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Application of Metronidazole Drug as Corrosion Inhibitor of Mild Steel in Hydrochloric Acid Medium

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Abstract

Application of metronidazole drug as corrosion inhibitor of mild steel in 1M hydrochloric acid medium is presented. Gravimetric, potentiodynamic polarization, electrochemical impedance spectroscopy and thermometric techniques were used for the study. Molecular species and functional groups of the metronidazole drug were analyzed by gas chromatography mass spectrophotometer (GCMS) and Fourier transform infrared (FTIR) spectroscopy respectively. Based on response surface methodology, the inhibition efficiency was optimized by central composite design of Design Expert Software Version 12. Scanning electron microscopic analysis was used to reveal texture of the mild steel surface. Analyses of the results showed that metronidazole drug contains heterocyclic compounds and heteroatoms of nitrogen and oxygen, which makes it suitable for the corrosion inhibition function. Major constituents of metronidazole drug include metronidazole, 9-octadecenoic acid and methyl ester. The leading functional groups include C=O stretch, ≡C-H stretch, C≡N stretch and N=O stretch. Adsorption of molecules of the inhibitor on mild steel surface was spontaneous and of physical adsorption mechanism. At temperature of 313K, attractive, lateral interaction, and size parameters were obtained as 2.3838, -2.4605 and 0.5721 respectively. Positive/negative signs of these values indicate that: molecular species of the inhibitor were attracted to the mild steel surface; repulsion exists in the adsorption layer; and the adsorbed species of the inhibitor were bulky. A quadratic model adequately described the inhibition efficiency of metronidazole, with optimum efficiency of 91.48%. Electrochemical studies revealed metronidazole as mixed-type inhibitor capable of controlling cathodic and anodic corrosion. For the thermometric technique, maximum inhibition efficiency of 93.27% and corresponding reaction number of 0.0297 ^{0}C/min. were obtained at 0.8 g/L inhibitor concentration. Surface texture of the mild steel samples confirmed that metronidazole is an effective corrosion inhibitor of mild steel in hydrochloric medium.

Keywords: Metronidazole, Corrosion, Mild Steel, Hydrochloric acid

1. Introduction

Mild steel is well-recognized as a medium carbon steel (Uppal and Bhatia, 2009; Aggarwal, 2010). It is widely applied in engineering and allied industries. Its usefulness is challenged by corrosion. Corrosion causes enormous destruction of metals with corresponding economic and environmental consequences (Trethewey and Chamberlain, 1995; Shreir et al, 2000; Taleb and Mohamed, 2011). In view of these, several steps are taken by researchers and industrialists to mitigate effects of corrosion on mild steel and allied metals (Teleb and Mohamed, 2011; Uwah et al, 2013). Industrial corrosion mitigation measures include pickling, cleaning and descaling operations. Of these three, pickling has been seen as the most effective technique. It uses aggressive solution (such as HCl) to dissolve oxide formation and other related materials on metal surface. Corrosion inhibition additives are often added to the pickling solution in order to prevent any form of side effect. Practice of using inhibitors has proven to be the cheapest and environmentally benign method for corrosion control in corrosive environment (Chigondo and Chigondo, 2010;

Umoren and Solomon, 2014; Kamal and Sethuraman, 2012; Okafor et al, 2008; Singh et al, 2010; Loto, 2017; Raja and Sethuraman, 2008; Loto et al, 2011; Loto et al, 2014). A small concentration of inhibitor can effectively reduce corrosion rate of metal (Znini et al, 2012; Odewunmi et al, 2015; Omotioma and Onukwuli, 2016). It creates protective barrier that prevents metal deterioration (Anadebe et al, 2018). Vast synthetic substances have been investigated as potential corrosion inhibitors (Prathibha et al, 2012; Qiang et al, 2018). It has been established that most organic molecules containing heteroatoms are highly efficient in inhibiting corrosion (Buchweishaija, 2009; Omotioma and Onukwuli, 2016; Anadebe et al, 2018).

Despite the significance of inhibition efficiency of synthetic substances, most of them are expensive, carcinogenic and non-biodegradable (Al-Sawaad, 2010; Kang *et al*, 2012). Based on these deficiencies, efforts are geared towards deployment of environmentally friendly, effective and readily available corrosion inhibitors. Currently, researchers' interest is on identification and / or development of green corrosion inhibitors (Rajeswari et al, 2014; Hamdani et al, 2015). In this regard, possible candidates are plant extracts and pharmaceutical drugs. However, use of plant extracts is bedeviled with some shortcomings. First, recipes for plant extracts of proven safety data are yet to be developed. Second, plant extracts' composition is location-dependent (Ojezele and Agunbiade, 2013); thus hampering their universal application. Pharmaceutical drugs on the other hand, are already developed recipes that have been subjected to well-controlled clinical pharmaceutical research and evaluation, following international approved clinical trial protocols; and as such are readily available in the shelves of pharmacy shops for purchase and immediate use. Use of pharmaceutical drugs as corrosion inhibitors will as well mitigate incidences of expired drugs, thus widening their range of useful applications. Previous investigations on use of pharmaceutical drugs as inhibitors had been mainly on antibacterial and anti-fungal drugs (Golestani et al, 2014). There is need to investigate antacid and antibiotic drugs such as metronidazole as potential inhibitors.

Obot et al (2013) examined corrosion inhibition of mild steel in 0.5 M HCl using metronidazole, but use of thermometric technique that determines the relationship between reaction number and inhibition efficiency was ignored. Also, application of metronidazole in 1M acid solution (typical of pickling medium) was not studied. Although, Hamzah (2020) investigated corrosion inhibition of mild steel in 1M HCl using metronidazole drug, thermometric method of analyzing the corrosion process was not reported. Also, lateral interaction, attractive and size parameters of the adsorption isotherms that explain physical mechanism of the corrosion inhibition process were not reported in both studies. Furthermore, mathematical model that relates inhibition efficiency of metronidazole with corrosion inhibition factors was not generated. Thus, this study is intended to investigate corrosion control of mild steel in 1M solution of HCl using metronidazole drug. This is to obtain and establish comprehensive adsorption parameters, relationship between reaction number and inhibition efficiency, optimum inhibition parameters, and mathematical model of the inhibition efficiency.

2.0 Materials and Method

2.1 Materials and Equipment

Materials/reagents used in this work include mild steel (coupon), distilled water, HCl (acid medium) and metronidazole drug (inhibitor). The chemicals used were of analytical grades. Equipment employed in the study were Fourier transform infrared spectrophotometer, gas chromatography-mass spectrometer, potentiostat/galvanostat 263 electrochemical system workstation, and scanning electron microscopy.

2.2 Preparation of the Inhibitor Concentrations

Metronidazole drug used as corrosion inhibitor was purchased from Uche Phamacy, Old UNTH Road, Enugu. 10g of metronidazole drug was dissolved in 1 L HCl solution. From the stock solution (10 g/L), inhibitor test solutions of 0.2, 0.4, 0.6, 0.8 and 1.0 g/L concentrations were prepared.

2.3 Metals Preparation

The mild steel with composition of Mn (0.13%), P (0.22%), Si (0.05%), S (0.12%), C (0.24%), Cr (0.02%), Ni (0.07), and Fe (99.15 %) was cut into coupons (4cm x 3cm x 0.1cm). The coupons were cleaned, polished, degreased, washed and dried.

2.4 Characterization of the Inhibitor

2.4.1 GC MS analysis of the inhibitor

Metronidazole drug was analyzed using by chromatography-mass spectrophotometer (Agt. Tech. model 7890A and 5977B MSD). The method used is similar to that of El Ouariachi et al (2010) and Rosaline-Vimela et al (2012). The gas chromatography-mass spectrophotometer combined the features of gas chromatography (GC) and mass spectrometry (MS) to identify different substances within a test sample of the inhibitor. In the GC, the metronidazole drug was separated into individual substances when heated. The heated substances were carried through a column with an inert gas. As the separated substances emerged from the column opening, they flew into the MS. The MS identified the compounds of the inhibitor by the mass of the analyte molecule.

2.4.2 Determination of the functional groups of the inhibitor by FTIR analysis

Fourier transform infrared spec. (Cary 630, Agt. Tech. USA) was used for the determination of the functional groups of the inhibitor. The FTIR spectrophotometer collected high spectral resolution data over a wide spectra range. Fourier transform (a mathematical process) converted the raw data into actual spectrum, where appropriate functional groups were obtained (Onukwuli and Omotioma, 2016).

2.5 Gravimetric Technique

2.5.1 Consideration of one factor at-a-time

On the basis of one factor at-a-time, the gravimetric technique was carried out at different inhibitor concentration, temperatures and time. Loss in weight of mild steel was determined in the absence and presence of the inhibitor in the acid medium following the method employed by Onukwuli and Omotioma (2016) and Onukwuli and Omotioma (2019). So, weight loss (Δw), corrosion rate (CR), inhibition efficiency (IE) and degree of surface coverage (ϴ) were evaluated using Equations (1), (2), (3) and (4) respectively (Onukwuli and Omotioma, 2016; Onukwuli and Omotioma, 2019).

$$\Delta w = w_i - w_f \tag{1}$$

$$CR = \frac{w_i - w_f}{At} \tag{2}$$

$$IE\% = \frac{\omega_0 - \omega_1}{\omega_0} * 100 \tag{3}$$

$$\theta = \frac{\omega_0 - \omega_1}{\omega_0} \tag{4}$$

where initial and final weight of mild steel were denoted with w_i and w_f respectively; the weight loss values in presence and absence of inhibitor were denoted with ω_1 and ω_0 respectively. A is the mild steel's area, and t stands for immersion time.

2.5.2 Adsorption isotherms consideration

Values of ϴ (degree of surface coverage) were used to test Langmuir, Frumkin, Temkin and Flory-Huggins adsorption isotherms.

1. Langmuir isotherm

Langmuir isotherm was employed as expressed by previous works (Li and Deng, 2012; Patel et al, 2013; Onukwuli and Omotioma, 2019):

$$log\frac{C}{\theta} = \log C - logK \quad (5)$$

where C stands for inhibitor conc., while K is the equilibrium constant.

2. Frumkin isotherm

Frumkin adsorption isotherm as used by (Nwabanne and Okafor, 2011) was adopted:

$$\log\left((C) * \left(\frac{\theta}{1-\theta}\right)\right) = 2.303logK + 2\alpha\theta \quad (6)$$

where α stands for lateral interaction term.

3. Temkin isotherm

Temkin isotherm as expressed by (Nwabanne and Okafor, 2011) was employed:

$$\theta = -\frac{2.303\,logK}{2a} - \frac{2.303\,logC}{2a} \quad (7)$$

where 'a' is the attractive parameter, while C is the inhibitor's concentration.

4. Flory-Huggins isotherm

Flory-Huggins model as expressed by (Nwabanne and Okafor, 2011; Alinnor and Ejikeme, 2012) was used:

$$\log\left(\frac{\theta}{C}\right) = \log K + xlog(1-\theta) \quad (8)$$

where x stands for size parameter.

Gibb's free energy of adsorption (ΔG_{ads}) was evaluated using (Nwabanne and Okafor, 2011; Alinnor and Ejikeme, 2012):

$$\Delta G_{ads} = -2.303RTlog(55.5K) \quad (9)$$

where R is 8.314 kJ/kmol.K, T is temperature. K is the equilibrium constant for each of the Langmuir, Frumkin, Temkin and Flory-Huggins isotherms.

2.6 Gravimetric technique by RSM

On response surface methodology, Design Expert Software was used to examine interactive effects of inhibitor's concentration, temperature and time on the inhibition efficiency of metronidazole. Optimum inhibition parameters and mathematical model were obtained in line with the protocol of previous reports (Omotioma and Onukwuli, 2016; Anadebe et al, 2018).

2.7 Electrochemical Studies

Electrochemical (potentiodynamic polarization and electrochemical impedance spectroscopy) experiments on metronidazole as inhibitor were carried out by employing the technique used by Oguzie *et al* (2010), Ihebrodike *et al* (2012) and Anadebe et al (2018). Potentiostat/galvanostat 263 electrochemical system workstation (with conventional three-electrode corrosion cell) aided the investigation. Graphite rod and saturated calomel electrode were used as a counter and reference electrodes, respectively. Mild steel specimen fixed in epoxy resin with a surface area of 1 cm^2 functioned as the working electrode. Electrochemical measurements were accomplished in aerated and unstirred solution at the end of 1800 s of immersion. It allowed the open circuit potential (OCP) to attain steady state (Anadebe et al, 2018). Temperature was fixed at 30±1 ^{0}C. The efficiency of metronidazole was determined by:

$$IE\,\% = \frac{i_{corr(uninh)} - i_{corr(inh)}}{i_{corr(uninh)}} \times 100 \quad (10)$$

where $i_{corr(uninh)}$ and $i_{corr(inh)}$ stand for the corrosion current density values in the absence and presence of inhibitor respectively.

2.8 Thermometric technique

Thermometric measurements were carried out using water bath with thermostat set at 30 ^{0}C. The temperatures of the system containing uninhibited (free) and inhibited mild steel samples were monitored until steady temperature was reached in each case. The reaction number (RN) and inhibitor efficiency (IE) were determined using Equations 11 and 12 respectively (Eddy *et al*, 2012; Onukwuli and Omotioma, 2016).

$$RN = \frac{T_m - T_i}{t} \quad (11)$$

$$IE\% = \left(1 - \frac{RN_{add}}{RN_{free}}\right) * 100 \quad (12)$$

where T_i and T_m are the initial and maximum temperatures (in ^{0}C) respectively, t is the time in minutes taken to reach maximum temperature, RN_{free} and RN_{add} are the reaction numbers for free and inhibited media respectively.

2.9 Morphological Analysis of the Mild Steel Surface

Surface textures of the mild steel samples (in the presence and absence of the inhibitor) were examined by scanning electron microscopy (model: Rhenom Prox, P. W. Eindhoven, Netherlands).

3.0 Results and Discussions

3.1 Characteristics of the Inhibitor (Drug)

3.1.1 Chemical compositions of the inhibitor as determined by GC MS

The chromatogram of metronidazole is shown in Figure 1. The identified peaks represent metronidazole, 9-octadecenoic acid and methyl ester. Chemical structures and physicochemical properties of these constituents make metronidazole a suitable corrosion inhibitor. Presence of heterocyclic molecules is an indication that the drug will be effective corrosion inhibitor. This is based on the report of Al-Sawaad et al (2010) that heterocyclic molecules enhance effectiveness of corrosion inhibitor.

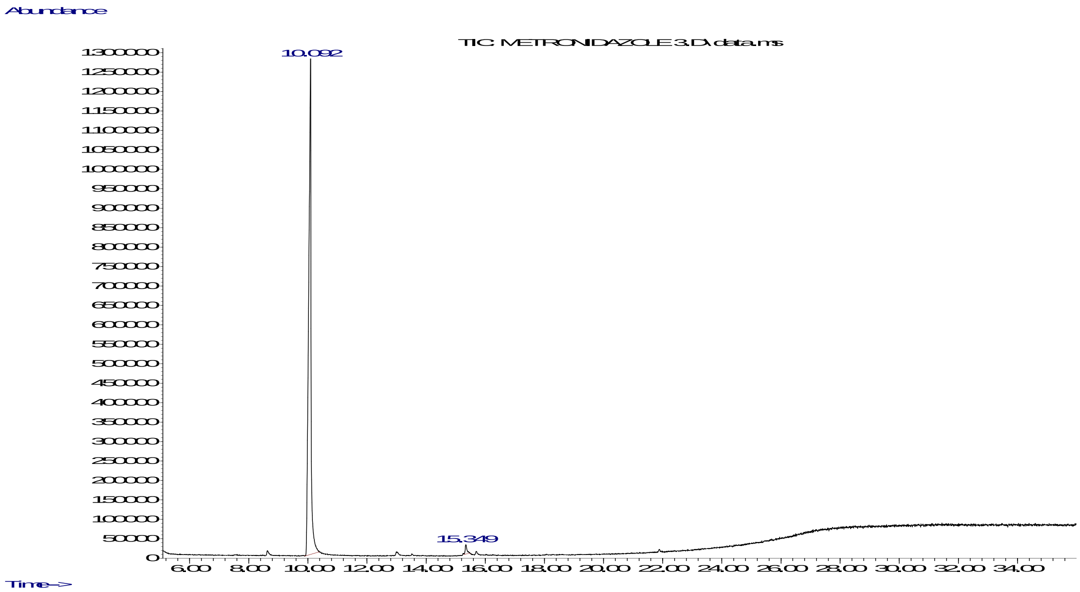

Figure 1: Chromatogram of metronidazole

3.1.2 Functional groups of the inhibitor as determined by FTIR spectroscopy

The spectrum of Figure 2 shows relationship between transmittance and wave number. Peaks of the spectrum denote the functional groups of the inhibitor (Onukwuli and Omotioma, 2016; Eddy *et al*, 2012). Functional groups of metronidazole were revealed as ≡C-H stretch, C-H stretch, O-H stretch, C≡N stretch, C-O stretch, N=O stretch, =C-H bend, and =C-O-C symmetric and asymmetric stretch. These polar functional groups and the structural multiple bonds (double and triple) can act as adsorption centers during mild steal-inhibitor interactions. The presence of the heteroatoms depicts that metronidazole is a potential corrosion inhibitor. This is in line with the assertion that nature of inhibitor’s functional groups affects its performance (Rani and Basu, 2012; Umoren et al, 2016; Onukwuli and Omotioma, 2016; Qiang et al, 2018).

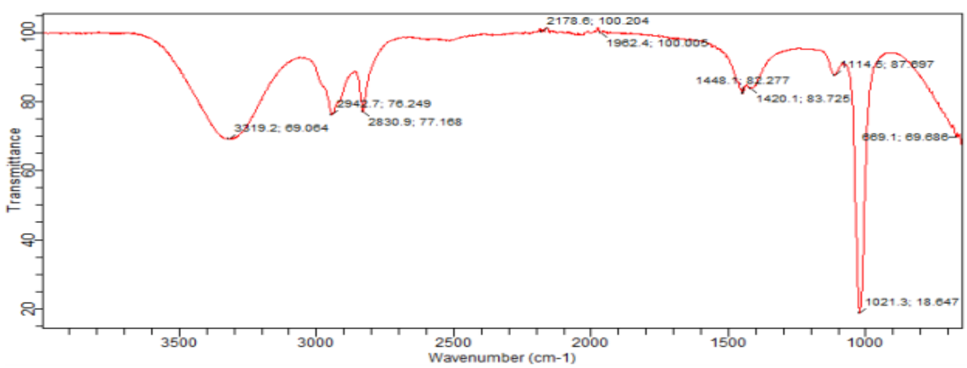

Figure 2: FTIR spectrum of metronidazole

3.2 Gravimetric Results

Gravimetric results of mild steel in HCl medium are presented in Tables 1 - 3. The results are shown on the basis of one factor at-a-time. Effects of time, inhibitor concentration and temperature on weight loss, corrosion rate, inhibition efficiency and degree of surface coverage are presented in Tables 1, 2 and 3 respectively. The corrosion rate reduced with increased in inhibitor concentration. This may be attributed to action and formation of an insoluble physical diffusion barrier on the mild steel surface that prevented the mild steel reaction and deterioration (Al-Sawaad et al, 2010). Inhibition efficiency increased with increase in inhibitor concentration and time. The increase in inhibition efficiency with increase in concentration of the inhibitor can be attributed to increased adsorption of the inhibitor on the mild steel surface. The inhibition efficiency decreased with increase in temperature. This is because increase in temperature generally facilitates desorption of physically adsorbed inhibitor molecules. Decrease in inhibition efficiency with increase in temperature can also be attributed to increase in the solubility of the protective films and of any reaction products precipitated on the surface of the metal that may inhibit the reaction.

Table 1: Effect of time on the corrosion control

Time (hr)	ΔW_0 (g)	CR_0 (mg/cm^2hr)	ΔW_1 (g)	CR_1 (mg/cm^2hr)	IE (%)	Ɵ
1.0	0.13	10.833	0.03	2.500	76.92	0.7692
2.0	0.34	14.167	0.04	1.667	88.24	0.8824
3.0	0.53	14.722	0.04	1.111	92.45	0.9245
4.0	0.55	11.458	0.06	1.250	89.09	0.8909
5.0	0.57	9.500	0.08	1.333	85.96	0.8596

Table 2: Effect of inhibitor concentration on the corrosion control

Inh. Conc. (g/L)	ΔW_0 (g)	CR_0 (mg/cm^2hr)	ΔW_1 (g)	CR_1 (mg/cm^2hr)	IE (%)	Ɵ
0.0	0.53	14.722				
0.2			0.20	5.556	62.26	0.6226
0.4			0.17	4.722	67.92	0.6792
0.6			0.09	2.500	83.02	0.8302
0.8			0.04	1.111	92.45	0.9245
1.0			0.05	1.389	90.57	0.9057

Table 3: Effect of temperature on the corrosion control

Temp. (K)	ΔW_0 (g)	CR_0 (mg/cm^2hr)	ΔW_1 (g)	CR_1 (mg/cm^2hr)	IE (%)	Ɵ
303	0.49	13.611	0.06	1.667	87.76	0.8776
313	0.53	14.722	0.04	1.111	92.45	0.9245
323	0.56	15.556	0.10	2.778	82.14	0.8214
333	0.6	16.667	0.15	4.167	75.00	0.7500
343	0.62	17.222	0.17	4.722	72.58	0.7258

3.2.1 Adsorption isotherm

The experimental data were fitted into Langmuir adsorption isotherm. The graphical analysis of log(C/θ) against log(C) is presented in Figure 3. Trendline function in Microsoft Excel Software was employed in the determination of the correlation coefficient and equilibrium constant from the Langmuir isotherm. Log(C/θ) against log(C) showed linear graph. It indicates adherence to Langmuir adsorption isotherm (Vasudha and Shanmuga, 2013; Onukwuli and Omotioma, 2016).

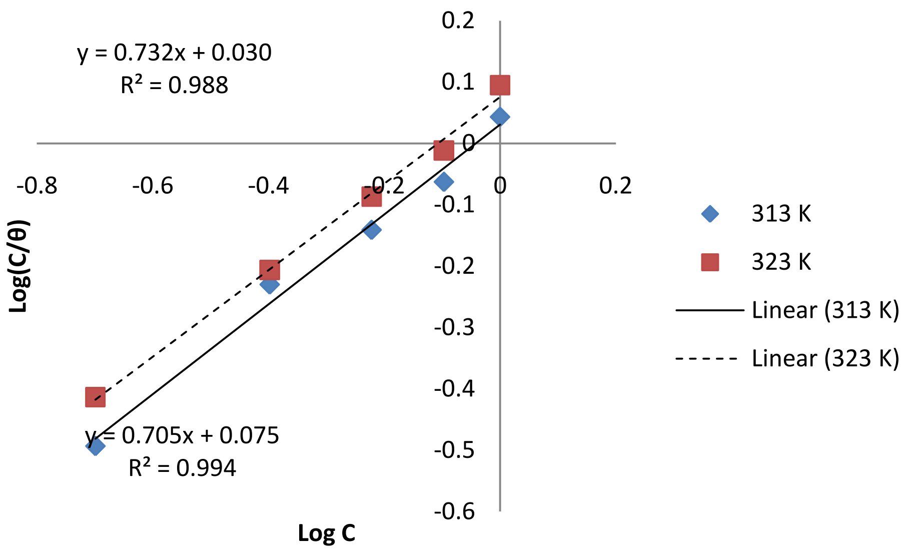

Figure 3: Log(C/ θ) versus logC of the corrosion control with metronidazole

3.2.2 Adsorption parameters

Parameters of the Langmuir, Temkin, Frumkin and Flory-Huggins isotherms are presented in Table 4. Langmuir isotherm gave the highest values of R^2 (very close to one), indicating strong adherence to Langmuir adsorption isotherm (Vasudha and Shanmuga, 2013; Nnanna *et al*, 2013; Anadebe et al, 2019). At temperature of 313K, attractive, lateral interaction, and size parameters were obtained as 2.3838, -2.4605 and 0.5721 respectively. From the Frumkin adsorption parameters, the lateral interaction term (α) gave positive values suggesting attractive behaviour of the inhibitor on the mild steel surface (Nwabanne and Okafor, 2011). From the Temkin adsorption parameters, the attractive parameter values (a) were negative, indicating that repulsion exists in the adsorption layer (Nnanna *et al*, 2013; Omotioma and Onukwuli, 2016). From the Flory-Huggins parameters, the values of the size parameter (x) were all positive. This showed that the adsorbed species of the inhibitor was bulky (Nwabanne and Okafor, 2011; Onukwuli and Omotioma, 2016).

In addition to confirmation of inhibitor adsorption from the data fitted to the isotherms, it is important to consider thermodynamic parameters associated with the adsorption process (Ihebrodike et al, 2012). Such parameters include adsorption equilibrium constant (K) and standard Gibb free energy of adsorption (ΔG_{ads}). K values obtained from the isotherms (Langmuir, Frumkin, Temkin and Flory-Huggins isotherms) were used to obtain the values of ΔG_{ads}. The values of ΔG_{ads} are negative and less than the threshold value of -40000 J/mol required for chemical adsorption. This is in agreement with the works of Nwabanne and Okafor (2011) and Ndibe *et al* (2011). It was revealed that adsorption of the inhibitor was spontaneous and obeyed mechanism of physical adsorption. Obtained negative value of ΔG_{ads} suggests spontaneous adsorption process and that the adsorbed layer is stable. Mechanism of action of a corrosion inhibitor may be connected to the electron density and polarization of the functional groups (Ihebrodike et al, 2012).

Table 4: Parameters of adsorption for the corrosion control using metronidazole

Adsorption Isotherm	Temperature (K)	R^2	K	ΔG_{ads} (J/mol)	Isotherm property	
Langmuir	313	0.9889	1.0732	-10637.5		
Isotherm	323	0.9949	1.1830	-11239.0		
Temkim	313	0.9097	85.4476	-22030.4	a	-2.4605
Isotherm	323	0.9684	71.9615	-22272.9		-2.5761
Frumkin	313	0.9863	29.9640	-19303.0	α	2.3838
Isotherm	323	0.9929	17.5954	-18489.8		2.121
Flory-Huggins	313	0.7629	4.1267	-14143.0	x	0.5721
Isotherm	323	0.9051	5.0327	-15128.0		1.0344

3.3 RSM Result Analysis

The RSM results of the corrosion control with metronidazole are displayed in Table 5. The interactive effects of inhibitor concentration (0.6 g/L – 1.0g/L), temperature (303K – 323K) and time (1hr – 5hrs) on the IE revealed that highest value of the IE was obtained at the mid points of the considered factors. This observation suggests that relationships among concentration, temperature and time are parabolic in nature. The variations of inhibition efficiency with concentration, temperature and time were further analyzed using graphs and mathematical models determined by response surface methodology (RSM) of Design Expert Software.

Table 5: RSM results of the corrosion control

Std.	Run.	Factor 1 A: Inhibitor conc. g/L	Factor 2 B: Temperature K	Factor 3 C: Time Hr	Response Inhibition efficiency %
6	1	1.0	303	5	78.35
5	2	0.6	303	5	67.43
18	3	0.8	313	3	88.68
17	4	0.8	313	3	88.68
15	5	0.8	313	3	88.68
12	6	0.8	323	3	73.21
11	7	0.8	303	3	75.51
3	8	0.6	323	1	49.00
13	9	0.8	313	1	76.92
20	10	0.8	313	3	88.68
7	11	0.6	323	5	65.24
19	12	0.8	313	3	88.68
8	13	1.0	323	5	53.21
9	14	0.6	313	3	77.36
10	15	1.0	313	3	84.91
1	16	0.6	303	1	50.00
2	17	1.0	303	1	60.05
16	18	0.8	313	3	88.68
4	19	1.0	323	1	50.04
14	20	0.8	313	5	87.72

3.3.1 Analysis of variance (ANOVA) of the RSM results

ANOVA for corrosion control with metronidazole is displayed in Table 6. The model F-value of 107.32 suggests that the model is significant. P-values less than 0.05 indicate that the terms of the model are significant. As such, A, B, C, AC, A^2, B^2, C^2 are significant model terms. The predicted R^2 of 0.9094 is in rational agreement with the adjusted R^2 of 0.9805; because the difference is less than 0.2.

Table 6: ANOVA for the corrosion control with metronidazole

Source	Sum of Squares	Df	Mean Square	F-value	p-value	
Model	4892.59	9	543.62	107.32	< 0.0001	Significant
A-Inhibitor concentration	158.48	1	158.48	31.29	0.0002	
B-Temperature	105.24	1	105.24	20.78	0.0010	
C-Time	337.33	1	337.33	66.59	< 0.0001	
AB	9.12	1	9.12	1.80	0.2094	
AC	37.67	1	37.67	7.44	0.0213	
BC	9.86	1	9.86	1.95	0.1932	
A^2	217.27	1	217.27	42.89	< 0.0001	
B^2	316.83	1	316.83	62.55	< 0.0001	
C^2	557.92	1	557.92	110.14	< 0.0001	
Residual	50.65	10	5.07			
Lack of Fit	50.65	5	10.13			
Pure Error	0.0000	5	0.0000			
Cor Total	4943.25	19				
Std. Dev.	2.25		R^2		0.9898	
Mean	76.81		Adjusted R^2		0.9805	
C.V. %	2.93		Predicted R^2		0.9094	
			Adequate Precision		26.7374	

3.3.2 Mathematical models of inhibition efficiency of metronidazole

Mathematical model (in terms of significant and non-significant terms) of the inhibition efficiency (IE) of metronidazole was obtained as:

$$IE = + 93.7 + 3.98A - 3.24B + 5.81C - 1.07AB + 2.17AC - 1.BC - 8.89A^2 - 1\ 0.73B^2 - 14.24C^2 \qquad (13)$$

The coded model is suitable for identifying the relative impact of the factors by comparing the factor coefficients. The inhibition efficiency depended on the inhibitor concentration (C, g/L), temperature (T, K) and time (t, hr). The positive signs in the mathematical model implied synergistic effect, while the negative signs represented antagonistic effect. In each case, the highest power of at least one of the independent variables is 2, which showed that the model is a quadratic equation. Considering only the significant terms, the model is reduced to:

$$IE = + 93.7 + 3.98A - 3.24B + 5.81C + 2.17AC - 8.89A^2 - 1\ 0.73B^2 - 14.24C^2 \qquad (14)$$

3.3.3 Analysis of graphical results of metronidazole inhibition efficiency (IE)

Graphical analyses of IE on corrosion control of mild steel in HCl are shown in Figures 4 – 7. Plot of predicted versus actual inhibition efficiency showed a linear graph. It depicts that the model can adequately describe the inhibition efficiency of metronidazole. The 3-D plots revealed the interactive effects of the factors of inhibitor concentration, temperature and time on the inhibition efficiency. Each of the 3-D plots gives a parabolic graph showing the optimum inhibition efficiency. Inhibition efficiency of metronidazole for the corrosion control of mild steel in HCl medium was obtained as 91.48% at inhibitor concentration of 0.83g/L, temperature of 316.9K and immersion time of 3.1hrs. The result of the model was validated by comparing it with that of the experimental (92.12%). Percentage deviation of 0.69% was recorded (less than 5%), which is an indication that the model can adequately predict the inhibition efficiency of metronidazole. This high value of IE recorded showed that metronidazole can be applied in various maintenance operations such as oil well acidizing and pickling of pipelines.

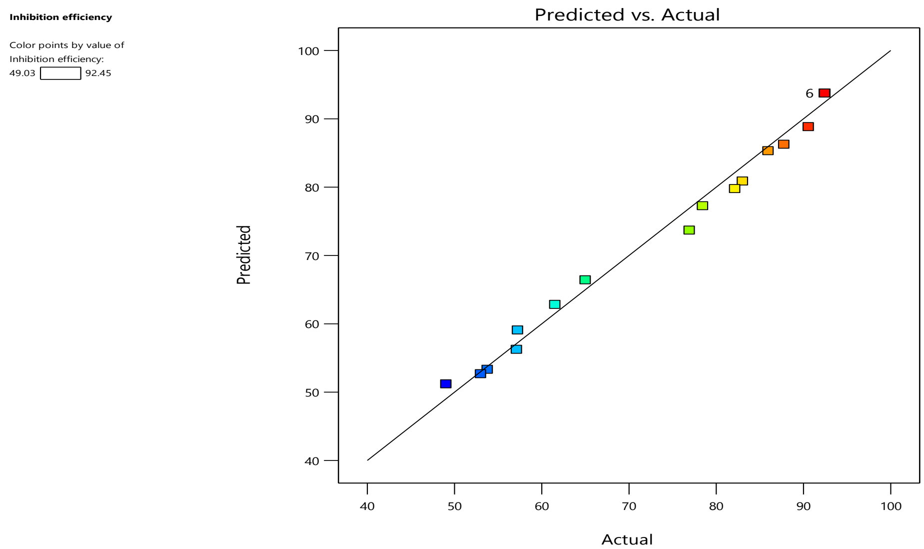

Figure 4: Predicted versus actual inhibition efficiency of metronidazole for mild steel in HCl

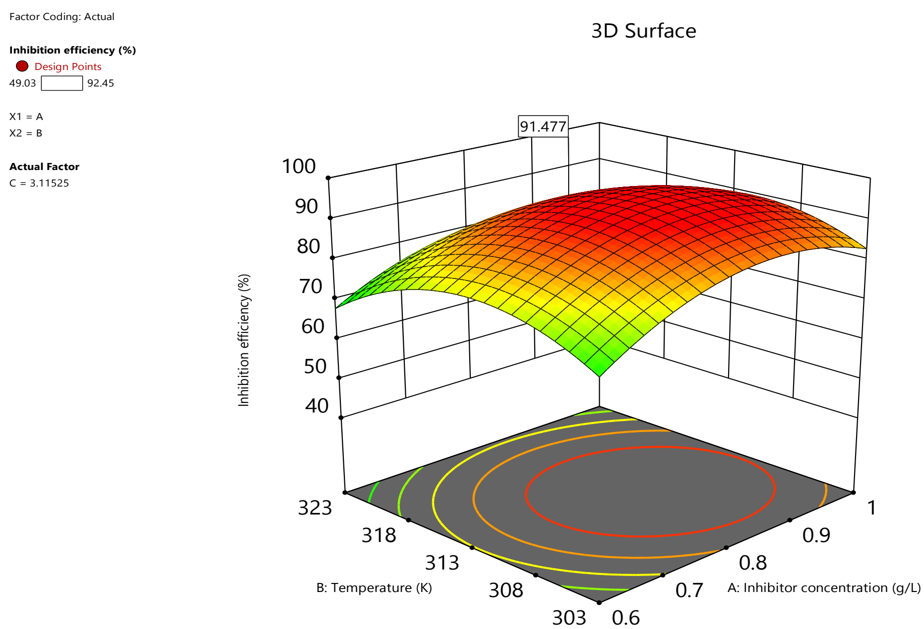

Figure 5: Inhibition efficiency versus inhibitor conc. and temperature

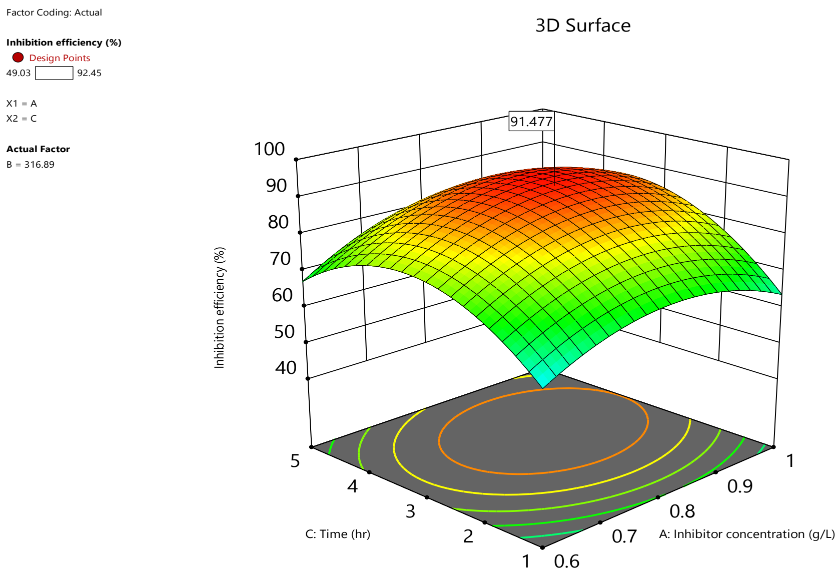

Figure 6: Inhibition efficiency versus inhibitor conc. and immersion time

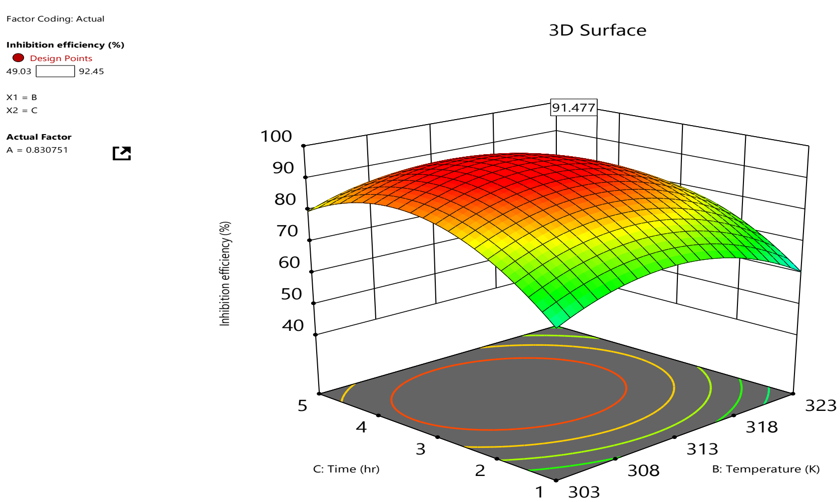

Figure 7: Inhibition efficiency versus temperature and immersion time

3.4 Electrochemical Results

Results of electrochemical impedance spectroscopy and potentiodynamic polarization are presented in Figures 8 - 9. In the electrochemical studies, the inhibitor was denoted as; metronidazole (MNZ). Electrochemical impedance spectra of mild steel in HCl solution in the absence and presence of metronidazole are shown in Figure 8. The spectra are in three categories; Nyquist, Bode phase angle and Bode mag plots. In each of the plots, trend curves of uninhibited and inhibited HCl with 0.6g/L and 0.8g/L metronidazole were presented**.** Impedance spectra were evaluated at the respective corrosion potential, and they were analyzed in terms of equivalent circuit. The impedance spectra described the semicircles in the complex plane.

The displayed semi-circle is an indication that charge transfer process occurred with charge transfer resistance in parallel with the interfacial capacitance. It has been established that huge charge transfer resistance is directly related to rate of corrosion. The semicircles were depressed into real axis of the Nyquist plot due to the roughness of the mild steel surface. The observed dispersing effect can be described by power law dependent capacity (khaled, 2003; khaled and Qahtani, 2009; Anadebe et al, 2018). EIS is an essential method of monitoring electrochemical charges with critical understanding of physical processes occurring at the metal/ electrolyte interface. Circumference of the

Nyquist semicircle is connected to charge transfer process. It was revealed that middle of this depressed semicircle was gently shifted below the real axis. The impedance spectra have a depressed semicircle which may be attributed to the effect of frequency dispersion. Addition of metronidazole drug to the acid medium enhanced the magnitude of the impedance spectrum. It signifies the inhibiting strength of the constituents of the metronidazole which impeded adverse electrochemical reactions.

Figure 9 shows the potentiodynamic polarization curves. The polarization curves showed that metronidazole acted as a mixed type inhibitor because the curves shifted in both cathodic and anodic sides of the plot. The observation is in agreement with the assertion that mixed type inhibitor is useful in controlling anodic and cathodic corrosion (Oguzie *et al*, 2010; Omotioma and Onukwulu, 2016; Khaled, 2003; Ihebrodike *et al*, 2012; Torres *et al*, 2011). The metronidazole can be used to control both anodic and cathodic corrosions.

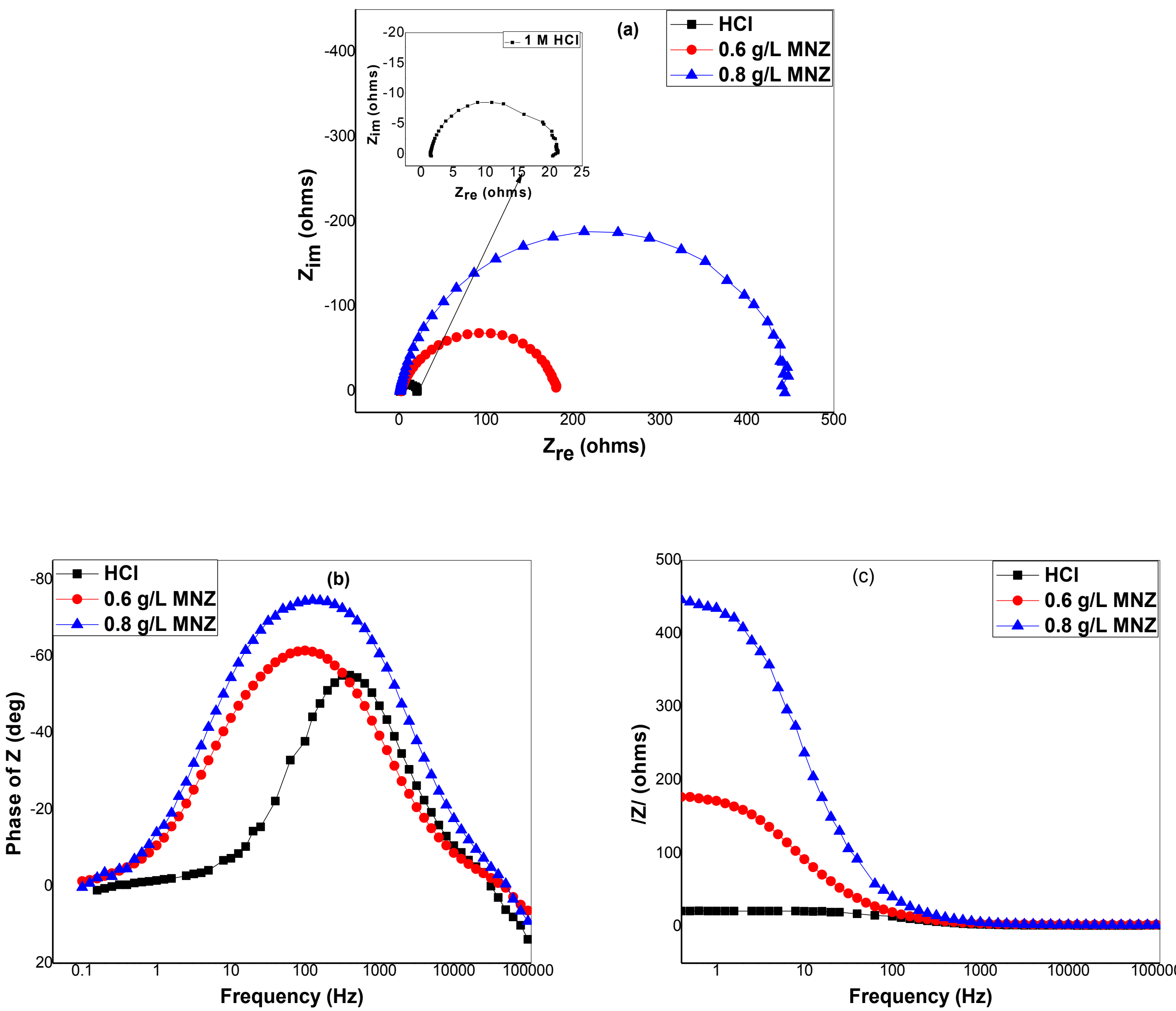

Figure 8: Electrochemical impedance spectra of the corrosion control: (a) Nyquist and (b) Bode phase angle and (c) Bode mag plots.

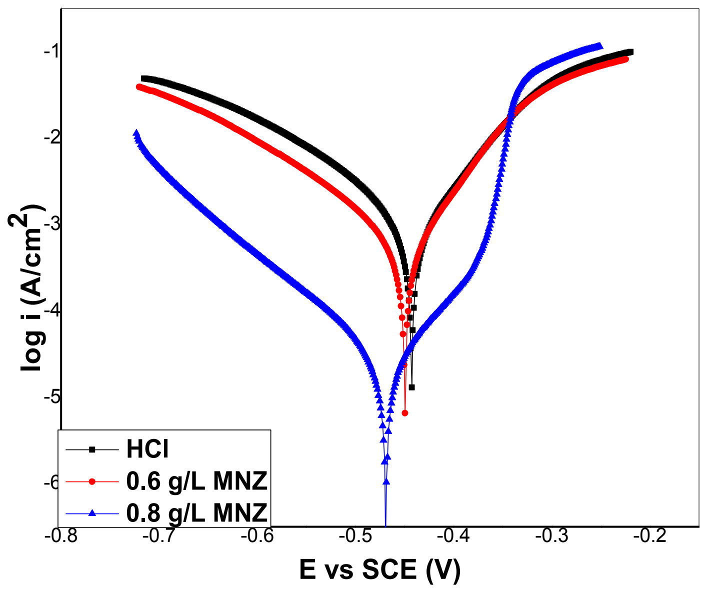

Figure 9: Potentiodynamic polarization curves of the corrosion control by of metronidazole.

Table 7 presents the electrochemical parameter of mild steel in HCl in the absence and presence of metronidazole. Maximum value of inhibition efficiency of metronidazole was recorded as 95.6% at concentration of 0.8g/L; The mechanism of action of inhibitor depended on the electron density and polarizability of the functional groups present in the molecule. It involves complex inhibition mechanisms because most of the functional groups as well as their reaction products inhibit the corrosion reaction in different ways. Some of the constituents of the inhibitor may have been adsorbed as protonated species and some molecular species, with the predominant adsorption mode depending on the prevailing test conditions at any time (Oguzie *et al*, 2010; Ihebrodike *et al*, 2012; Torres *et al*, 2011; Anadebe et al, 2019).

Table 7: Electrochemical parameters for mild steel in HCl in the absence and presence of metronidazole.

System	R_s (Ω cm^2)	R_{ct} (Ω cm^2)	N	IE (%)	E_{corr} (mV)	I_{corr} (μA/cm^2)	IE%
HCl	1.916	20.2	0.89		- 426.8	235.4	
0.6 g/L MNZ	2.321	176.2	0.89	88.5	- 443.5	25.3	89.3
0.8 g/L MNZ	2.332	428.7	0.89	95.3	- 478.5	10.4	95.6

3.5 Thermometric Results

Effects of concentration of inhibitor on the reaction number and inhibition efficiency of metronidazole are displayed in Tables 8. Reaction number decreased with increase in concentration of the inhibitor. It revealed that inhibition efficiency is inversely related to the reaction number. This is in agreement with the findings of Onukwuli and Omotioma (2016). Maximum inhibition efficiency of 93.27% and corresponding reaction number of 0.0297 ^{0}C/min. were obtained at 0.8 g/L inhibitor concentration.

Table 8: Effect of inhibitor concentration on the IE of mild steel in the acid media

Inhibitor conc., g/L	Reaction number (^{0}C/min.)	Inhibition efficiency (%)
0.0	0.4418	
0.2	0.2115	52.14
0.4	0.1119	74.66
0.6	0.0817	81.51
0.8	0.0297	93.27
1.0	0.0506	88.55

3.6 Surface Morphologies of the Metals

The micrographs of mild steel samples in the uninhibited and inhibited HCl medium are displayed in Figures 10 and 11 respectively. There was significant difference in the surface texture of the mild steel samples. The electron micrographs showed that the surface was harshly damaged owing to corrosion in the absence of the metronidazole drug, but there is a much smaller damage on the mild steel surface in the presence of the inhibitor. This is in agreement with the previous study by Loto and Popoola (2012).

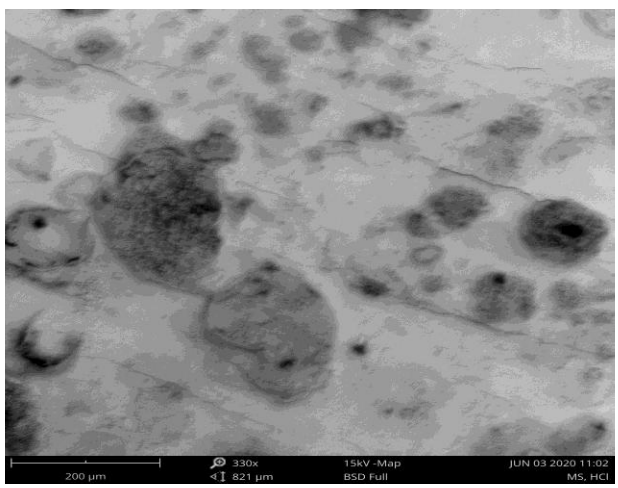

Figure 10: SEM Analysis of mild steel in HCl

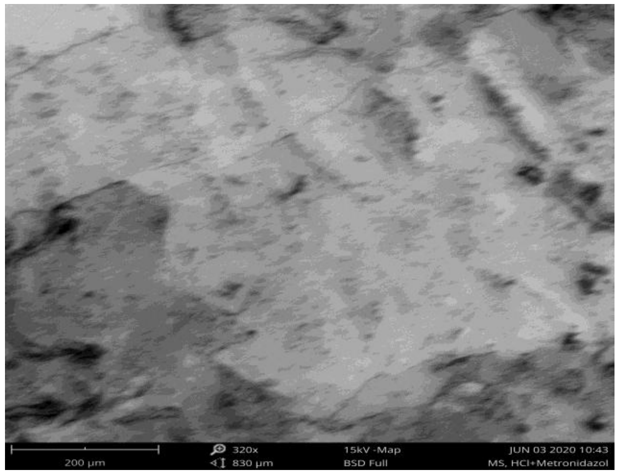

Figure 11: SEM Analysis of mild steel in HCl with Metronidazole

4.0. Conclusion

From the analyses of the experimental results, the following conclusions can be made:
Metronidazole drug contains heterocyclic compounds and heteroatoms of nitrogen and oxygen that make it suitable for corrosion control of mild steel in HCl medium. There was strong synergy among the functional groups of the inhibitor for the corrosion control function.

At temperature of 313K, attractive, lateral interaction, and size parameters were obtained as 2.3838, -2.4605 and 0.5721 respectively. Positive/negative signs of these values indicate that: molecular species of the inhibitor were attracted to the mild steel surface; repulsion exists in the adsorption layer; and the adsorbed species of the inhibitor were bulky. Quadratic model adequately relates inhibition efficiency of metronidazole with corrosion inhibition factors. Electrochemical studies revealed metronidazole as mixed-type inhibitor capable of controlling cathodic and anodic corrosion.

For the thermometric technique, maximum inhibition efficiency of 93.27% and corresponding reaction number of 0.0297 ^{0}C/min. were obtained at 0.8 g/L inhibitor concentration. The inhibition efficiency is inversely related to the reaction number. Surface texture of the mild steel samples confirmed that metronidazole is an effective corrosion inhibitor of mild steel in hydrochloric medium.

Nomenclature

Weight loss	=	Δw (g),
Corrosion rate	=	CR (mg/cm^{2}hr)
Inhibition efficiency	=	IE (%)
Activation energy	=	E_a (kJmol^{-1})
Heat of adsorption	=	Q_{ads} (kJmol^{-1})
Gibb's free energy of adsorption	=	ΔG_{ads} (kJ/mol)

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