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4-Ethylcyclohexanonethiosemicarbazone as Corrosion Inhibitor for Iron Metal in 0.5N Hydrochloric Acid Solutions

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Abstract : The corrosion inhibition of iron (Fe) metal in acidic medium (0.5N HCl) in the presence of synthesized4-ethylcyclohexanonethiosemicarbazone (ECHTSC) has been investigated by the weight loss method. The protective layer of thiosemicarbazone on Fe surface was confirmed by scanning electron microscopy (SEM). Inhibition efficiency, corrosion rate and surface coverage were evaluated at different concentrations of thiosemicarbazone in 0.5N HCl. The adsorption equilibrium constant (K_{ads}) and standard free energy of adsorption (ΔG_{ads}) were calculated. The values of free energy of adsorption (ΔG_{ads}) revealed that the inhibitor was adsorbed on the Fe surface via both physical and chemical adsorption nmechanisms.

Keywords: 4-ethylcyclohexanonethiosemicarbazone(ECHTSC), Iron (Fe), Adsorption, Acidic Medium**,** SEM.

Introduction:

There is one of the very serious problem ofthe corrosion of materials for industrial processes, generating huge financial losses. Metallic industrial structures are often exposed to conditions that facilitate corrosive processes. For example, acidic solutions, which are widely used in acid pickling, industrial acid cleaning and oil refinery equipment cleaning, promote the acceleration of metallic corrosion, affecting the performance and durability of the treated equipments[1-5].

For the past several decades, thiosemicarbazone and their derivatives have been investigated for biological importance and hundreds of transition-metal complexes have been prepared and structurally characterized[6].In recent years, the efficiency of thiosemicarbazone compounds as organic corrosion inhibitors has been studied in a wide range[7-15]. The high activity and efficiency of these compounds against corrosion was due to the presence of both nitrogen and sulfur in their structures. The goal of the present work was to study the performance and inhibition characteristics of thiosemicarbazone(ECHTSC) as corrosion inhibitor for iron metal (Fe) in HCl using weight loss technique. The choice of this compound was based on the consideration that it contains good π-electron conjugation, enhancing its coordination and an abundance of heteroatoms, enhancing its adsorption onto the surface of iron metal. Industrial important metals like Fe metal tend to corrode in presence of acid (HCl).In order to determine the inhibitory efficiency of ECHTSC on theFe corrosion SEM was also used in this study.

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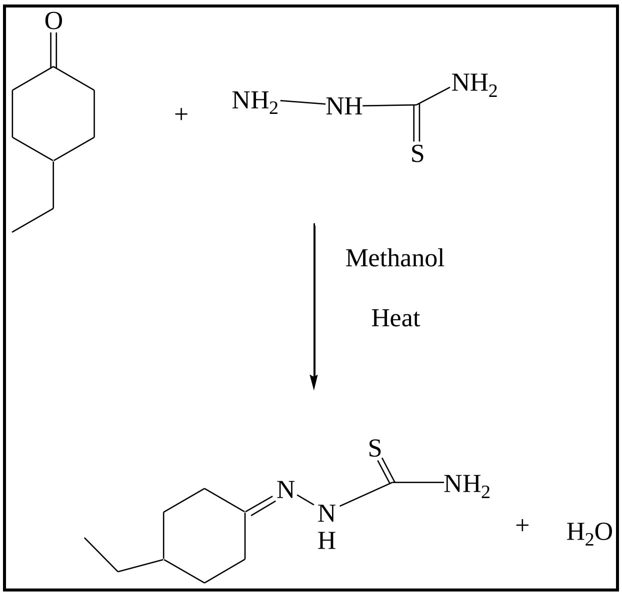
Experiment work:

Synthesis of compound (ECHTSC):

The thiosemicarbazone (4-ethylcyclohexanonethiosemicarbazone (ECHTSC)) was synthesized[16-17]from 4-ethylcyclohexanone and thiosemicarbazide in equal molar ratio in methanol (Scheme I). The structure of compound was characterized by IR studies.Absence of a υ(C=O) band (1745 cm^{-1}) of ketone and presence of υ(C=N) band occured[18] at 1622-1632 cm^{-1} in the spectra of thiosemicarbazone indicating the condensation between ketonic group of 4-ethylcyclohexanone and amino group of thiosemicarbazide.



Scheme I: Synthesis of 4-ethylcyclohexanonethiosemicarbazone (ECHTSC)

Preparation of metal coupons

For corrosion purpose we have used Fe metal coupons of 99.5% purity. The metal coupons were cut to dimensions of 3*2*0.2 cm and the surface was abraded with different embery papers from 220 to 1000 grades and washed with acetone and alcohol. The cleaned metal coupons were then washed with doubly distilled water and finally dried before use.

Weight loss experiment

Gravimetric method was used to calculate the corrosion parameters. Different iron metal coupons were immersed in hanging positions in 0.5N HCl solutionscontaining different inhibitor concentrations.Variable concentrations of inhibitor starting from 0.01 (g/L) by weight in the range of 0.02, 0.03, 0.04, and 0.05 (g/L) were used. Coupons weighed before and after the immersion in 0.5N HCl with and without inhibitor.The difference between the weight of coupon after immersion time and initial weight of the coupon was considered as the mass loss. Using the parameter of mass loss we calculated the rate of corrosion.The rate of corrosion, percentage inhibition efficiency (IE, %) and degree of surface coverage (θ) were calculated from the following 1-3 equations[19-21].

Electrochemical measurements:

Rate of Corrosion (mmpy)

$$=(87.6W)/(dAt) \qquad (1)$$

In above equation, W represents mass loss in mg, d represents density of the metal (gcm^{-3}), A represents surface area of the coupon in square cm and trepresents immersion time in hours.

The inhibition efficiencies at different inhibitor concentrations were calculated using the following equation[22]:

$$IE (\%) = [1-(Wi/Wo)] \times 100 \qquad (2)$$

At the room temperature, Wo and Wi are the mass loss of the iron metal without and with inhibitor amount in HCl acid solution respectively. The degree of surface coverage (θ) was evaluated from equation (3)

$$\theta = 1 - (Wi/Wo) \qquad (3)$$

Result and Discussion:

Tables 1-5 represent the parameters for iron corrosion in 0.5N HCl at different concentration of compounds depicting weight loss, percentage inhibitor efficiency, rate of corrosion and surface coverage (θ).Surface coverage for iron metal was determined in the absence and presence of the additive (inhibitor) at different concentrations varying from 0.01 to 0.05 g/L.

Table 1:Calculated values of inhibition efficiency, rate of corrosion and surface coverage(at room temperature) for iron metal immersed in 0.5 N HCl without and with inhibitor (immersion time: 4 h)

Amount of inhibitor (g/L)	Weight loss (g)	Percentage Inhibitor Efficiency	Rate of Corrosion (mmpy)	Surface Coverage by Inhibitor(θ)
0.00	0.1361		8.870	
.01	0.0711	47.75	4.633	0.4775
.02	0.0658	51.6	4.288	0.516
.03	0.0408	70.02	2.659	0.7002
.04	0.0388	71.49	2.528	0.7149
.05	0.0345	74.65	2.248	0.7465

Table 2: Calculated values of inhibition efficiency, rate of corrosion and surface coverage (at room temperature) for iron metal immersed in 0.5 N HCl without and with inhibitor (immersion time: 8 h)

Amount of Inhibitor (g/L)	Weight Loss (g)	Percentage Inhibitor Efficiency	Rate of Corrosion (mmpy)	Surface Coverage by Inhibitor(θ)
0.00	0.2409		7.850	
0.01	0.0784	67.45	2.548	0.6745
0.02	0.0772	67.95	2.509	0.6795
0.03	0.0387	83.93	1.257	0.8393
0.04	0.0378	84.30	1.228	0.8430
0.05	0.0353	85.34	1.147	0.8534

Table 3: Calculated values of inhibition efficiency, rate of corrosion and surface coverage (at room temperature) for iron metal immersed in 0.5 N HClwithout and with inhibitor (immersion time: 16 h)

Amount of Inhibitor (g/L)	Weight Loss (g)	Percentage Inhibitor Efficiency	Rate of Corrosion (mmpy)	Surface Coverage by Inhibitor(θ)
0.00	0.2084		3.395	
0.01	0.0826	60.36	1.345	0.6036
0.02	0.0398	80.90	0.648	0.8090
0.03	0.037	82.24	0.602	0.8224
0.04	0.0355	82.96	0.578	0.8296
0.05	0.0337	83.82	0.549	0.8382

Table 4: Calculated values of inhibition efficiency, rate of corrosion and surface coverage (at room temperature) for iron metal immersed in 0.5 N HClwithout and with inhibitor (immersion time: 32 h)

Amount of Inhibitor (g/L)	Weight Loss (g)	Percentage Inhibitor Efficiency	Rate of Corrosion (mmpy)	Surface Coverage by Inhibitor(θ)
0.00	0.2409		1.962	
0.01	0.1769	26.56	1.441	0.2656
0.02	0.0718	70.19	0.584	0.7019
0.03	0.0709	70.56	0.5776	0.7056
0.04	0.0625	74.05	0.509	0.7405
0.05	0.0604	74.92	0.492	0.7492

Table 5: Calculated values of inhibition efficiency, rate of corrosion and surface coverage (at room temperature) for iron metal immersed in 0.5 N HCl without and with inhibitor (immersion time: 120 h)

Amount of Inhibitor (g/L)	Weight Loss (g)	Percentage Inhibitor Efficiency	Rate of Corrosion (mmpy)	Surface Coverage by Inhibitor(θ)
0.00	0.3536		0.768	
0.01	0.292	17.42	0.634	0.1742
0.02	0.2446	30.82	0.5313	0.3082
0.03	0.2117	40.13	0.459	0.4013
0.04	0.1313	62.86	0.285	0.6286
0.05	0.1104	68.77	0.239	0.6877

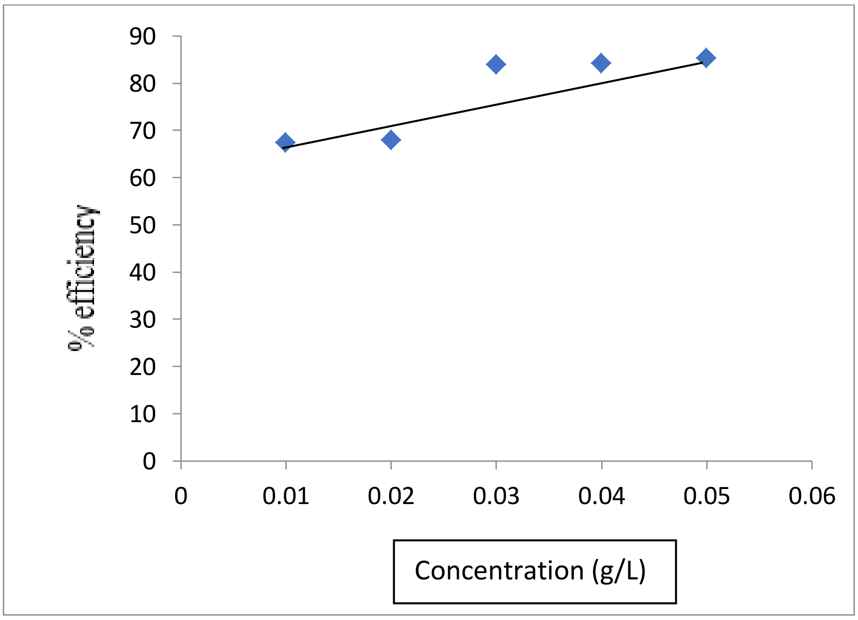


Figure 1: Variation of the % inhibition efficiency for iron metal immersed in 0.5 N HCl in the presence of .01-.05 g/L concentration of ECHTSC for 8 h.

From tables 1-5 and figure 1 it was observedthat weight loss of coupons without inhibitor increases with immersion time and weight loss of coupons is decreased with increased conc. of inhibitor. The percentage of inhibition efficiency and surface coverage by inhibitor(θ) increases with increasing inhibitor concentration.Surface coverage by inhibitor is further confirmed by the surface morphology. Maximum inhibition efficiency is reported for 8h immersion time. Rate of corrosion also decreases with increasing inhibitor concentration.

Thermodynamic and Adsorption considerations:

The spontaneous corrosion of iron in acidic solutions can be represented by the anodic dissolution reaction:

$FeFe^{+2} + 2e^{-} \quad \longrightarrow$

Accompanied by the correspondingcathodic reaction:

$2H^{+} + 2e^{-} H_2 \quad \longrightarrow$

The values of rate constant are obtained using kinetics first order rate law[23]:

$\log(Wi - \Delta W_t) = -(k/2.303)\, t + \log Wi$ (4) ————

In above formula Wi is the starting weight of metal coupon and $\Delta W_t$is the weight loss during immersion time t. The value of half life was obtained by the following formula:

$t_{½} = 0.693/k$ (5) ————

Table 6: Kinetic data of iron with different amount of thiosemicarbazone (immersiontime 8 h)

Concentration of inhibitor(g/L)	**k(s^{-1})**	**$t_{½}$(s)**
0.00	$8.0*10^{-7}$	$8.6*10^{5}$
0.01	$2.4*10^{-7}$	$28.88*10^{5}$
0.02	$3.2*10^{-7}$	$21.6*10^{5}$
0.03	$0.8*10^{-7}$	$86.62*10^{5}$
0.04	$17.5*10^{-7}$	$3.93*10^{5}$
0.05	$1.59*10^{-7}$	$43.33*10^{5}$

As far as the inhibition process is concerned it is generally assumed that the adsorption of the inhibitor at the metal surface is the first step of the procedure of inhibition in the presence of the corrosive acid media.Experimental values evaluated for surface coverage (θ) were applied for many isotherm equations related to adsorption like Langmuir, El-Awady, Frumkin, Freundlich and Florry-Huggins.However, the best correlation was obtained using the Langmuir adsorption isotherm model. According to this isotherm, θ is related to the C and equilibrium constant of adsorption K_{ads}, using following equation:

$C/\theta = 1/K_{ads} + C$ (6)

Thermodynamic-kinetic model of El-Awady et al is given by:

$\log \theta/1-\theta = \log K + y\log C$ (7)

Where C is the concentration of additive (inhibitor), K_{ads} is the equilibrium constant of adsorption process and $K_{ads} = K^{1/y}$

The equilibrium constant for the adsorption process from Langmuir adsorption isotherm model is related to the standard Gibbs free energy of adsorption by the following expression

$\Delta G_{ads} = 2.303RT\log(55.5\, K_{ads})$ (8)

Where R is the universal gas constant, T is the absolute temperature, and 55.5 is the concentration of water in solution (mol L^{-1}).

Table 7: Langmuir adsorption parameters for the iron metal with thiosemicarbazone in 0.5 N HCl(at room temperature) for different immersion time

Immersion time	K_{ads}	$LogK_{ads}$.	Slope	ΔG_{ads} ($KJmol^{-1}$)	R^2
4 h	81.30	1.9100	1.0928	21.525	0.9744
8 h	181.81	2.259	1.0553	23.583	0.9896
16 h	238.095	2.3767	1.0956	24.277	0.996
32 h	48.30	1.683	0.838	20.186	0.7936
120 h	17.301	1.2380	0.294	17.562	0.4328

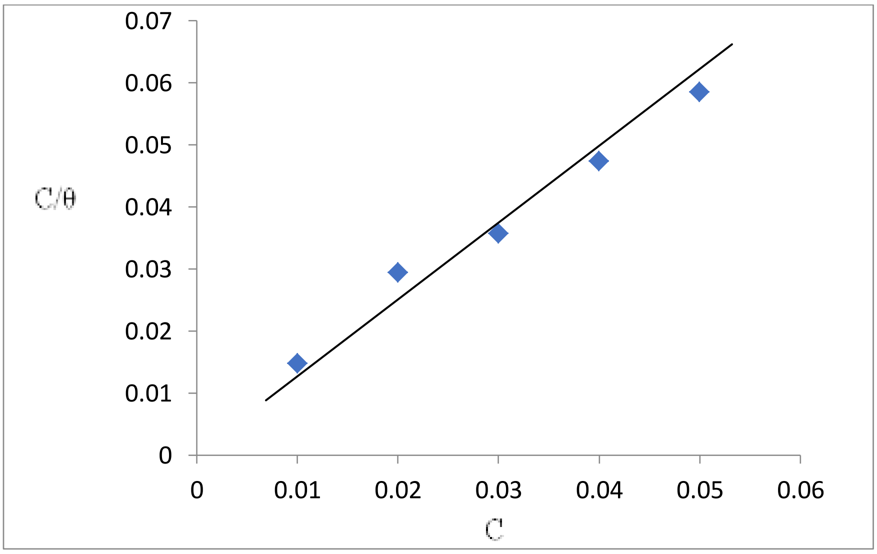


Figure 2: Langmuir adsorption isotherm (C/θ v/s C) for iron metal in 0.5 N HCl (immersion time 8h)

Table 8: Thermodynamic-Kinetic model parameters for the adsorption of thiosemicarbazone on the surface of iron metal in 0.5N HCl (at room temperature)

Immersion time	logK	$logK_{ads}$=log $K^{1/y}$	Slope (Y)	ΔG_{ads} ($KJmol^{-1}$)	1/Y
4 h	1.5069	1.19920	0.7968	17.333	1.2550
8 h	1.7492	1.30148	0.7438	17.936	1.3444
16 h	1.7366	1.2735	0.7333	17.771	1.3636
32 h	2.244	2.6951	1.2601	26.155	0.8326
120 h	2.2141	3.270	1.4771	29.545	0.6770

Data obtained from the weight loss method were used to analyse the adsorption mechanism. The plot of C/θ v/s C is represented in figure 2 and straight line has been observed, with slope nearly equal to unity, indicating that inhibitor adsorb according to the Langmuir adsorption isotherm.

The K_{ads} value may be taken as a measure of the strength of the adsorption forces between the inhibitor molecules and the metal surface[24]. The negative values of ΔG_{ads} indicate that the adsorption of compound on metal is proceeding spontaneously and is accompanied by a highly efficient adsorption[25]. When ΔG_{ads} reached the value of around -20 $KJmol^{-1}$, the electrostatic interaction between the charged inhibitor molecules and metal causes physical adsorption, ΔG_{ads} values become more negative than -40 KJ mol^{-1}, a sharing of electrons from the inhibitor molecules to the metal surface occurred to form a coordinated type of bond (chemical adsorption process)[26-27].The obtained ΔG_{ads} values for the studied inhibitor are in the range of from -17 to -29 $KJmole^{-1}$ indicating that adsorption of on iron metal surface involves combination of both physical and chemical adsorption. Parameters obtained from Langmuir adsorption isotherm indicated that the inhibition efficiency was maximum at 8 h immersion time might be due to chemisorption. As immersion time increases from 8 h to 120 h chemisorption may be converted to physisorption causing decrease of inhibition efficiency. As we increase the immersion time from 8 h to 16 h, inhibition efficiency decreases from 85.34% to 83.82%. Further increase of immersion time upto 32 h inhibition efficiency decrease from 83.82% to 74.92% and at 120 h immersion time inhibition efficiency is reported 68.77%. These parameters suggest desorption of the adsorbed compound over longer test period.

Scanning Electron Microscopy (SEM):

The surface morphology of the formed layers on the Iron metal surface after its immersion in the solutions of 0.5N HCl in the absence and in the presence of the inhibitor (various concentration) was carried out. The specimens were taken out, and dried and the SEM photographs of the surfaces of the specimens were investigated by ZEISS EVO 18 instrument. Surface morphology of Fe metal was studied by scanning electron microscopy after 8 h and 120 h immersion in 0.5 N HCl before and after addition of the inhibitor at room temperature. **Figure 4(a)** showed the SEM obtained of polished Fe metal without being exposed to the corrosive environment and it clear that the Fe sample before immersion seems smooth and shows some abrading scratches on the surface while, **Figure 4(b and b')** showed strongly damaged of Fe metal surface due to the formation of corrosion products after immersion in 0.5 N HCl solution for 8h and 120h respectively. As displaying aggressive attack of the corroding medium on the Fe metal surface. In contrast, **Figure 4(c and c')** SEM image of Fe surface after immersion in 0.5 N HCl for 8h and 120h in the presence of 0.05 g/L of thiosemicarbazone compound shows that the Fe metal surface was corroded only negligibly.

The result obtained from SEM supported the parameters of weight loss measurement that there was a decrease in contact between the Fe metal and the aggressive medium. Thus, a good absorptive protection layer formed by 4-ethylcyclohexanonethiosemicarbazonecan efficiently inhibit the corrosion of Fe metal. When we compare both fig. 4c and 4c' it is observed that 4c is less corroded.

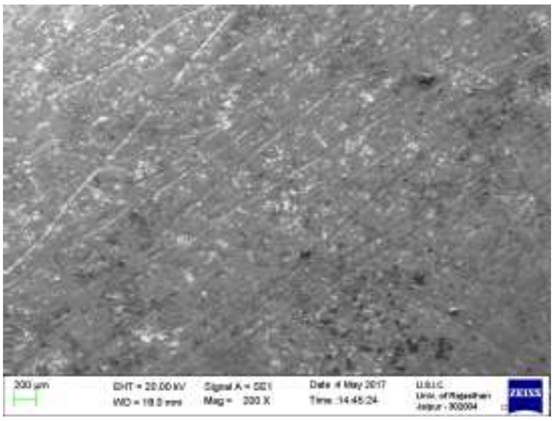


Figure 4(a): SEM image of iron metal before immersion (polished)

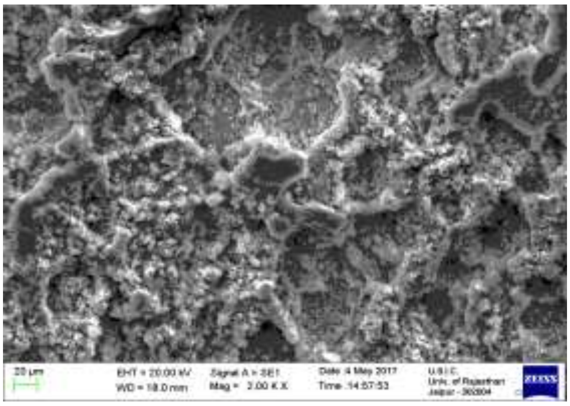


Figure 4(b): SEM image of iron metal in 0.5N HCl after 8 h of immersion without inhibitor (blank)

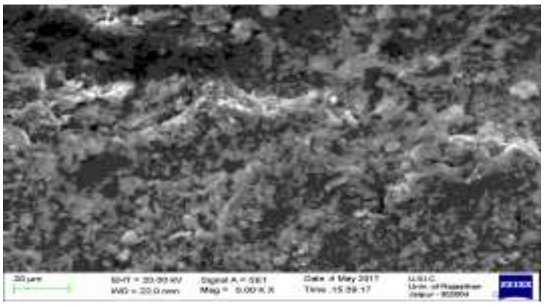


Figure 4(b'): SEM image of iron metal in 0.5 N HCl after 120 h of immersion without inhibitor (blank)

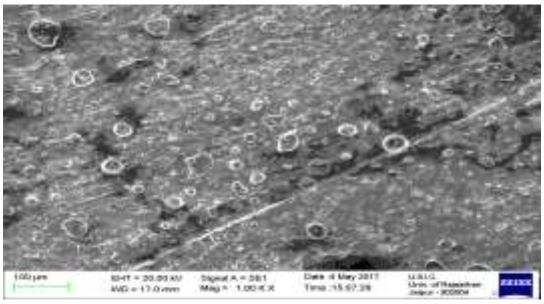


Figure 4(c): SEM image of iron metal in 0.5 N HCl after 8 h of immersion with inhibitor (0.05 g /L conc.)

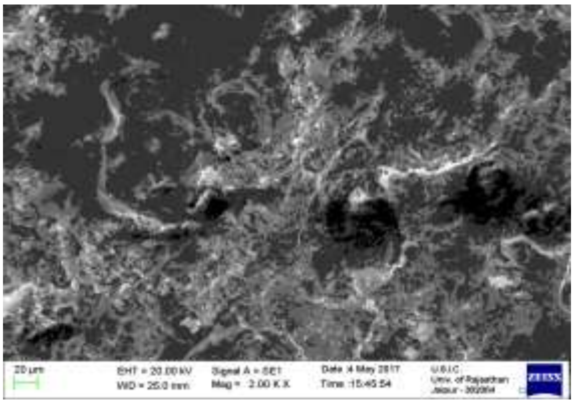


Figure 4(c'): SEM image of iron metal in 0.5 N HCl after 120 h of immersion with inhibitor (0.05 g/L conc.)

Conclusion:

By considering the experimental data and figures, we can conclude present research work in following manners:

1. The corrosion of Fe metal in 0.5NHCl solution can be inhibited by the use of thiosemicarbazone compound.
2. As the concentration of thiosemicarbazone increases, the inhibition efficiency of Fe metal increases.
3. The adsorption of thiosemicarbazone molecules on the metal surface in 0.5N HCl solution obeyed Langmuir adsorption isotherm model.
4. Surface study with SEM showed that a film of inhibitor was formed on the metal surface and the inhibition efficiency η (%) of the thiosemicarbazone decreased with increasing immersion time (from 8 h to 120 h).

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