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Corrosion inhibition properties of the combined admixture of thiocarbanilide and hexadecyltrimethylammoniumbromide on mild steel in dilute acid solutions

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Abstract: The synergistic effect of the combined admixture of thiocarbanilide and hexadecyltrimethylammoniumbromide on the electrochemical corrosion behavior and inhibition of mild steel in 1 M H_2SO_4 and HCl acid media was evaluated through weight loss analysis, potentiodynamic polarization technique, and IR spectroscopy. Results show that the admixture performed effectively in both acid solutions with an average HTH inhibition efficiency of 86.2 and 82% in H_2SO_4 acid from weight loss and potentiodynamic polarization test while the corresponding values in HCl acid are 79 and 80%, respectively. Thermodynamic calculations showed that the compound chemically adsorbed onto the steel surface blocking the diffusion of corrosive anions and simultaneously suppressing the redox electrochemical process responsible for corrosion. Infrared spectroscopic images revealed the presence of the functional groups of the organic compound responsible for corrosion inhibition.

ABOUT THE AUTHORS

Roland T. Loto is a senior lecturer and researcher in the Department of Mechanical Engineering, Covenant University, Ota, Ogun State, Nigeria. He is a proven scholar and research scientist in the field of metallic corrosion reactions phenomena, materials characterization, corrosion measurement, control and prevention covering a very broad spectrum of technical areas and activities. His research aims to proffer solutions to the current depreciating effect of metallic degradation and failure in service in various engineering and industrial applications.

Cleophas A. Loto has over 60 research publications including reviews in top international journals and has consistently served as reviewer in respectable journals due to his in-depth knowledge and technical expertise. He has a doctor of technology (DTech) in Metallurgical and Materials Engineering (2014) from Tshwane University of Technology, Pretoria, South Africa, master's degree (MSc) in Metallurgical and Materials Engineering (2007) from University of Lagos, Lagos, Nigeria, and a bachelor of technology in Mechanical Engineering (2002) from Ladoke Akintola University of Technology, Oyo State, Nigeria.

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PUBLIC INTEREST STATEMENT

The economic impact and problems resulting from corrosion has drawn strong attention from scientists and engineers worldwide. Corrosion of mild steel in industrial environments is a major concern in chemical processing plants, oil and gas industry, manufacturing, automobile industry, marine operations, boiler plants, and power generation plants due to the considerable cost involved in the replacement of metallic parts in their various applications. The consequence often leads to plant shutdowns, breakdown of industrial equipment, reduced efficiency, industrial downtime, high maintenance cost due to replacement of damaged part, wastage of valuable resources, and expensive overdesign. Corrosion inhibition is of great practical importance, being extensively employed in curtailing wastage of engineering materials and minimizing costs of corrosion control. A great number of studies are being devoted to the subject of corrosion inhibitors. Identification of the functional groups in organic compounds responsible for corrosion inhibition is important in the development of organic corrosion inhibitors of mild steels.

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Statistical derivations through Analysis of variance analysis confirmed that the inhibitor concentration is the only variable responsible for the inhibition efficiency values. Adsorption of the compound obeyed the Langmuir isotherm model.

Subjects: Chemistry; Material Science; Corrosion-Materials Science

Keywords: adsorption; corrosion, mild steel; inhibitor; acid

1. Introduction

Carbon steel is one of the most important engineering material extensively applied in automotive, construction, consumer, marine, mining and chemical processing industries, and petrochemical plants for applications involving acids, alkalis, and chloride environments due to its low cost and ready availability. There are several grades of carbon steels, published, registered, and standardized worldwide with varying chemical and physical compositions. It provides material properties that are acceptable for many applications as such their corrosion is a fundamental academic and industrial concern. They suffer from pitting and general corrosion which result in them being continually re-placed after rapid severe deterioration. Corrosion represents a significant cost burden and major industrial setback being the largest cause of plant shutdown, equipment breakdown, and accidents in processing allied industries. Selection of materials of construction which are completely resistant to corrosion from corrosive fluids is possible, but the cost of such an approach is most often restric-tive (Corrosion in Process Industries, n.d.).

Corrosion inhibiting compounds are extensively applied industrially to minimize the deterioration rate of metallic alloys interacting with corrosive environments, however most corrosion inhibitors are costly and environmentally unfriendly (Ashassi-Sorkhabi, Majidi, & Seyyedi, 2004; El-Etre, 1998, 2003). Organic compounds have been evaluated to be effective corrosion inhibitors for ferrous alloys through the formation of a chelate on the metal surface. This involves electron transfer between the compound and the valence electrons on the steel surface resulting in covalent bonding adsorption process (Ajmal, Mideen, & Quraishi, 1994). Most common inhibiting organic compounds contain O, N, and/or S atoms (Fang & Li, 2002). Electrochemical interactions between their functional groups and the metal play an important role in corrosion inhibition due to the free electron pair they possess. The inhibitor structure consisting of adsorption sites in the molecule, the charge density, the mo-lecular size, adsorption mode, and the precipitation of metallic complexes has a strong influence on the efficiency of inhibitors (Obot & Obi-Egbedi, 2008; Obot, Obi-Egbedi, Umoren, & Ebenso, 2010; Soltani, Behpour, Ghoreishi, & Naeimi, 2010). Inhibitor efficiency is a product of environmental char-acteristics, the properties of the metal surface, and electrochemical potential at the boundary layer. A significant number of studies have been done on the corrosion inhibition of carbon steel in acidic media (Aljourani, Golozar, & Raeissi, 2010; Ghareba & Omanovic, 2010; Hosseini, Mertens, Ghorbani, & Arshadi, 2003; Moussa, El-Far, & El-Shafei, 2007; Raman & Labine, 1986; Singh & Quraishi, 2010; Singh, Quraishi, & Ebenso, 2011; Zucchi, Trabanelli, & Brunoro, 1992).

Previous research on thiocarbanilide and hexadecyl trimethyl ammonium bromide separately gave mixed results. Singh (1993) studied the effect of thiourea and its derivatives thiourea; allylthi-ourea; N,N′-diethylthiourea; N,N′-di-isopropylthiourea; phenylthiourea; thiocarbanilide; and symdio-tolylthiourea on cold-rolled mild steel in 1 M H_2SO_4 at 40°C. Results show that the derivatives accelerated corrosion reactions and H_2 pickup at higher concentrations. Al-Faiyz (2007) showed in his work that the inhibition efficiency of thiourea increases with the increase in temperature and thiourea concentration for repeatedly recrystallized microalloyed steel. The inhibition effect of N-(2-thiophenyl)-N/-phenyl thiourea on the corrosion of mild steel in H_2SO_4 and HCl acid was evaluated by Shetty, Shetty, and Nayak (2006). The thiourea derivative performed effectively with greater inhibi-tion efficiency in HCl than H_2SO_4. The combined admixture of thiourea and hexamethylenetetramine effectively inhibited the corrosion of N80 steel, forming strong bonds and stable films on the steel surface (Hu, Wang, Yu, Zou, & Wang, 2015). Loto, Loto, Joseph, and Olanrewaju (2016) studied the

corrosion inhibition effect of thiocarbanilide on high carbon steel in dilute H_2SO_4 and HCl acid. The compound effectively inhibited the steel with inhibition efficiencies above 70%.

The corrosion inhibition effect of hexadecyl trimethyl ammonium bromide on high carbon steel in H_2SO_4 acid was studied at temperatures 30–60°C through weight loss. Results showed that the compound effectively inhibited the steel obeying the Langmuir's adsorption isotherm (Osman, 1998). Langmuir–Blodgett monolayers of hexadecyl trimethyl ammonium bromide deposited onto carbon steels surface were investigated by Guo, Xing, Shan, Lu, and Xi (1994) through polarization resistance and cyclic voltammetry. The monolayers were observed to effectively inhibit the corrosion process in neutral and acidic solution. Inhibition mechanism was based on the blocking effect with the assistance of the charge effect in acidic solution. Sharma, Chawla, and Singh (2009) studied the inhibitive effect of cetyl trimethylammonium bromide on the corrosion of mild steel in H_2SO_4 acid at various temperatures through galvanostatic and potentiostatic techniques and scanning electron microscopy. The compound performed effectively with respect to concentration of the inhibiting compound. 4-hydroxy-3-methoxy-benzaldehyde was evaluated for its corrosion inhibition properties on aluminum in HCl. The compound acts as a good inhibitor with inhibition efficiency increasing with the increase in concentration of the compound (El-Etre, 2001). The corrosion inhibition effect of 4-hydroxy-3-methoxy-benzaldehyde and 3,4-dihydroxy-benzaldehyde in HCl was investigated with results confirming the synergistic effectiveness of the compound. Corrosion rate increased with the increase in concentration of the compound (Emregül & Hayvalı, 2004). This research aims to investigate the synergistic effect of the admixture of thiocarbanilide and hexadecyltrimethylammonium-bromide (HTH) on mild steel in dilute acid solutions of 1 M H_2SO_4 and 1 M HCl through weight loss analysis, potentiodynamic polarization test, and numerical analysis through Analysis of variance (ANOVA) and infrared spectroscopy.

2. Materials and methods

2.1. Material
Mild steel purchased from the Steel Works, Owode, Nigeria and analyzed at the Materials Characterization Laboratory, Department of Mechanical Engineering, Covenant University, Ota, Ogun State, Nigeria gave an average nominal percentage (%) composition as shown in Table 1. The steel has a cylindrical dimension of 16 mm diameter.

2.2. Inhibitor
Combined admixture of thiocarbanilide and HTH, (a solid white powdery compound) was individually obtained in synthesized form from SMM Instruments, South Africa and used in equal proportions and every concentration studied. Their structural formulas are shown in Figure 1, and the properties are given in Table 2.

HTH was prepared in molar concentrations of 2.11×10^{-6}, 4.22×10^{-6}, 6.33×10^{-6}, 8.44×10^{-6}, 1.05×10^{-5} and 1.27×10^{-5} Mol/L, respectively, per 200 mL of the acid solution.

Table 1. Percentage nominal composition of mild steel

Element symbol	C	Si	Mn	P	S	Cu	Ni	Al	Fe
% composition	0.401	0.169	0.440	0.005	0.012	0.080	0.008	0.025	98.86

Table 2. Properties of the HTH inhibiting compound

S/N	Compound	Molecular formula	Molar mass (gmol^{-1})
1	Thiocarbanilide	$C_{13}H_{12}N_2S$	228.31
2	Hexadecyltrimethylammoniumbromide	$C_{19}H_{42}BrN$	364.45

Figure 1. Chemical structure of (a) thiocarbanilide and (b) HTH.

(a) (b)
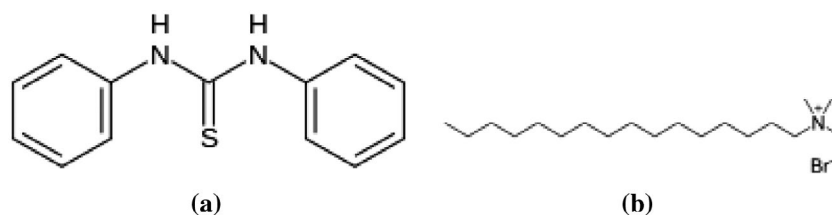
2.3. Acid test solution

About 1 M H_2SO_4 and HCl acid solution were prepared by dilution of an analytical grade of H_2SO_4 acid (98%) and HCl acid (37%) with distilled water and used as the corrosive test environment.

2.4. Preparation of mild steel samples

The mild steels were machined into 14 test samples with an average length of 5 mm and metallographically prepared with silicon carbide abrasive papers of 80, 120, 220, 800, and 1,000 grits before being polished with 6–1 μm diamond liquid, rinsed with distilled water and acetone, dried, and later stored in a dessicator for weight loss analysis and potentiodynamic polarization test in accordance with ASTM G1-03(2011).

2.5. Weight loss analysis

Weighed steel samples were individually immersed fully into 200 mL of the dilute acid media for 432 h at ambient temperature of 25°C. Each sample was removed from the solution at 24 h interval, rinsed with distilled water and acetone, dried, and reweighed according to ASTM G31-72(2004). Graphical illustrations of corrosion rate, $\curlyvee$ (η) and percentage inhibition efficiency (η) vs. exposure time *T* were plotted from the data obtained during the exposure hours. The corrosion rate ($\curlyvee$) calculation is defined as (Venkatesan, Anand, & Matheswaran, 2009):

$$\curlyvee = \left[\frac{87.6\tilde{\omega}}{DAT} \right] \tag{1}$$

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

Inhibition efficiency (η) was calculated from the relationship:

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

where $\tilde{\omega}_1$ and $\tilde{\omega}_2$ are the weight loss with and without specific concentrations of HTH. η was calculated at all HTH concentrations throughout the exposure period.

Surface coverage is determined from the mathematical relationship given below (Abbasova et al., 2013; Sethi, Chaturvedi, & Mathur, 2007):

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

where θ is the amount of HTH compound, adsorbed per gram of the mild steel. $\tilde{\omega}_1$ and $\tilde{\omega}_2$ are the weight loss of the mild steel coupon with and without predetermined concentrations of HTH in the acid solutions.

2.6. Potentiodynamic polarization technique

Potentiodynamic polarization test was performed with cylindrical mild steel electrodes mounted in acrylic resin with an unconcealed surface area of 154 mm². The steel electrode was prepared according to ASTM G59-97(2014). Studies were performed at 25°C ambient temperature with Digi-Ivy 2300

potentiostat and electrode cell containing 200 mL of the acid media, with and without HTH compound. Platinum 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). The corrosion current density (j_{corr}) and corrosion potential (E_{corr}) were calculated from the Tafel plots of potential vs. log current. The corrosion rate (Υ) and the percentage inhibition efficiency (η_2) were determined from Equation (4).

$$\Upsilon = \frac{0.00327 \times J_{corr} \times E_q}{D} \qquad (4)$$

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 (Ahmad, 2006; Choi, Nesic, & Ling, 2011).

The percentage inhibition efficiency (η_2) was calculated from corrosion rate values using the equation given below:

$$\eta_2 = 1 - \left[\frac{\Upsilon_2}{\Upsilon_1} \right] \times 100 \qquad (5)$$

where Υ_1 and Υ_2 are the corrosion rates with and without HTH inhibitor.

2.7. Infrared spectroscopy
The HTH inhibiting compound in H_2SO_4 and HCl acid was exposed to a range of infrared ray beams. The transmittance and reflectance of the infrared rays at different frequencies was translated into an IR absorption plot consisting of spectra peaks. The spectral pattern was analyzed and matched according to IR absorption table to identify the functional group responsible for the corrosion inhibition mechanism in the compound.

Figure 2. Polarization plot for mild steel in 1 M H_2SO_4 acid at 0–0.75% HTH.
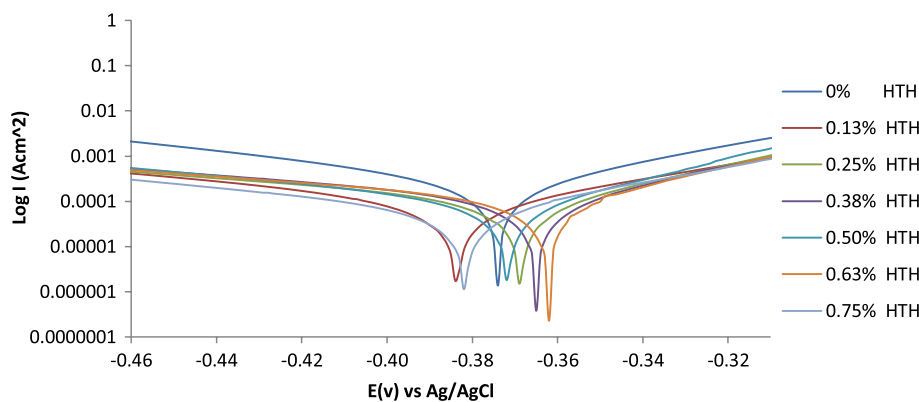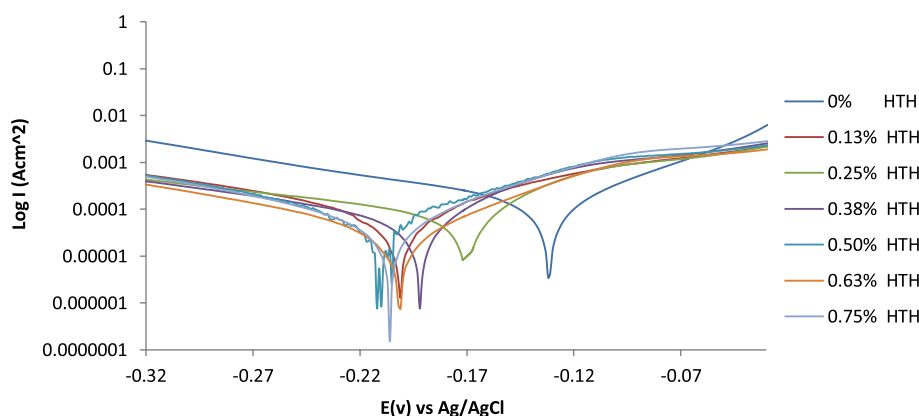

Figure 3. Polarization plot for mild steel in 1 M HCl acid at 0–0.75% HTH.

3. Result and discussion

3.1. Potentiodynamic polarization

The potentiodynamic polarization plots of HTH compound on the corrosion inhibition of the mild steel specimen in 1 M H_2SO_4 and HCl acids are presented in Figures 2 and 3. Tables 3 and 4 show the data obtained from the polarization scans. Observation of Table 3 shows remarkable difference in corrosion rate values between the inhibited and uninhibited steel specimens in 0% and 0.13–0.75% HTH in H_2SO_4 acid solution. At 0% HTH the mild steel oxidizes resulting in the formation of a porous oxide. Growth of the oxide continues leading to the formation of pores and channels within the oxide layer which further accelerates the corrosion. The presence of corrosive ions within the acid solution increases the corrosion rate mainly due to depassivation effect in iron dissolution. There is a layer of the mixture of corrosion products on the metal surface; this non-protective layer will form additional reaction sites (Chin & Nobe, 1972; Deyab, 2007; Macdonald, 2007; Wang, Shi, Hong, Kang, & Jepson, 2001). The corrosion rate reduced dramatically after 0% HTH and remained generally the same till 0.75% HTH. This is due to the electrochemical reactions of HTH within the solution which result in the formation of a passivating, adherent corrosion product that interferes with the access to the corrosive ions to the metal surface. Metallic corrosion is complex and non-homogeneous due to the presence of numerous anodic and cathodic reaction sites. Corrosion inhibiting compounds tends to interact with the sites, through retardation of the redox electrochemical process and/or inhibition of the diffusion of active corrosive ions from the acid solution to the steel. Increase in HTH concentration did not affect the corrosion rate values thus its inhibition efficiency is independent of the variation in inhibitor concentration. At 0.13% HTH concentration in H_2SO_4 acid solution, the inhibition efficiency is 80%, while at 0.75% HTH, the inhibition efficiency is 81%. Similar trend in values were obtained for HTH in HCl solution (Table 4).

Table 3. Potentiodynamic polarization results for mild steel in 1 M H_2SO_4 for 0–0.75% HTH									
Sample	Inhibitor concentration (%)	Corrosion rate (mm/y)	Inhibition efficiency (%)	Corrosion current (A)	Corrosion current density (A/cm²)	Corrosion potential (V)	Polarization resistance, R_p (Ω)	Cathodic Tafel slope (B_c)	Anodic Tafel slope, B_a (V/dec)
0	0	6.64	0	8.82E-04	5.73E-04	−0.351	29.14	−0.105	7.687
1	0.13	1.33	80	1.77E-04	1.15E-04	−0.397	145.40	−7.863	7.598
2	0.25	1.22	82	1.62E-04	1.05E-04	−0.379	91.05	−4.090	8.378
3	0.38	1.13	83	1.51E-04	9.78E-05	−0.348	109.50	−4.539	7.943
4	0.50	1.28	81	1.70E-04	1.11E-04	−0.382	71.30	−4.174	8.028
5	0.63	0.99	85	1.31E-04	8.51E-05	−0.374	103.60	−4.423	7.281
6	0.75	1.28	81	1.70E-04	1.11E-04	−0.346	150.80	−6.279	8.054

Table 4. Potentiodynamic polarization results for mild steel in 1 M HCl at for 0–0.75% HTH									
Sample	Inhibitor concentration (%)	Corrosion rate (mm/y)	Inhibition efficiency (%)	Corrosion current (A)	Corrosion current density (A/cm²)	Corrosion potential (V)	Polarization resistance, R_p (Ω)	Cathodic Tafel Slope (B_c)	Anodic Tafel Slope, B_a (V/dec)
0	0	2.94	0	3.91E-04	2.54E-04	−0.132	125.60	−6.258	17.070
1	0.13	0.68	77	9.02E-05	5.86E-05	−0.201	285.00	−7.536	9.320
2	0.25	0.59	80	7.89E-05	5.12E-05	−0.170	216.10	−5.227	6.094
3	0.38	0.66	78	8.72E-05	5.66E-05	−0.192	294.70	−6.603	8.953
4	0.50	0.70	76	9.29E-05	6.03E-05	−0.212	276.60	−8.198	13.510
5	0.63	0.34	88	4.54E-05	2.95E-05	−0.201	566.40	−8.340	15.200
6	0.75	0.54	82	7.12E-05	4.62E-05	−0.206	361.00	−8.855	13.510

The significant change in corrosion rate between inhibited and uninhibited mild steel samples corresponds with changes in corrosion current values. Observation of the results shows that HTH compound has similar electrochemical behavior in H_2SO_4 and HCl acid, respectively. HTH being an organic compound with heteroatoms protonates in the acid media forming cationic molecules which react with the corrosive ions of SO_4^{2-} and Cl^-, and consequentially build up a protective hydrophobic film of adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte (Gentil, 2003). The potentiodynamic polarization plots in Figures 2 and 3 show active–passive behavior under the inhibiting action of HTH compound. The corrosion potential generally transits to cathodic corrosion potentials suggesting that the mechanism of inhibition by HTH is through geometric blockage of the reaction sites whereby the main cathodic reactions involving hydrogen evolution and oxygen reduction reactions are suppressed through selective precipitation of insoluble compounds on cathodic areas to increase the surface impedance and limit the diffusion of reducible species. This promotes passivation of the steel through adsorption and hinders the deterioration of the steel as the inhibitor coverage decreases the number of surface metal atoms released into the solution. It explains why the inhibitor is independent of concentration, thus considerably very effective. The anodic Tafel slopes for H_2SO_4 and cathodic slopes for HCl were moderately affected by changes in HTH concentration suggesting that in part that the corrosion inhibition reactions were slightly influenced (Hosseini & Azimi, 2009). From Butler–Volmer relationship, Equation (6), (Brett & Brett, 1993):

$$I = I_{corr} \left\{ \exp\left[\frac{2.3(E - E_{oc})}{B_a} \right] - \exp\left[\frac{2.3(E_{oc} - E)}{B_c} \right] \right\} \tag{6}$$

where E_{oc} is the open circuit potential, I_{corr} is the corrosion current, B_a is the anodic Tafel slope B_c is the cathodic Tafel slope. B_a and B_c measures the symmetry of the activation barrier for anodic and cathodic reaction. The ratio of cathodic and anodic reaction constants does not change significantly. It shows that the protective film has similar effect on the anodic and cathodic reaction. It will not only block the cathodic reaction sites but also the anodic reaction. This proves the blocking effect as a reason for the decrease in the corrosion current.

The change in metal/solution interface from active deterioration to the passive state is due generally to the adsorption of HTH molecules on the metal surface, creating a non-porous barrier (Chao, Lin, & Macdonald, 1981). Adsorption occurs through electrostatic attraction between ionic charges or dipoles of the adsorbed HTH cations and the ionized valence atoms on the metal surface (Bockris & Swinkels, 1964; Intropor, 1962). The pi-electrons of HTH functional groups possibly overlap with the vacant d-orbitals of the metal surface resulting in a strong covalent bond. The maximum change in corrosion potential in H_2SO_4 is 46 mV in the cathodic direction while in HCl it is 80 mV in the cathodic direction, thus HTH is a mixed type inhibitor in H_2SO_4 acids with dominant control over the cathodic reactions however HTH also actively inhibits the anodic reactions occurring on the metal surface. In HCl acid HTH is a cathodic type inhibitor (Şahin, Bilgiç, & Yılmaz, 2002; Susai, Mary, Noreen, & Ramaraj, 2002).

3.2. Weight loss measurements

Data obtained from weight loss analysis for weight loss ($\tilde{\omega}$), corrosion rate (γ) and percentage inhibition efficiency (η) in H_2SO_4 and HCl acids are shown in Tables 5 and 6. Figures 4(a) and (b) and 5(a) and (b) show the plot of corrosion rate and percentage inhibition efficiency against immersion time in the acid media. The data from both acid solutions are generally the same further proving that similar electrochemical reactions occurred. The presence of HTH suppressed the redox electrochemical process responsible for corrosion attack. From the previous discussion on potentiodynamic polarization, the adsorption of HTH cations is through selective precipitation on the reactive sites on the mild steel; as a result the release of metal cations into the solution through the action of sulfate and chloride anions was effectively inhibited. This explanation is confirmed from the significant difference in corrosion rate between the HTH inhibited and uninhibited metal samples (Tables 5 and 6). The corrosion rate is slightly higher in H_2SO_4 than HCl acid due to its ability to completely ionize in the

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solution releasing two protons (Equations 7 and 8) that strongly react with the steel surface compared to HCl which releases one proton (Equation 8).

$$H_2SO_4 \longrightarrow HSO_4^- + H^+ \tag{7}$$

$$HSO_4^- \longrightarrow SO_4^{2-} + H^+ \tag{8}$$

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^- \tag{9}$$

HTH inhibitor has higher inhibition efficiency in H_2SO_4 acid despite the high dissociation constant of the acid. This can be explained on the basis that in H_2SO_4 HTH protonates strongly allowing more molecules to release electrons, the phenomenon increases the reactivity of the compound enabling strong interaction with the steel surface. As observed in polarization study, the corrosion rate in H_2SO_4 and HCl acid remained generally the same at all HTH concentrations.

Due to the large molecular weight of the cetrimonium bromide component of HTH ($C_{16}H_{33}^-N^+(CH_3)_3Br^-$), the compound easily attached itself to the mild steel through intermolecular attraction. The compound consists of hydrophilic and hydrophobic parts. The hydrophilic part of the compound $^+N(CH_3)_3$ enhances its solubility in the solution, being charge-polarized as positively charged polyatomic ions of the structure NR_4^+, R being an alkyl group or an aryl group are capable of hydrogen bonding. This facilitates adsorption to the steel while the main hydrophobic part (C_6H_{33}) enables substitutional adsorption mechanism. These attributes allow chemical interaction with the steel at steel/solution interface through covalent bonding resulting from electrostatic attraction between the nitrogen cations and steel surface due to the specific adsorption of bromide ion onto the steel causing a negatively charged steel surface (El Maghraby & Soror, 2010; Luo, Guan, & Han, 1998). The thiocarbanilide part of the mixture contains mainly multiple bonds in addition to heteroatoms within the molecules that are strongly polar, offering an electron-rich reaction center that facilitates adsorption on the metal surface (Gad & Tamous, 1990; Quaternary Ammonium Cation, n.d.). Adsorption occurs on the cathodic and anodic sites through the π-electrons of structural rings and the lone pair of electrons of nitrogen and sulfur, atoms, which decreases anodic dissolution of the steel. Due to their inherent hydrophilic protonated amino and imino groups they can firmly adsorb on the negatively charged steel surface, while their hydrophobic substituent orientates the inhibitor during adsorption to form a polymolecular barrier layer that reliably screens the metal from the corrosive medium by means of their strong affinity to metal.

3.3. Adsorption isotherm

The mechanism of adsorption of HTH compound on mild steel is a surface phenomenon through which HTH cations diffuse towards the surface of the steel and adsorb through intermolecular or electrostatic/covalent adsorption at specific temperature. The ionization potential, metal surface properties, electronic behavior, extent of adsorption of ions present, and the electrochemical potential at metal/solution-interface are responsible for the mechanism and type of adsorption. The adsorption characteristics of HTH compound was studied to further understand the mechanism of interaction between the compound and mild steel (Allen, Mckay, & Porter, 2004; Limousin et al., 2007; Tosun & Ergun, 2006). Langmuir isotherm model amongst tested models had the best fit for the results retrieved for HTH in H_2SO_4 and HCl acid, respectively.

Generally isotherms are of the form:

$$kc = g(\theta, x) \exp(-f\theta) \tag{10}$$

where $g(\theta, x)$ is the configurational factor subject to the physical model and assumptions involved in the emanation of the isotherms.

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The general form of the Langmuir equation is shown below:

$$\left[\frac{\theta}{1-\theta}\right] = K_{ads}C \tag{11}$$

rearranging Equation (11)

$$\theta = \left[\frac{K_{ads}C}{1 + K_{ads}C}\right] \tag{12}$$

where θ is the value of surface coverage on the metal alloy, C is HTH concentration in the acid solution, and K_{ads} is the equilibrium constant of the adsorption process. The plots of $\frac{C}{\theta}$ vs. the HTH concentration C were linear (Figure 6(a) and (b)) confirming Langmuir adsorption.

According to Langmuir, HTH cations occupy specific adsorption sites at the metal/ion solution interface resulting in the slight deviation of the slope from unity in Figure 6(a) and (b) (Abiola, 2006; Bockris, 1970). Adsorption of organic molecules is a substitutional reaction whereby molecules of water are removed from the steel surface through the hydrophobic component of the compound's functional group. The amount of steel passed into the electrolyte is related to the extent of coverage of HTH inhibitor over the mild steel surface. It can be assumed that the metal surface is covered with water dipoles, thus for adsorption of the cations of the organic compound to occur the water dipoles must be replaced by the cation from the electrochemical reaction as follows (Damaskin & Frumkin, 1971; Susuki, 1990):

$$nH_2O_{electrode} + Organic_{solution} \iff Organic_{electrode} + nH_2O_{solution} \tag{13}$$

Table 5. Data for mild steel in 1 M H_2SO_4 at specific concentrations of HTH from weight loss						
Samples	Weight loss (g)	Corrosion rate (mm/y)	HTH inhibition efficiency (%)	HTH concentration (%)	HTH concentration (molarity)	Surface coverage (θ)
A	6.080	0.0223	0	0	0	0
B	0.803	0.0029	86.81	0.13	2.11E-06	0.868
C	0.737	0.0027	87.89	0.25	4.22E-06	0.773
D	0.763	0.0028	87.47	0.38	6.33E-06	0.875
E	0.917	0.0034	84.93	0.50	8.44E-06	0.774
F	0.960	0.0035	84.23	0.63	1.05E-05	0.842
G	0.863	0.0032	85.82	0.75	1.27E-05	0.858

Table 6. Data for mild steel in 1 M HCl at specific concentrations of HTH from weight loss						
Samples	Weight loss (g)	Corrosion rate (mm/y)	HTH inhibition efficiency (%)	HTH concentration (%)	HTH concentration (molarity)	Surface coverage (θ)
A	1.620	0.0059	0	0	0	0
B	0.318	0.0012	80.36	0.13	2.11E-06	0.804
C	0.326	0.0012	79.88	0.25	4.22E-06	0.799
D	0.339	0.0012	79.09	0.38	6.33E-06	0.791
E	0.380	0.0014	76.53	0.50	8.44E-06	0.765
F	0.296	0.0011	81.74	0.63	1.05E-05	0.817
G	0.356	0.0013	78.00	0.75	1.27E-05	0.780

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Figure 4. Plot of (a) corrosion rate vs. exposure time and (b) inhibition efficiency vs. exposure time in 1 M H_2SO_4 at 0–0.75% HTH.
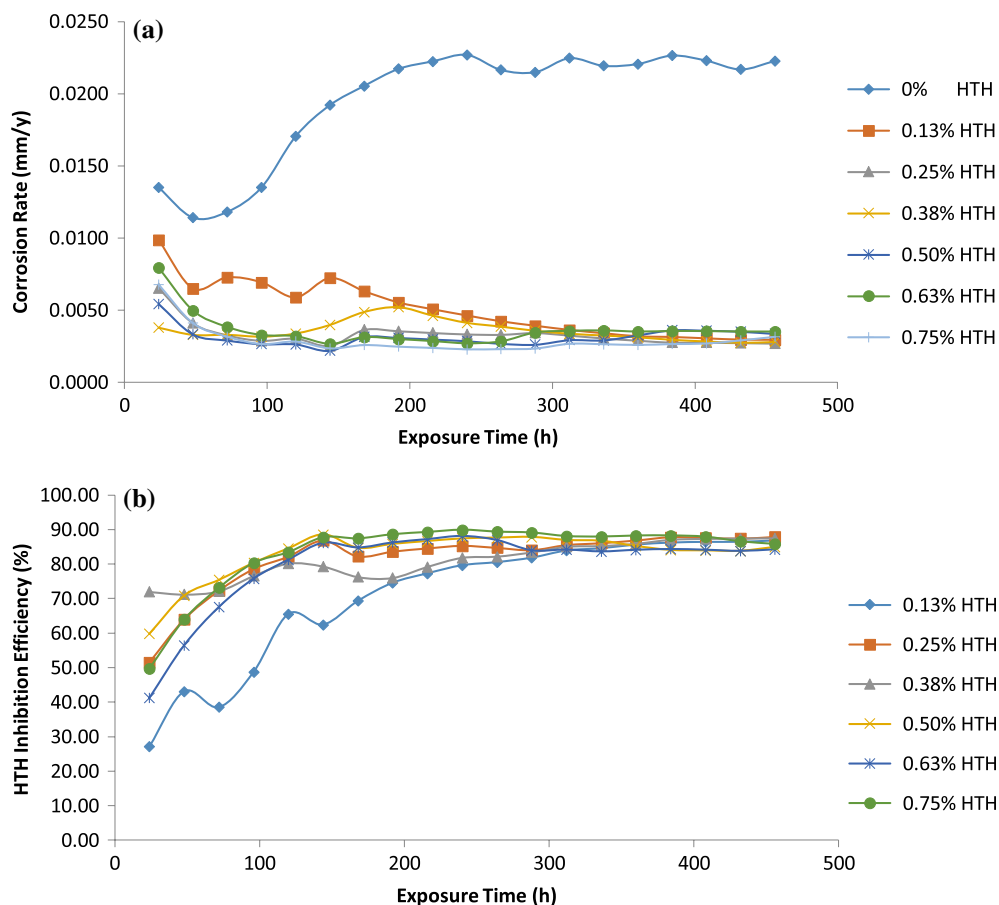
Increase in HTH concentration causes changes in the energy of interaction with water molecules as HTH molecules adsorb on the steel with increase in concentration of HTH molecules.

### 3.4. Thermodynamics of the corrosion process

From previous discussion on Langmuir adsorption isotherm, the thermodynamics of the substitutional process depends on the amount of water molecules (*n*) removed by HTH inhibitor. Calculated results of Gibbs free energy (ΔG°_{ads}) for the adsorption process as shown in Tables 7 and 8 can be evaluated from Equation (14) given below:

$$\Delta G_{ads} = -2.303\,RT \log\left[55.5\,K_{ads}\right] \tag{14}$$

Table 7. Data for Gibbs free energy, surface coverage and equilibrium constant of adsorption for 0–7.5% HTH in 1 M H_2SO_4

Samples	HTH concentration (%)	Surface coverage (θ)	Equilibrium constant of adsorption (K)	Gibbs free energy, ΔG (kJ mol⁻¹)
A	0	0	0	0
B	0.13	0.868	3115184.6	−47.00
C	0.25	0.773	806177.8	−43.65
D	0.38	0.875	1101928.0	−44.43
E	0.50	0.774	406509.0	−41.96
F	0.63	0.842	505908.9	−42.50
G	0.75	0.858	477550.7	−42.36

Figure 5. Plot of (a) corrosion rate vs. exposure time and (b) inhibition efficiency vs. exposure time in 1 M HCl at 0–0.75% HTH.
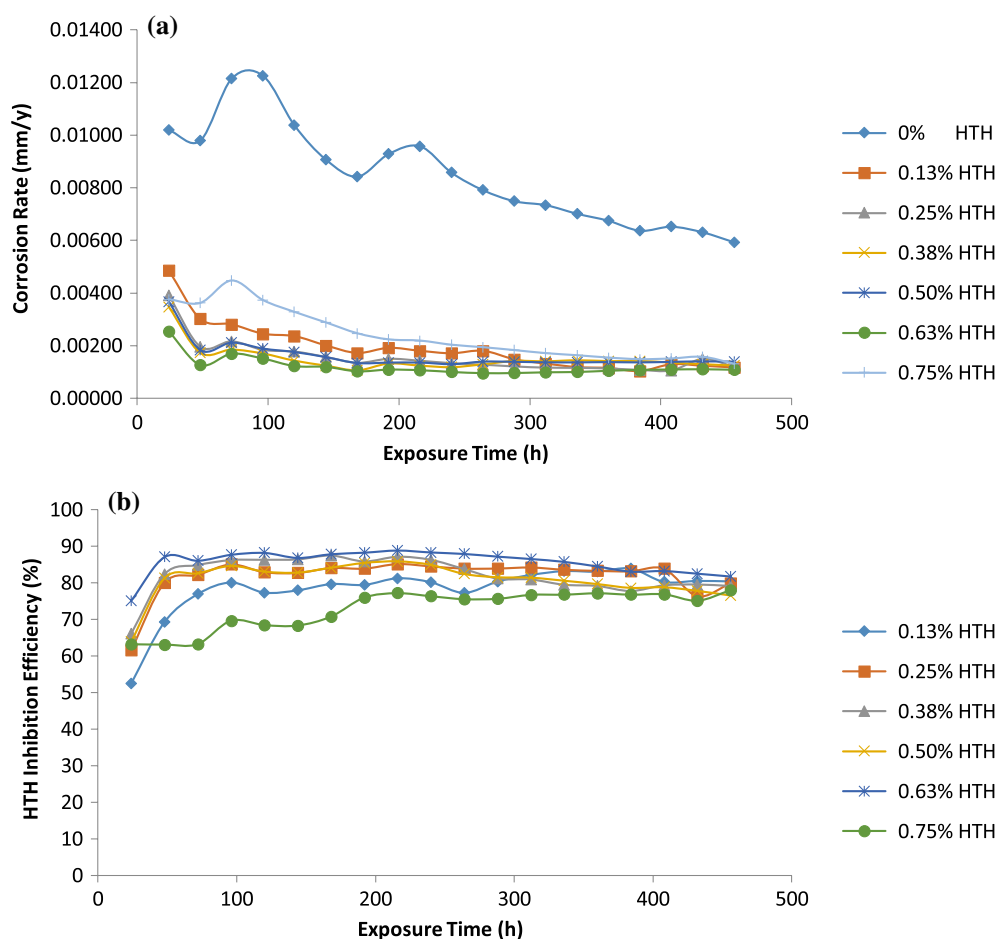
where 55.5 is the molar concentration of water in the solution, R is the universal gas constant, T is the absolute temperature, and K_{ads} is the equilibrium constant of adsorption. K_{ads} is related to surface coverage (θ) by the following equation:

$$K_{ads}C = \left[\frac{\theta}{1 - \theta} \right] \tag{15}$$

The non-homogeneous nature (presence of flaws, impurities, cracks, and vacancies) of the steel surface is responsible for the changes in ΔG°_{ads} of HTH as the surface coverage value changes

Samples	HTH concentration (%)	Surface coverage (θ)	Equilibrium constant of adsorption (k)	Gibbs free energy, ΔG (kJ mol^{-1})
Table 8. Data for Gibbs free energy, surface coverage and equilibrium constant of adsorption for 0–7.5% HTH in 1 M HCl				
A	0	0	0	0
B	0.13	0.804	1940478.3	−45.83
C	0.25	0.799	941343.0	−44.04
D	0.38	0.791	597871.9	−42.91
E	0.50	0.765	386519.1	−41.83
F	0.63	0.817	424679.2	−42.07
G	0.75	0.780	280265.6	−41.04

Figure 6. Plot of $\frac{C}{\theta}$ vs. HTH concentration (*C*) (a) in 1 M H$_2$SO$_4$ and (b) in 1 M HCl.
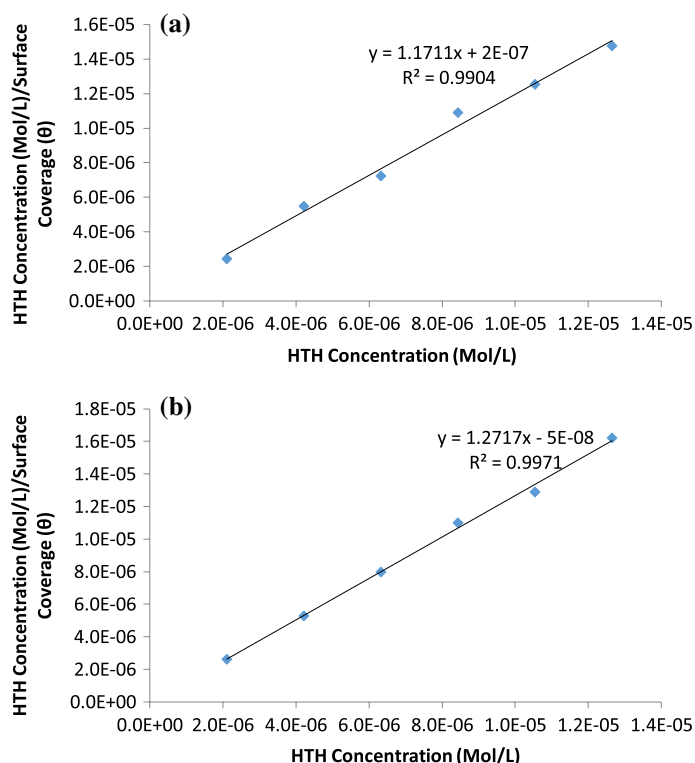
(Damaskin & Frumkin, 1971; Li, Deng, Fu, & Mu, 2009; Lowmunkhong, Ungthararak, & Sutthivaiyakit, 2010). This relationship is responsible for the differences in adsorption energies presented in the tables. The negative values of ΔG°_{ads} shows the adsorption is spontaneous. Values of ΔG°_{ads} around −20 kJ mol^{-1} depicts physisorption adsorption mechanism, while ΔG°_{ads} 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 ΔG°_{ads} value in H$_2$SO$_4$ is −47.00 kJ mol^{-1} at 0.13% HTH while the lowest is −41.96 kJ mol^{-1} at 0.50% HTH. In HCl the highest ΔG°_{ads} value is −45.83 kJ mol^{-1} at 0.13% while the lowest is 41.04 kJ mol^{-1} at 0.75% HTH. The values of ΔG°_{ads} for HTH adsorption on mild steel in H$_2$SO$_4$ and HCl acid solution show chemisorption interaction (Benali, Benmehdi, Hasnaoui, Selles, & Salghi, 2013).

Figure 7. IR spectra of HTH inhibiting compound in H$_2$SO$_4$ acid before and after mild steel corrosion.
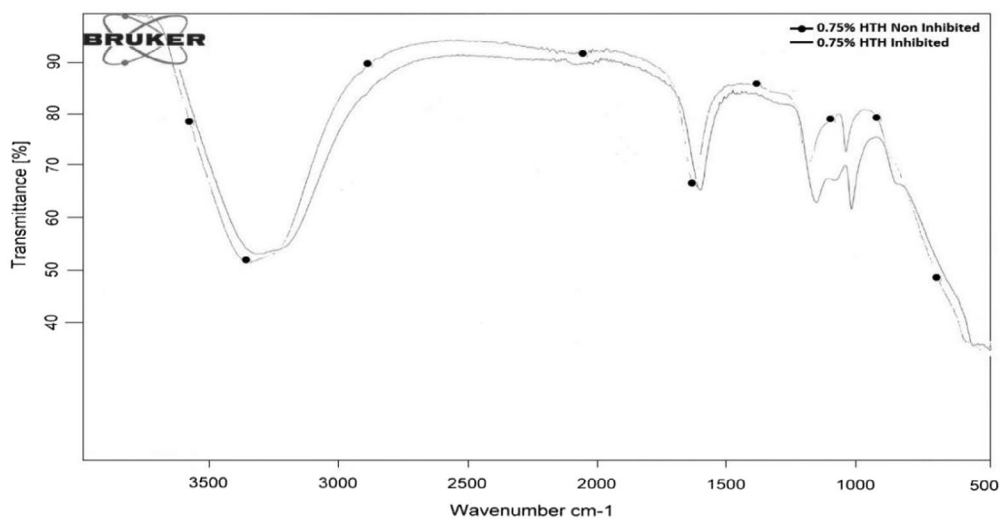
Figure 8. IR spectra of HTH inhibiting compound in HCl acid before and after mild steel corrosion.
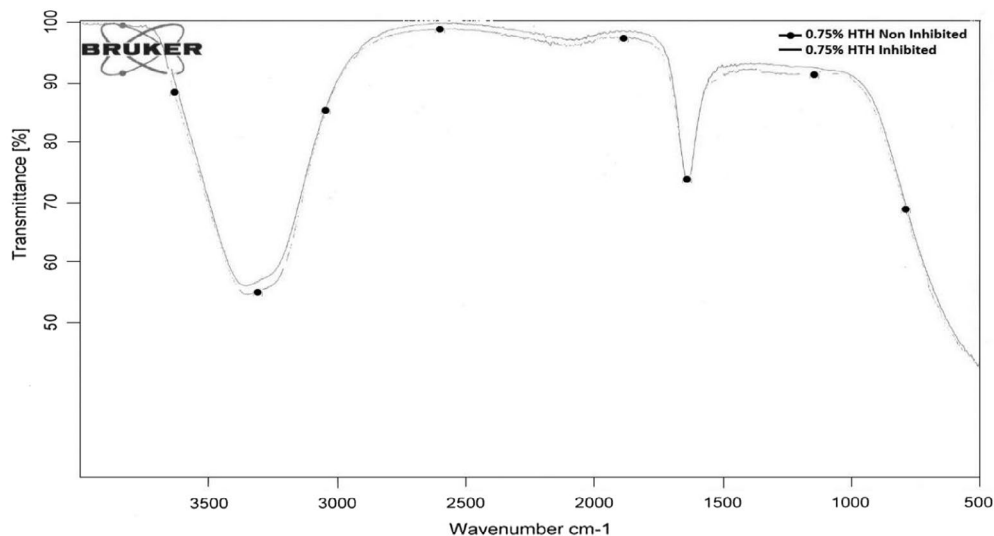
3.5. IR spectroscopy

The identification, properties, and nature of adsorption of HTH compound on the corrosion inhibition of mild steel in the dilute acid media was studied through IR spectroscopy. Figure 7 shows the spectra peaks for HTH compound in H_2SO_4 acid before and after the corrosion test (without and with the presence of mild steel sample) superimposed on each other, while Figure 8 shows the spectra peaks for HTH inhibiting compound in HCl acid solution before and after the corrosion test superimposed on each other. The characteristic IR absorptions are presented in Table 9. Observation and comparison the of the spectra peaks before corrosion test (Figure 7) with Table 9 show peak values at 3,355.12, 1,635.38, 1,190.73, and 1,049.97 cm^{-1} which correspond with the presence of N–H stretch primary and secondary amines and amides, N–H bend primary amines, C–H wag alkyl halides, and C–N stretch aliphatic amines functional groups. The comparison of spectra peaks after corrosion test (Figure 7) with Table 9 shows similar functional groups at slightly different peak values of 3,345.63, 1,631.37, 1,182.56, 1,184.56, and 1,049.03 cm^{-1}.

The differences in spectra peaks between the HTH compounds (before and after the corrosion test) are shown in the superimposed image in Figure 7. The slight decrease in transmittance indicators for the figure shows that the functional groups earlier mentioned were actively involved in the inhibition of the steel by adsorption through chemisorption mechanism. The groups are responsible for the formation of stable complexes between the iron constituents and functional groups present in the HTH compound forming covalent or coordinate bonds between the anionic components of HTH and vacant Fe d-orbital. The metal-inhibitor bond usually leads to suppression of the redox electrochemical process through inhibition of the electrolytic transport and diffusion of corrosive ions responsible for material degradation (Ngobiri et al., 2015). The corrosion retarding mechanism dominates at all HTH concentrations due to strong adsorption resulting from the donation of lone pair of electrons from oxygen and nitrogen to vacant d orbital of the metal. The spectra peaks of

Table 9. Table of characteristic IR absorptions (extracted)		
Wavenumber (cm^{-1})	**Bond**	**Functional group**
3,400–3,250 (m)	N–H stretch	Primary, secondary amines, amides
1,650–1,580 (m)	N–H bend	Primary amines
1,300–1,150 (m)	C–H wag (–CH$_2$X)	Alkyl halides
1,250–1,020 (m)	C–N stretch	Aliphatic amines
850–550 (m)	C–Cl stretch	Alkyl halides

3,347.61 and 1,636.90 cm^{-1} for HTH compound before and after the corrosion test in HCl acid (Figure 8) consists of N–H stretch, primary secondary amines, amides and N–H bend, primary amine functional groups responsible for corrosion inhibition by HTH, however the superimposed image shows that the spectral diagrams are closely similar. It is suggested that HTH essentially inhibited the mild steel corrosion through film formation by blocking the active sites on the surface but not necessarily changing the mechanism of the corrosion process.

3.6. Statistical analysis

Numerical analysis through ANOVA at a confidence level of 95% (significance level of $\alpha = 0.05$) was used to determine the statistical significance of HTH concentration and time of exposure on HTH inhibition efficiency results according to Equations (16 and 17). Results (Tables 10 and 11) from ANOVA showed that HTH concentration only is statistically relevant on HTH inhibition efficiency values with F-values of 25.92 in H_2SO_4 solution and 5.38 in HCl solution. The values are significantly higher than the significance factor (significance F) in Tables 10 and 11, proving that they are significant at the level of probability employed. The statistical influence of HTH concentration is 266.3% in H_2SO_4. It shows that HTH concentration had a strong electrochemical influence on the corrosion inhibition behavior of HTH in contrast to the exposure time which is insignificant. For HCl acid the same phenomenon is observed with the statistical influence of HTH concentration at 79.09%.

The Sum of squares among columns (exposure time) was obtained with Equation (16).

$$SS_c = \frac{\sum T_c^2}{nr} - \frac{T^2}{N} \tag{16}$$

Table 10. ANOVA for HTH inhibition efficiency in 1 M H_2SO_4 (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	*F* (%)
						Significance *F*	
Among columns	Inhibitor concentration	51,796.22	5	10,359.24	25.92	2.53	266.295
Among rows	Exposure time	−44,335.40	6	−7,389.23	−18.49	2.42	−227.937
Residual	Residual	11,989.87	30	399.66			
Total	Total	19,450.69	41				

Table 11. ANOVA for HTH 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	*F* (%)
						Significance *F*	
Among columns	Inhibitor concentration	45,626.86	5	9,125.37	5.38	2.53	79.09
Among rows	Exposure time	−38,830.06	6	−6,471.68	−3.81	2.42	−67.31
Residual	Residual	50,893.46	30	1,696.45			
Total	Total	57,690.26	41				

Sum of squares among rows (inhibitor concentration)

$$SS_r = \frac{\sum T_r^2}{nc} - \frac{T^2}{N} \qquad (17)$$

Total sum of squares

$$SS_{Total} = \sum x^2 - \frac{T^2}{N} \qquad (18)$$

4. Conclusion

The electrochemical performance of HTH on mild steel corrosion inhibition showed the organic admixture to be very effective. Calculated results showed the compound to be mixed type in H_2SO_4 with dominant cathodic inhibiting properties and cathodic type in HCl acid. The inhibition efficiency remained generally the same at all HTH concentrations studied due to the strong action of the functional groups and heteroatoms of the admixture which synergistically enabled and maintained a strong protective film over the steel surface. Evaluation of the thermodynamic properties of HTH confirms chemisorption mechanism on the mild steel surface and the adsorption obeyed the Langmuir adsorption isotherms. Infrared spectra images confirmed the presence of functional groups of the organic compound responsible for corrosion inhibition. Statistical derivations showed the overwhelming influence and statistical significance of inhibitor concentration only on HTH inhibition efficiency values in contrast to exposure time.

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