

Experimental Analysis of Mild Steel Corrosion in Aqueous Medium

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Abstract

Corrosion is one of the major problems in almost all the industries. The loss due to corrosion is about 3 – 4 % of GNP in the developed countries and it is even more in the developing countries. Mild steel is a commonly material which is widely used in almost all the manufacturing sectors and is very prone to the corrosion, especially in acidic environment. Therefore, it is essential to control the corrosion of mild steel in acid medium to reduce the unexpected economic loss due to corrosion. The inhibition is one of the simplest mechanisms used for extenuating the corrosion of metallic components, predominantly in aqueous medium. The present study, tries to evaluate the influence of N-benzyl-N'-phenyl thiourea (BPTU) on the corrosion behavior of mild steel in 0.1M HCl medium using the Tafel extrapolation method and the results are cross checked with linear polarization technique. It is evident from the study that the Tafel extrapolation and the linear polarization results are closely matches with each other. The investigation reveals that BPTU works as an efficient anodic inhibitor for mild steel corrosion in HCl solution and the protective efficiency (PE) of more than 97 % is noticed even at very low concentration of BPTU. The investigation also reveals that BPTU is chemically adsorbed on the steel surface, following Temkin's adsorption isotherm. The presence of BPTU significantly reduces the anodic dissolution of the mild steel and the PE of the compound deduced is linearly varies with the concentrations of the inhibitor.

Keywords: low carbon steel; inhibition; activation energy; corrosion; hetero atoms; adsorption; elemental analyses

INTRODUCTION

The use of inhibitor is a simple, cost effective, and trouble-free method for preventing the metallic corrosion in acidic medium [1]. It reduces the corrosion rate either by reducing the probability of its occurrence or by reducing the rate of attack by forming a thin adsorption film on the metal surface or by doing both. The adsorption mainly depends on the

functional group and aromaticity of the organic compounds [2, 3]. The majority of the inhibitors/organic compounds contain hetero atoms such as N and S through which they quickly adsorbed on the metal surface, and thus, retard the rate of electrochemical reactions. Among these inhibitors, derivatives of thiourea are extensively used for mitigating the metallic corrosion, especially in the acid media [4, 5].

Mild Steel is a major material of construction that is usually used in industries for handling acid solutions due to its low cost and simple fabrication technique. Since the mild steel is very prone to corrosion in acid solution, it is required to study and control the corrosion of mild steel or low carbon steel for the effective production of goods and services. Among the mineral acids, HCl is known to be a working horse in the pre-treatment of metals and alloys. The use of this acid in pickling and cleaning of metals and in other chemical processes is cost-effective and trouble free compared to other mineral acids [6, 7]. The selection of inhibitor is primarily depends on the type of acid and its concentration, solution temperature, and the type of metal or alloy to be exposed in the acidic solution. Considering the corrosion inhibition process in acid pickling, good inhibitors should be effective in metal dissolution, no delay in the pickling process, effective at low concentrations and high temperatures, thermally and chemically stable and they should have a good surfactant and foaming characteristics [8].

Since the derivatives of thiourea are most effective in preventing the metallic corrosion in acid media, the authors decided to synthesize and study the influence of BPTU on mild steel corrosion in 0.1M HCl medium with different concentrations (0.00002, 0.00004, 0.00006mol/L) of BPTU at 28 and 50°C using the Tafel extrapolation technique. The selection of this compound as inhibitor is also due to the fact that the method used for synthesizing BPTU is very simple and cost-effective. The main hub of this study is to determine the protection ability of this compound against the mild steel corrosion in HCl solution with very low concentrations at room and elevated temperature.

MATERIALS AND METHODS

Specimen preparation

The mild steel specimen of chemical composition (wt %): C: 0.205; Si: 0.06; Mn: 0.55; S: 0.047; P: 0.039, and balance Fe is used in the current work. The specimen is mirror polished with emery papers, cleaned with distilled water and dried in air. A Teflon holder is used for exposing 0.786 cm² area of the specimen in the corrosive medium.

Preparation of BPTU

N-benzyl-N'-phenyl thiourea (BPTU) is synthesized by studying the reported method of synthesizing the similar compounds [9]. The benzyl amine and phenyl-isothiocyanate are used for synthesizing this compound and the ethanol is used for re-crystallization. The purity of this compound is tested by elemental analysis (shown in Table 1) and melting point (158°C). The molecular formula of the compound is also given in Table 1.

Table 1: Molecular formula and the elemental analyses of BPTU

Inhibitors	Molecular formula	Calculated (found)%				
		C	H	N	O	S
BPTU	C ₁₄ H ₁₄ N ₂ S	69.39 (69.26)	5.82 (5.79)	11.56 (11.60)	-	13.23 (13.19)

Tafel extrapolation study

Tafel extrapolation study is conducted by using a Wenking potentiostat (LB95L) and a three electrode cell as shown in Fig. 2.



Figure 2: Experimental set up

The steady state rest potential (RP) is noted after 25 – 30 min. for conducting the experiments at 28 and 50°C. The potential range used in this study is ± 250 mV vs. RP and the potential is varied in steps of 20 mV/min from the cathodic side for measuring the corrosion current (I) for the blank and the inhibited solutions. Then, the Tafel plot of potential vs. log I is drawn for determining the corrosion current density (i_{corr})

and the corrosion potential (E_{corr}). The straight line region of the Tafel plot, shown in Fig. 3 is used for obtaining i_{corr} and E_{corr}. The corrosion rate is calculated using the equation 1 and the linear polarization method is used for cross checking the Tafel results.

$$\text{Corrosion rate (CR), mpy} = \frac{0.129 \times \text{Eq. Wt} \times i_{\text{corr}}}{D} \quad (1)$$

where, i_{corr} in μA/cm², Eq. wt. is the equivalent weight of the specimen taken as 27.925 grams, D is the density of the specimen taken as 7.86 g/cc.

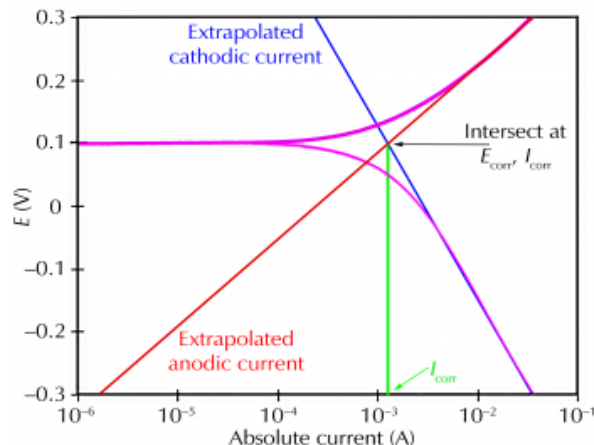


Figure 3: Schematic illustration of Tafel plot

Linear polarization study

The linear polarization study is conducted with ± 20 mV vs. RP. The scanning rate of 5mV / min is used for measuring the corrosion current (I) for both 28 and 50°C. The plot of E vs. I is drawn and the slope of E vs. I is used for calculating i_{corr} as shown in the equation 2. The schematic representation of linear polarization plot is shown in Fig. 4.

$$i_{\text{corr}} = 0.026 / \text{slope} \quad (2)$$

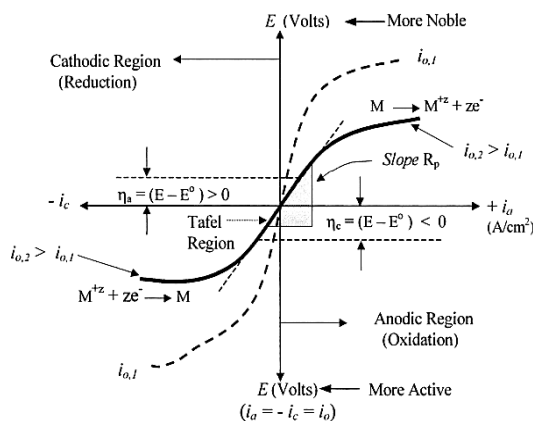


Figure 4: Schematic illustration of linear polarization plot

The inhibition efficiency (IE)/protection efficiency (PE), and the degree of surface coverage (θ) are determined using the equations 3 and 4.

$$\%IE = \left[\frac{(i_{corr} - i_{corr(inh)})}{i_{corr}} \right] \times 100 \quad (3)$$

where, i_{corr} and $i_{corr(inh)}$ are the current densities for blank and inhibited solutions respectively.

$$\theta = \left[\frac{(i_{corr} - i_{corr(inh)})}{i_{corr}} \right] \quad (4)$$

RESULTS AND DISCUSSION

Effect of inhibitor concentration

The Tafel results for the corrosion of mild steel in the blank and the inhibited solutions of HCl at 28 and 50°C are presented in Table 3.

Table 3: Tafel results of BPTU for mild steel corrosion

C (mol/L)	28 °C				50 °C			
	E_{corr} (mV)	i_{corr} (mA/cm ²)	CR (mpy)	IE (%)	E_{corr} (mV)	i_{corr} (mA/cm ²)	CR (mpy)	IE (%)
0	-550	636.13	291.55	-	-540	1195.93	548.11	-
0.00002	-507	29.39	13.47	95.38	-511	70.56	32.34	94.10
0.00004	-505	22.45	10.29	96.47	-510	58.10	26.63	95.14
0.00006	-503	15.90	7.29	97.50	-508	44.85	20.56	96.25

It is evident from the Table 3 that corrosion rate and corrosion current density of the low carbon steel increases drastically in the absence of BPTU from 28 to 50 °C. This may be due to increase in conductance of the corrosive medium with increase in temperature. However, in the presence inhibitor, the corrosion of mild steel decreased substantially at both the temperatures studied. It is also evident from the Table 3 that PE/IE of the compound investigated is linearly varies with the concentration of BPTU. The increase in IE may be owing to increase in the formation of the adsorption film on the steel surface, which retards the electrochemical reactions. The linear polarization results obtained for mild steel corrosion are shown in Table 4. From Tables 3 and 4, it is observed that there is a very little deviation among the Tafel extrapolation and linear polarization results. This confirms the accuracy of the Tafel results obtained for low carbon steel corrosion.

Table 4: Linear polarization results for mild steel corrosion

C (mol/L)	28 °C				50 °C			
	E_{corr} (mV)	i_{corr} (mA/cm ²)	CR (mpy)	IE (%)	E_{corr} (mV)	i_{corr} (mA/cm ²)	CR (mpy)	IE (%)
0	-550	612.01	280.49	-	-540	1157.82	530.64	-
0.00002	-510	26.32	12.06	95.70	-515	66.57	30.51	94.25
0.00004	-506	19.64	9.00	96.79	-509	53.26	24.41	95.40
0.00006	-500	14.20	6.51	97.68	-505	41.10	18.84	96.45

The Tafel plot for mild steel corrosion in 0.00006 mol/L of BPTU at 28°C is shown as a sample in Fig. 5.

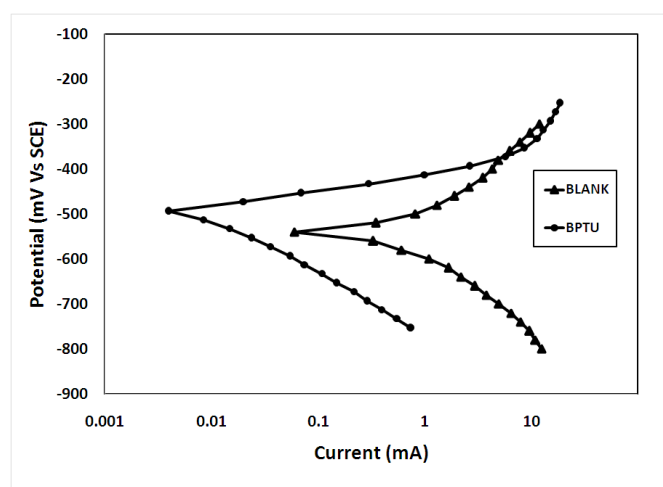


Figure 5: Tafel plot for mild steel corrosion at 28°C

From Fig. 5, it is seen that the Tafel curve shifts to the left in the presence of BPTU. This also indicates that there is a noticeable reduction in corrosion current in the presence of inhibitor. This considerable decrease in corrosion current in the presence BPTU is a clear evidence for the effectiveness of BPTU in preventing the corrosion of steel surface in HCl medium. From Fig. 5, it is also seen that corrosion potential (E_{corr}) shifts in the upward/positive direction in the presence of inhibitor. This shift in E_{corr} in the positive direction, indicating that the compound investigated is primarily working as an anodic inhibitor for low carbon steel corrosion in HCl solution [10]. The similar trends are also noticed in 0.00002 and 0.00004mol/L of BPTU at 28°C and in 0.00002 – 0.00006 mol/L of BPTU at 50°C.

Effect of temperature on IE

It is apparent from the results shown in Table 3 that there is a marginal decrease in IE of the compound with increase in temperature of the corrosive medium. This demonstrated that

the investigated compound is insensible to the temperatures studied. The highest IE exhibited by the compound in 0.00006 mol/L at 28 and 50°C are 97.68% and 96.45% respectively. This confirms that BPTU did not lose its inhibiting ability much in the elevated temperature. The good performance demonstrated by the compound even at very low concentration may be owing to the existence of the nitrogen and the sulphur atoms and π - electrons of the aromatic ring in the molecular structure of BPTU, makes it adsorbed quickly on the steel surface [11].

Mechanism of adsorption

The adsorption mechanism of the inhibitor on to the metal surface is known by determining the free energy of adsorption (ΔG_{ads}) and the activation energy (E_a). The following relationships help for determining ΔG_{ads} and E_a values [12].

$$\Delta G_{ads} = -RT \ln (55.5K) \quad (5)$$

where, R is the universal gas constant in J/k/mol, T is the temperature in Kelvin and 55.5 is the concentration of water in mol /L and K is the equilibrium constant.

$$K = \theta / C (1-\theta) \quad (6)$$

where, θ is the degree of surface coverage on the metal surface and C is the concentration of inhibitor in mol /L.

$$\ln (r_2 / r_1) = -E_a \Delta T / (R \times T_2 \times T_1) \quad (7)$$

Where, r_1 and r_2 are the corrosion rates at temperature T_1 and T_2 and ΔT is the difference in temperatures.

The ΔG_{ads} values for the compound studied are more than 40 kJ/mol (Table 5) demonstrating that the adsorption of BPTU is governed by a chemisorption mechanism [13]. The chemisorption or a chemical adsorption is also confirmed from the influence of inhibitor on the corrosion potential (E_{corr}). The presence of BPTU shifts the E_{corr} in the positive direction, indicating the suppression of the electrochemical reactions by chemisorption of the electron rich N - S atoms function ability to the positive centers of the metal [14]. The negative values of ΔG_{ads} shown in Table 5 indicate the rapid adsorption and a strong interface between the metal and the molecules of BPTU [15]. It is observed that the E_a value in the presence of inhibitor is more than that of the blank solution. This confirms that the dissolution of the steel surface is reduced and the compound is also more efficient at lower temperatures [16, 17].

Table 5: Results of E_a and ΔG_{ads} in 0.00006 mol/L of BPTU

System	E_a (kJ/mol)	- ΔG_{ads} (kJ/mol)	
		28°C	50°C
0.1 M HCl	23.20	-	-
BPTU	45.83	43.55	45.61

The process of adsorption of inhibitor on to the steel surface is also known by the Temkin's adsorption isotherm plot, which is shown in Fig. 6. From Fig. 6, it is observed that θ has a straight relationship with $\log C$, indicating that adsorbed of BPTU on the steel surface obeys Temkin's isotherm model. This signifies the mono - layer adsorption of the inhibitor on uniform or a homogeneous steel surface [18].

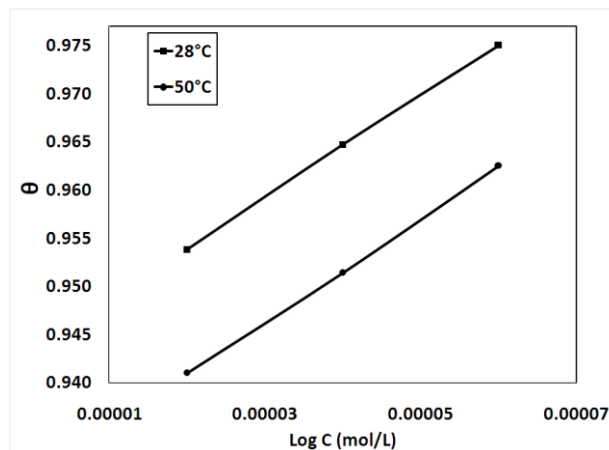
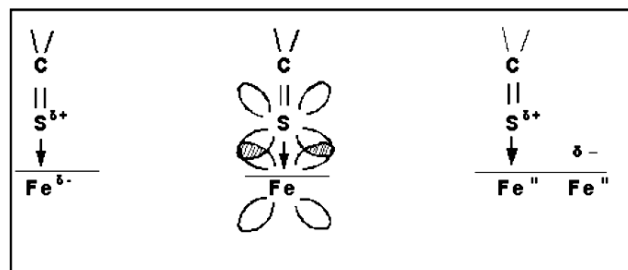


Figure 6: Adsorption isotherm plot for mild steel

The stages of adsorption of the organic compound is shown in Fig. 7(a, b and c). The adsorbed compound on the metal surface will introduce a partial negative charge at the point of attraction (Fig. 7a). The attraction of negative charges of the inhibitor molecules and the positive active centres of the iron atoms becomes stronger due to the strong electrostatic forces developed during the chemisorption stage. The S - atom has a vacant d - orbital of symmetry, that is compatible with some of the d - orbitals of the metal atoms. The π - electrons present in the molecules of the inhibitor can overlap with the sulphur d -orbital and thus, forming a partial $d\pi - d\pi$ bond (Fig.7 b). The intensity of the negative charge present in the metal atom can be minimized either by back donating to the S atom as shown in Fig. 7c or by concentration of the charge at some convenient distance from the adsorbed molecule (Fig. 7c). However, these processes will take place simultaneously[19].



a) Initial adsorption b) $d\pi - d\pi$ overlapping
 c) Shift of negative charge

Figure 7: Stages of adsorption of inhibitor molecules on steel surface

The bonding between the molecules of the inhibitor and the metal is described in terms of the concepts of “hard-soft acids and bases” and electrosorption valency. Inhibiting efficiency varies with the nature of substituents present in the molecules of the inhibitor as electron densities changed at the functional group. The substituents (nucleophilic or electrophilic) increase the electron density which develops the stronger electrostatic or adsorption forces. The IE of the compound increases due to this stronger electrostatic forces between the metal and the inhibitor molecules [20]. The corrosion inhibition properties of the compound studied may be acknowledged with the existence of the N. and the S atoms, and the π - electrons on the benzene ring. The sulphur atom present in the compound has a permanent negative charge, whereas, the nitrogen atom has a permanent positive charge. As the molecules approach the metal surface, the electric field of double layer enhances the polarization of the molecules and induces additional charges on both S and N atoms, which increases the adsorption of inhibitor molecules on the steel surface [21].

CONCLUSIONS

1. The study reveals that BPTU acts as an exceptionally good anodic inhibitor for mild steel corrosion in HCl solution.
2. The presence of BPTU increases the corrosive resistance of mild steel by forming a stable film on its surface.
3. The investigation shows that the compound adsorbed on the steel surface follows Temkin's adsorption isotherm.
4. The compound investigated prevent the corrosion of mild steel through the chemisorption mechanism.
5. The result reveals that IE increases with increase in the concentrations of BPTU.
6. The result of the study also reveals that BPTU is insensitive to the temperatures studied.
7. The exceptionally good performance exhibited by BPTU even in very low concentrations and at elevated temperature, indicating that it can be proficiently used for mitigating the corrosion of low carbon steel in HCl medium.

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REFERENCES

- [1] Bentiss, F., Traisnel, M., and M., Legrenee, M., 2000, “Inhibitor effect of triazole derivatives on corrosion of mild steel in acidic media,” *British Corrosion Journal*, 35(4), pp. 315–320.
- [2] Khamis, E., 1990, “The Effect of Temperature on the Acidic Dissolution of Steel in the Presence of Inhibitors,” *Corrosion*, 46(6), pp. 476–484.
- [3] Quraishi, M. A., and Sharma, H. K., 2003, “4-Amino-3-butyl-5-mercapto-1,2,4-triazole: a new corrosion inhibitor for mild steel in sulphuric acid,” *Materials Chemistry and Physics*, 78(1), pp. 18–21.
- [4] Reeta Agrawal, and Nambodhiri T. K. G., 1990, “The inhibition of sulphuric acid corrosion of 410 stainless steel by thioureas,” *Corrosion Science*, 30(1), pp. 37–52.
- [5] Wilhelm, S. M., and Abayarathna, D., 1994, “Inhibition of hydrogen absorption by steels in wet hydrogen sulfide refinery environments,” *Corrosion*, 50(2), pp. 152–159.
- [6] Ostovari, A., Hoseinie, S. M., Peikari, M., Shadzadeh, S. R., and Hashemi, S. J., 2009, “Corrosion inhibition of mild steel in 1 M HCl solution by henna extract: A comparative study of the inhibition by henna and its constituents (lawsone, gallic acid, α -D-glucose and tannic acid),” *Corrosion Science*, 51(9), pp. 1935–1949.
- [7] Kaan Emregul, C., and Mustafa Hayvali, 2006, “Studies on the effect of newly synthesized schiff based compounds from phenazone and vanillin on the corrosion of steel in 2 M HCl,” *Corrosion Science*, 48, pp.797–81.
- [8] Schmitt, G., 1984, “Application of inhibitors for acid media: report prepared for the European federation of corrosion working party on inhibitors” *British Corrosion Journal*, 19, pp. 165–176.
- [9] Moore, M. L., and Crossly, F. S., 2003, “Organic Synthesis,” Horning, E.C., (ed.), John Wiley and Son's Publication, New York.
- [10] Divakara Shetty, S., Nagaraja Shetty., Faiz Parvaz., Karthik Agnihotri., and Parthiv Mewawala, 2017, “Investigating the inhibiting action of thiourea derivative on the mild steel corrosion in acid medium”, *International Journal of Applied Engineering Research*, 12, pp. 323–3242.
- [11] Tamil Selvi, S., Raman, V., and Rajendran., 2003, “Corrosion inhibition of mild steel by benzotriazole derivatives in acid medium,” *Journal of Applied Electrochemistry*, 33, pp.1175–1182.

- [12] Quaroishi, M. A., and Sardar, R., 2004, "Effect of some nitrogen and sulphur based synthetic inhibitors on corrosion inhibition of mild steel in acid solutions," *Indian Journal of Chemical Technology*, 11(1), pp. 103–107.
- [13] Quraishi, M. A., Jamal, D., and Singh, R. N., 2002, "Expand article tools inhibition of mild steel corrosion in the presence of fatty acid thiosemicarbazides," *Corrosion*, 58(3), pp. 201–207.
- [14] Ali, S. A., El-Shareef, A. M., Al-Ghamdi, R. F., and Saeed, M. T., 2005, "The isoxazolidines: the effects of steric factor and hydrophobic chain length on the corrosion inhibition of mild steel in acidic medium," *Corrosion Science*, 47(11), pp. 2659–2678.
- [15] Savithri, B. V., and Mayanna, S., 1996, "Tetrabutyl ammonium iodide, cetyl pyridinium bromide and cetyl trimethyl ammonium bromide as corrosion inhibitors for mild steel in sulphuric acid," *Indian Journal of Chemical Technology*, 3(5), pp. 256– 258.
- [16] Quraishi, M. A., and Sharma, H. K., 2004, "Inhibition of mild steel corrosion in formic and acetic acid solutions," *Indian Journal of Chemical Technology*, 11, pp. 331–336.
- [17] Vishwanatham, S., and Emranuzzaman, 1998, "Inhibition effect of some aniline compounds on corrosion of mild steel in 3% HF," *Indian Journal of Chemical Technology*, 5, pp. 246–250.
- [18] Stoyanova, A. E., Sokolova, E. L., and Raicheva, S. N., 1997, "The inhibition of mild steel corrosion in 1 M HCl in the presence of linear and cyclic thiocarbamides-effect of concentration and temperature of the corrosion medium on their protective action," *Corrosion Science*, 39(9), pp. 1595–1604.
- [19] Donnelly, B., Downie, T. C., Grzeskowiak, R., Hamburg, H. R., and Short, D., 1974, "A study of the inhibiting properties of some derivatives of thiourea" *Corrosion Science*, 14(10), pp. 597–606.
- [20] Thomas, J. G. N., 2000, "In corrosion," Ed. L.L. Shreir, L. L., Jarman, R. A., and Bustein. G. T., Vol. 2, Butterworth – Heinemann, U.K, pp. 17–58.
- [21] Ateya. B. G., Abo-Elkhair, B. M., and Abdel-Hamid I. A., 1976, "Thiosemicarbazides as an inhibitor for acid corrosion of iron," *Corrosion Science*, 16, pp. 163–169.