

6-methyl-4,5-dihydropyridazin-3(2H)-one as a novel corrosion inhibitor for mild steel in acidic media

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Abstract

The inhibition behavior of 6-methyl-4,5-dihydropyridazin-3(2H)-one (TR) on mild steel in 1 M HCl and 0.5 M H₂SO₄ containing different concentration of TR was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy studies. It has been observed that corrosion rate decreases and inhibition efficiencies increases with increasing in TR concentration and immersion time in case of HCl. The recorded electrochemical data indicated the basic modification of mild steel surface as a result in a decrease in the corrosion rate. Corrosion inhibition could be explained by considering an interaction between metal surface and the inhibitor.

Keywords: Corrosion inhibition, Mild steel, Acidic media, Polarization, Impedance

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1. Introduction :

Metals generally tend to move to its original state by corrosion process. Mild steel is an alloy form of iron, which undergoes corrosion easily in acidic medium. Acidic solutions are extensively used in chemical laboratories and in several industrial processes such as acid pickling, acid cleaning, acid descaling and oil wet cleaning etc. Also mild steel is used under different conditions in chemical and allied industries for handling alkaline, acid and salt solutions. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion [1]. Most of the efficient inhibitors used in industry are organic compounds which mainly contain oxygen, sulphur, nitrogen atoms and multiple bonds in the molecule through which they are adsorbed on metal surface [2–6]. Moreover, many *N*-heterocyclic compounds have been proved to be effective inhibitors for the corrosion of metals and alloys in aqueous media [7–13].

This work deals with the study of the corrosion inhibition properties of 6-methyl-4,5-dihydropyridazin-3(2*H*)-one (TR). The choice of this compound was based on the consideration that this compound contains π -electrons and heteroatoms such as N and O, which induce greater adsorption of the inhibitor molecule onto the surface of mild steel. The aim of this study was to determine the inhibition efficiency of (TR) as a novel inhibitor for the corrosion of mild steel in 1M HCl and 0.5 M H₂SO₄.

2. Experimental method:

2.1. Materials:

Mild steel specimens of the following chemical composition (wt.%) were used for the experiment: C=0.11, Si=0.24, Mn=0.47, Cr=0.12, Mo=0.02, Ni=0.1, Al=0.03, Cu=0.14, W=0.06, Co<0.0012, V<0.003 and the remainder Fe. The structural formula of inhibitor is shown in Fig. 1. Its concentration was varied from 10⁻⁴ M to 10⁻² M. The electrolyte solution 1M HCl and 0.5M H₂SO₄ were prepared from commercial 37% HCl and 98% H₂SO₄, respectively, and distilled water.

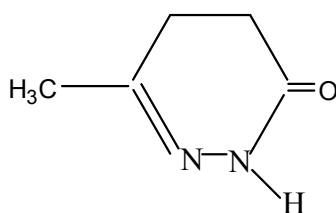


Fig.1 : molecular structure of inhibitor

2.2. Gravimetric measurements:

The mild steel sheets of 2cm×5cm×0.05cm were abraded with emery paper (grade from 400 to 1200) and then washed with distilled water and acetone, dried at room temperature. After weighing accurately, the specimens were immersed in corrosive medium with and without the addition of different concentrations of inhibitor for 6 h. The mild steel sheets were then taken out, washed with distilled water and acetone, dried and weighed accurately. The average weight loss of three substrate sheets could be obtained. The inhibition efficiency (IE %) of inhibitors on the corrosion of mild steel was calculated as follows:

$$IE\% = \frac{\omega_0 - \omega}{\omega_0} \times 100 \quad (1)$$

Where ω_0 and ω are the values of the average weight loss without and with addition of the inhibitors, respectively.

2.3. Electrochemical measurements

Electrochemical measurements were conducted in a conventional three-electrode cylindrical glass cell at 20°C with a platinum counter electrode (CE) and a saturated calomel electrode (SCE) as the reference electrode. The working electrode (WE) was in the form of a square cut from mild steel embedded in epoxy resin of polytetrafluoroethylene (PTFE) so that the flat surface was the only surface in the electrolyte. The working surface area was 1cm². The polarization curves were recorded by using a potentiostat/galvanostat (PGZ100). The potential increased with a speed of 1 mV/s and started from potential of -750 mV to -100 mV vs. SCE for 1M HCl and 0.5M H₂SO₄ at 20°C. The IE% was defined as:

$$IE\% = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0} \times 100 \quad (2)$$

Where i_{corr}^0 and i_{corr} are the corrosion current densities values without and with inhibitor, respectively.

2.4. EIS measurements:

The electrochemical impedance spectroscopy measurements were carried out using a transfer function analyser (VoltaLab PGZ 100), with a small amplitude ac. Signal (10 mV rms), over a frequency domain from 100 KHz to 10 mHz at 20°C. The results were then analysed in terms of equivalent electrical circuit using bouckamp program [14]. The charge transfer resistance R_{ct} , is obtained from the diameter of the semicircle in Nyquist representation. The inhibition efficiency of the inhibitor has been found from the relationship:

$$IE\% = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \quad (3)$$

Where R_{ct}^0 and R_{ct} are the charge transfer resistance values in the absence and the presence of inhibitor, respectively.

3. Results and discussion:

3.1. Gravimetric measurements:

Tables 1 and 2 show the result for mild steel in corrosive medium in the absence and presence of TR at 20°C. The inhibition efficiency was greater than 92% and 21% in case of 1M HCl and 0.5M H₂SO₄, respectively. TR inhabited the corrosion of mild steel in both acids. As corrosion rate decreased, inhibition efficiency increased with increasing TR concentration in the test solution. This inhibition can be due the formation of an organic film on the metal surface through sharing electrons between nitrogen or oxygen and iron atoms.

However, inhibition efficiency values are maximum in case of 1M HCl than 0.5M H₂SO₄. This is probably due to the lesser surface coverage in H₂SO₄ solution. Again chloride ions have a greater adsorption tendency than sulphate ions on steel [15].

Table 1: inhibition efficiency for various concentration of TR for the corrosion of mild steel in 1 M HCl obtained from weight loss measurements at 20°C (6h of immersion)

Inhibitor conc. (M)	Corrosion rate (mg.cm ⁻² .h ⁻¹)	inhibition efficiency, IE (%)
Blank	3.026	---
10 ⁻⁴	0.241	92
10 ⁻³	0.110	96
5 × 10 ⁻³	0.057	98
10 ⁻²	0.045	98

Table 2: inhibition efficiency for various concentration of TR for the corrosion of mild steel in 0.5M H₂SO₄ obtained from weight loss measurements at 20°C (6h of immersion)

Inhibitor conc. (M)	Corrosion rate (mg.cm ⁻² .h ⁻¹)	inhibition efficiency, IE (%)
Blank	7.243	---
10 ⁻³	5.728	21
5 × 10 ⁻³	4.657	35
10 ⁻²	4.100	43
5 × 10 ⁻²	3.237	55

3.2. Potentiostatic polarization study:

Figures 2 and 3 show polarization curves for mild steel in 1M HCl and 0.5M H₂SO₄ with and without various concentration of TR. TR suppressed the cathodic and anodic reactions. It is clear that the addition of TR hindered the acid attack on the mild steel electrode and a comparison of curves in both cases, showed that, with respect to the blank, increasing the concentration of inhibitor gave rise to a consistent decrease in anodic and cathodic current densities indicating that TR acts as a mixed type inhibitor [16,17]. The polarization parameters such as corrosion potential (E_{corr}) and corrosion current densities (i_{corr}) obtained by extrapolation of the Tafel lines are listed in table 3 and 4. The calculated percentage inhibition efficiency (IE%) of TR are also given. Analysis of these data show that i_{corr} decreased with addition of TR in 1M HCl and 0.5M H₂SO₄, can be due to increase in the blocked fraction of the electrode surface by adsorption.

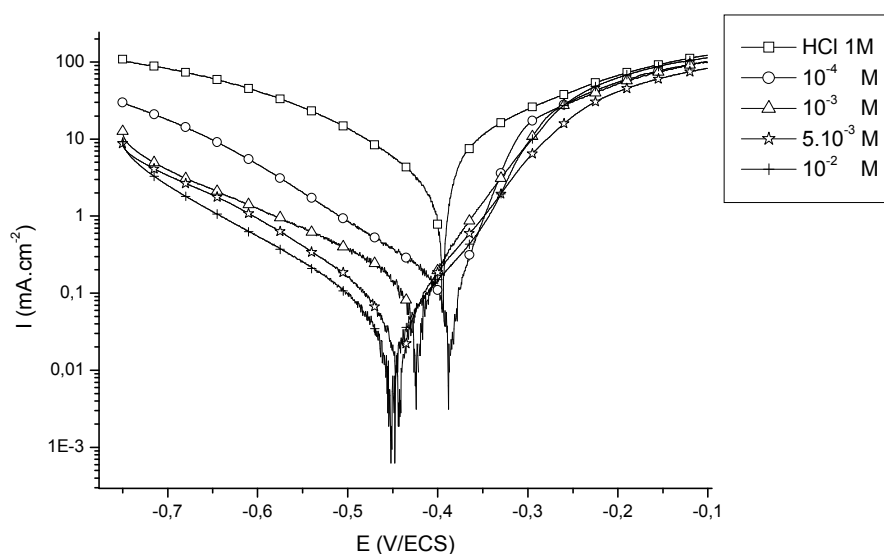


Fig.2 : Polarization curves of mild steel recorded in 1M HCl containing different concentration of TR at 20°C

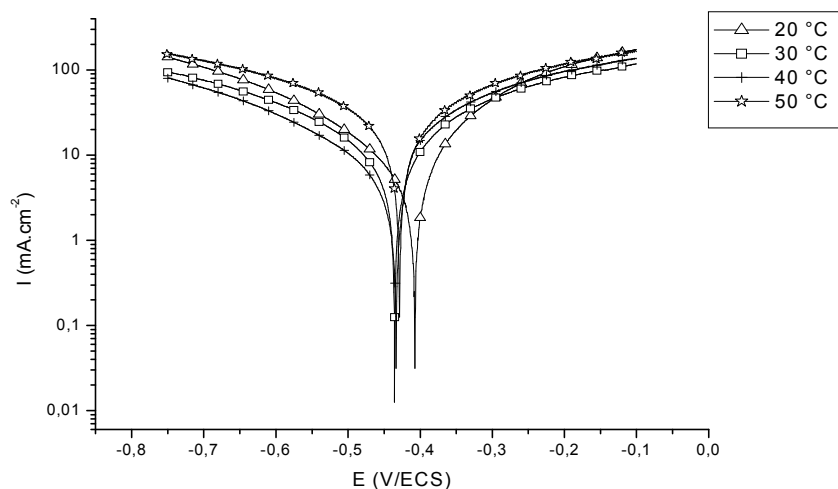


Fig.3 : Polarization curves of mild steel recorded in 0.5M H₂SO₄ containing different concentration of TR at 20°C

Table 3: electrochemical parameters for the corrosion of mild steel 1M HCl containing different concentration of TR at 20°C (30 min of immersion)

Conc. (M)	E _{corr} (mV/sce)	i _{corr} (μA.cm ⁻²)	-β _c (mV.dec ⁻¹)	IE (%)
00	-396	1072	125	----
10 ⁻⁴	-387	108	120	89
10 ⁻³	-424	84	131	92
5×10 ⁻³	-443	50	118	95
10 ⁻²	-453	31	109	97

Table 4: electrochemical parameters for the corrosion of mild steel in 0.5 M H₂SO₄ containing different concentration of TR at 20°C (30min of immersion)

Conc. (M)	E _{corr} (mV/sce)	i _{corr} (μA.cm ⁻²)	-β _c (mV.dec ⁻¹)	IE (%)
00	-409	3749	127	-----
5×10 ⁻⁴	-416	1230	135	67
10 ⁻³	-406	1142	132	69
5×10 ⁻³	-410	1094	156	70
10 ⁻²	-405	940	138	75
5×10 ⁻²	-405	793	147	79

3.3. Electrochemical impedance spectroscopy study :

The results described blow can be interpreted in terms of the equivalent circuit of the double layer shown in figure 4, which has been used previously to model the iron-acid interface [18].

The corrosion behavior of mild steel in different corrosive media in the presence of various concentration of TR was investigated by EIS at 20°C and is given in figures 5 and 6. The best

semicircle can be fitted through the data point in the Nyquist plot using Bockamp program [14]. The impedance diagrams obtained were not perfect semicircles. This feature had been attributed to frequency dispersion [19]. It is apparent from this plots that the impedance response of mild steel in uninhibited 1M HCl and 0.5M H₂SO₄ solutions has significantly changed after the addition of TR. This indicated that the impedance of inhibited substrate increases with increasing inhibitor concentration in both acids.

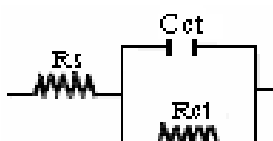


Fig.4: Electrical equivalent circuit for the metal-acid interface

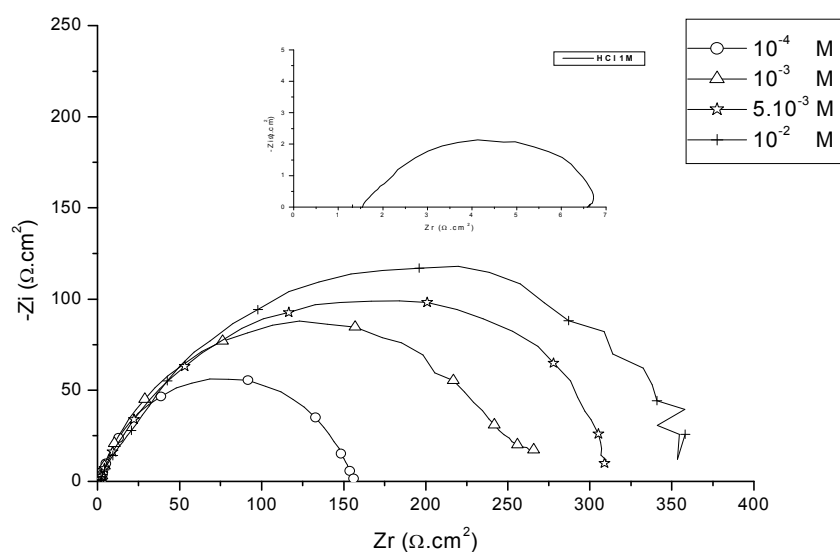


Fig. 5: Nyquist plots of mild steel in 1M HCl in presence of different concentrations of TR at 20 °C

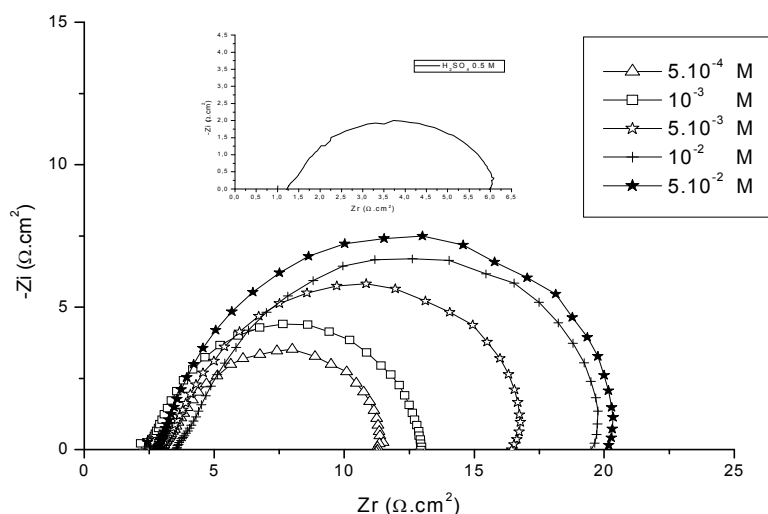


Fig. 6: Nyquist plots of mild steel in 0.5M H₂SO₄ in presence of different concentrations of TR at 20 °C

The corrosion kinetic parameters such as charge transfer resistance (R_{ct}), double layer capacitance (C_{ct}) and inhibition efficiency (IE%) are given in tables 5 and 6. The greatest effect was observed at 10^{-2} M of TR in 1M HCl and at 5×10^{-2} M in 0.5M H₂SO₄. When the concentration of inhibitor increases, C_{ct} values decrease. Decrease in the C_{ct} , which can result from decrease in local dielectric constant and/or an increase in the thickness of electrical double layer, suggested that the TR molecules function by adsorption at metal-solution interface [18]. Similar behavior is observed in both media [17].

It is well known that the inhibitive action of organic compounds containing S, N and/or O is due to the formation of a co-ordinate type bond between the metal and the lone pair of electrons in additive. The tendency to form a co-ordinate bond and hence the extent of inhibition can be enhanced by increasing the effective electron density at the functional group of the additive [20]. In aromatic or heterocyclic ring compounds the effective electron density at the functional group can be varied by introducing different substituents in the ring leading to variations of the molecules structure.

The adsorption of TR on the metal surface can occur either directly on the basis of donor-acceptor interactions between the π -electrons of the inhibitor and the vacant d-orbitals of iron surface atoms or an interaction of inhibitor with already adsorbed sulphate or chloride ions [21, 22].

Table 5: Data obtained from EIS measurements for mild steel in 1M HCl in the presence of different concentrations of TR.

Conc. (M)	$R_{ct} (\Omega.cm^2)$	$C_{ct} (\mu F.cm^{-2})$	IE (%)
00	6	165	---
10^{-4}	156	12	96
10^{-3}	270	8	97
5×10^{-3}	309	7	98
10^{-2}	350	7	98

Table 6: Data obtained from EIS measurements for mild steel in 0.5M H_2SO_4 in the presence of different concentrations of TR.

Conc. (M)	$R_{ct} (\Omega.cm^2)$	$C_{ct} (\mu F.cm^{-2})$	IE (%)
00	5	168	---
5×10^{-4}	12	59	58
10^{-3}	13	56	61
5×10^{-3}	17	48	70
10^{-2}	19	36	73
5×10^{-2}	20	35	75

3.4. Effect of temperature:

The effect of temperature on inhibition efficiency was determined in 1M HCl and 0.5M H_2SO_4 containing 10^{-2} M of TR at temperature range 20-50°C using potentiodynamic polarization curves. The results are given in table 7. As expected, the corrosion current density increased one order of magnitude with increasing temperature both in uninhibited and inhibited solutions, and the values of inhibition efficiency of TR were slightly decreased in the temperature range as a result of the higher dissolution of mild steel at higher temperature, which might cause the desorption of TR from the mild steel surface.

Table 7: The influence of temperature on the electrochemical parameters for mild steel electrode immersed in corrosive media + 10^{-2} M of TR.

	Temperature (°C)	$E_{corr} (mV/sce)$	$i_{corr} (\mu A.cm^{-2})$	IE%
Blank solution (1M HCl)	20	-396	1072	-
	30	-395	1664	-
	40	-396	2158	-
	50	-404	2743	-
10^{-2} of TR	20	-453	31	99
	30	-417	66	96
	40	-398	166	92
	50	-398	408	85

Blank solution (0.5 M H ₂ SO ₄)	20	-409	3749	-
	30	-434	4358	-
	40	-440	5332	-
	50	-426	6739	-
10 ⁻² M of TR	20	-405	793	79
	30	-436	1522	65
	40	-430	2255	57
	50	-428	3245	52

Corrosion current density for mild steel increased more rapidly with temperature in the absence of inhibitor (blank solution). These result confirmed that the TR acts as an efficient inhibitor in the range of temperature studied. The values of the apparent effective activation energy E_a were calculated from the Arrhenius equation:

$$i_{corr} = K' e^{-\frac{E_a}{RT}} \quad (4)$$

Where i_{corr} is the corrosion current density, K' the Arrhenius pre-exponential factor, T the absolute temperature and R is the universal gas constant.

The plots of logarithm of the corrosion current density versus reciprocal temperature T^{-1} are given in Figures 7 and 8. The plots obtained are straight lines and the slope of each one gives its activation energy E_a . It is evident that for the corrosion of mild steel in 1M HCl and 0.5M H₂SO₄, the E_a value was found equal to 23 kJ.mol⁻¹ and 15.39 kJ.mol⁻¹, respectively. In the presence of TR which function as an effective inhibitor, the E_a values are higher and equal to 68 kJ.mol⁻¹ in HCl and 36.51 kJ.mol⁻¹ in 0.5M H₂SO₄. According to Gomma [23], the kinetic of such a corrosion process acquires the character of a diffusion process in which at lower temperature the quantity of inhibitor present at the metal surface is greater than that at higher temperatures. The negative slope of E_a indicates the adsorption of organic compound on the electrode surface [24].

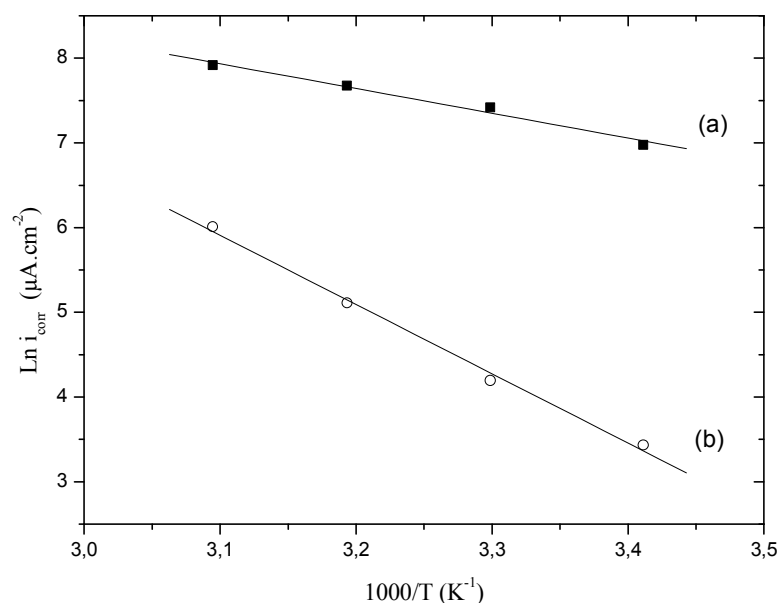


Fig.7: Arrhenius slopes calculated from corrosion current density for mild steel in: (a) 1M HCl and (b) 1M HCl + 10^{-2} M of TR.

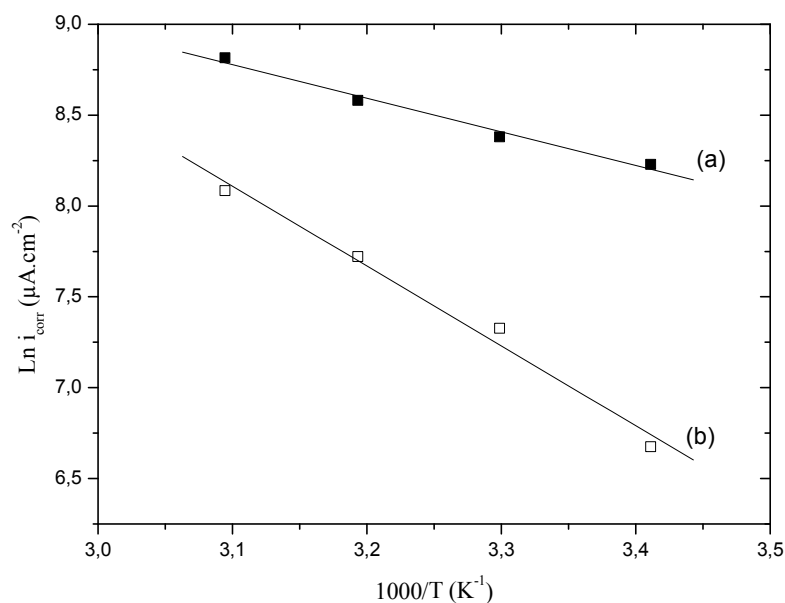


Fig.8: Arrhenius slopes calculated from corrosion current density for mild steel in: (a) 0.5M H₂SO₄ and (b) 0.5M H₂SO₄ + 10^{-2} M of TR

3.5. Immersion time:

Figures 9 and 10 show the impedance spectra after different immersion times in 1M HCl and 0.5M H₂SO₄ in the presence of 10^{-2} M TR. The evolution of the characteristics parameters associated with the capacitive loop with time is summarized in Table 8.

In case of H_2SO_4 , The diameter of the capacitive loop decreases in size with increasing immersion time. These results indicate that the adsorption model, arrangement and orientation of TR on the surface of the mild steel, change with time.

In case of HCl , The diameter of the capacitive loop increases in size with increasing immersion time. These results indicate that the immersion time increases the chlorides quantity which will be adsorbed on the surface helping to the formation of the inhibitor layer. However as soon as all the active sites become saturated with inhibitor. Furthermore, the change in the C_{ct} values may be caused by the gradual replacement of water molecules by the chloride anion and by the adsorption of the organic molecules on the metal surface, decreasing the extent of dissolution reaction.

This difference in the inhibition in both acids can be explained by that, in case of H_2SO_4 , FeSO_4 is less soluble than FeCl_2 and stay more efficiency on the steel surface. Less organic molecules are chemisorbed and therefore C_{ct} values are more important [25,26] (see table8).

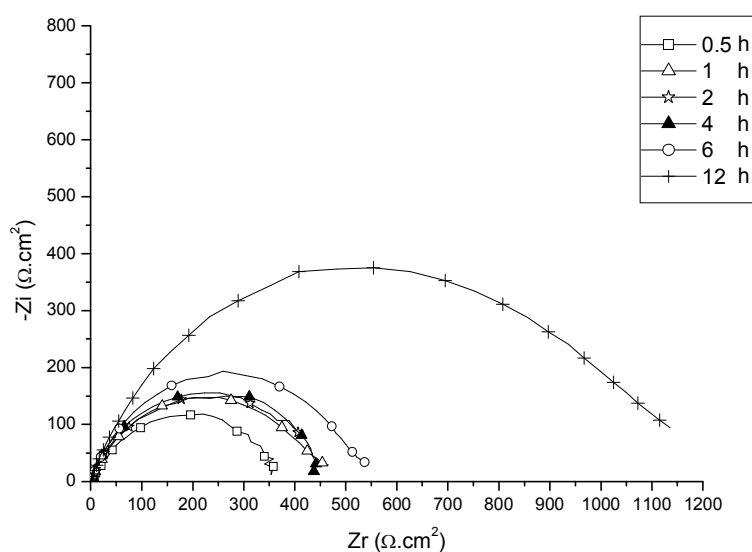


Fig.9: Nyquist diagrams for mild steel in 1M HCl containing 10^{-2} M of TR at different immersion time over open circuit potential.

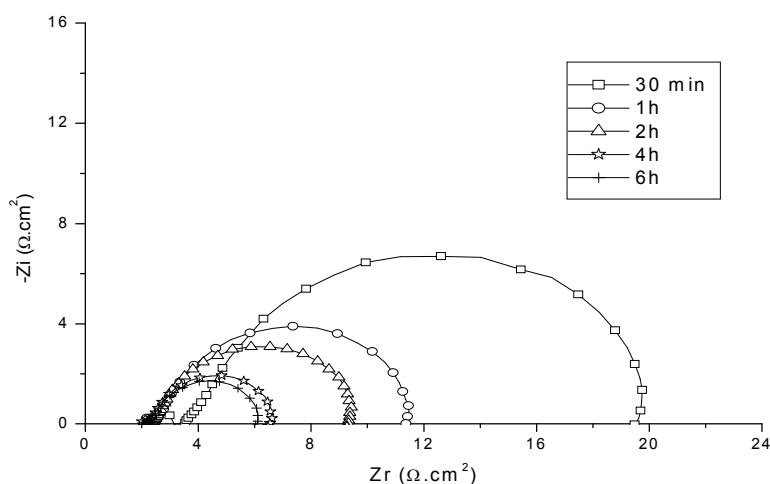


Fig.10: Nyquist diagrams for mild steel in 0.5M H₂SO₄ containing 10⁻² M of TR at different immersion time over open circuit potential.

Table 8: The influence of immersion time on the electrochemical parameters for mild steel electrode immersed in corrosive media + 10⁻² M of TR.

	Immersion time (h)	R _{ct} (Ω.cm ²)	C _{ct} (μF.cm ⁻²)	IE (%)
1M HCl	1/2	350	7	97
	1	447	6	98
	2	448	6	98
	4	449	6	98
	6	520	6	98
	12	1160	5	99
0.5 M H ₂ SO ₄	1/2	20	35	75
	1	11.5	47	56
	2	9.5	55	47
	4	6.6	59	24
	6	6.1	59	18

4. Conclusion

- (1) The TR shows good inhibiting properties for mild steel in both media in practically 1.0 M HCl medium.
- (2) In both medium, this compound was found to affect both the anodic and cathodic processes and acts as mixed-type inhibitor.
- (3) This compound inhibits corrosion by adsorption mechanism and the adsorption leads to the formation of a protective adsorbed film on the metal surface film which suppresses the dissolution reaction.
- (4) Inhibition efficiency values are maximum in case of 1M HCl than 0.5M H₂SO₄.

(5) The inhibition efficiency increases with increasing immersion time, in case of HCL, this study indicates that the TR inhibitor was strongly adsorbed on the mild steel.

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