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CORROSION INHIBITION OF 2-AMINO-5 ETHYL-1, 3, 4-THIADIAZOLE ON MILD STEEL IN HYDROCHLORIC ACID

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ABSTRACT

Corrosion inhibition of mild steel in 0.5M hydrochloric acid solutions by 2- amino- 5 ethyl- 1, 3, 4-thiadiazole(TTD) was studied using weight loss, open circuit potential measurement and potentiodynamic polarization technique. The compoundshowedmaximum inhibition efficiency of 93.7 and 97% at highest TTD concentration from weight-loss and potentiodynamic polarization test. Results from corrosion potential monitoring showed the inhibiting compound well within passivation values throughout the exposure period.Inhibition efficiency varied with inhibitor concentration and the mechanism of inhibition is attributed to chemical interaction and adsorption form thermodynamic calculations. Adsorption of the compound obeyed the Langmuir and Frumkin isotherm model. Scanning electron microscopy characterization showed the formation of protective precipitates on the steel surface while statistical derivations confirmed the overwhelming statistical significance of inhibitor concentration against exposure time on inhibition efficiency.

Keywords: Corrosion; thiadiazole; hydrochloric acid, steel, inhibition.

INTRODUCTION

Metallic corrosion has been a worldwide industrial problem that has the attention of scientist and engineers researching into and developing new corrosion control techniques (Liu *et al*., 2001; Collins *et al*., 1993; Ekpe *et al*., 1995). Corrosion inhibiting compounds are of immense importance and extensively employed in curtailing wastage of metallic alloys in applicationssuch as in acid pickling of steel, chemical cleaning and processing, ore production, chemical processing plants, automobile industries, oil well acidification etc (Ashassi-Sorkhabi *et al*., 2009; Singh *et al*., 1995). Chromate based compounds and inorganic inhibiting agents are commonly used for corrosion inhibition, however their application is being highly restricted due to their toxic nature and impact (Fontana, 1986; Abboud *et al*., 2009; Sinko, 2001; Manahan, 1994). Currently there has been unusual attention on the use of organic compounds due to their promising corrosion inhibition properties and environmentally friendly (Krim *et al*., 2008; Quraishi and Shukla, 2009; Devarayan, 2012). Application of nitrogen and sulphur containing heterocyclic organic compounds for the corrosion inhibition of mild steel in acidic solutions has been studied by a number of authors (Ita and Offiong, 1997; Abiola *et al*., 2004; Rastoyi *et al*., 2005; James *et al*., 2005; Ita and Offiong, 1997). Heterocyclic compounds act by adsorption onto the alloy surface through the heteroatom and triple or conjugated double bonds within their molecular structures (Thomas, 1980-1981). A number of heterocyclic compounds have been used for the corrosion inhibition of ferrous alloys in acid solutions (Bentiss*et al*., 2000; Cruz *et al*., 2004; Bouklah*et al*., 2005; Popova *et al*., 2004). In this investigation 2 Amino, 5 ethyl, 1, 3, 4-thiadiazole was observed for its corrosion inhibition properties and performance on mild steel in dilute hydrochloric acid.

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MATERIALS AND METHODS

Material

The mild steel used for this research was obtained in the open market and analyzed at the Applied Microscopy and Triboelectrochemical Research Laboratory, Department of Chemical and Metallurgical Engineering, Tshwane University of Technology, South Africa. The mild steel has the nominal per cent composition: 0.301C, 0.169Si, 0.440Mn, 0.005P, 0.012S, 0.080Cu, 0.008Ni, 0.025Al, and the rest being Fe.

Inhibitor

2- Amino, 5- ethyl- 1, 3, 4-thiadiazole (TTD) a colorless, solid flakeobtained from SMM Instruments South Africa is the inhibitor used. The structural formula of TTD is shown in figure 1. The molecular formula is $C_4H_7N_3S$, while the molar mass is 129.18 g mol^{-1}.

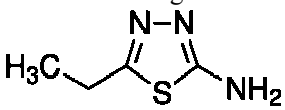


Fig. 1. Chemical structure of 2- Amino- 5 ethyl- 1, 3, 4-thiadiazole (TTD).

TTD was prepared in concentrations of 0.125%, 0.25%, 0.375%, 0.5%, 0.625% and 0.75%, respectively.

Test Media

0.5M hydrochloric acid with 3.5% recrystallised sodium chloride of Analar grade were used as the corrosion test media.

Preparation of Test Specimens

A cylindrical mild steel rod with a diameter of 14.5 mm was carefully machined and cut into a number of test specimens of average dimensions in length of 6 mm. A 3 mm hole was drilled at the centre for suspension. The steel specimens were then thoroughly rinsed with distilled water and cleansed with acetone for weight loss analysis. The linear polarization technique involved grinding the two surface ends of each specimen with silicon carbide abrasive papers of 80, 120, 220,800 and 1000 grits before being polished with 6.0μm to 1.0μm diamond paste, washed with distilled water, rinsed with acetone, dried and stored in a dessicator before the test.

Weight-loss Experiments

Weighted test species were fully and separately immersed in 200ml of the test media at specific concentrations of the TTD for 360 h at ambient temperature of 25°C. Each of the test specimens was taken out every 72 h, washed with distilled water, rinsed with acetone, dried and re-weighed. Plots of weight-loss (mg), corrosion rate (mm/y) inhibitor concentration versus exposure time (h) (Figs. 2, 3 and 4) for the test media and those of percentage inhibition efficiency (%*IE*) (calculated) versus percentage TTD concentration (Fig. 5) were made from table 1.

The corrosion rate (*R*) calculation is from this equation 1:

$$R = \left[\frac{87.6W}{DAT}\right] \quad (1)$$

Where *W* is the weight loss in milligrams, *D* is the density in g/cm^3, A is the area in cm^2, and T is the time of exposure in hours. The %*IE* was calculated from the relationship in equation 2.

$$\%IE = \left[\frac{W1 - W2}{W1}\right] = 100 \quad (2)$$

$W_1$and W_2 are the weight loss of mild steel coupon in free and inhibited acid chloride solutions respectively in the presence of predetermined concentrations of TTD. The %*IE* was calculated for all the inhibitors every 72 h during the course of the experiment, while the surface coverage is calculated from the relationship:

$$\theta = \left[1 - \frac{W2}{W1}\right] \quad (3)$$

Where θ is the substance amount of adsorbate adsorbed per gram (or kg) of the adsorbent.

Open Circuit Potential Measurement

A two-electrode electrochemical cell with a silver/silver chloride was used as reference electrode. The measurements of OCP were obtained with Autolab PGSTAT 30 ECO CHIMIE potentiostat. Resin mounted test electrodes/specimens with exposed surface of 165 mm^2 were fully and separately immersed in 200ml of the test media (acid chloride) at specific concentrations of TTD for a total of 288 h. The potential of each of the test electrodes was measured every 48 h. Plots of potential (mV) versus immersion time (hrs) (Fig. 6) for the test media were made from the tabulated values in table 2.

Linear Polarization Resistance

Linear polarization measurements were carried out using, a cylindrical coupon embedded in resin plastic mounts with exposed surface of 165 mm^2. The electrode was polished with different grades of silicon carbide paper, polished to 6μm, rinsed by distilled water and dried with acetone. The studies were performed at ambient temperature with Autolab PGSTAT 30 ECO CHIMIE potentiostat and electrode cell containing 200 ml of electrolyte, with and without the inhibitor. A graphite rod was used as the auxiliary electrode and silver chloride electrode (Ag/AgCl) was used as the reference electrode. The steady state open circuit potential (OCP) was noted. The potentiodynamic studies were then made from -1.5V *versus* OCP to +1.5 mV *versus* OCP at a scan rate of 0.00166V/s and the corrosion currents were registered. The corrosion current density (I_{corr}) and corrosion potential (E_{corr}) were determined from the Tafel plots of potential *versus* log *I*. The corrosion rate (*R*),the degree of surface coverage (θ) and the percentage inhibition efficiency (%*IE*) were calculated as follows

$$R = \frac{0.00327\ xicorrxeq.wt}{D} \quad (4)$$

Where I_{corr} is the current density in μA/cm^2, *D* is the density in g/cm^3; *eq.wt* is the specimen equivalent weight in grams. The percentage inhibition efficiency (%*IE*) was calculated from corrosion rate values using the equation.

$$\%IE = 1 - \left[\frac{R2}{R1}\right] = 100 \quad (5)$$

where*R*1and *R*2 are the corrosion rates in absence and presence of TTD, respectively.

Scanning Electron Microscopy Characterization

The surface morphology of the uninhibited and inhibited steel specimens were investigated after weight-loss

analysis in 0.5 M HCl solutions using Jeol scanning electron microscope for which SEM micrographs were recorded

Statistical Analysis

Two-factor single level statistical analysis using ANOVA test (F-test) was performed so as to investigate the significant effect of inhibitor concentration and exposure time, ascertaining their statistical significance on the inhibition efficiency values of TTD in the acid media.

RESULTS AND DISCUSSION

Weight-loss measurements

Weight-loss of mild steel at specific time intervals, in the absence and presence of TTD concentrations in 0.5M HCl acid at ambient temperature of 25°C was studied. The values of weight-loss (*W*), corrosion rate (*R*) and the percentage inhibition efficiency (%*IE*) are presented in table 2. The corrosion rates decreased progressively in HCl with increase in TTD concentration. Figures 2, 3 and4shows the variation of weight-loss, corrosion rate and percentage inhibition efficiency versus exposure time at specific TTD concentrations while figure 5 shows the variation of %*IE* with TTD concentration. The curves obtained showa progressive increase in%*IE* values with the addition of TTD at all concentrations in HCl.

The inhibition efficiency in HCl declined from 0.125 - 0.5% TTD well below effective inhibiting values. This could be due to lateral repulsion between the molecules of TTD or formation of secondary precipitates resulting in desorption and penetration of the protective film by the corrosive species. At 0.625% TTD concentration there is a sharp increase in inhibition efficiency till 0.75% TTD concentration. Comparison of the %*IE* values of TTD in both acid solutions shows the inhibitor to be highly protective at specific concentrations.

Polarization studies

Potentiostatic potential was cursorily examined –1.5 V to +1.5 V vs. Ag/AgCl at a scan rate of 0.00166 mV s^{-1} for equilibrium state analysis. The effect of the addition of TTD on the anodic and cathodic polarization curves of

Table 1. Data obtained from weight loss measurements for MS in 0.5M HCl solution at specific concentrations of the TTD at 432 h.

Sample	Corrosion Rate (mm/y)	Inhibitor Concentration (%)	Inhibition Efficiency (%)	Weight Loss (mg)	Inhibitor Concentration (Molarity)	Surface Coverage (θ)
A	13.62	0	0	2.735	0	0
B	3.51	0.125	72.14	0.762	9.68E-06	0.721
C	4.97	0.25	62.74	1.019	1.94E-05	0.627
D	5.80	0.375	55.58	1.215	2.90E-05	0.556
E	7.65	0.5	39.23	1.662	3.87E-05	0.392
F	1.03	0.625	90.64	0.256	4.84E-05	0.906
G	0.66	0.75	93.6	0.175	5.81E-05	0.936

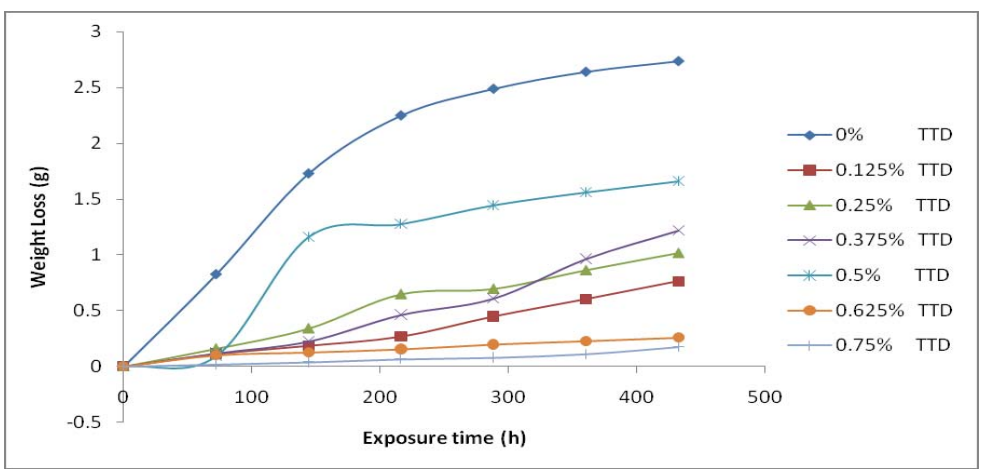


Fig. 2. Variation of weight-loss with exposure time for samples (A – G) in 0.5M HCl solution at specific TTD concentrations.

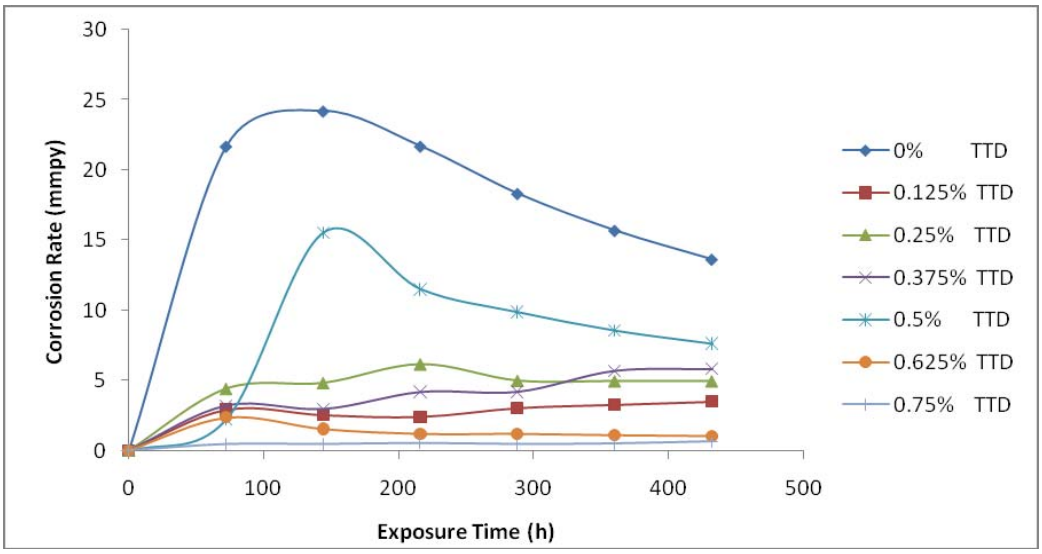


Fig. 3. Effect of percentage concentration of TTD on the corrosion rate of MS in 0.5M HCl.

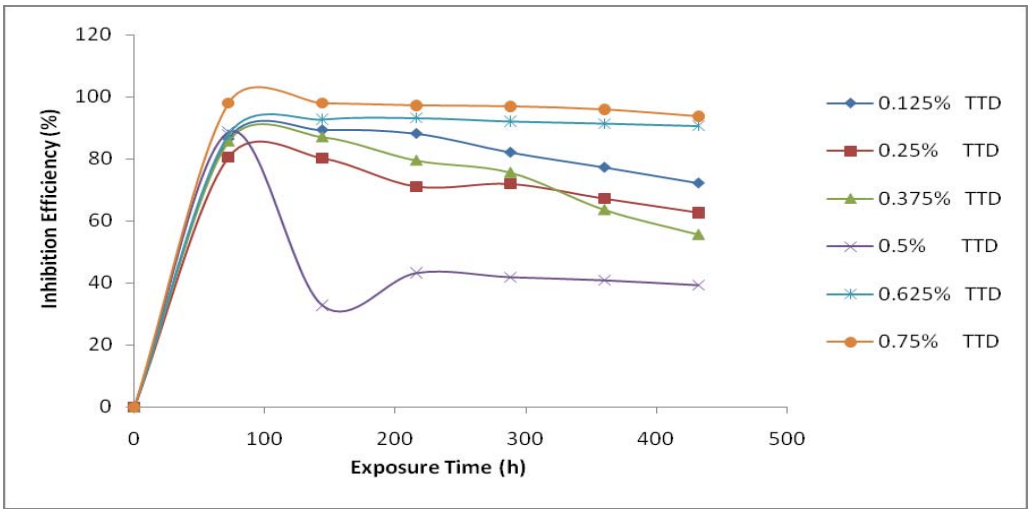


Fig. 4. Plot of inhibition efficiencies of sample (A-G) versus exposure time in 0.5M HCl solution/TTD during the exposure period.

mild steel in 0.5M HCl solutions is shown in figure 6. The performance of TTD on the corrosion inhibition of mild is independent of its concentration as observed in table 2. The corrosion rates in the acid solutions decreased in proportion despite the differential values in the electrochemical parameters while figure 7 depicts the electrochemical relationship between TTD concentration and inhibition efficiency of TTD. Changes in the redox Tafel constants occurred due to the electrolytic impact of TTD on the corrosion process. This altered the redox reactions responsible for corrosion as a result of the formation of a compact barrier film on the steel electrode surface.

The corrosion inhibition property of TTD on mild steel in the acid solution is of mixed inhibitiontype due to its electrochemical influence on the Tafel constants of the electrochemical reaction and differential values in the corrosion potential observed.The tendency for cathodic inhibition is much more dominant with the corrosion potential values shifting to less noble potentials over the TTD concentrations studied. The maximum displacement in HCl for the corrosion potential is 51mV in the cathodic direction, thus conventionally it is a mixed type inhibitor, but the mechanism of inhibition is dominantly cathodic (Eduok *et al*., 2010; Trowsdale *et al*., 1996). This causesthe selective precipitation of TTD cations on cathodic sites resulting in the suppression of hydrogen evolution and oxygen reduction reactions.

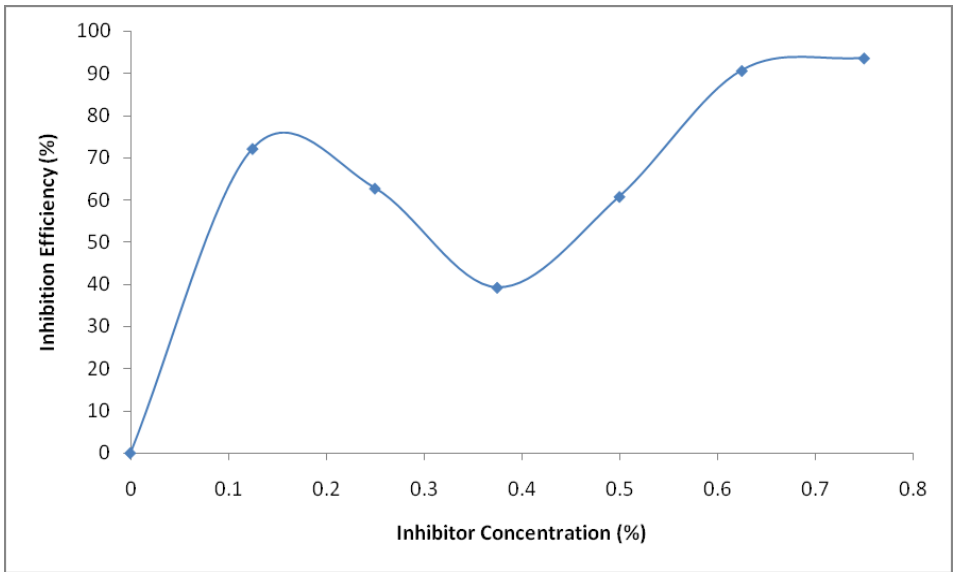


Fig. 5. Variation of Inhibition efficiency of versus inhibitor concentrations from weight loss analysis in 0.5 M HCl solution/TTD.

Table 2. Data obtained from polarization resistance measurements for MS in 0.5M HCl solution at specific concentrations of the TTD.

Sample	Inhibitor Concentration (%)	*ba* (V/dec)	*bc* (V/dec)	E_{corr}, Obs (V)	I_{corr} (A/cm²)	i_{corr} (A)	Corrosion rate (mm/yr)	*R*p (Ω)	Inhibition Efficiency (%)
A	0	0.249	0.070	-0.351	0.000401	0.000662	4.67	35.899	0
B	0.125	0.245	0.171	-0.384	7.47E-05	0.000123	0.87	355.41	81.37
C	0.25	0.279	0.161	-0.368	0.000111	0.000181	1.28	245.23	72.59
D	0.375	0.051	0.302	-0.396	0.000145	0.00024	1.69	79.040	63.81
E	0.5	0.201	0.087	-0.390	0.000236	0.000389	2.74	67.860	41.33
F	0.625	0.303	0.065	-0.318	2.93E-05	4.84E-05	0.34	480.77	92.72
G	0.75	0.082	0.042	-0.429	1.21E-05	1.99E-05	0.14	606.82	97.00

Open Circuit Potential Measurement

The corrosion potential values for TTD are shown in table 3, while figure 8 shows the corresponding relationship between corrosion potential values and exposure time. There is a potential displacement to less noble potentials from 0.125% TTD to 0.5% TTD even the potential values at 1.25% TTD - 2.5% TTD are well within passivity potentials, after which the potential values at 0.375% TTD – 0.5% TTD are within the zones of active corrosion. At 0.625% TTD – 0.75% TTD there is a sharp potential displacement to values within the zone of effective inhibition (total suppression of the corrosion process). This is further confirmed from the weight-loss method. The non linear potential values in HCl from 0.125% TTD to 0.75% TTD is most probably due to desorption of the inhibitor from the steel surface. The desorption is a product of the formation of secondary precipitates which accelerates the corrosion process and lateral repulsion between the cations of TTD compounds due to the specific nature of the inhibitor at the concentrations involved.Comparison of the potential values shows TTD influence to be more thermodynamically stable than in HCl due to the aggressive nature and adsorption of the chloride ions from the HCl solution.

Scanning Electron Microscopy Analysis

The SEM images of figure 9 (a & b) shows surfaces which has been electrochemically altered due to competitive adsorption of TTD molecules which results in the displacement of Cl^- ions initially adsorbed onto the specimen's surface. The resulting topography consist of solid and impervious precipitates of TTD molecules formed over the entire surface of MS due to charge transfer and chemical interaction with the valence orbital of iron constituting the bulk of MS constituent elements. This is responsible for the unusual topographic image because the cationic molecules of TTD form complexes on the surface which effective prevents diffusion of the corrosive anions. Results from weight loss and

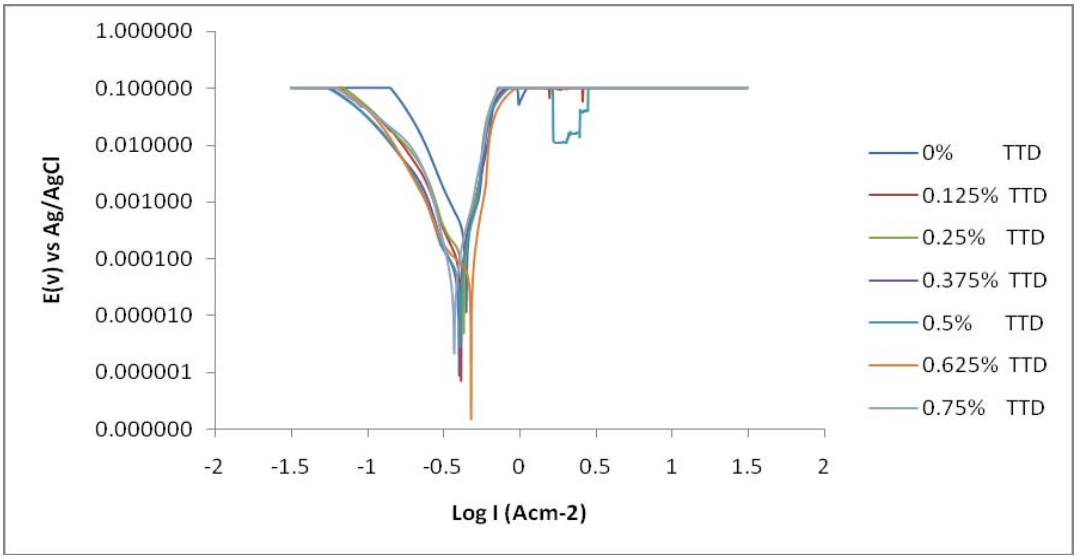


Fig. 6. Comparison plot of polarization scans for MS in 0.5M HCl solution at specific concentrations of TTD (0%-0.75% TTD).

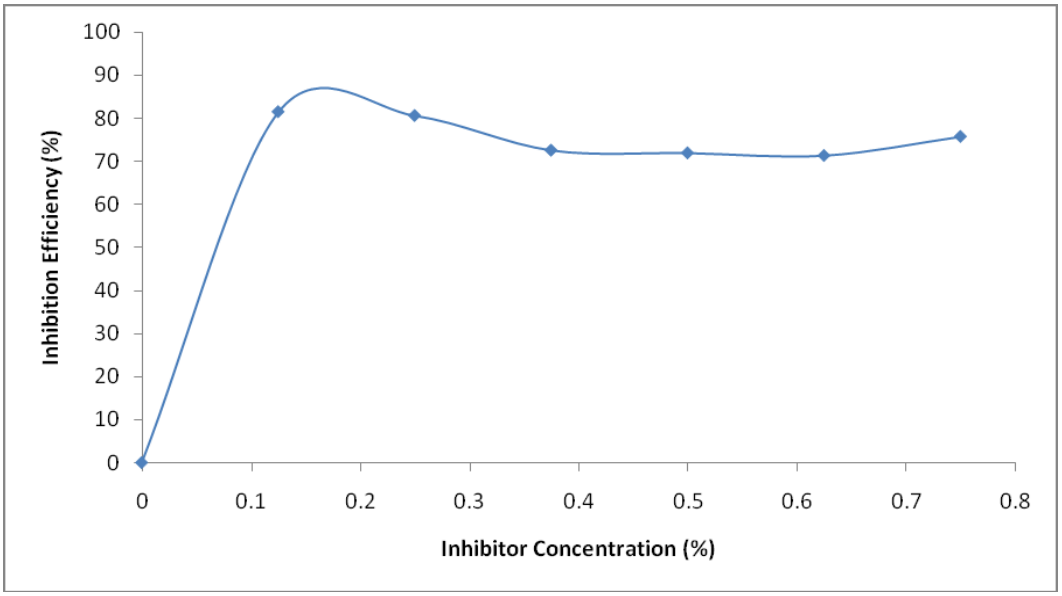


Fig. 7. The relationship between %*IE* and inhibitor concentration for polarization test in 0.5M HCl solution/TTD.

potentiodynamic polarization furthers corroborates the effectiveness of the protective film resulting from the significant electrochemical influence TTD has on the corrosion process. The contrast in the micrographs from both solutions is due to the molecular nature and specific inhibiting action of TTD the varying acid solutions.

Adsorption Isotherms and Thermodynamics of the Corrosion Process

The mechanism of corrosion inhibition can be explained on the basis of the adsorption behaviour of the adsorbate on the metal surface (Deyab and Abd El-Rehim, 2013). Adsorption isotherms are very important in determining the mechanism of organo - electrochemical reactions. The adsorptive behaviour of the organic compounds is an important part of this study, as it provides important clues to the nature of the metal-inhibitor interaction. Langmuir and Frumkin adsorption isotherms were applied to describe the adsorption mechanism for the inhibiting compounds in acid solutions, as they best fit the experimental results.

The isotherms are of the general form.

$$f(\theta, x)\exp(-2a\theta) = K \qquad (6)$$

where f (θ, x) is the configurational factor which depends upon the physical model and assumption underlying the derivative of the isotherm, θ is the surface coverage, C is

Table 3. Data obtained from potential measurements for mild steel in 0.5M HCl in presence of specific concentrations of the TTD.

TTD Concentration (%) / Exposure Time (h)	0	0.125	0.25	0.375	0.5	0.625	0.75
0	-459	-346	-413	-438	-469	-314	-317
48	-451	-331	-397	-423	-450	-309	-312
96	-445	-324	-383	-415	-437	-304	-301
144	-431	-319	-374	-396	-413	-299	-293
192	-433	-313	-368	-388	-416	-295	-289
240	-438	-310	-359	-375	-411	-287	-281
288	-442	-302	-356	-367	-427	-282	-279

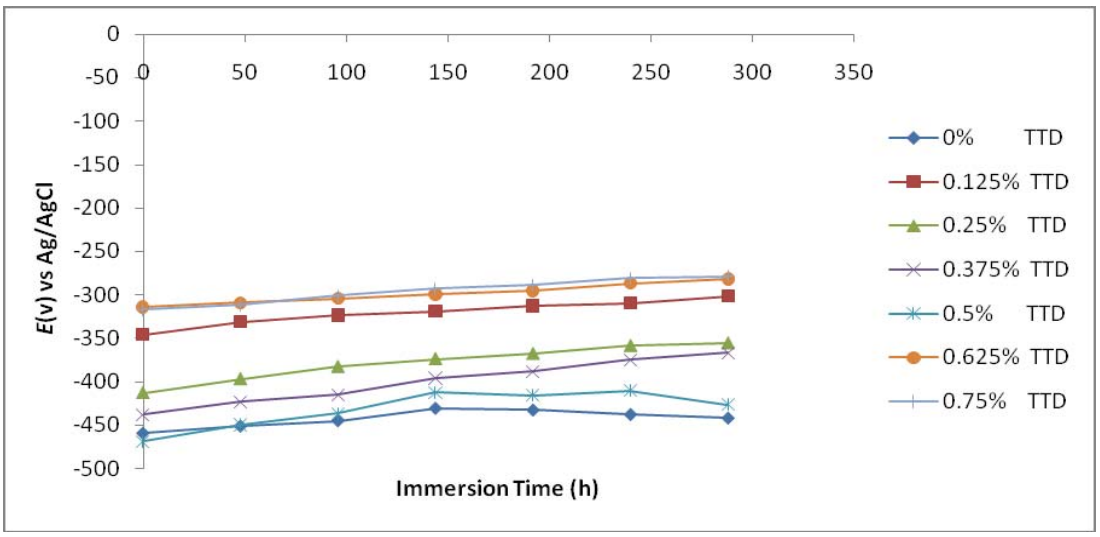


Fig. 8. Variation of potential with immersion time for TTD concentrations in 0.5M HCl.

the inhibitor concentration, x is the size ration, 'a' is the molecular interaction parameter and K is the equilibrium constant of adsorption process.

The conventional form of the Langmuir isotherm is,

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

and rearranging gives

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

whereθ is the degree of coverage on the metal surface, C is the inhibitor concentration in the electrolyte, and K_{ads} is the equilibrium constant of the adsorption process.

Langmuir isotherm proposes the following;

(i) The molecular interaction between the adsorbates on the metal surface is fixed.
(ii) The Gibbs free energy does not depend on the surface coverage values
(iii) There is no effect of lateral interaction among the adsorbates onthe value of Gibbs free energy (Ashish and Quraishi, 2011).

The plot of C/θ versus AMB concentration (C) (Fig. 10) fitted the Langmuir adsorption isotherm.

Frumkin isotherm assumes unit coverage at high inhibitor concentrations and that the electrode surface is inhomogeneous i.e. the lateral interaction effect is not negligible. In this way, only the active surface of the electrode, on which adsorption occurs, is taken into account. Frumkin adsorption isotherm can be expressed according to equation 9.

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

Where K is the adsorption-desorption constant and α is the lateral interaction term describing the interaction in adsorbed layer.

Plots of θ/1- θ versus inhibitor concentration(C) as presented in figure 11 is linear with slight deviation which shows the applicability of Frumkin isotherm. The lateral interaction term (α) calculated from the slope of the Frumkin isotherm (Table 4) shows the intermolecular attraction between the TTD molecules on the surface of

MS decreases progressively with increase in TTD concentration; however its overall influence on the inhibition efficiency is negligible.

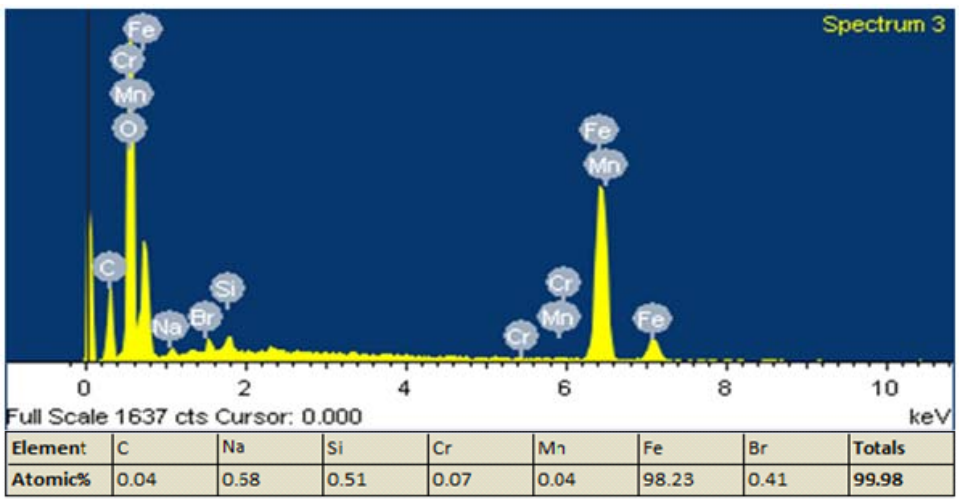
Table 4. Relationship between lateral interaction parameter and surface coverage (θ) in 0.5 M HCl MS.

Lateral Interaction Parameter (α)	Surface Coverage (θ)
0	0
2.156	0.721
2.478	0.627
2.798	0.556
3.964	0.392
1.716	0.906
1.661	0.936

Values of ΔG_{ads} around -20 kJ/mol are consistent with physisorption; those around -40 kJ/mol or higher involve charge sharing to form a coordinate type of bond chemisorption (Vračar and Drazic, 2002). The value of ΔG_{ads} in HCl for MS under the action of the organic compounds as shown in table 5 reveals the strong adsorption of TTD molecules onto the steel surface. The negative values of ΔG_{ads} showed that the adsorption of inhibitor molecules on the metal surface is spontaneous. The values of ΔG_{ads} calculated ranged between −38.00 and −40.94 kJ mol^{-1} for TTD (Table 5) in HCl. The values in HCl are consistent with chemical interaction and adsorption onto the MS surface.

The value of ΔG_{ads} obtained shows that the molecules chemisorb on the steel producing a bond resistant to penetration and competitive adsorption from the corrosive species. The intermolecular bonding is sufficiently strong to prevent displacement of adsorbed inhibitor molecules

(a)



(b)

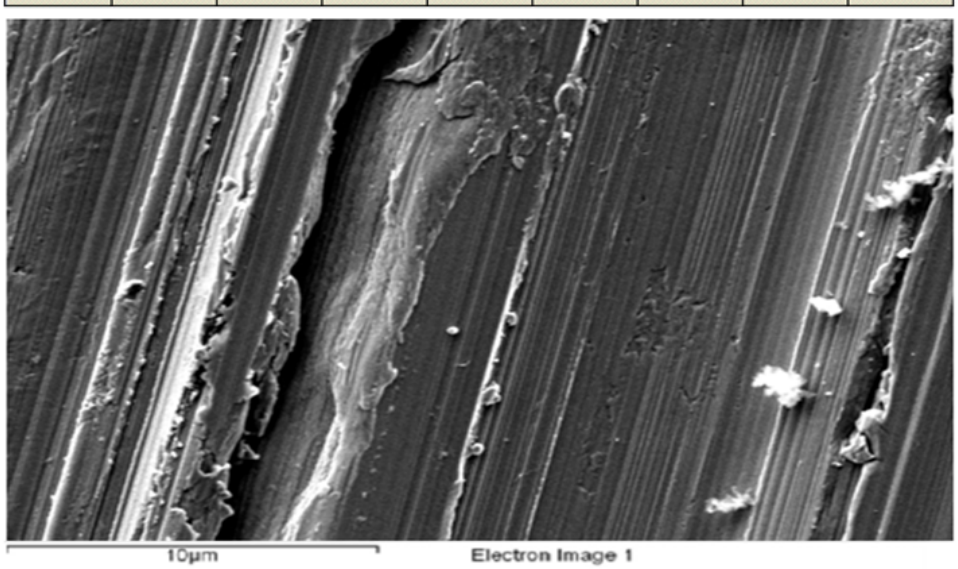
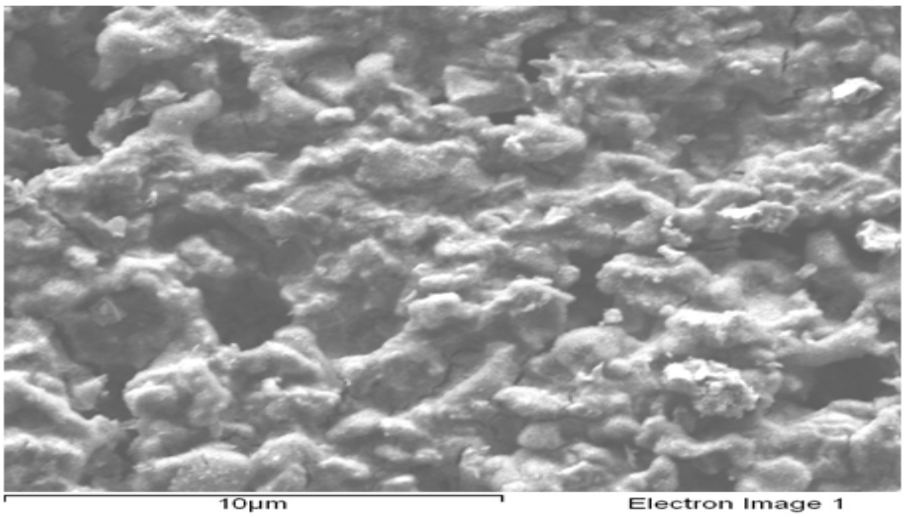


Fig. 9. SEM micrographs of: a) Energy dispersive spectrometer analysis of Mild, b) Mild steel before immersion in 0.5 M HCl.

(c)



(d)

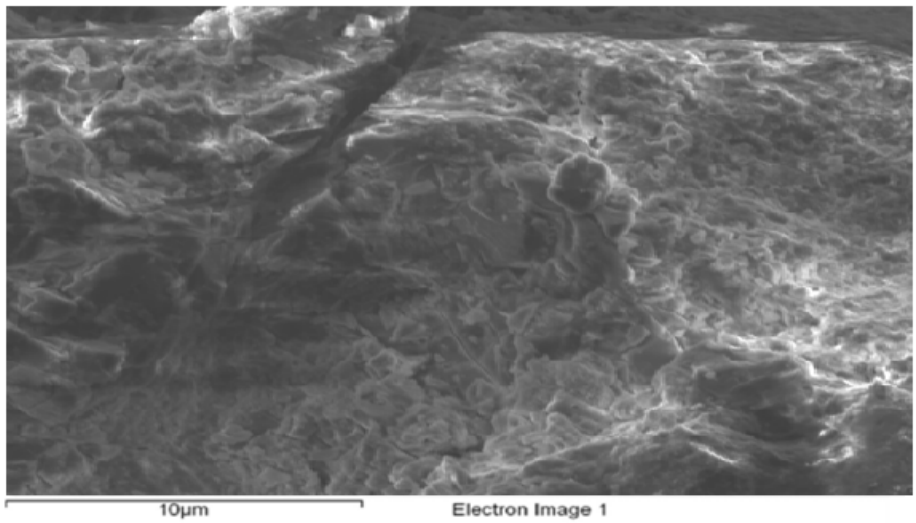


Fig. 9. SEM micrographs of: c) Mild steel after immersion in 0.5 M HCl, d) Mild steel after immersion in 0.5 M HCl with TTD addition.

along the surface. The precipitates formed are stable in the acid solution throughout the exposure period.

Statistical Analysis

Two-factor single level experimental ANOVA test (F-test) was used to analyse the separate and combined effects of the percentage concentrations of TTD and exposure time on the inhibition efficiency of TTD in the corrosion inhibition of mild steels in 0.5M HCl solutions and to investigate the statistical significance of the effects. The F-test was used to examine the amount of variation within each of the samples relative to the amount of variation between the samples.

The Sum of squares among columns (exposure time) was obtained with the following equations.

$$SS_c = \frac{\sum T_c^2}{nr} - \frac{T^2}{N} \qquad (10)$$

Sum of Squares among rows (inhibitor concentration)

$$SS_r = \frac{\sum T_r^2}{nc} - \frac{T^2}{N} \qquad (11)$$

Total Sum of Squares

$$SS_{Total} = \sum x^2 - \frac{T^2}{N} \qquad (12)$$

The results using the ANOVA test is tabulated (Table 4) as shown.

The ANOVA results (Table 6, Fig. 12) in the acid solution shows the overwhelming influence of inhibitor concentration on the inhibition efficiency with F-values of 98.46 (Table 6). This greater than significance factor at α=0.05 (level of significance or probability). The F-values of exposure time in both acids are less significant

Table 5. Data obtained for the values of Gibbs free energy, Surface coverage and equilibrium constant of adsorption at varying concentrations of TTD in 0.5 M HCl for MS.

Samples	Surface Coverage (θ)	Equilibrium Constant of Adsorption (K_{ads})	Free energy of Adsorption (ΔG_{ads}) (kJ/mol)
B	0.721	267483	-40.91
C	0.627	86804.3	-38.12
D	0.556	43138.9	-36.40
E	0.392	16682.4	-34.06
F	0.906	200074	-40.23
G	0.936	251783	-40.80

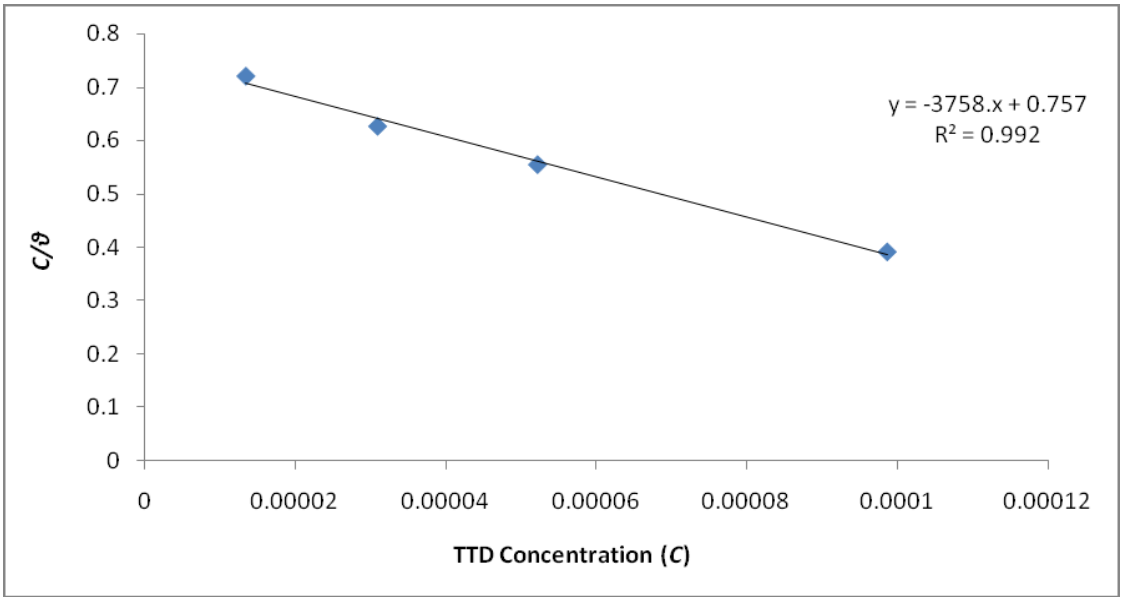


Fig. 10. Relationship between C/θ and TTD concentration (C) in 0.5 M HCl for MS.

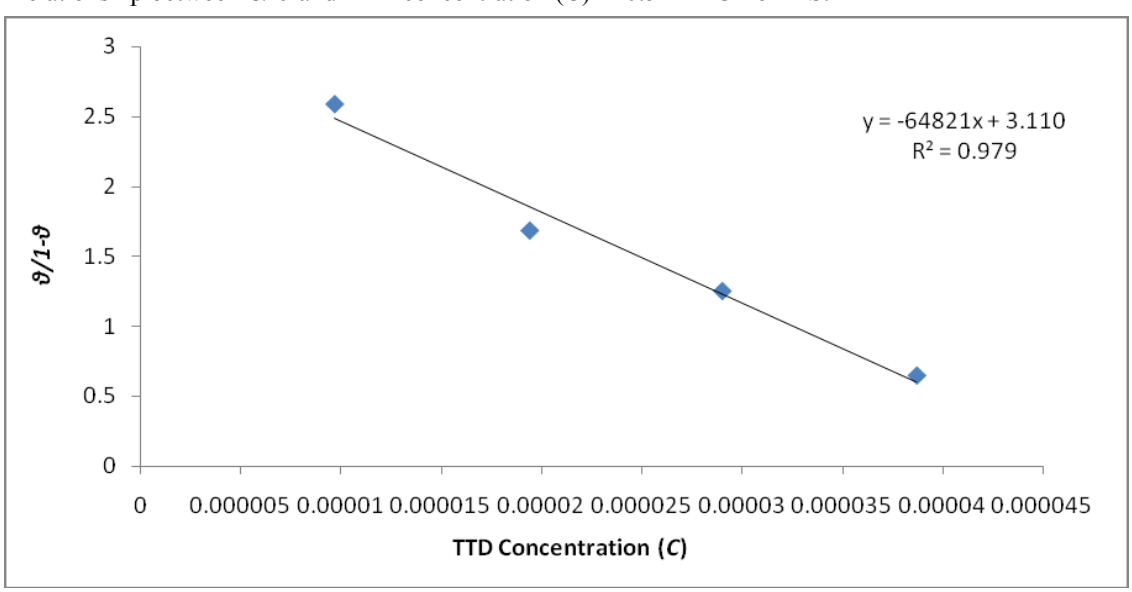


Fig. 11. Relationship between θ/1- θ and TTD concentration (C) in 0.5 M HCl for MS.

Table 6. Analysis of variance (ANOVA) for inhibition efficiency of TTD inhibitor in 0.5M HCl (at 95% confidence level).

TTD HCl					Min. MSR at 95% confidence	
Source of Variation	Sum of Squares	Degree of Freedom	Mean Square	Mean Square Ratio	Significance F	F(%)
Inhibitor concentration	7059.73	5	1411.95	139.41	2.71	85.7
Exposure Time	743.31	4	185.83	18.35	2.87	8.76
Residual	202.56	20	10.13			
Total	8005.60	29				

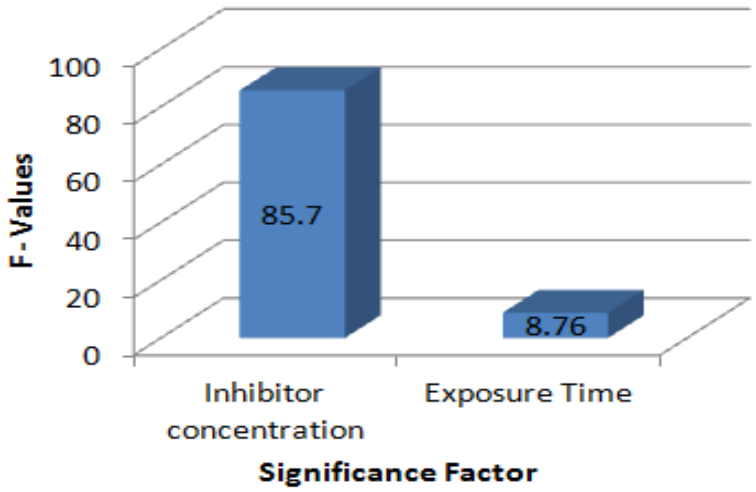


Fig. 12. Influence of inhibitor concentration and exposure time on inhibition efficiency of TTD in 0.5M HCl.

compared to inhibitor concentration but greater than the significant factor hence they are statistically relevant with F-values of 15.14. The statistical influence of the inhibitor concentration in HCl is 85.7% while the inf luence of the exposure time is 8.76%. The inhibitor concentration and exposure time are significant model terms influencing inhibition efficiency of TTD on the corrosion of the steel specimen with greater influence from the percentage concentration of TTD.

CONCLUSION

2-amino- 5 ethyl- 1, 3, 4 thiadiazole (TTD) performed effectively with excellent results in the acid media. Thecorrosion reduced with increase in TTD concentration. TTD showed mixed inhibiting tendencies at all concentration studied, though the tendency for cathodic inhibition is more pertinent with the corrosion potential values shifting to less noble values over the TTD concentrations studied. Results deduced from thermodynamic calculations showed the electrochemical interaction to be by chemisorption mechanism. SEM characterization shows surfaces which has been electrochemically altered due to adsorption of TTD molecules onto the specimen's surface resulting in topography which consists of solid and impervious precipitates of TTD compound. Statistical analysis through ANOVA revealed only the inhibitor concentration to be statistically relevant on the inhibition efficiency of TTD.

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