

Adsorption and corrosion inhibition properties of thiocarbanilide on the electrochemical behavior of high carbon steel in dilute acid solutions



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ABSTRACT

The inhibition performance of thiocarbanilide on the electrochemical corrosion behavior of high carbon steel in 1 M H₂SO₄ and HCl acid solutions was studied through weight loss method and potentiodynamic polarization test. Data obtained showed that the organic compound performed effectively in acid solutions at all concentrations with an average thiocarbanilide inhibition efficiency above 70% in H₂SO₄ acid and 80% in HCl acid from weight loss and potentiodynamic polarization test respectively. Results from corrosion thermodynamic calculations showed that the adsorption of thiocarbanilide onto the steel was through chemisorption mechanism whereby the redox electrochemical process responsible for corrosion and the electrolytic transport of corrosive anions were simultaneously suppressed. Statistical derivations through ANOVA analysis confirm that the influences of both the inhibitor concentration and exposure time on inhibition efficiency values are negligible. Adsorption of the compound was determined to obey the Langmuir and Frumkin isotherm model.

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Introduction

Carbon steel is the most versatile and highly applicable engineering material, accounting for about 85% of the total yearly steel production worldwide. It represents the largest single classification of metallic alloys applied in tonnage and total cost [1]. Carbon steel corrosion has been a problem of enormous practical importance due to its high cost on the national economy. Despite its relatively limited corrosion resistance carbon steel is used in marine applications, petroleum production and refining, chemical processing, pipelines, mining, construction, metal-processing equipment, fossil fuel power and nuclear power plants. However steels exposed to aqueous environments are strongly susceptible to corrosion due to their thermodynamic instability therein [2]. This is more evident in acidic media because of the increased industrial applications of acid solutions [3]. The corrosion issue consists of the major portion of the overall expenditure for petrochemical companies worldwide, occurring at all stages from down-hole to surface equipment and processing facilities. Corrosion problems are also usually associated with operational problems and maintenance of plants and equipment causing periodic but limited or complete process shut-

down, resulting in serious economic losses [4]. Applicable corrosion control and prevention methods have been shown to help mitigate against potential disasters capable of causing loss of life, negative social impacts, damage to water resource and environmental pollution. This is the reason for the existence of entire industries devoted to providing protective systems for iron and steel. Historically, corrosion inhibitors has been observed to have excellent anti-corrosive properties, however, a significant proportion of them caused secondary effect, damaging the environment. Thus research for environmentally friendly inhibitors, like the organic inhibitors is ongoing [5–12]. Previous research has shown that compounds of organic origin have good corrosion inhibition properties for steel in acidic chloride environments [13–19]. The chemical compounds protect through adsorption mechanism by chemisorbing at the metal/solution interface on the metal surface forming a protective barrier against corrosion. The paradox is subject to the nature and surface charge of the metal, the nature and type of corrosive solution and the molecular structure of the inhibiting compound [20]. The aim of this study is to investigate the electrochemical and corrosion inhibition property of thiocarbanilide a sulfur-containing compound of great industrial potential for high carbon steel protection against corrosion in 1 M H₂SO₄ and HCl acid by using weight loss and electrochemical (anodic and cathodic Tafel polarization), optical microscopy and numerical analysis through ANOVA.

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Materials and methods

Material

High carbon steel obtained commercially from the open market in Lagos, Nigeria was analyzed at the Materials Characterization Laboratory, Department of Mechanical Engineering, Covenant University, Ota, Ogun State, Nigeria. The steel has an average nominal composition (%) depicted in Table 1. The energy dispersive spectrometer analysis is shown in Fig. 1.

Inhibitor

Thiocarbamide (TCB) a solid white powdery substance sourced from Merck Chemicals, South Africa in synthesized form is the inhibiting compound used. The structural formula is shown in Fig. 2, and the properties in Table 2.

TCB was prepared in molar concentrations of 5.48×10^6 , 1.10×10^5 , 1.64×10^5 , 2.19×10^5 , 2.74×10^5 and 1.27×10^5 per 0.2 L of the acid test media.

Corrosive test media

Dilute concentrations of 1 M H₂SO₄ and HCl acid media were prepared with analytical grade H₂SO₄ (98%) and HCl acid (37%) with deionized water and used as the corrosive test environment.

Preparation of high carbon steel specimens

Cylindrical steel specimens were mechanically cut into 14 test pieces, each with an average dimension of 0.7 cm radius and 0.7 cm length. The two exposed surface ends of the steel were ground with silicon carbide abrasive papers of 80, 120, 220, 800 and 1000 grits before polishing with 6 μm–1 μm diamond liquid, rinsed with distilled water and acetone, dried and later stored in a desiccator for weight-loss analysis, and potentiodynamic polarization resistance technique in accordance with ASTM G1 – 03 (2011) [21].

Weight-loss analysis

Steel samples of predetermined weight were separately immersed in 0.2 L of the corrosive test solution for 240 h at ambient temperature of 25 °C [22]. The samples were each removed from the acid solution after 24 h consecutively, rinsed with distilled water and acetone, dried and re-weighed in accordance with ASTM G31-12a [23]. Plots of corrosion rate, ν (mm/y) and percentage inhibition efficiency (η) versus exposure time T were plotted from the results computed during the exposure hours. The corrosion rate (ν) calculation was determined from Eq. (1) [24].

$$\nu = \frac{87.6\tilde{\omega}}{DAT} \quad (1)$$

where $\tilde{\omega}$ is the weight loss in mg, D is the density in g/cm³, A is the total area in cm² and 87.6 is a constant.

Inhibition efficiency (η) was calculated from (2)

$$\eta = \left[\frac{\tilde{\omega}_1 - \tilde{\omega}_2}{\tilde{\omega}_1} \right] \times 100 \quad (2)$$

where $\tilde{\omega}_1$ and $\tilde{\omega}_2$ are the weight loss of the specimens in the presence and absence of specific concentrations of TCB. η was calculated for every TCB concentration throughout the exposure period.

Surface coverage was determined from Eq. (3) [25,26].

$$\theta = \left[1 - \frac{\tilde{\omega}_2}{\tilde{\omega}_1} \right] \quad (3)$$

where θ is the quantitative amount of TCB compound, adsorbed per gram on the steel specimens. $\tilde{\omega}_1$ and $\tilde{\omega}_2$ are the weight loss of the specimen in the presence and absence of predetermined concentrations of TCB in acid media.

Potentiodynamic polarization technique

Potentiodynamic polarization test was performed with cylindrical high carbon steel electrodes mounted in acrylic resin with an uncoated surface area of 154 mm². The steel electrode was prepared according to ASTM G59-97 (2014) [27]. The studies were performed at 25 °C ambient temperature with Digi-Ivy 2300 potentiostat and electrode cell containing 0.2 L of the acid media, with and without TCB compound. Platinum rod was used as the counter electrode and silver chloride electrode (Ag/AgCl) was employed as the reference electrode. Potentiodynamic measurement was performed from –1.5 V to +1.5 V at a scan rate of 0.0016 V/s according to ASTM G102-89 (2015) [28]. The corrosion current density (j_{corr}) and corrosion potential (E_{corr}) were calculated from the Tafel plots of potential versus log current. The corrosion rate (ν) and the percentage inhibition efficiency (η_2) were from Eq. (4).

$$r = \frac{0.00327 \times j_{\text{corr}} \times E_q}{D} \quad (4)$$

where j_{corr} is the current density in μA/cm², D is the density in g/cm³; E_q is the specimen equivalent weight in grams. 0.00327 is a constant for corrosion rate calculation in mm/y [29,30]. The percentage inhibition efficiency (η_2) was calculated from corrosion rate values using Eq. (5) below;

$$\eta_2 = 1 - \left[\frac{\nu_2}{\nu_1} \right] \times 100 \quad (5)$$

where ν_1 and ν_2 are the corrosion rates with and without TCB inhibitor.

Results and discussion

Potentiodynamic polarization

The anodic and cathodic polarization plots of the electrochemical influence of TCB inhibitor on the corrosion of high carbon steel in 1 M H₂SO₄ and HCl acid solutions are shown in Figs. 3 and 4. Tables 3 and 4 show the results obtained from the polarization scans. Observation of the corrosion rates in Table 3 shows the significant difference in corrosion rate values for TCB inhibited and uninhibited steel samples at 0.0025–0.0150% TCB & 0% TCB. At 0% TCB significant anodic dissolution of the carbon steel sample occurred with the formation of pores, pits and channels within the porous oxide layer. The SO₄²⁻ ions within the acid solution are responsible for the corrosion reactions that occurred on the steel surface. The remarkable decrease in corrosion rate occurred from 0.0025% to 0.0150% TCB. These values are generally the same with the average inhibition efficiency of 70% due to the electrochemical action of TCB in the acid solution. Metallic corrosion is complex and non-homogeneous due to the presence of numerous anodic and cathodic reaction cells. Corrosion inhibiting compounds tend to interact with the cells, through retardation of the redox

Table 1
Nominal composition (%) of high carbon steel.

Element symbol	C	Sb	Mn	Mo	Ni	Cs	Fe
% Composition	2.40	0.04	0.69	0.08	0.01	0.02	96.76

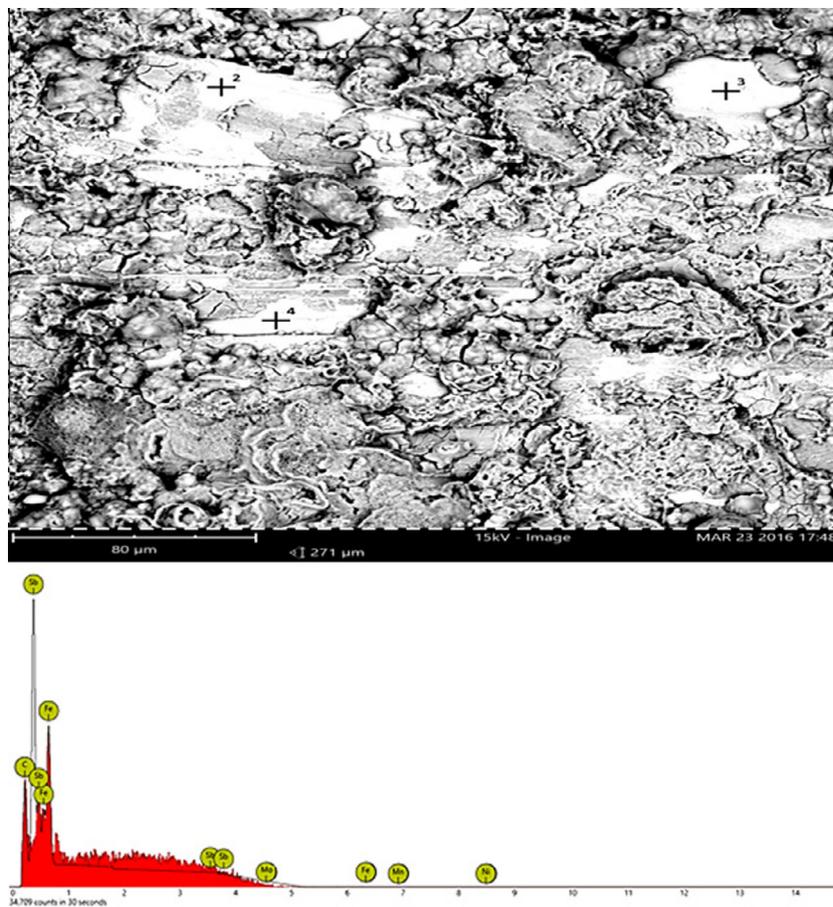


Fig. 1. Energy dispersive spectrometer analysis of high carbon steel specimen.

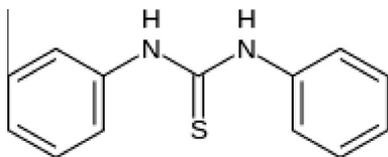


Fig. 2. Chemical structure of thiocarbanilide.

Table 2
Properties of the TCB compound.

S/N	Compound	Molecular formula	Molar mass (g mol ⁻¹)
1	Thiocarbanilide	C ₁₃ H ₁₂ N ₂ S	228.31

electrochemical process and/or inhibition of the diffusion of active corrosive anions from the acid solution to the steel. Changes in TCB concentration have no significant effect on the inhibition efficiency values. TCB inhibition performance is independent of its inhibitor concentration. At 0.0025% TCB the inhibition efficiency is 73.91%, while at 0.0150% TCB, the inhibition efficiency is 73.70%.

The electrochemical performance of TCB in HCl slightly contrasts its behavior in H₂SO₄ from observation of lower corrosion rate and higher inhibition efficiency values in Table 4. The change in corrosion rate corresponds with changes in corrosion current values. The anode–cathode polarization plots in Figs. 3 and 4 show active–passive behavior under the inhibiting action of the TCB compound. The corrosion potential generally alternates between

cathodic and anodic corrosion potentials suggesting that the mechanism of inhibition by TCB is through surface coverage of the steel preventing anodic deterioration and selective blockage of the reaction sites whereby the main cathodic reactions involving hydrogen evolution and oxygen reduction reactions are suppressed through precipitation of insoluble compounds on cathodic areas to increase the surface impedance and limit the diffusion of reducible species [31]. TCB reacts with the corrosion product, initially formed, resulting in a cohesive and insoluble film on the metal surface i.e. with the displaced metal ions produced on the anode, forming generally insoluble compounds which deposit on the steel surface as an insoluble film and impermeable to metallic ion. This promotes passivation of the steel through adsorption and hinders its deterioration as the inhibitor surface coverage decreases the number of surface metal atoms at which corrosion reactions can occur. This observation is confirmed from the anodic and cathodic potentials in Tables 3 and 4. Changes in potentials indicate that TCB has a significant influence on the mechanistic aspects of corrosion i.e. the mechanism of the corrosion process was significantly influenced.

The maximum change in corrosion potential in H₂SO₄ is 17 mV in the anodic direction while in HCl it is 27 mV in the cathodic direction, thus TCB is a mixed type inhibitor in both acids [32,33]. TCB compound has a number of lone pairs of electrons in the atoms within its molecular structure. This enables the availability of electrons to the unoccupied orbital on the steel surface leading to the formation of stable covalent bonds i.e. TCB chemically adsorbs on the steel reducing the active surface area of the steel, thus retarding the rate of the corrosion process through formation of a protective coating [34,35].

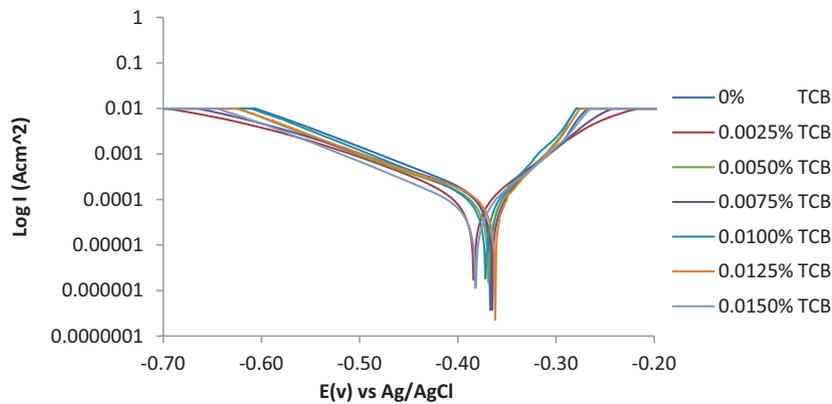


Fig. 3. Anodic-cathodic polarization plots for high carbon steel in 1 M H₂SO₄ for 0–0.0150% TCB.

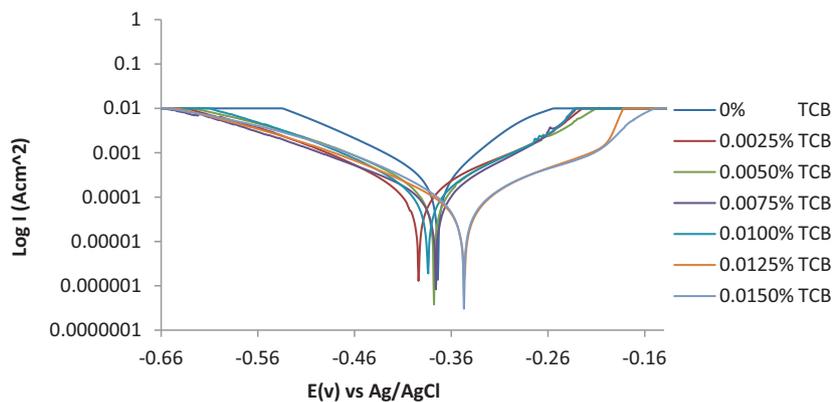


Fig. 4. Anodic-cathodic polarization plots for high carbon steel in 1 M HCl for 0–0.0150% TCB.

Table 3

Anodic-cathodic polarization results for high carbon steel in 1 M H₂SO₄ for 0–0.0150% TCB.

Sample	TCB conc. (%)	Corrosion rate (mm/y)	TCB inhibition efficiency (%)	Corrosion current (A)	Corrosion current density (A/cm ²)	Corrosion potential (V)	Polarization resistance, R _p	Cathodic tafel slope (Bc)	Anodic tafel slope (Ba)
0	0.0000	1.44	0	1.91E-04	1.24 × 10 ⁻⁴	-0.367	134.60	-8.451	27.670
1	0.0025	0.38	73.91	4.98E-05	3.23 × 10 ⁻⁵	-0.384	200.50	-8.428	15.750
2	0.0050	0.39	72.98	5.16E-05	3.35 × 10 ⁻⁵	-0.369	164.80	-7.215	33.800
3	0.0075	0.41	71.29	5.48E-05	3.56 × 10 ⁻⁵	-0.365	152.70	-7.126	17.380
4	0.0100	0.42	70.66	5.60E-05	3.64 × 10 ⁻⁵	-0.372	160.40	-8.775	26.330
5	0.0125	0.43	70.10	5.71E-05	3.71 × 10 ⁻⁵	-0.362	142.00	-6.910	30.540
6	0.0150	0.38	73.70	5.02E-05	3.26 × 10 ⁻⁵	-0.382	177.40	-9.013	19.920

Table 4

Anodic-cathodic polarization results for high carbon steel in 1 M HCl for 0–0.0150% TCB.

Sample	TCB conc. (%)	Corrosion rate (mm/y)	TCB inhibition efficiency (%)	Corrosion current (A)	Corrosion current density (A/cm ²)	Corrosion potential (V)	Polarization resistance, R _p	Cathodic tafel slope (Bc)	Anodic tafel slope (Ba)
0	0.0000	3.06	0	4.05E-04	2.63 × 10 ⁻⁴	-0.374	63.38	-10.330	13.870
1	0.0025	0.54	82	7.16E-05	4.65 × 10 ⁻⁵	-0.394	164.10	-9.899	8.895
2	0.0050	0.62	80	8.19E-05	5.32 × 10 ⁻⁵	-0.378	138.20	-9.501	9.823
3	0.0075	0.52	83	6.83E-05	4.44 × 10 ⁻⁵	-0.376	172.10	-8.318	11.280
4	0.0100	0.68	78	9.04E-05	5.87 × 10 ⁻⁵	-0.384	156.30	-9.971	10.060
5	0.0125	0.62	80	8.29E-05	5.38 × 10 ⁻⁵	-0.347	310.10	-9.626	8.420
6	0.0150	0.67	78	8.94E-05	5.80 × 10 ⁻⁵	-0.347	287.60	-10.120	7.597

Weight-loss measurements

Results from weight loss measurement of the high carbon steel specimens for weight loss ($\bar{\omega}$), corrosion rate (γ) and percentage

inhibition efficiency (η) in H₂SO₄ and HCl acids are depicted in Tables 5 and 6. Figs. 5(a), (b) and Figs. 6(a), (b) show the plot of corrosion rate and percentage inhibition efficiency versus exposure time in the acid media. Observation of the results from H₂SO₄ acid

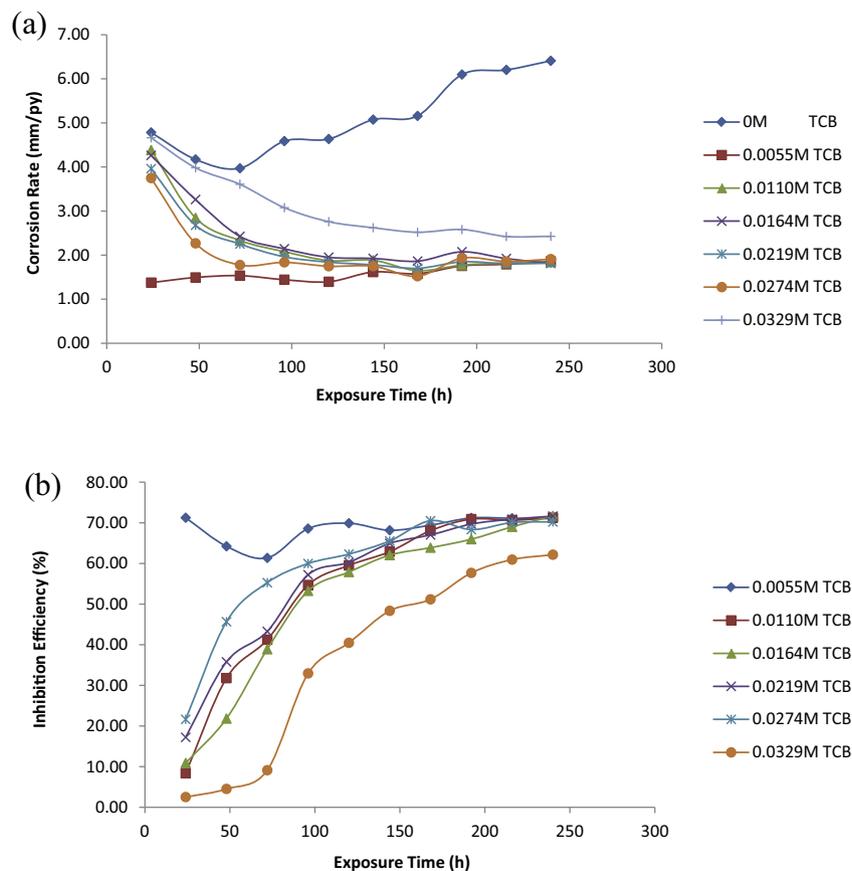
Table 5Data for high carbon steel in 1 M H₂SO₄ at predetermined concentrations of TCB from weight loss analysis.

Samples	Weight loss (mg)	Corrosion rate (mm/y)	TCB concentration (%)	TCB concentration (molarity * 10 ³)	TCB inhibition efficiency (%)	TCB surface coverage (θ)
A	0.848	6.409	0	0	0	0
B	0.246	1.857	0.0025	5.48×10^{-6}	71.02	0.710
C	0.244	1.842	0.0050	1.10×10^{-5}	71.27	0.713
D	0.240	1.814	0.0075	1.64×10^{-5}	71.69	0.717
E	0.241	1.818	0.0100	2.19×10^{-5}	71.63	0.716
F	0.253	1.909	0.0125	2.74×10^{-5}	70.22	0.702
G	0.321	2.426	0.0150	3.29×10^{-5}	62.15	0.622

Table 6

Data for mild steel in 1 M HCl at predetermined concentrations of TCB from weight loss analysis.

Samples	Weight loss (mg)	Corrosion rate (mm/y)	TCB concentration (%)	TCB concentration (Molarity * 10 ³)	TCB inhibition efficiency (%)	TCB surface coverage (θ)
A	1.852	13.998	0	0	0	0
B	0.346	2.615	0.0025	5.48×10^{-6}	81.32	0.813
C	0.320	2.420	0.0050	1.10×10^{-5}	82.71	0.827
D	0.312	2.361	0.0075	1.64×10^{-5}	83.14	0.831
E	0.363	2.742	0.0100	2.19×10^{-5}	80.41	0.804
F	0.323	2.440	0.0125	2.74×10^{-5}	82.57	0.826
G	0.317	2.396	0.0150	3.29×10^{-5}	82.89	0.829

**Fig. 5.** Plot of (a) corrosion rate versus exposure time (b) inhibition efficiency versus exposure time for high carbon steel in 1 M H₂SO₄ at 0 M–0.0329 M TCB.

shows TCB inhibition efficiencies at all TCB concentrations studied to be generally above 70% due to increased surface coverage by the adsorbed TCB molecules, with the exception of 3.29×10^{-5} M TCB concentration where the inhibition efficiency decreased to 62% as a result of desorption of TCB or modification in the adsorbed TCB species. It is suggested that the modification accelerates the cathodic reaction causing a reduction in inhibition efficiency [36]. Some

authors [37] have suggested the decrease in inhibition efficiency to be due to the reduction of TCB to release corrosion accelerating ions, others have suggested it to be due to protonation based on the belief that protonated species facilitates the hydrogen evolution reaction, and thus corrosion. This observation is further confirmed from the corrosion rate values where the corrosion rate the carbon steel sample at 0 M TCB has significantly higher corro-

sion rate value of 6.409 mm/y compared to the values for samples immersed in acid solutions with TCB. The values for TCB inhibition efficiencies in HCl acid are significantly higher than values in H₂SO₄ acid at all TCB concentrations with average inhibition efficiency above 80%. The results show that the corrosion inhibition properties and electrochemical behavior of TCB on the high carbon steels in both acids is appreciable as TCB suppressed the redox electrochemical reactions responsible for corrosion degradation. The molecular structure of TCB consists mainly of multiple bonds and heteroatoms within its structure which are strongly polar and capable of releasing electrons from its reaction center which facilitates its adsorption on carbon steel surface [38,39]. TCB being an organic compound tends to form a very thin and protective adsorbed film that leads to the general decrease in the corrosion rate of the carbon steel specimens due to the suppression of the anodic reaction, the cathodic reaction, or both [40]. The adsorption mechanism of the corrosion inhibition process occurs on the reactive sites of the steel through the π -electrons of structural rings and the lone pair of electrons of nitrogen and sulfur atoms [41,42].

Adsorption isotherm

The mechanism of adsorption of TCB compound on high carbon steel is a surface phenomenon through which TCB ionized molecules are attracted to the steel surface and adsorb through intermolecular or electrostatic mechanism. The ionization potential, surface characteristics of the metal, electronic behavior, degree of adsorption of ions present and the electrochemical potential at metal/solution-interface are responsible for the mechanism and type of adsorption. Adsorption isotherms describe the behavior of

the inhibitor molecules and provide information about the interaction of the inhibitor molecules with the metal surface [43]. The adsorption characteristics of TCB compound were analyzed to further establish the interaction mechanism between TCB and the carbon steel [43–45]. Langmuir and Frumkin isotherm produced the best fit for TCB in H₂SO₄ and HCl acid.

The isotherms are of the general form shown in Eq. (6)

$$kc = g(\theta, x)\exp(-f\theta) \quad (6)$$

where $g(\theta, x)$ is the configurational factor subject to the physical model and assumptions involved in the emanation of the isotherms. The general form of the Langmuir equation is shown below,

$$\left[\frac{\theta}{1-\theta} \right] = K_{ads}C \quad (7)$$

rearranging Eq. (7)

$$\left[\frac{c}{\theta} = \frac{1}{\theta} \right] + C \quad (8)$$

where θ is the value of surface coverage on the steel alloy, C is TCB concentration in the acid solution, and K_{ads} is the equilibrium constant of the adsorption process. The plots of TCB concentration/surface coverage versus the TCB concentration were linear in H₂SO₄ and HCl acid [Fig. 7(a) and (b)] confirming Langmuir adsorption.

According to Langmuir model TCB molecules occupy specific adsorption sites at the metal/solution interface resulting in the slight deviation of the slope from unity as shown in the correlation coefficient values in Fig. 7(a) and (b) [46,47]. Fig. 8(a) and (b) shows the Frumkin adsorption isotherm for TCB for high carbon steel in both acids. The correlation factor in H₂SO₄ is 0.0602 while

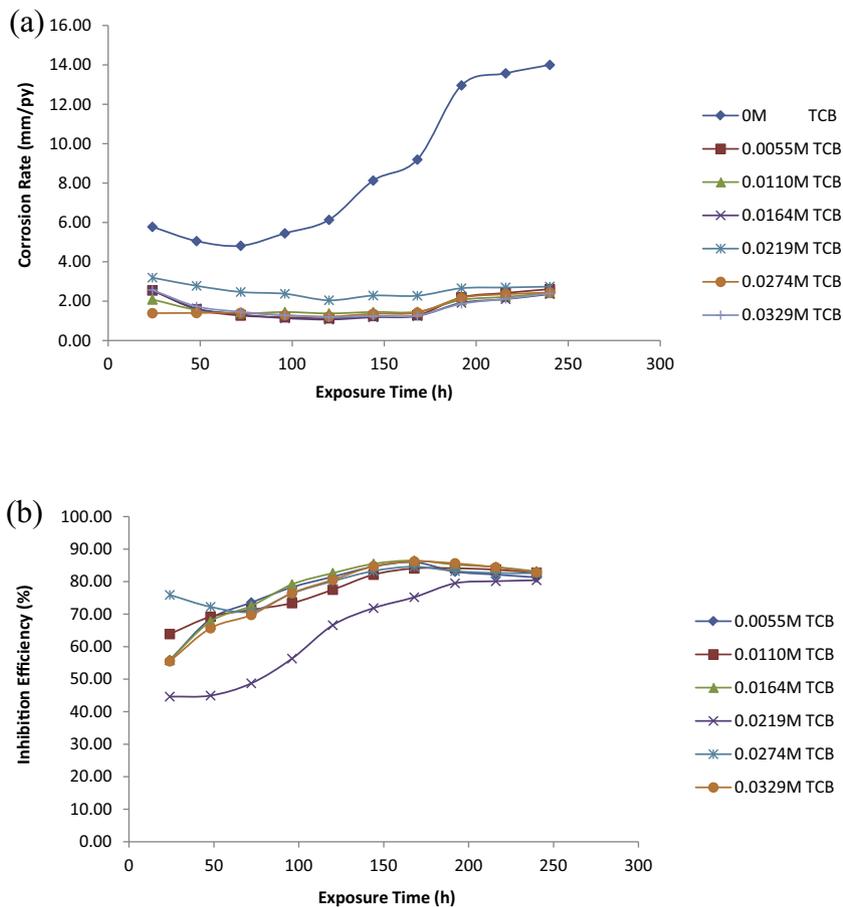


Fig. 6. Plot of (a) corrosion rate versus exposure time (b) inhibition efficiency versus exposure time high carbon steel in 1 M HCl at 0 M–0.0329 M TCB.

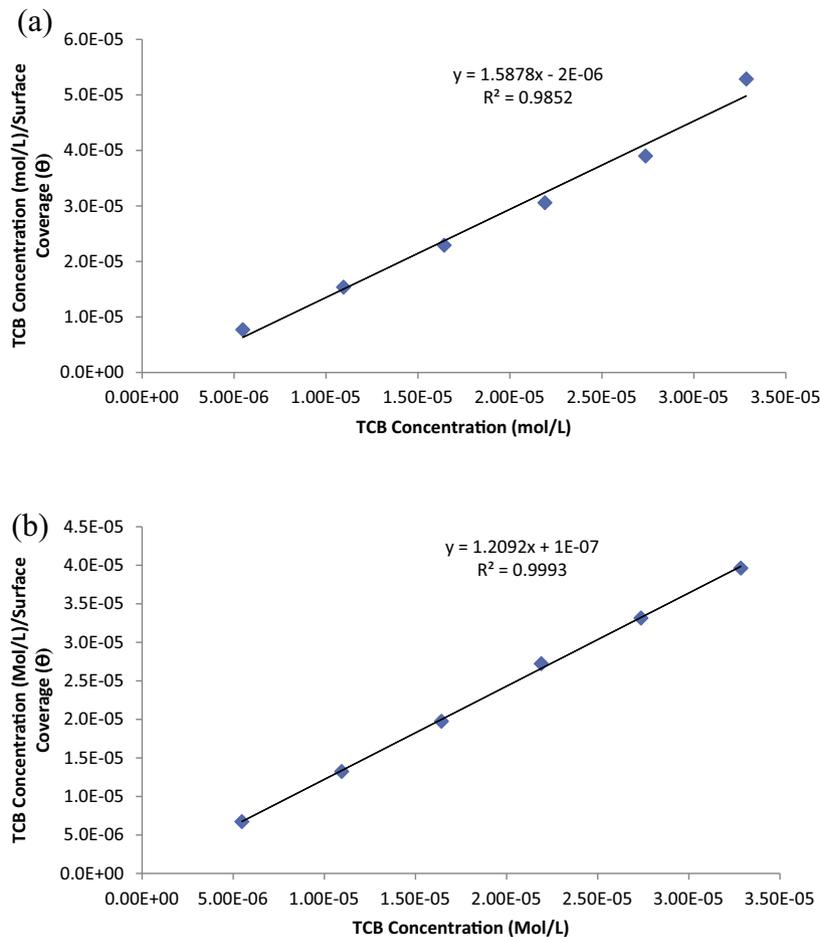


Fig. 7. Plot of TCB concentration/surface coverage versus the TCB concentration (a) in 1 M H₂SO₄, (b) in 1 M HCl.

in HCl is the factor is 0.4724. Frumkin isotherm assumes unit coverage at specific TCB concentrations and that the carbon steel surface is heterogeneous i.e. the effect of lateral interaction is significant, thus the active surface of the steel where adsorption takes place is accounted for. Frumkin adsorption isotherm can be expressed according to Eq. (9). K is the adsorption–desorption constant and α is the lateral interaction term describing the interaction in adsorbed layer

$$\text{Log} \left\{ C \times \left(\frac{\theta}{1-\theta} \right) \right\} = 2.303 \log K + 2\alpha\theta \quad (9)$$

Increase in TCB concentration in the acid solutions results in changes in the interaction energy with water molecules as TCB molecules ionize and adsorb on the carbon steel. The amount of carbon steel released into the acid solution is related to the extent of coverage of TCB over the carbon steel surface. With the assumption that the steel surface is covered with water dipoles, adsorption of the TCB occurs through substitution of the water dipoles by TCB cations [48,49].

Thermodynamics of the corrosion process

The thermodynamics of the substitutional process depends on the amount of water molecules (n) removed by TCB inhibiting compound. Results determined for Gibbs free energy ($\Delta G_{\text{ads}}^{\circ}$) for the adsorption process shown in Tables 7 and 8 were calculated from Eq. (10) below.

$$\Delta G_{\text{ads}} = -2.303RT \log[55.5K_{\text{ads}}] \quad (10)$$

where 55.5 is the molar concentration of water in the solution, R is the universal gas constant, T is the absolute temperature and K_{ads} is the equilibrium constant of adsorption. K_{ads} is related to surface coverage (θ) from the following equation.

$$K_{\text{ads}}C = \left[\frac{\theta}{1-\theta} \right] \quad (11)$$

The heterogeneous surface properties (i.e. flaws, impurities, cracks and vacancies) of the steel are responsible for the differential values of $\Delta G_{\text{ads}}^{\circ}$ of TCB compound as the surface coverage value changes [48,50–51]. This relationship is responsible for the differences in adsorption energies depicted on the tables. The negative values of $\Delta G_{\text{ads}}^{\circ}$ shows the adsorption is spontaneous. Values of $\Delta G_{\text{ads}}^{\circ}$ around -20 kJ mol^{-1} depicts physisorption adsorption mechanism, while $\Delta G_{\text{ads}}^{\circ}$ around -40 kJ mol^{-1} depicts chemisorption adsorption reactions. The reaction involves (charge sharing or transfer between the inhibitor cations and the valence electrons of the metal forming a co-ordinate covalent bond). The highest $\Delta G_{\text{ads}}^{\circ}$ value in H₂SO₄ is $-42.20 \text{ kJ mol}^{-1}$ at $5.48 \times 10^6 \text{ M}$ TCB while the lowest is $-36.76 \text{ kJ mol}^{-1}$ at $3.29 \times 10^5 \text{ M}$ TCB. In HCl the highest $\Delta G_{\text{ads}}^{\circ}$ value is $-43.26 \text{ kJ mol}^{-1}$ at $5.48 \times 10^6 \text{ M}$ while the lowest is $41.04 \text{ kJ mol}^{-1}$ at $3.29 \times 10^5 \text{ M}$ TCB. thus at the lowest TCB concentration in H₂SO₄ and HCl acid the carbon steel was most inhibited from corrosion. The values of $\Delta G_{\text{ads}}^{\circ}$ for TCB adsorption on carbon steel shows chemisorption interaction [52,53].

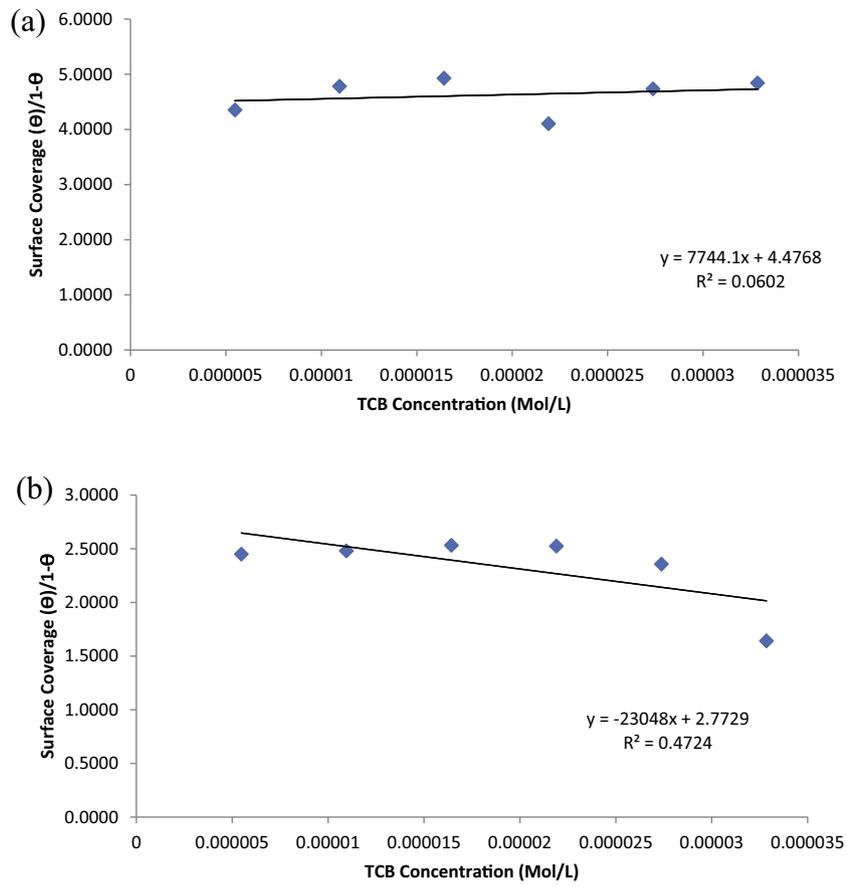


Fig. 8. Plot of $\frac{\theta}{1-\theta}$ versus TCB concentration (C) (a) in 1 M H_2SO_4 , (b) in 1 M HCl.

Table 7
Results for Gibbs free energy, surface coverage and equilibrium constant of adsorption for TCB inhibitor in 1 M H_2SO_4 .

Samples	TCB concentration (Mol $\times 10^3$)	TCB surface coverage (θ)	Equilibrium constant of adsorption (K)	Gibbs free energy, ΔG (kJ/Mol)
A	0	0	0	0
B	5.48×10^6	0.710	447,535	-42.20
C	1.10×10^5	0.713	226,483	-40.51
D	1.64×10^5	0.717	154,165	-39.56
E	2.19×10^5	0.716	115,289	-38.83
F	2.74×10^5	0.702	86114.1	-38.11
G	3.29×10^5	0.622	49984.2	-36.76

Table 8
Data for Gibbs free energy, surface coverage and equilibrium constant of adsorption for TCB inhibitor in 1 M HCl.

Samples	TCB concentration (Mol $\times 10^3$)	TCB surface coverage (θ)	Equilibrium constant of adsorption (K)	Gibbs free energy, ΔG (kJ/Mol)
A	0	0	0	0
B	5.48×10^6	0.813	795,170	-43.62
C	1.10×10^5	0.827	436,814	-42.14
D	1.64×10^5	0.831	300,113	-41.21
E	2.19×10^5	0.804	187,409	-40.04
F	2.74×10^5	0.826	173,024	-39.84
G	3.29×10^5	0.829	147,437	-39.44

Statistical analysis

Statistical analysis through ANOVA at a confidence level of 95% (significance level of $\alpha = 0.05$) was applied to quantify the statistical importance of TCB concentrations and immersion time on the inhibition efficiency values of TCB with respect to Eqs. (11)–(13). Data obtained from ANOVA analysis (Tables 9 and 10) showed that the concentrations of TCB studied is the only variable that seems to be statistically relevant to TCB inhibition efficiency results, however with F -values of 0.66 in H_2SO_4 solution and 2.38 in HCl solution it is not because the values are significantly lower than the significance factor (significance F) in Tables 7 and 8, proving that they are not significant at the level of probability applied. The statistical influence of TCB concentration is 10.1% in H_2SO_4 . It shows that TCB concentration has a negligible electrochemical influence on the corrosion inhibition behavior of TCB, likewise the exposure

time. For HCl acid the same phenomenon is observed with the statistical influence of TCB concentration at 35.1%.

The Sum of squares among columns (exposure time) was obtained with Eq. (12).

$$SS_c = \frac{\sum T_c^2}{nr} - \frac{T^2}{N} \quad (12)$$

Sum of squares among rows (inhibitor concentration)

$$SS_r = \frac{\sum T_r^2}{nc} - \frac{T^2}{N} \quad (13)$$

Total Sum of squares

$$SS_{\text{Total}} = \sum x^2 - \frac{T^2}{N} \quad (14)$$

Table 9Analysis of variance (ANOVA) for TCB inhibition efficiency in 1 M H₂SO₄ (at 95% confidence level).

Source of variation	Source of variation	Sum of squares	Degree of freedom	Mean square	Mean square ratio (F)	Min. MSR at 95% confidence	
						Significance F	F (%)
Among columns	Inhibitor concentration	23459.49	5	4691.90	0.66	2.53	10.1
Among rows	Exposure time	−5962.13	6	−993.69	−0.14	2.42	−2.57
Residual	Residual	214792.31	30	7159.74			
Total	Total	232289.67	41				

Table 10

Analysis of variance (ANOVA) for TCB inhibition efficiency in 1 M HCl (at 95% confidence level).

Source of variation	Source of variation	Sum of squares	Degree of freedom	Mean square	Mean square ratio (F)	Min. MSR at 95% confidence	
						Significance F	F (%)
Among columns	Inhibitor concentration	38984.19	5	7796.84	2.38	2.53	35.1
Among rows	Exposure time	−28945.27	6	−4824.21	−1.47	2.42	−26.73
Residual	Residual	98254.56	30	3275.15			
Total	Total	108293.49	41				

Conclusion

Results of the electrochemical performance of TCB organic compound on the corrosion inhibition of high carbon steel in dilute H₂SO₄ and HCl acid confirms the organic derivative to be highly effective. The compound was determined to be mixed type in both acids with dominant anodic inhibition in H₂SO₄ and cathodic in HCl. The inhibition efficiency remained generally the same at all TCB concentrations evaluated due to the effective action of the functional groups and heteroatoms of the compound which facilitated and maintained an adherent protective covering over the steel surface. Thermodynamic evaluation of TCB confirms chemisorption adsorption mechanism on the carbon steel surface and the adsorption obeyed the Langmuir and Frumkin adsorption isotherms. Statistical analysis show that TCB concentration and exposure time had negligible influence on its inhibition efficiency values.

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