
Adsorption Isotherm,
Corrosion Rate,
Inhibition Efficiency.

ABSTRACT

The adsorption and inhibitive efficiency of *Millingtonia hortensis* leaves extract on mild steel in 1N HCl and 1N H_2SO_4 acid in the temperature range (303 to 343k) are investigated by mass loss measurements. The value of inhibition efficiency increased with increase of inhibitor concentration and decreased at **333K. ΔG_{ads} adsorption value in the range 12 – 24 KJ / mol is suggestive of physisorption processs.** Adsorption of inhibitor on the metal surface was found to obey Langmuir and Temkin adsorption isotherm. The values of activation energy (ΔE_a), free energy of adsorption (ΔG_{ads}), enthalpy of adsorption (ΔH) and entropy of adsorption (ΔS) were calculated.

INTRODUCTION

The corrosion of engineering materials is known to lower performance efficiency and lead to reduced service life, in severe cases it could serve as a precursor to catastrophic failures which result in grave losses. The use of inhibitors has been well documented as an effective method of protecting metallic materials from corrosion. Many industrial processes have put to use inorganic inhibitors for corrosion protection but as a result of cost and toxicity, attention is currently shifted towards the use of more eco-friendly inhibitors. Organic substances *(plant based)* containing functional groups with oxygen, nitrogen and /or sulphur atoms in a conjugate system have been reported to exhibit good inhibiting properties. This has made plant extracts an important choice for environmentally friendly, readily available and renewable source for wide range of inhibitors referred to as green inhibitors. Some of the advantages of green inhibitors are low cost of processing, biodegradability, and absence of heavy metals or other toxic compounds which pose great hazard to the environment (1). Some investigations in recent time have been made into the corrosion inhibiting properties of natural products of plant origin, which showed good inhibition efficiencies.

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This area of research is important because in addition to being inexpensive, natural products are readily available, eco-friendly and renewable sources of materials.

Nicotiana tabacum(2),Punica granatum (3), *Azadirachta indica*(4), red peanut skin (5), *Piper nigrum*(6), *Manihot esculentum* (7), Lawsonia inermis (8), *Jatropha Curcas*(9), *Hibiscus cannabinus* (10), *glutaric acid (GA) in conjunction with Zn^{2+} and diethylene triamine penta (methylene phosphonic acid) [DTPMP]* (11), *Acacia drepanolobium* (12), *Citrullus colocynthis* (13) are also used as corrosion inhibitor.

Plant products contain alkaloids, flavonoids, carbohydrates, proteins, steroids and terpenoids. These organic compounds contain π-electron centres and functional groups such as –C=C, -OR, $-NR_2$ and/or –SR. The inhibiting action of natural products is attributed to the presence of these organic compounds as phyto chemical constituents. The aim of the present work is to study the inhibition efficiency of *Millingtonia hortensis* for the corrosion of mild steel in acid medium 1N HCl and 1N H_2SO_4 and to evaluate thermodynamic parameters of corrosion inhibition process for the adsorption of inhibitor on mild steel metal surface.

MATERIALS AND METHODS

Experimental

Sample Preparation

In preparing the specimens for the experiment, the specimens of mild steel were cut into 5x1cm and 2mm thickness. These samples were degreased, dried, weighed and stored in a desiccator. The initial weight of each sample was taken and recorded.

Preparation of the extract

The leaves of *Millingtonia hortensis* were collected shade dried and made into powder. 25g of this powder was refluxed with 500ml of 1N HCl acid solution. The solution was refluxed for 3hours and left overnight. The refluxed solution was then filtered carefully and the filtrate volume was made up to 500ml. From this 5% stock solution, different dilutions ranging from 0.05% to 3.0% v/v concentration s of the extract was prepared for the study.

Determination of corrosion rate

The rate of dissolution of metal is calculated in terms of corrosion rate using the expression,

Corrosion Rate (CR)= (534xW) / DAT (mpy)

where,

mpy= mils per year
W= loss in weight in milligrams
D= density in g/cm^3 (7.9 g/cm^3)
A= area in square inch
T= time in hours.

Determination of inhibition efficiency

The percentage inhibition efficiency of the inhibitor is expressed as,

$$\text{Inhibitor Efficiency (\%)} = \frac{\text{Weight loss without inhibitor - Weight loss with inhibitor}}{\text{Weight loss without inhibitor}} \times 100$$

Adsorption isotherm

In the present study the values of surface coverage (θ) were evaluated using the values of inhibition efficiency at different temperature, using the formula

θ= (IE% / 100) and the following adsorption isotherm equations have been considered
Langmuire isotherm
$\log (\theta / (1 - \theta)) = \log K + x \log c$
Temkin isotherm
$a^{\theta} = \ln Kc$

Determination of thermodynamic parameters

Determination of activation energy (E_a)

The activation energy for adsorption of the inhibitor at different concentrations of the inhibitor at various temperatures was determined by plotting log corrosion rate Vs 1/T.

From the slope activation energy (E_a) was calculated from the formula,

$E_a = -2.303 \times R \times \text{Slope}$

Where R is the gas constant (8.314J)

Determination of change in free energy of adsorption (aG^{o}_{ads})

The free energy of adsorption has been calculated from the equilibrium constant of adsorption using the expression,

$$K = \frac{1}{55.5} \exp\left(\frac{\Delta G_{ads}}{RT}\right)$$

where,

$K = \frac{\theta}{C(1 - \theta)}$ (from Langmuir equation)

θ=degree of coverage on the metal surface
C=concentration of inhibitor
$\Delta G_{ads} = -RT \ln (55.5k)$

Determination of change in enthalpy and entropy of adsorption

Enthalpy of adsorption (ΔH_{ads}) and entropy of adsorption (ΔS_{ads}) are calculated from the values of free energy of adsorption (ΔG_{ads}) using Gibbs- Helmholtz relationship,

$\Delta G_{ads} = \Delta H_{ads} - T \Delta S_{ads}$

A plot of ΔG_{ads} Vs T was drawn. The slopes of these lines are equal to entropy (ΔS) and intercept corresponds to enthalpy (ΔH) of adsorption.

RESULTS AND DISCUSSION

The effect of concentration of the inhibitor on the IE of plant extract and corrosion rate of mild steel in 1N HCl and 1N H_2SO_4 shows that corrosion inhibition by the plant extract is taking place by adsorption mechanism. With the increase in concentration of the plant extracts, more phytoconstituents are being adsorbed on the surface, enhancing more uniform surface coverage, which decreases the corrosion. The adsorption of the phytoconstituents on the metal surface makes a barrier for mass and charge transfers and thus protects the metal surface from corrosion. The degree of protection increases with the increase in surface fraction occupied by the adsorbed molecules. The surface coverage parameter θ is calculated from the IE values, which is used to represent the fraction of the surface occupied by the adsorbed molecules.

TEMPERATURE STUDIES

Temperature plays a major role on the rate of the electrochemical corrosion of metal. Temperature can modify the interaction between mild steel and the acidic media in the presence and absence of inhibitor. IE increases with increase in temperature. The decrease in corrosion rate with extract concentration may be due to the competition between forces of adsorption and desorption of phytochemicals of the MHL extract.

Table 1. Effect of temperature on mild steel corrosion in 1N HCl in absence and presence of MHL extract

Concentration of MHL extract (v/v%)	303 K		313 K		323 K		333 K		343 K	
	CR (mpy)	IE %	CR (mpy)	IE %	CR (mpy)	IE %	CR (mpy)	IE %	CR (mpy)	IE %
Blank	492.79	-	1011.75	-	6746.47	-	16022.31	-	9716.31	-
0.05	252.94	48.67	492.79	51.29	689.04	89.79	11818.31	26.24	3759.18	61.31
0.10	148.27	69.91	270.38	73.28	632.35	90.63	8503.95	46.92	2337.50	75.94
0.50	117.75	76.10	392.49	61.21	623.62	90.76	985.59	93.85	915.81	90.57
1.00	109.03	77.87	218.05	78.45	723.93	89.27	514.60	96.79	532.04	94.52
1.50	87.22	82.30	100.30	90.09	279.10	95.86	741.37	95.37	523.32	94.61
2.00	78.50	84.07	100.30	90.09	266.02	96.06	470.99	97.06	841.67	91.34
2.50	65.42	86.70	143.91	85.78	440.46	93.47	414.30	97.41	693.40	92.86
3.00	52.33	89.93	157.00	84.48	209.33	96.90	758.81	95.26	488.43	94.97

Table 2. Effect of temperature on mild steel corrosion in 1 N H_2SO_4 in absence and presence of MHL extract

Concentration of MHL extract (v/v%)	303 K		313 K		323 K		333 K		343 K	
	CR (mpy)	IE%	CR (mpy)	IE%	CR (mpy)	IE%	CR (mpy)	IE%	CR (mpy)	IE%
Blank	1731.3	-	5268.0	-	9916.91	-	12782.0	-	22664.1	-
0.05	257.30	85.14	627.98	88.08	963.78	90.28	8032.96	37.15	2555.55	88.72
0.10	191.88	88.92	654.15	87.58	553.85	94.42	5093.65	60.15	2119.45	90.65
0.50	91.58	94.71	462.27	91.23	606.18	93.89	850.40	93.35	1474.02	93.50
1.00	61.05	96.47	571.29	89.16	357.60	96.39	1151.30	90.99	2058.39	90.92
1.50	17.44	98.99	309.63	94.12	313.99	96.83	702.12	94.51	1081.53	95.23
2.00	17.44	98.99	597.46	88.66	287.83	97.10	636.71	95.02	1814.18	92.00

Table 3. E_a for mild steel in 1N HCL without and with the presence ofvarious concentrations of MHL extract

Concentration of MHL extract (v/v%)	E_a (kJ/mol)
Blank	76.20
0.05	74.27
0.10	77.86
0.50	44.02
1.00	35.52
1.50	48.45
2.00	54.24
2.50	50.34
3.00	52.69

Table 4. E_a for mild steel in 1N H_2SO_4 without and with the presence of various concentrations of MHL extract

Concentration of MHL extract(v/v%)	E_a (kJ/mol)
Blank	52.44
0.05	62.23
0.10	59.63
0.50	53.78
1.00	67.23
1.50	79.40
2.00	81.66

For a physical adsorption mechanism, values of IE of an inhibitor decreases with temperature while for a chemical adsorption mechanism, values of IE increases with temperature (Ebenso 2003a, b and 2004).

Effect of temperature on CR of mild steel in 1N HCl and IE of plant extract

The effect of temperature on the IE of the plant extract and corrosion rate of mild steel in HCl in the absence and presence of MHL extract was studied in the temperature range of 303K to 343K using weight loss measurements. The results obtained for the different concentrations of the inhibitor are presented in Table 1. As the temperature rises the corrosion rate of mild steel increases in HCl acid medium. For different concentrations of inhibitor, as the temperature increases the corrosion rate is found to increase. Increase in CR with temperature may be due to the fact that increase in temperature usually accelerates corrosive processes, particularly in media in which volume of hydrogen evolved at higher temperature is significantly higher than that evolved at lower temperature, which gives rise to higher dissolution of metal in acidic medium. At all temperatures corrosion rate is found to decrease and inhibition efficiency is found to increase with inhibitor concentration. The extent of increase in corrosion rates is more pronounced as the temperature is increased. Hence the corrosion inhibition is by the physical adsorption of the plant constituents on to the metal surface and as the temperature increases they are desorbed exposing the metal surface to the corrosive medium. IE of MHL extract increases with inhibitor concentrations. The IE is 97.06% maximum at 333K at 2% v/v of MHL extract. The inhibition is due to the presence of plant constituents of the leaves extract. Adsorption and desorption of inhibitor molecule continuously occur at the metal surface and the equilibrium is established between these two processes at a particular temperature.

Effect of temperature on CR of mild steel in 1N H_2SO_4 and IE of plant extracts

To find out the effectiveness of the inhibitor at higher temperature in H_2SO_4 medium the experiment was carried out at different temperatures from 303K to 343K in 1N H_2SO_4 for different concentrations of the inhibitors and the results are presented in Table 2. The data reveal that the IE increases with rise in temperature as well as the concentration. The presence of inhibitor decreases the CR of mild steel in case of MHL extract in 1N H_2SO_4. At the temperature 333 K for 2% v/v of MHL extract shows 95.02% of inhibition efficiency. Increase in CR of mild steel with temperature is more pronounced in H_2SO_4 than in HCl.

Energy of Activation for the dissolution of metal in acidic medium

The activation energy (E_a) at different temperature has been calculated for different concentration of the inhibitor.

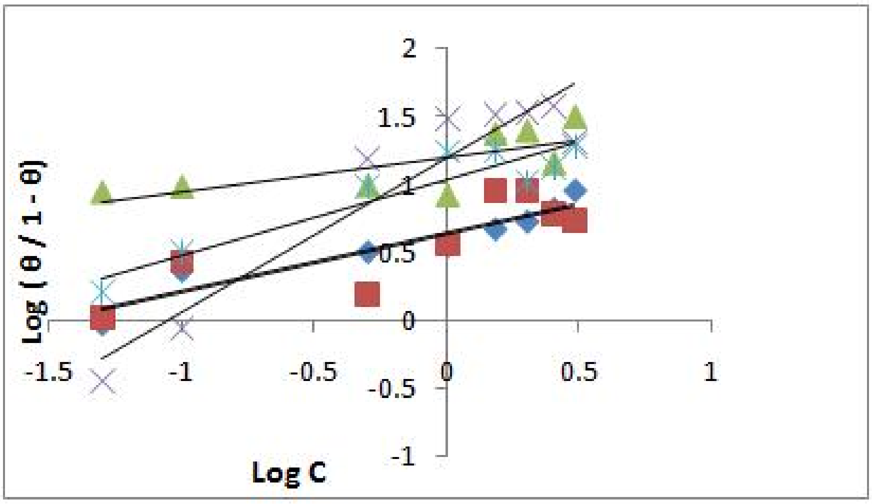

Figure 1. Arrhenius plot for mild steel in 1N HCl in presence and absence of MHL extract

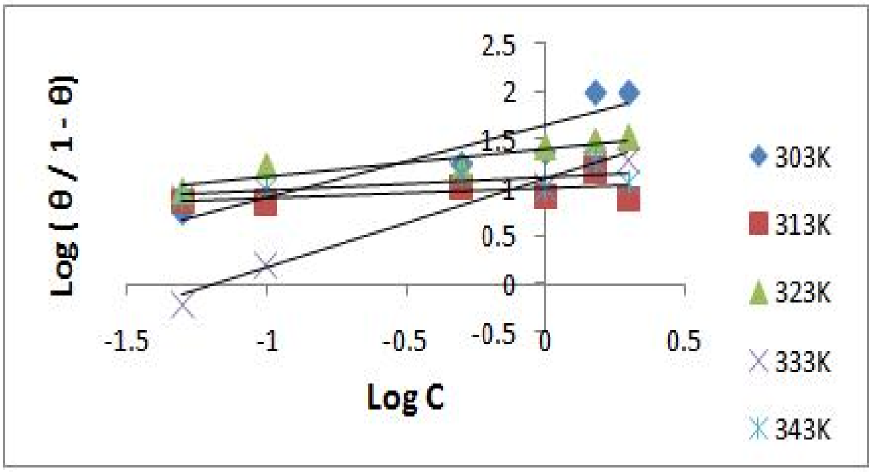

Figure 2. Arrhenius plot for mild steel in 1N H_2SO_4 in presence and absence of MHL extract

Table 5. Thermodynamic parameters of adsorption on mild steel surface in 1N HCl containing different concentrations of the inhibitor

			$-\Delta G_{ads}$ (kJ/mol)			ΔS_{ads} (kJ/K^{-1})	$-\Delta H_{ads}$ (kJ/mol)
Conc (v/v %)	303K	313K	323K	333K	343K		
0.05	17.54	18.33	24.71	21.31	22.70	0.1329	22.0101
0.10	18.03	19.01	23.16	21.38	22.75	0.1181	17.2749
0.50	14.75	13.40	18.84	21.44	22.80	0.2417	59.8123
1.00	13.28	13.72	16.38	21.51	22.86	0.2693	69.4471
1.50	12.89	15.09	18.21	21.57	22.91	0.2651	67.4961
2.00	12.53	14.34	17.44	21.64	22.96	0.2816	73.1701
2.50	12.58	12.77	15.25	21.70	23.01	0.2979	79.1757
3.00	12.86	11.88	17.15	21.76	23.06	0.3026	80.3992

Table 6. Thermodynamic parameters of adsorption on mild steel surface in 1N H_2SO_4 containing different concentrations of the inhibitor

Conc			$-\Delta G_{ads}$ (kJ/mol)			ΔS_{ads}	$-\Delta H_{ads}$
(v/v%)	(303K)	(313K)	(323K)	(333K)	(343K)	(kJ/K^{-1})	(kJ/mol)
0.05	22.03	23.43	24.79	17.93	25.85	0.0214	15.8938
0.10	21.14	21.50	24.54	18.61	24.47	0.0377	9.8749
0.50	19.11	18.33	19.96	20.33	21.01	0.0580	1.0140
1.00	18.10	15.91	19.59	17.50	18.00	0.0139	13.3303
1.50	20.65	16.59	18.86	17.85	18.81	-0.0242	26.3686
2.00	19.93	13.98	18.32	17.34	16.41	-0.0368	29.0824

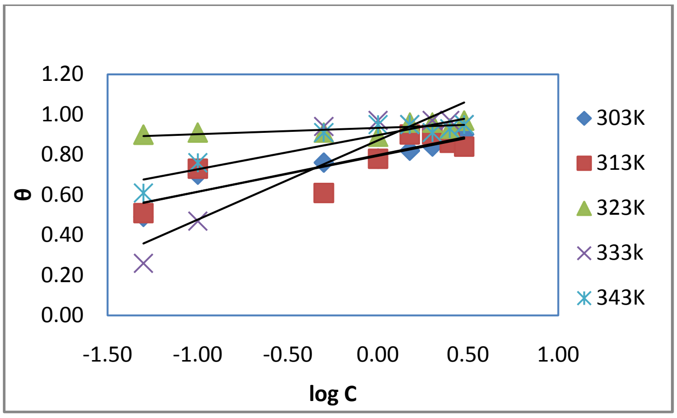

Figure 3. Temkin isotherm for various concentrations of MHL extract in 1N HCl

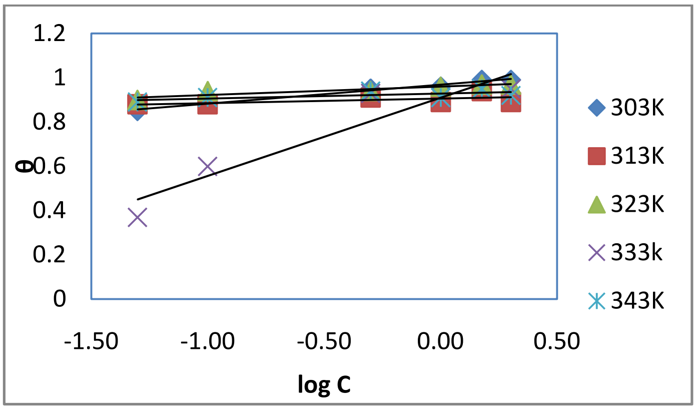

Figure 4. Temkin isotherm for various concentrations of MHL extract in 1N H_2SO_4

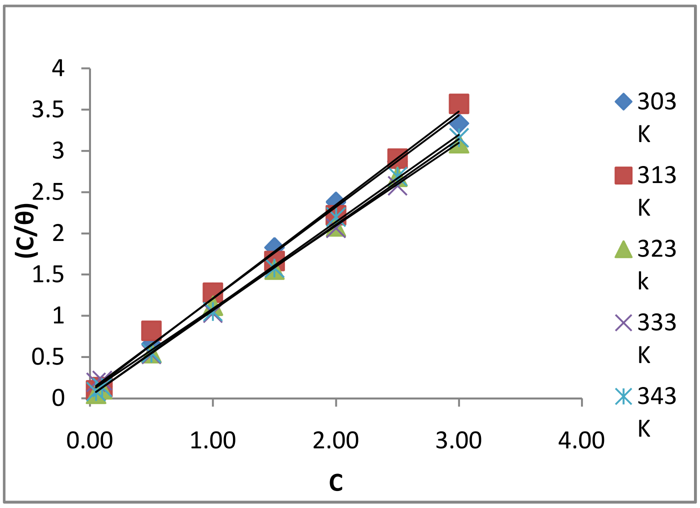

Figure 5. Langmuir isotherm for various concentrations of MHL extract in 1N HCl

The values of E_a for corrosion of mild steel using MHL inhibitor in 1N HCl and 1N H_2SO_4 are given in the Tables 3 and 4. The apparent E_a value calculated showed that there is an increase in activation energy for inhibited acid than that of uninhibited acid. Thus the reactive centers on the inhibitors block the active sites for corrosion resulting in the decrease in corrosion rate with increase in the activation energy. E_a is calculated using Arrhenius Equation

Log corrosion rate = $A^{-(Ea/RT)}$

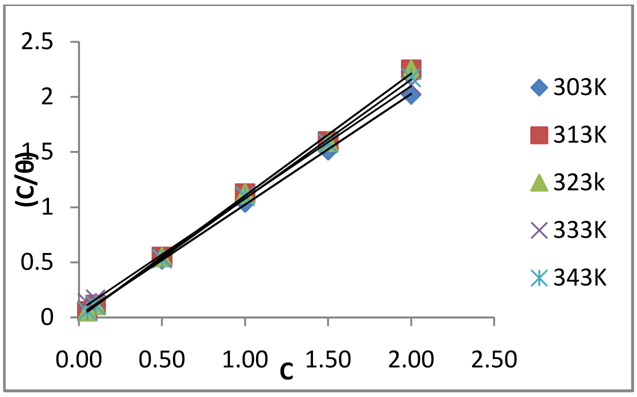

Figure 6. Langmuir isotherm for various concentrations of MHL extract in 1N H_2SO_4

Where A is the pre exponential factor and E_a is the apparent activation energy. The Arrhenius plots for the plant extract in 1N HCl and 1N H_2SO_4 medium are shown in Figures 1and 2. As the concentration of the inhibitor is increased, the activation energy also increases for all the concentrations of the inhibitor in 1N HCl medium. The result shows that the addition of the plant extract to the acidic medium decreases metal dissolution. The hindrance is due to the formation of inhibitor layer between the mild steel and acidic media. Hence the leaf extracts *Millingtonia hortensis* acts as a very good inhibitor for mild steel in 1N HCl acid. The E_a for 1N HCl increases upto 1% v/v of the inhibitor and again for further increase in the concentration of the inhibitor the E_a values decreases. E_a values for the plant extract in 1N H_2SO_4 increases from 0.5% v/v of the inhibitor concentration and then decreases at higher concentration.

Thermodynamic parameters for adsorption of the plant extract on mild steel in 1N HCl and 1N H_2SO_4

Thermodynamic parameters for adsorption of the plant extract in 1N HCl and 1N H_2SO_4 acid medium are given in the Tables 5 and 6. The negative values of free energy of adsorption (ΔG°_{ads}), indicate the spontaneity of inhibitor molecule of the metal surface. In the present study the values of ΔG°_{ads} calculated are in the range -11.88 kJ / mol to -24.70 kJ / mol in HCl medium and -13.98 kJ / mol to -25.85 kJ / mol for H_2SO_4 medium. This indicates that the plant constituents are absorbed on the metal surface by strong physical adsorption process. Negative sign indicates that adsorption of the plant constituents on the metal surface is a spontaneous process. Adsorption of plant constituents on the metal surface in hydrochloric acid and sulphuric acid medium were found to be an exothermic process and indicated by the negative ΔH_{ads} which range between -17.27 kJ / mol to -80.39 kJ / mol in 1N HCl and -1.01 kJ / mol to -29.08 kJ / mol in 1N H_2SO_4.

ADSORPTION STUDIES

Corrosion inhibition is a surface phenomenon. The interaction of the surface inhibitor can be estimated from the experimental data. The inhibition efficiency depends on the type, number of active sites at the metal surface, charge density, molecular size of the inhibitor, metal inhibitor interactions and the metallic complex formation. Adsorption isotherms give information on metal inhibitor interaction. Adsorption isotherms are very important in determining the mechanism of the inhibition reaction.

Most frequently used adsorption isotherms are Langmuir and Temkin isotherms. The experimental data obtained with different inhibitor concentrations of the plant extracts in the HCl and H_2SO_4 media at different temperatures from 303K to 343K were applied to different adsorption isotherm equations and isotherms are given in figures

Conclusion

- The protection efficiency of the inhibitor depends on its concentration, immersion time and temperature.
- The comparative study of the plant extract shows better inhibitive effect in H_2SO_4 medium than in HCl medium.
- The adsorption on the metal surface was found to obey Langmuir and Temkin isotherms.
- The optimum temperature for the corrosion inhibition with the leaf extract in 1N HCl was 333K **(97.41%)** and 1N H_2SO_4 was 323K **(97.10%)**.
- The negative value of ΔG_{ads} and its magnitude indicate the spontaneous physical adsorption of the constituents of the inhibitor on the metal surface.
- Adsorption of inhibitor species on mild steel surface in 1N HCl and 1N H_2SO_4 suggest physisorption mechanism.

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