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Der Pharma Chemica, 2009, 1(2): 249-257
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X

Environment friendly acid corrosion inhibition of mild steel by *Ricinus communis* Leaves

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Abstract

Large extent of mild steel corrosion occurs during acid pickling and surface cleaning. Various synthetic chemicals have been studied as corrosion inhibitors and reported. But pure synthetic chemicals are costly. Some of them are toxic and their disposal creates pollution problems. In the present study the acid extract of *Ricinus Communis* leaves have been investigated as a cheap and eco-friendly corrosion inhibitor for mild steel in 1M HCl medium by weight loss and polarization techniques. Using various concentrations of inhibitor, studies were carried out for ½ h, 1 h, 3 h, 7 h and 24 h immersion times and at different temperatures. The results indicate *Ricinus communis* leaves to be a good corrosion inhibitor for mild steel. The inhibition efficiency was found to increase with inhibitor concentration. Inhibition efficiency of 97.19% at 2.5%v/v inhibitor concentration was obtained. The potentiodynamic polarization results reveal that the extract behave like mixed type inhibitor.

Key words: Acid corrosion, corrosion inhibitors, mild steel, polarization methods

Introduction

Carbon steel is used in a wide range of industrial applications such as erecting boilers, drums, heat exchangers, tanks etc. Hydrochloric acid is generally used for the removal of undesirable scale and rust in several industrial processes, but this leads to base metal attack. Hence inhibitors are commonly used to minimize metal dissolution and acid consumption [1,2].Unfortunately many of the inhibitors used are inorganic salts or organic compounds with toxic properties or limited solubility. Increasing awareness of health and ecological risks has drawn attention in finding more suitable inhibitors, which are non-toxic. Earlier research studies have substantially proved that certain natural parts of plant origin containing various organic compounds have corrosion inhibitive action [3-11].

A thorough review on literature showed that there is no study on the agro waste of *Ricinus communis* leaves as corrosion inhibitor. In the present work, the electrochemical behaviour of mild steel in 1M HCl in the absence and presence of *Ricinus communis leaves* is studied by potentiodynamic polarization, electrochemical impedance and weight-loss measurements.

Results and Discussion

Weight loss measurements

Table 1 gives the values of inhibition efficiency obtained from the weight loss measurements for different concentrations of *Ricinus communis* at various immersion times in 1M HCl at 303 K. The optimum concentration required to achieve an efficiency of 97% is found to be 2.5%. It is hence inferred from the obtained data that there is a strong correlation between inhibitor efficiency and concentration of the inhibitor.

Table 1 Inhibition efficiencies for corrosion of mild steel in 1M HCl with different conc. of *Ricinus communis* at 303K

Conc(%) (v/v)	Inhibition efficiency P (%)				
	½ h	1 h	3h	7h	24h
Blank	-	-	-	-	-
0.005	34.52	45.36	53.02	53.32	72.96
0.010	36.48	49.54	67.50	80.07	80.83
0.050	44.84	65.81	72.01	82.72	83.89
0.100	49.91	70.65	76.91	85.61	86.68
0.150	55.60	72.41	78.53	86.57	90.75
0.200	57.85	74.50	80.65	87.85	92.11
0.500	63.44	75.57	83.38	87.91	92.35
1.000	64.53	76.96	84.77	91.52	92.94
1.500	65.26	78.49	86.58	91.90	94.11
2.500	67.37	81.94	86.62	92.20	97.19

The inhibition of corrosion of metals by organic compounds [14] is attributed to either the adsorption of inhibitor molecule or the formation of a layer of insoluble complex of the metal on the surface which acts as a barrier between the metal surface and the corrosive medium. Since no insoluble material was observed on the surface of the metal, the inhibitive action of the extract may be due to its adsorption on the metal surface. At lower concentrations the components of the extract is adsorbed at the surface with a low percent coverage. As the concentration increases the amount adsorbed increases leading to a higher degree of coverage and consequently higher corrosion inhibition.

Polarization measurements

Figure 1 shows the polarization curves of mild steel in 1M HCl blank solution and in the presence of different concentrations (0.005-2.5%) of the extract. The increase in concentration of the extract led to both anodic and cathodic current inhibition, but the reduction in the anodic current was more significant than that of the cathodic current. This shows that the addition of *Ricinus communis* reduces anodic dissolution and also retards the hydrogen evolution reaction.

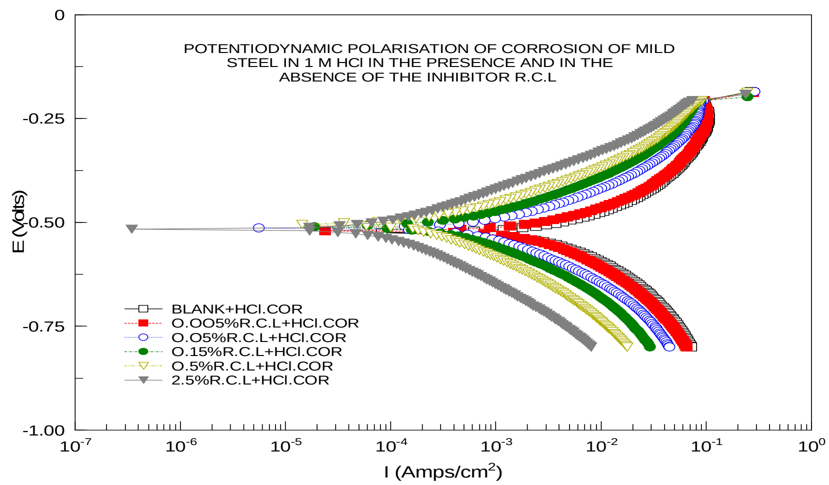

Figure 1: Potentiodynamic Polarization curves for mild steel in 1M HCl containing different concentrations of *Ricinus communis* extract

Table 2 gives the values of kinetic corrosion parameters as to the corrosion potential E_{corr}, corrosion current density I_{corr} , Tafel slopes b_a and b_c, and inhibition efficiency for the corrosion of mild steel in 1M HCl blank solution and in the presence of various concentrations (0.005-2.5%) of the extract. It can be seen that the E_{corr} values are shifted positively which suggests the extract functions as a mixed type of inhibitor. In the entire concentrations b_a is greater than the b_c suggesting that though the inhibition is under mixed control the effect of the inhibitor on the anodic polarization is more pronounced than on the cathodic polarization.

Table 2: Electrochemical parameters for corrosion of mild steel in 1M HCl with various concentrations of *Ricinus communis* extract at 303 K

Conc (%) (v/v)	$-E_{corr}$ mV	I_{corr} μACm^{-2}	b_a mV/dec	b_c mV/dec	I.E (%)	Rp (Ω Cm^2)	I.E (%)
Blank	525.25	5.382	201.60	141.60	-	6.92	-
0.005	520.34	3.921	197.00	126.26	27.15	8.83	21.63
0.050	513.96	0.089	125.93	95.58	98.35	24.61	71.88
0.150	510.27	0.049	123.74	92.09	99.09	46.65	85.17
0.500	504.00	0.028	139.32	86.89	99.48	76.94	91.00
2.500	516.30	0.009	130.28	93.57	99.83	227.54	96.96

Electrochemical impedance spectroscopy

Impedance diagrams obtained for mild steel in 1M HCl in the presence of various concentrations of *Ricinus communis* are shown in figure 2. These diagrams are not perfect semicircles. The difference has been attributed to frequency dispersion [15].

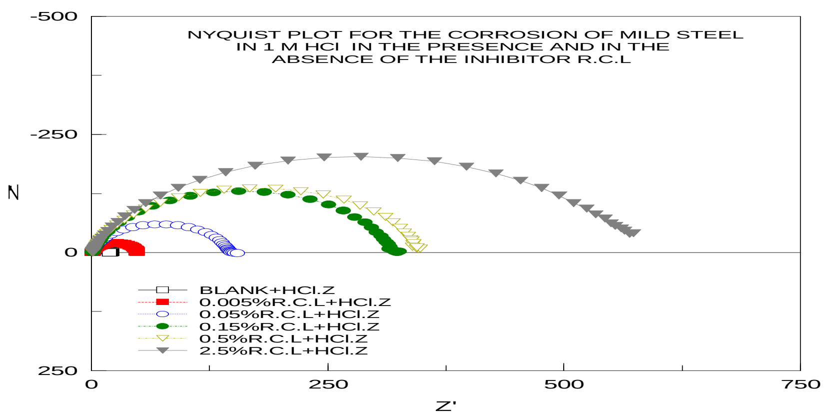

Figure 2: Nyquist plot of mild steel in 1M HCl with various concentrations of RC at 303K

The fact that impedance diagrams have a semicircular appearance shows that the corrosion of steel is controlled by a charge transfer process and the presence of inhibitor does not alter the mechanism of dissolution of steel in HCl.

Table 3 Impedance parameters for the corrosion of mild steel in 1M HCl containing different concentrations of *Ricinus communis* at 303 K

Conc (%) (v/v)	Rct (ΩCm^2)	Cdl (μFCm^{-2})	I.E (%)
Blank	19.64	165.18	-
0.005	47.64	148.1	58.77
0.050	146.91	96.16	86.63
0.150	318.55	80.31	93.83
0.500	345.97	75.09	94.32
2.500	581.53	66.34	96.62

Table 3 gives the values of the charge transfer resistance $R_{ct,}$ double layer capacitance C_{dl} and inhibitor efficiency obtained from the above plots. It can be seen that the presence of *Ricinus communis* enhances the values of R_{ct} and reduces the C_{dl} values. The decrease in C_{dl} may be due to the adsorption of the phytochemical constituents of *Ricinus communis* to form an adherent film on the metal surface and suggests that the coverage of the metal surface with this film decreases the double layer thickness.

Effect of temperature

Temperature can modify the interaction between the mild steel electrons and the acidic media in absence and presence of the inhibitor. Mass loss method was adopted for corrosion of mild steel in 1 M HCl in absence and presence of various concentrations of the inhibitor at different temperatures. The plot of log (corrosion rate) against 1/T gave straight lines (Figure 4). The values of the slopes of these straight lines permit the calculation of the Arrhenius activation energy

$$Ea^* \ [\ \log I_{corr} = (-Ea^* / 2.303\ RT) + const]$$

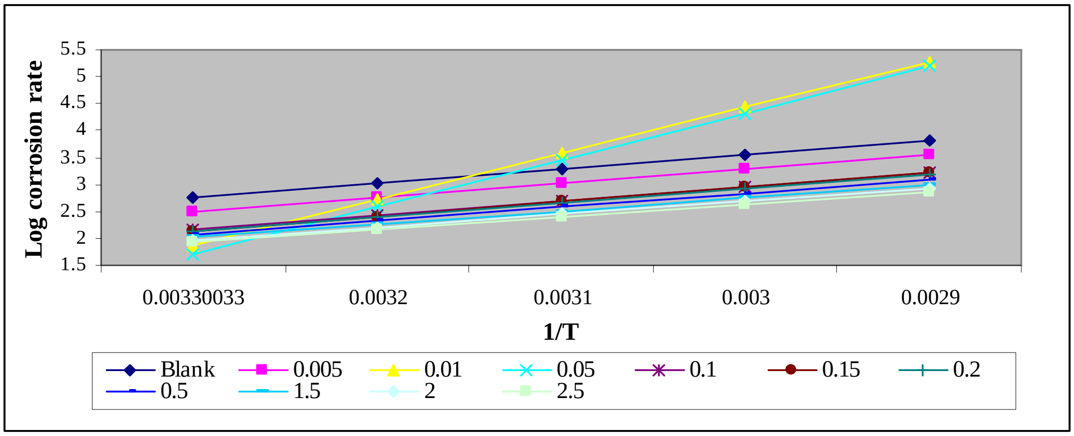

Figure 4: Arrhenius plots for mild steel dissolution process in 1M HCl containing different concentrations of *Ricinus communis*

Table 4 Activation energy (Ea) and thermodynamic parameters for corrosion of mild steel in 1M HCl containing different concentrations of *Ricinus communis* extract

Conc (%) (v/v)	Activation energy (E_a) KJ/mol	Free energy of adsorption (-ΔG) KJ/mol					Heat of adsorption (ΔH) KJ/mol	Entropy changes (ΔS) J/deg/mol
		303 K	313 K	323 K	333 K	343 K		
Blank	33.24	-	-	-	-	-	-	-
0.005	35.31	22.36	23.77	25.18	26.58	27.99	- 20.223	0.141
0.010	35.94	21.41	22.63	23.84	25.06	26.27	0.065	0.121
0.050	59.33	18.24	19.11	19.98	20.86	21.73	0.031	0.087
0.100	40.40	17.04	17.79	18.55	19.30	20.06	0.075	0.075
0.150	41.90	16.56	17.19	17.84	18.48	19.12	0.008	0.064
0.200	39.96	16.23	16.87	17.51	18.16	18.79	0.003	0.064
0.500	39.02	14.53	15.03	15.53	16.02	16.52	- 0.015	0.049
1.500	33.49	12.18	12.69	13.19	13.69	14.20	- 0.029	0.050
2.000	27.74	11.79	12.34	12.89	13.43	14.03	0.055	0.055
2.500	25.15	10.18	11.14	12.11	13.07	13.98	0.096	0.096

The calculations show that Ea increases in the presence of *Ricinus communis* extract which indicate that the inhibition probably occurs via formation of a physisorbed monolayer on the metal surface. The reduction in the activation energy at a higher concentration of the inhibitor may be attributed to chemisorption of the inhibitor on the steel surface. It also indicates that the inhibitors are more effective at lower temperatures for lower concentration and higher temperature for higher concentration. The low and negative values of ΔG_{ads} indicate the spontaneous adsorption of inhibitor on the surface of the mild steel. It also suggests the strong interaction of inhibitor molecules on to the mild steel surface. The ΔH values are found to be below 10 KJ/mol, which indicate physical adsorption over the surface of mild steel. The negative values (-20.22 KJ/mol) of ΔH shows the adsorption process is exothermic in nature. The change in entropy (ΔS) was found to be greater than zero (0.14 J/deg/mol) in 1M HCl at 0.005%. This indicates that the reaction is irreversible.

Adsorption isotherms

Since the inhibition of corrosion by the inhibitor involves the adsorption of the inhibitor on to the surface of the metal, the phenomenon of interaction between the metal surface and inhibitor can better be understood in terms of adsorption isotherms. Degree of surface coverage (θ) for different inhibitor concentrations at various immersion times was evaluated by the weight loss method. Data were tested graphically by fitting to Langmuir, Freundlich and Temkin adsorption isotherms (figures 5, 6 &7).

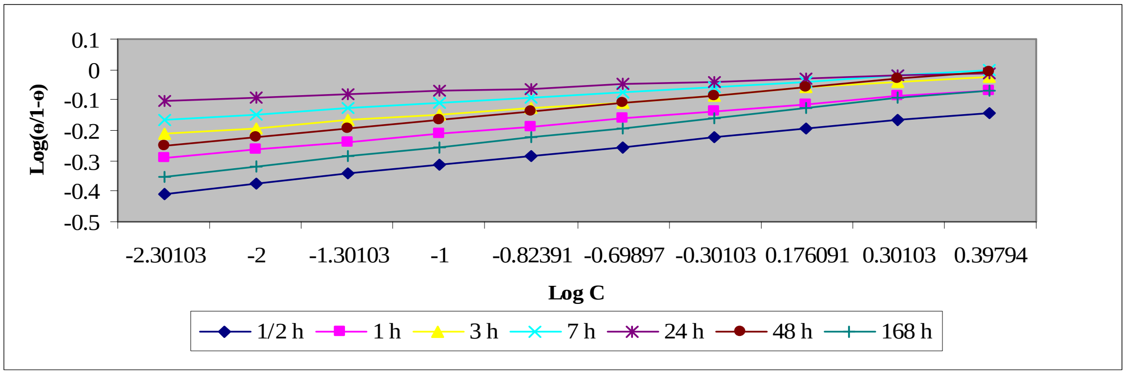

Figure 5: Langmuir isotherm plots for the adsorption of *Ricinus communis* inhibitor in 1M HCl

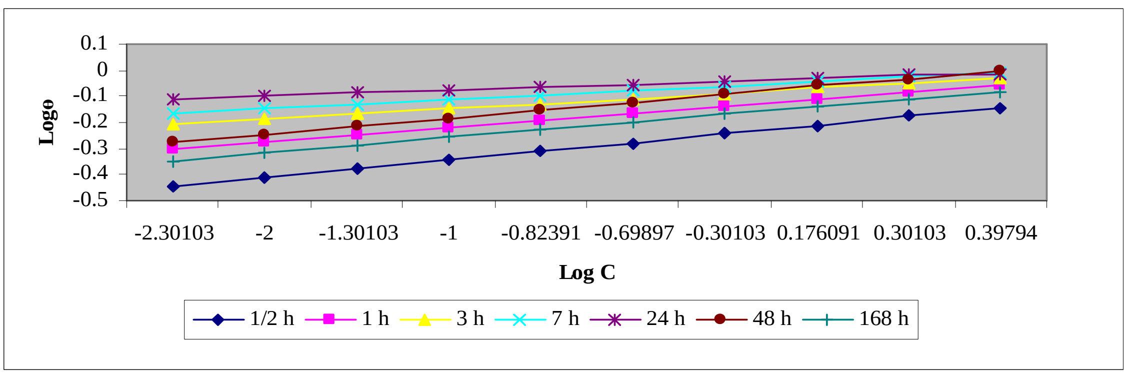

Figure 6: Freundlich isotherm plots for the adsorption of *Ricinus communis* inhibitor in 1M HCl

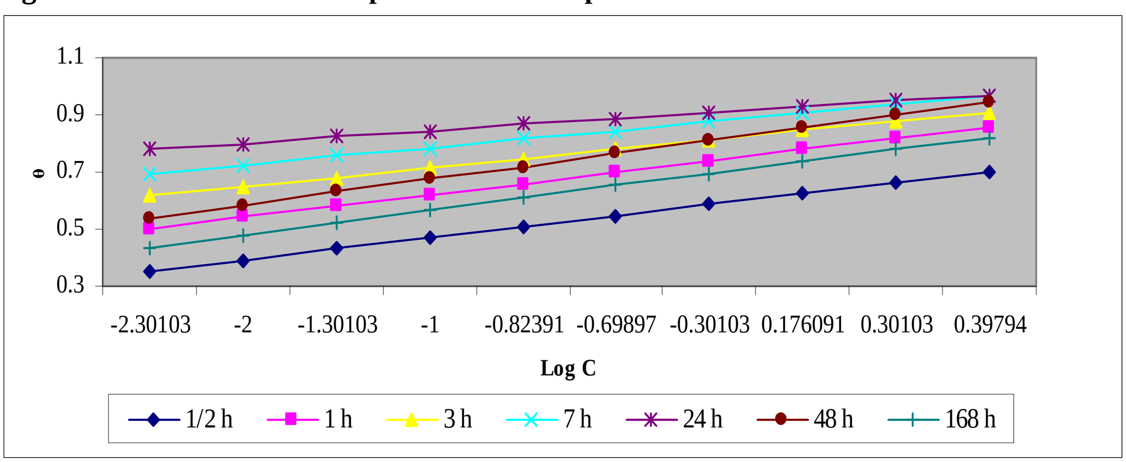

Figure 7: Temkin isotherm plots for the adsorption of *Ricinus communis* inhibitor in 1M HCl

From the figures, it is well evident that all three isotherms tested obeyed with the adsorption models. In the present investigation the Langmuir curves obtained from the extract were reasonably linear (correlation coefficient > 0.9). The slight deviation may be because of the fact that there is no interaction amongst the adsorbed molecules. This is not true in the case of organic molecules having polar atoms of groups which are adsorbed on the anodic and cathodic sides of the metal surface. Such adsorbed species may interact by mutual repulsion or attraction, thus accounting for the deviation of the gradient from unity. The negative slopes of the Temkin isotherms mean that there are repulsive side interactions between adsorbed inhibitor molecules.

Materials and Methods

The *Ricinus communis* leaves extract was prepared by refluxing 50 grams of the powdered leaves in 1000 ml of 1M HCl for 3 hours and kept overnight and was filtered, Made up to 1000 ml to attain the stock solution. From this stock solution, different concentrations of the inhibitor were prepared. Solution of 1M HCl was prepared from a commercial grade acid. The composition of mild steel has been analyzed using ARL 3460 metal analyzer (Optical emission spectrometer). The metal was found to have the following elemental composition. Carbon-0.0715%, Silicon-0.0920%, Manganese-0.1747%, Phosphorus-0.0169%, Sulphur-0.0162%, Chromium-0.0095%, Molybdenum-0.0020%, Nickel-0.0048%, Vanadium-0.003%, Aluminium-0.0370%, Copper-0.0060%, Titanium-0.0008%, Niobium-0.0006%, Tungsten-0.0006%, Lead-0.0004% Boran-0.0007%, Antimony-0.0001%, Bismuth-0.0020%, Calcium-0.0005%, Zinc-0.0004%, Cerium-0.0001% and Iron-99.5618%.

The sheets of cold rolled mild steel, which is commercially available in the market, were machined into coupons of area 5 X 1 cm^2. Holes were drilled on the center of one end of all the coupons for suspension. These coupons were degreased, cleaned with emery paper and washed with distilled water. The panels were stored in desiccators in the absence of moisture before their use for the investigation.

Mass loss method

Mild steel coupon accurately weighed using Denver balance were fully immersed in triplicate in 100 ml of 1 M HCl in absence and presence of various concentrations of the extract. At the end of the test, the coupons were washed with distilled water, dried and then reweighed. The loss in mass is calculated from the difference between the before and end of the experiment weights and were averaged. The corrosion rate in mpy was calculated using the formula given in our earlier paper [12].

Electrochemical experiments were carried out in a glass cell with a capacity of 100ml. A platinum electrode and a saturated calomel electrode (SCE) were used as a counter electrode and a reference electrode respectively. The working electrode (WE) was mild steel coupon used for mass loss method but lacquered as to expose an area of 1 cm^2.

Potentiodynamic polarization was conducted using a Solartran Electrochemical measurement unit (1280 B) with a software package of Corrware and Z-view. The a.c impedance measurements were performed at corrosion potentials (E_{corr}) over a frequency range of 10 KHz to 20 MHZ, with a signal amplitude perturbation of 10mv. Nyquist plots were obtained from the results of these experiments. Values of the charge transfer resistance R_t were obtained from the plots by determining the difference in the values of impedance at low and high frequencies as suggested by Tsura *et al* [13].Values of the double-layer capacitance C_{dl} were calculated from the frequency at which the impedance imaginary component Z'' was maximum using the equation

$$f\,(Zi_{max}) = 1 / 2\pi\, C_{dl}\, R_t$$

Corrosion potentials and corrosion current densities were determined by extrapolating the cathodic and anodic Tafel regions from the potentiodynamic polarization curves. The intersect gives the corrosion current and corrosion potential.
Inhibition efficiencies P% were calculated as follows

$$IE\% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100$$

Where I_{corr} and I'_{corr} are the corrosion current densities in the absence and in presence of the inhibitor.
- Impedance measurement

$$IE\% = \frac{R_{t/inh} - R_t}{R_{t/inh}} \times 100$$

Where R_t and $R_{t/inh}$ are the charge transfer resistance values in absence and in presence of the inhibitor, respectively.

Conclusion

The conclusions drawn from the study are:

- The acid extract of *Ricinus communis* leaves behaved as a potent inhibitor to mild steel in 1M HCl. The protection efficiency of the inhibitor was found to increase with increase in concentration of the inhibitor showing a maximum efficiency of 97.19% at 2.5% v/v.
- The extract under study resists corrosion effectively even at higher temperature.
- The thermodynamic parameters obtained from the study indicate that the spontaneous adsorption of inhibitor on the surface of the mild steel is exothermic in nature.
- Adsorption models- Langmuir, Freundlich and Temkin isotherm fit well for the data proving the applicability of these models to the process.
- The results obtained from the polarization studies reveal that the extract behaved as a mixed type of inhibitor.

Acknowledgement

The authors would like to record their sincere thanks to the authorities of Avinashilingam University for Women, Coimbatore, for providing facilities to carry out this research work.

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Objectives

- Replacing highly toxic commercial inhibitors with non toxic, biodegradable, eco friendly plant materials
- Trying an easily available and cost effective plant materials

Methods adopted and materials

Metal selected: Mild steel(Extensively used in Boilers, Drums, Heat exchangers and tanks)
Acid medium : HCl (Commonly used in Pickling)

Weight loss method

- **Sample size :** Mild steel: 5cm x 1cm
- **Balance** : Denver – 220D
- **Temperature study** : Thermostat
- **Parameters**:
  - **Inhibitor concentrations**: 0.005,0.01,0.05,0.1,0.2, 0.5,1.0, 1.5 and 2.5%(v/v)
  - **Immersion periods:** ½ h, 1h, 3h, 7h and 24h
  - **Temperatures**: 30, 40, 50, 60 and 70 (±2) K.

Potentiodynamic polarization and impedance measurements

- **Instrument:** A Solatron Electrochemical Measurement Unit (1280 B) with a computer software corrware for potentiodynamic polarization and Z-view for impedance.

Conclusion:

- Optimum concentration : 2.5%v/v
- Optimum temperature : 323 K
- Maximum Efficiency : 97.19%
- Mechanism of action : Chemisorption, Spontaneous, Exothermic and Irreversible
- Adsorption obeys Langmuir, Freundlich and Temkin models
- Mode of inhibition : Mixed type