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Analytical Evaluation of Corrosion Inhibition Efficiency of Citrus limonum Extract on Zn Metal in 0.1M HNO3

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Abstract

The corrosion inhibition potential of *Citrus limonum* extract for zinc in nitric acid (HNO_3) medium was investigated using weight-loss measurements, Fourier Transform Infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM). The inhibition behaviour and corrosion mechanism were evaluated for zinc immersed in 0.1 M HNO_3 containing different concentrations of the plant extract over a temperature range of 303–333 K. Weight-loss results demonstrated that inhibition efficiency (IE) increased with increasing inhibitor concentration but decreased with increasing temperature throughout the test period. This temperature-dependent behaviour suggests that adsorption of *Citrus limonum* constituents onto the zinc surface occurs predominantly through physisorption. Kinetic and thermodynamic analyses revealed that both inhibited and uninhibited corrosion reactions of zinc in HNO_3 medium were spontaneous, followed first-order kinetics, were exothermic, and proceeded with an increasing degree of order. Analysis of the adsorption behaviour showed that the experimental data were best described by the Langmuir adsorption isotherm, indicating systematic surface coverage by adsorbed inhibitor species. SEM examination further revealed substantial differences between inhibited and uninhibited zinc surfaces, confirming that the *Citrus limonum* extract formed a protective covering on the metal surface, thereby reducing direct interaction between zinc and the corrosive acidic medium. Complementary FTIR analysis identified changes in characteristic functional groups of the extract, suggesting that some functional groups participated in bond formation and development of an adsorbed interfacial layer between zinc and inhibitor molecules. These findings confirm significant interactions between the inhibitor constituents and zinc surface and demonstrate the corrosion-protection potential of *Citrus limonum* in 0.1 M HNO_3.

Keywords
Citrus limonum,
Zinc,
Corrosion inhibition,
Adsorption

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1. Introduction

Corrosion is the deterioration of materials by chemical interaction with their environment [1]. The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than simple loss of a mass of a metal. Due to problems from corrosion that are confronting industries; several methods of corrosion control and prevention have been put in place. These include: cathodic protection, lubrication, anodic protection, alloying, coating, inhibition *Citrus limonum*. The choice and application of any of the methods is based on their efficiency, economic factors and the nature of the corrosive environment [2]. The use of inhibitors is one of the most practical methods for protection against corrosion in corrosive environments.

Inhibitors are chemicals that directly or indirectly coat a film on a metal surface to protect it from its environment [3]. Most of the known corrosion inhibitors are synthetic chemicals, expensive and very hazardous to environment. [4]. The use of natural products otherwise tagged green corrosion inhibitors‖ has been advocated because of the cost, toxic nature and environmentally unfriendliness of some of the inorganic and organic corrosion inhibitors. More so, they are readily available, cheap and a renewable source of materials. A lot of natural products were previously used as corrosion inhibitors for different metals in various environments and their optimum concentrations were reported [1, 5-12]. Very encouraging results have been obtained in this regard. An attempt at making a contribution to this growing research area has necessitated the present investigation, Therefore, the objective of the present study is to investigate the inhibitive and adsorption properties of ethanol extracts of *Citrus limonum* leaves for the corrosion of zinc in HNO_3 medium.

The of *Citrus Limonum* has been analyzed with some of the following major phytochemicals identified; a-farnesene (21.3%), octadedecane (11.7%), hexadecanoic acid (9.5%), dibutyl phthalate (9.1%), 1,2,3-trimethoxy-5-(2propenyl)- benzene (6.6%), neoisothujol (5.8%), 1,2,4-trimethoxy-5-(1- propenyl)-benzene (4.5%) 6,10,14trimethyl-2-pentadecanoic, 1-(2,3,6-trimethyl phenyl)-(E)-3-buten-2-one, geranyl acetone, hexadecanoic acid (21.0%) and 2-ethyl-3,6- dimtheylpyrazine (19.2%), (*Z*)-phytol (41.2%), fatty acid palmitic acid (11.0%), and the (*E*)-nerolidol (4.7%) [13-15]. The presence of these phytochemicals in the compound makes it suitable as a good corrosion inhibitor since they possess, -bond, aromatic system, conjugated bond, heteroatoms and long carbon chains [16].

2. Materials and Methods

2.1. Materials

The sheets of zinc, A72357 type used for this study were obtained from the Novara group Limited England. The composition of the zinc metal in (% wt) as determined by quantitative method of analysis using NEX CG Energy Dispersive X-ray Fluorescence Spectrometer (ED XRF) is Zn (99.591), Sr (0.227), Fe (0.094), Co (0.011), Ni (0.011), Si (0.021), and Zr (0.045). Each sheet was 0.4 mm in thickness and were mechanically pressed cut into 5 x 4 cm coupons for weight loss and 2 x 3 cm for electrochemical. The coupons were degreased by washing in absolute ethanol, dried in acetone and stored in moisture free desiccators before use [17].

Analar grade reagents were used. These included concentrated Trioxonitrate (V) acid, ethanol and silver nitrate.

2.2. Preparation of samples

Citrus limonum, is popularly known as 'fruit' in South west Nigeria or 'mbansan mbakara' in Efik, SouthSouth Nigeria. It was obtained from Gwange Ward, Damaturu, Yobe State (Lat. 11^0.44.820'N, Long. $011^0$58.153' E) in North-East Nigeria. The major phytochemicals in *Citrus Limonum* have been established as alkaloids, resins, steroids, tannins, saponins and phenols. The functional groups of –NH and -OH are present in the identified phytochemicals [18]. The leaves were washed with water, shade dried, grinded and soaked in a solution of ethanol for 48 hours. After 48 hours, the sample was filtered. The filtrate was subjected to evaporation at 338K (65^0C) in other to ensure the sample was free of ethanol.

The concentration of acid (HNO_3) used for the study were 0.1 M while the concentrations of the inhibitor were 0.1, 0.2, 0.3, 0.4 and 0.5 g (per liter of the acid solution). These were dissolved in 1liter solution containing 0.1 M of HNO_3 respectively.

2.3. Corrosion monitoring 2.3.1 Weight loss method

A previously weighed metal (zinc sheet) was completely immersed in 250 ml of the test solution (different concentrations of acid, inhibitor as described above) in an open beaker. The beaker was inserted into a water bath maintained at a temperature of 303 K. Similar experiments were repeated at 313 K, 323 K and 333 K. In each case, the weight of the sample before immersion was measured using Scaltec high precision balance (Model SPB31). Prior to measurement, each coupon was washed in 5 % chromic acid solution (containing 1% silver nitrate) and rinsed in de-ionised water.

The difference in weight for a period of 168 hours was taken as total weight loss. The inhibition efficiency (% I) for each inhibitor was calculated using equation 1 [19],

$$\%I = \left(1 - \frac{W_1}{W_2}\right) \times 100 \tag{1}$$

Where W_1 and W_2 are the weight losses (g/dm^3) for zinc in the presence and absence of inhibitor in HNO_3 solution respectively. The degree of surface coverage □ is given by the equation 2:

$$x = \left(1 - \frac{W_1}{W_2}\right) \tag{2}$$

The corrosion rates for zinc corrosion in different concentrations of the acid and other media have been determined for 168h immersion period from weight loss using Equation 3.

$$CR = \frac{W_1 - W_2}{At} \tag{3}$$

Where *CR* is the corrosion rate of zinc, *A* is the surface area of the zinc coupon in cm^2 and t is the period of immersion in hours.

2.3.2. FTIR Analysis

FTIR analysis of the *Citrus limonum* leaves and those of the corrosion products were carried out using Cary-630 Agilent Fourier Transform Infra-red Spectrophotometer. The analysis was carried out by scanning the sample through a wave number range of 650 to 4000 cm^{-1}.

2.3.3. Scanning electron Microscopy Studies

A scanning electron microscope (SEM) model JSM-5600 LV, was used to analyze the morphology of the zinc surface without and with inhibitor added. The sample was mounted on a metal stub and sputtered with gold in order to make the sample conductive, and the images were taken at an accelerating voltage of 10 kV using different magnifications.

3. Results and Discussions

3.1. Weight loss study

The variation of weight loss with time for the corrosion of zinc in HNO_3 solutions containing various concentrations of *Citrus limonum* leaves are presented in Figures 1 to 4. From the Figures, it can be seen that weight loss of zinc for the blank is higher than those obtained for solutions containing various concentrations of *Citrus Limonum* leave extract indicating that it inhibited the corrosion of zinc in HNO_3 solutions. Also, the weight loss of zinc decreases with increasing concentration of the *Citrus Limonum* leaves extract indicating that the leaf extract is an adsorption inhibitor. For an adsorption inhibitor, weight loss is expected to decrease with increase in concentration [1]. It can be deduced from the plots that weight loss of zinc increases with increase in the period of time and with increase in temperature indicating that the rate of corrosion of zinc increases with time and with increase in temperature.

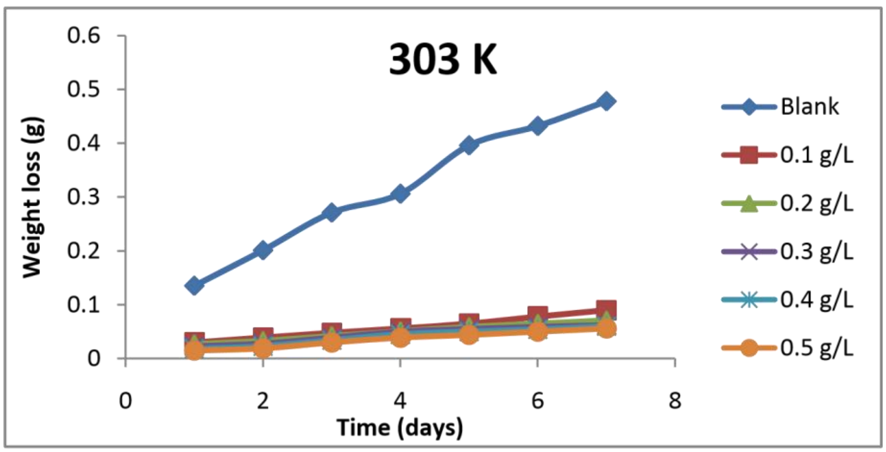


Figure 1: Variation of weight loss with time for the corrosion of zinc in 0.1 M HNO_3 containing various concentrations of Citrus Limonum as inhibitor at 303 K

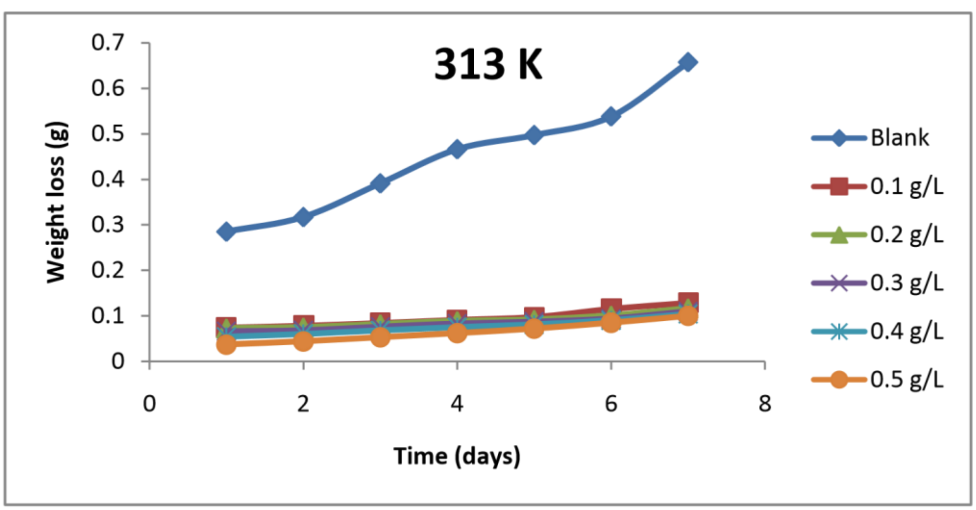


Figure 2: Variation of weight loss with time for the corrosion of zinc in 0.1 M HNO_3 containing various

concentrations of TC as inhibitor at 313 K

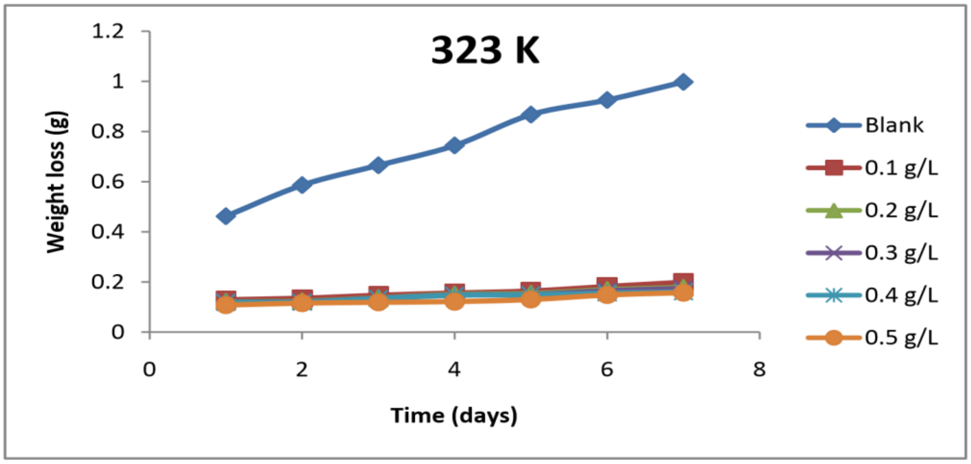


Figure 3: Variation of weight loss with time for the corrosion of zinc in 0.1 M HNO_3 containing various concentrations of TC as inhibitor at 323 K

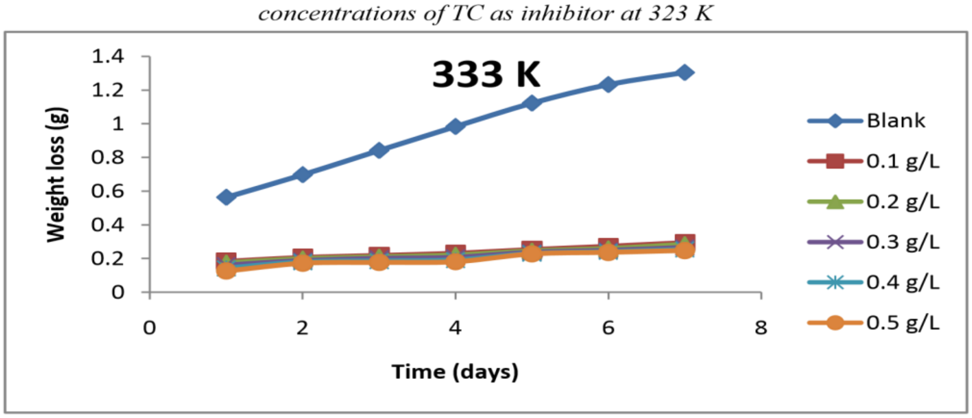


Figure 4: Variation of weight loss with time for the corrosion of zinc in 0.1 M HNO_3 containing various concentrations of Citrus Limonum as inhibitor at 333 K

Values of the corrosion rates of zinc in the absence and presence of extract of *Citrus Limonum*, and their corresponding percentage inhibition efficiencies obtained from equation 1 – 3 are recorded in Table 1. From the results obtained, it is evident that the corrosion rate of zinc in the presence of extract of *Citrus Limonum* have been found to decrease with increase in the concentration of the extract, indicating that the extract retarded the corrosion of zinc in 0.1 M HNO_3 and proportionately that the inhibition efficiencies of extract of *Citrus Limonum* increased with increase in the concentration of the extracts. From the values of the degree of surface coverage obtained, it can be deduced that *CITRUS LIMONUM* retarded the corrosion of zinc in solution of HNO_3, such that the rate of retardation decreases with increase in concentration but increases with increase in temperature.

Table 1: Corrosion rate (CR) of zinc, inhibition efficiencies (IE) and degree of surface coverage for *Citrus Limonum* leaves extract in various media

Temperature	**Systems**	**Corrosion rate ($gh^{-1}cm^{2}$)**	**I. E (%)**	**Degree of surface coverage (θ)**
303K	Blank (0.1 M HNO_3) at 303 K	0.000105		
	0.1 gl^{-1} of *Citrus Limonum* leaf extract at 303 K	0.0000515	71.05	0.7105
	0.2 gl^{-1} of *Citrus Limonum* leaf extract at 303 K	0.0000505	73.44	0.7344
	0.3 gl^{-1} of *Citrus Limonum* leaf extract at 303 K	0.0000501	76.18	0.7618
	0.4 gl^{-1} of *Citrus Limonum* leaf extract at 303 K	0.0000472	80.88	0.8088
	0.5 gl^{-1} of *Citrus Limonum* leaf extract at 303 K	0.0000460	84.10	0.8410
313K	Blank (0.1 M HNO_3) at 313 K	0.000211		
	0.1 gl^{-1} of *Citrus Limonum* leaf extract at 313 K	0.0000651	54.90	0.5490
	0.2 gl^{-1} of *Citrus Limonum* leaf extract at 313 K	0.0000643	60.32	0.6032
	0.3 gl^{-1} of *Citrus Limonum* leaf extract at 313 K	0.0000634	63.28	0.6328
	0.4 gl^{-1} of *Citrus Limonum* leaf extract at 313 K	0.0000625	65.43	0.6543
	0.5 gl^{-1} of *Citrus Limonum* leaf extract at 313 K	0.0000613	69.22	0.6922
323K	Blank (0.1 M HNO_3) at 323 K	0.000351		
	0.1 gl^{-1} of *Citrus Limonum* leaf extract at 323 K	0.0000676	51.39	0.5139
	0.2 gl^{-1} of *Citrus Limonum* leaf extract at 323 K	0.0000665	53.87	0.5387
	0.3 gl^{-1} of *Citrus Limonum* leaf extract at 323 K	0.0000656	57.03	0.5703
	0.4 gl^{-1} of *Citrus Limonum* leaf extract at 323 K	0.0000648	59.90	0.5990
	0.5 gl^{-1} of *Citrus Limonum* leaf extract at 323 K	0.0000614	63.73	0.6373
333K	Blank (0.1 M HNO_3) at 333 K	0.000393		
	0.1 gl^{-1} of *Citrus Limonum* leaf extract at 333 K	0.0000698	49.89	0.4989
	0.2 gl^{-1} of *Citrus Limonum* leaf extract at 333 K	0.0000689	52.94	0.5294
	0.3 gl^{-1} of *Citrus Limonum* leaf extract at 333 K	0.0000618	55.57	0.5557
	0.4 gl^{-1} of *Citrus Limonum* leaf extract at 333 K	0.0000571	57.94	0.5794
	0.5 gl^{-1} of *Citrus Limonum* leaf extract at 333 K	0.0000559	60.15	0.6015

3.2. Kinetic study

The kinetics of corrosion of zinc in 0.1 M HNO_3, solutions was studied at 303, 313, 323 and 333 K by fitting data obtained from weight loss measurements into equation 4.

$$-\log(\text{weight loss}) = \frac{k_1 t}{2.303} \quad (4)$$

where k_1 is the first order rate constant and t is the period of contact.

The test revealed that plotting of values of –log (weight loss) versus time (Figures 5 to 8) yielded straight line indicating that the corrosion reaction of zinc in solutions of HNO_3 is consistent with a first order kinetics [19-20]. Values of rate constants calculated from the slopes of the plots are presented in Table 2. The results obtained indicate that the rate constants decrease with increasing concentration of the respective inhibitor. Also, the rate constants were also found to increase with rise in temperature. The first order rate constant is related to the half-life of the corrosion reaction of zinc according to the following equation,

$$t_{1/2} = \frac{0.693}{k_1} \quad (5)$$

where $t_{1/2}$ is the half – life of the corrosion reaction of zinc.

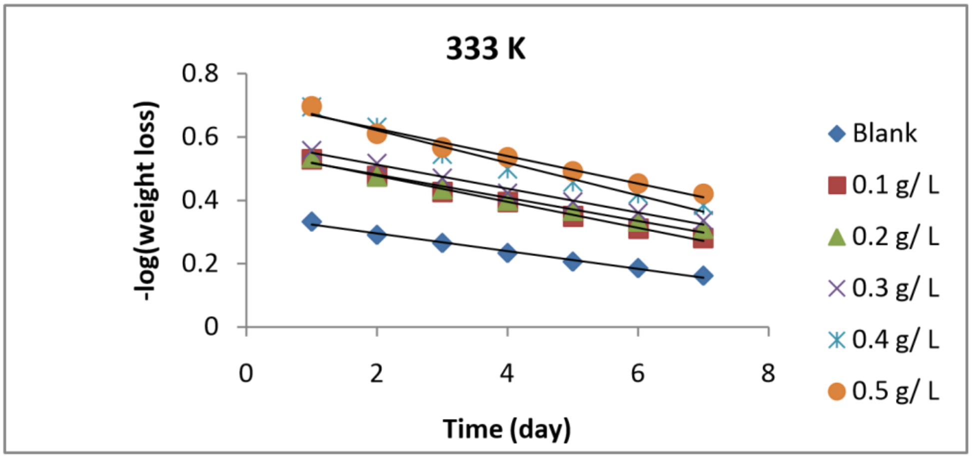


Figure 5: Variation of –log (weight loss) with time for the corrosion of zinc in 0.1 M HNO_3 containing various concentrations of TC at 333 K

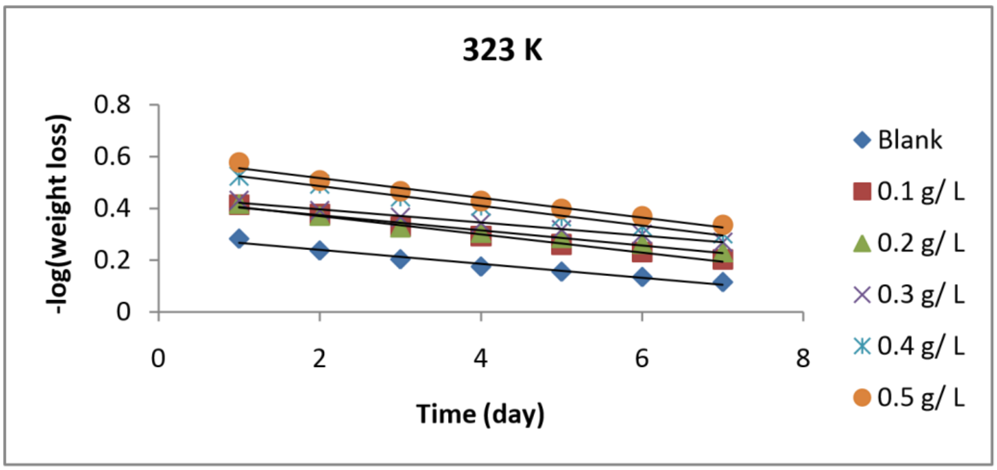


Figure 6: Variation of –log(weight loss) with time for the corrosion of zinc in 0.1 M HNO_3 containing various concentrations of TC at 323 K

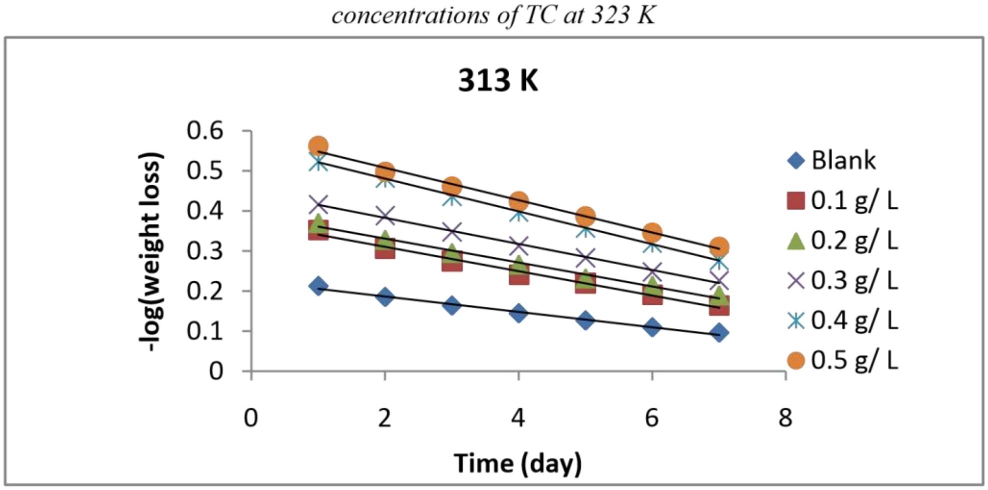


Figure 7: Variation of –log(weight loss) with time for the corrosion of zinc in 0.1 M HNO_3 containing various concentrations of Citrus Limonum at 313 K

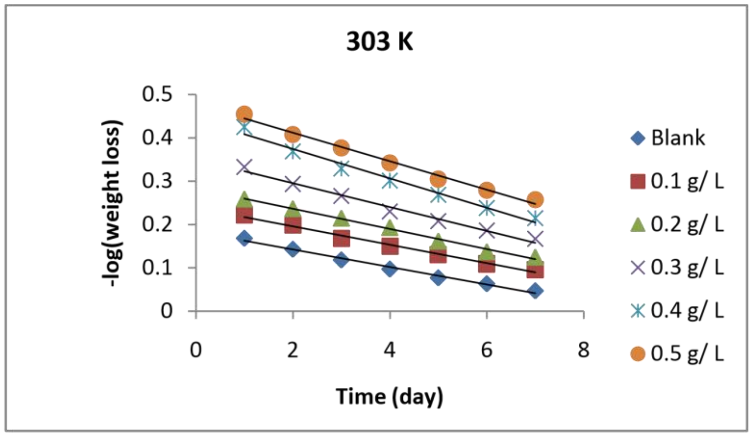


Figure 8: Variation of –log(weight loss) with time for the corrosion of zinc in 0.1 M HNO_3 containing various concentrations of Citrus Limonum at 303 K

Table 2: Kinetic parameters for the inhibition of the corrosion of zinc in 0.1 M HNO_3 by *Citrus Limonum*

Temperature	Inhibitor concentration	Slope	K_1	$t_{1/2}$ (day)
303 K	0.5g/L	0.0180	0.041454	16.71
	0.4 g/L	0.0252	0.058036	11.94
	0.3 g/L	0.0266	0.06126	11.31
	0.2 g/L	0.0279	0.064254	10.79
	0.1 g/L	0.0291	0.067017	10.34
	Blank	0.0309	0.071163	9.74
313 K	0.5g/L	0.0192	0.044218	15.67
	0.4 g/L	0.0285	0.065636	10.59
	0.3 g/L	0.0292	0.067248	10.31
	0.2 g/L	0.0315	0.072545	9.55
	0.1 g/L	0.0329	0.075769	9.15
	Blank	0.0344	0.079223	8.75
323 K	0.5g/L	0.0232	0.05343	12.97
	0.4 g/L	0.0328	0.075538	9.17
	0.3 g/L	0.0339	0.078072	8.88
	0.2 g/L	0.0357	0.082217	8.43
	0.1 g/L	0.0379	0.087284	7.94
	Blank	0.0388	0.089356	7.76
333 K	0.5g/L	0.0258	0.059417	11.66
	0.4 g/L	0.0409	0.094193	7.36
	0.3 g/L	0.0459	0.105708	6.56
	0.2 g/L	0.0469	0.108011	6.42
	0.1 g/L	0.0499	0.11492	6.03
	Blank	0.0529	0.121829	5.69

Using equation 5, values of the half-life for the various concentrations of the inhibitor were calculated and are also presented in Table 2. The results reveal that the half-life of zinc for the blank is lower than those obtained in the presence of the inhibitor indicating that the inhibitor increases the half-life of metal in HNO_3 solutions. Also, the half-lives were found to increase with increasing containing various concentrations of the inhibitor. The action of *Citrus Limonum* as inhibitor according to Eddy *et al.*, [21] may therefore be due to the type of interaction between the inhibitor and zinc surface.

3.3. Thermodynamic study

In order to calculate the activation energy of the corrosion reaction of zinc in 0.1 M HNO_3, the Arrhenius equation (Equation 6) was used.

$$ln(CR) = ln\,A - \frac{E_a}{RT} \quad (6)$$

Where CR is the corrosion rate of zinc, A is the Arrhenius or pre-exponential factor, R is the universal gas constant and T is the temperature. Equation 6 reveals that a plot of ln(CR) versus 1/T is expected to be linear, with slope and intercept equal to E_a/R and ln A respectively. Through the plot of ln(CR) versus 1/T (Figure 9), values of E_a were found to range from 9.97 to 11.29 J/mol (mean = 10.60J/mol). These values, together with the degree of linearity (R^2) are recorded in Table 3. From the results, it was seen that the degree of linearity of the plot was high confirming that Arrhenius equation is applicable to the inhibited corrosion reaction of zinc in 0.1 M HNO_3. The average value of E_a was found to be higher than the average value obtained for the blank indicating that *Citrus Limonum* retards the corrosion of zinc in the studied media

zinc in the studied media.

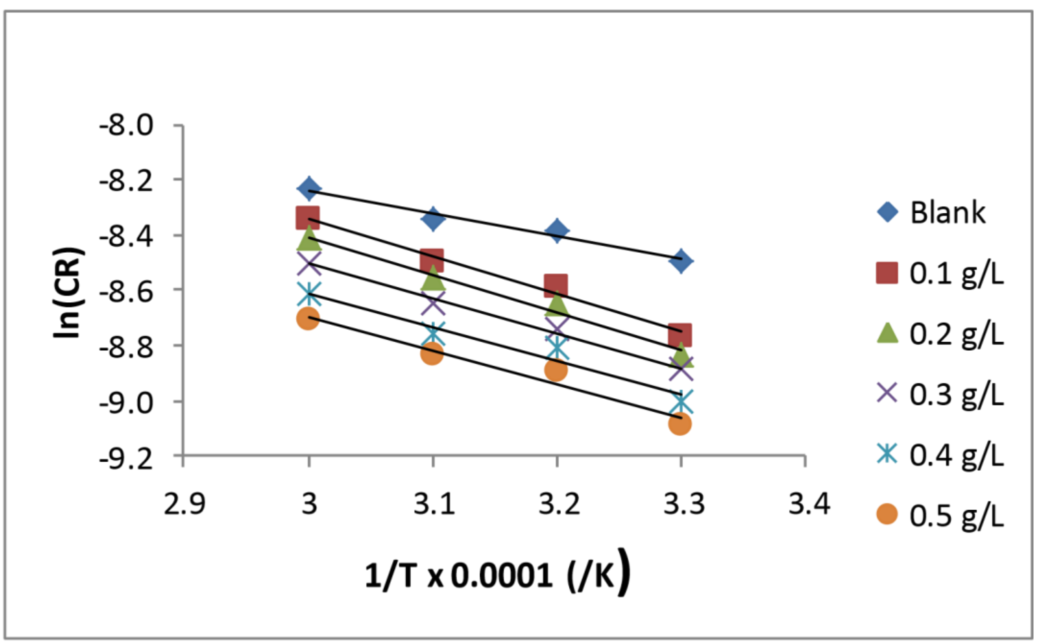


Figure 9: Arrhenius plots for the inhibition of the corrosion of Zinc in 0.1 M HNO_3 by TC

Table 3: Arrhenius parameters for the inhibition of the corrosion of zinc by *Citrus Limonum*

System	Slope	Intercept	E_a (J/mol)	A	R2
Blank	0.8215	-5.725	6.829951	0.00326	0.9708
0.1 g/L	1.3582	-4.2205	11.29207	0.01469	0.9865
0.2 g/L	1.3512	-4.304	11.23388	0.01351	0.9908
0.3 g/L	1.2454	-4.7821	10.35426	0.008378	0.9925
0.4 g/L	1.2199	-4.899	10.14225	0.007454	0.97888
0.5 g/L	1.1993	-5.1035	9.97	6.08E-06	0.9600

The transition state equation was used to calculate the thermodynamic parameters (free energy of adsorption, standard entropy change of adsorption and the standard enthalpy of adsorption of the inhibitor) of adsorption of *Citrus Limonum* on zinc surface. The transition state equation is represented as Equation 7.

$$CR = \frac{RT}{Nh} exp\left(\frac{\Delta S^0_{ads}}{T}\right) exp\left(\frac{-\Delta H^0_{ads}}{RT}\right) \quad 7$$

where CR is the corrosion rate at the temperature, T, R is the universal gas constant, N is the Avogadro's number, h is the Planck constant, ΔS^0_{ads} is the standard entropy change of adsorption and ΔH^0_{ads} is the standard enthalpy of adsorption of the inhibitor.
Rearrangement of equation 7 yields equation 8 and from the logarithm of both side of equation 8, equation 9 were obtained [16]:

$$\frac{CR}{T} = \frac{R}{Nh} exp\left(\frac{\Delta S^0_{ads}}{T}\right) exp\left(\frac{-\Delta H^0_{ads}}{RT}\right) \quad 8$$

$$log\left(\frac{CR}{T}\right) = log\left(\frac{R}{Nh}\right) + \frac{\Delta S^0_{ads}}{2.303R} - \frac{\Delta H^0_{ads}}{2.303RT} \quad 9$$

Applying equation 9 to our experimental data from weight loss by plotting values of log(CR/T) versus 1/T, a linear relationship with high degree of linearity was obtained as presented in Figure 10. From the slope and intercept of lines on the transition state plot, values of ΔH_{ads} and ΔS_{ads} were calculated and are recorded in Table 4. Mean value of ΔH_{ads} and ΔS_{ads} were found to be -18.527J/mol and 128.694J/mol respectively indicating that the inhibited corrosion reaction of zinc is exothermic and that the inhibition proceeded with increasing entropy.

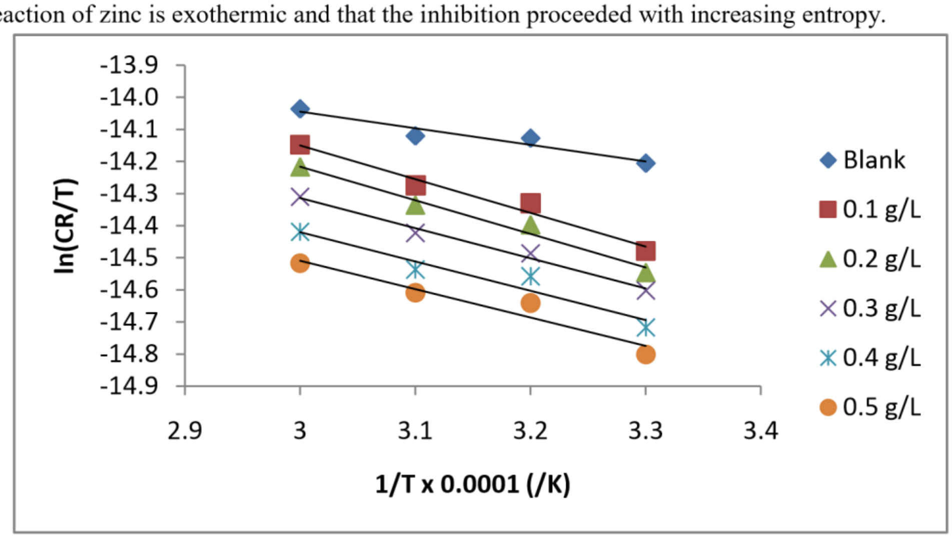


Figure 10: Transition state plots for the inhibition of the corrosion of zinc in 0.1 M HNO_3 by TC

Values of free energy of adsorption (ΔG_{ads}) of *Citrus Limonum* on zinc surface at 303 K were calculated using Gibb Helmotltz equation which is represented by Equation 10 (Ameh, 2014b):

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \quad (10)$$

By substituting values of ΔH_{ads} and ΔS_{ads}, values of ΔG_{ads} were obtained. These values are also recorded in Table 4. Average value of ΔG_{ads} was found to be -39049.14 (39.049kJ/mol). This value is less than the threshold value (- 40 kJ/mol) required for the mechanism of chemical adsorption [1]. Generally, values of ΔG^0_{ads} between 0 and -20 kJ/mol, are consistent with the mechanism of charge transfer from charged inhibitor's molecules to charged metal surface. Therefore, the adsorption of *Citrus Limonum* on the zinc surface is spontaneous and supports the mechanism of physical adsorption.

Table 4: Thermodynamic parameters for the adsorption of various concentration of *Citrus Limonum* on zinc surface

System	Slope	Intercept	ΔH^0_{ads} ($\frac{J}{mol}$)	ΔS^0_{ads} ($\frac{J}{mol}$)	ΔG^0_{ads} ($\frac{J}{mol}$)	R^2
Blank	0.517	-12.495	-9.89907	119.79	-36306.3	0.9335
0.1g/L	1.052	-10.991	-20.1427	132.22	-40082.8	0.9784
0.2g/L	1.049	-11.072	-20.08535	131.63	-39903.9	0.9803
0.3 g/L	0.939	-11.496	-17.97917	128.02	-38989.8	0.9851
0.4 g/L	0.913	-11.684	-17.48134	126.54	-38359.1	0.9375
0.5g/L	0.885	-11.859	-16.94522	125.06	-37910.1	0.9455

3.4. Adsorption study

The adsorption characteristics of *Citrus Limonum* was studied by fitting data obtained for the degree of surface coverage of the inhibitor into different adsorption isotherms including, Langmuir, Temkin, Flory Huggins, El awardy, Bockrisswinkle, Frumkin and Freundlich adsorption isotherms. The test revealed that the adsorption characteristics of the studied compounds are best described by the Langmuir adsorption isotherm, which can be expressed as follows,

$$\theta = K_{ads}C \times 1/(1+K_{ads}C) \quad (11)$$

where C is the concentration of the inhibitor in the bulk electrolyte, θ is the degree of surface coverage of the inhibitor and K_{ads} is the equilibrium constant of adsorption. Transformation of equation 11 yields equation 12, $\log(C/\theta) = \log C - \log K_{ads}$ 12

From equation 12, the plots of $\log(C/\theta)$ versus $\log C$ should yield straight lines provided the assumptions establishing the Langmuir adsorption isotherm are valid. Figure 11 show the Langmuir isotherm for the adsorption of *Citrus Limonum* on zinc surface. The adsorption parameters deduced from the isotherms are presented in Table 5. From the results obtained, it can be seen that the slopes and R^2 values for the Langmuir plots are very close to unity indicating strong adherence of the adsorption data to the Langmuir adsorption model.

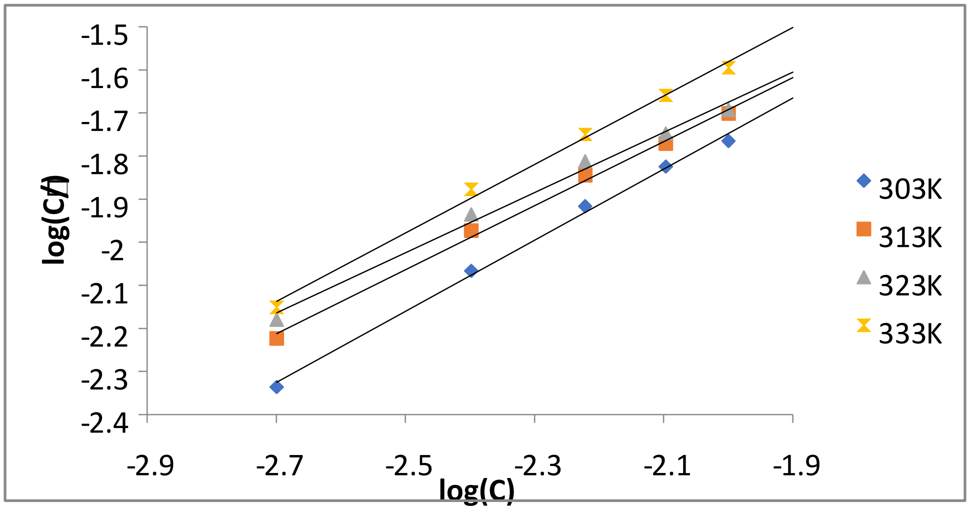


Figure 11: Langmuir isotherm for the adsorption of Citrus Limonum on zinc surface in 0.1 M at various temperatures

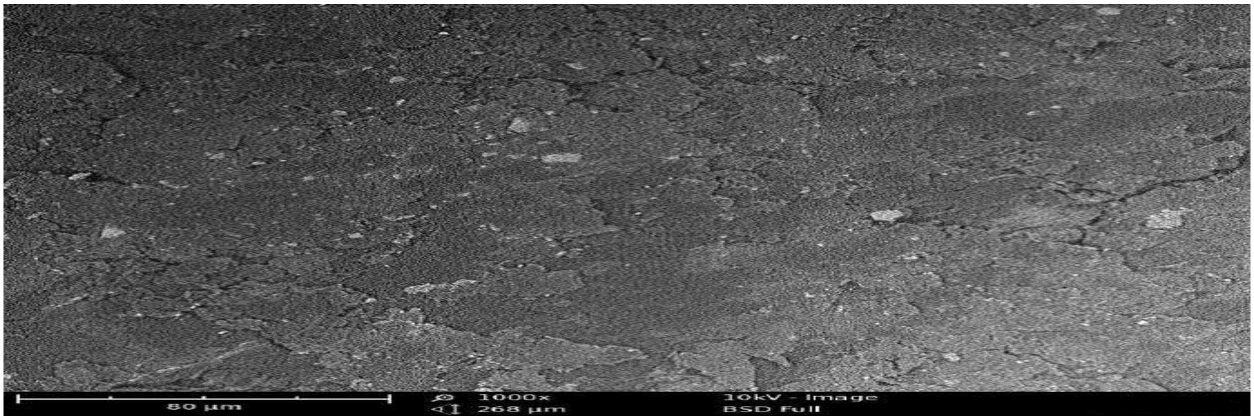
Table 5: Langmuir parameters for the corrosion of zinc in acid containing various concentrations of the studied inhibitors at various temperatures

T(K)	slope	log K_{ad}	R^2
303	0.808	0.3322	0.9989
313	0.8368	0.2222	0.9945
323	0.8137	0.2361	0.9992
333	0.8270	0.1552	0.997

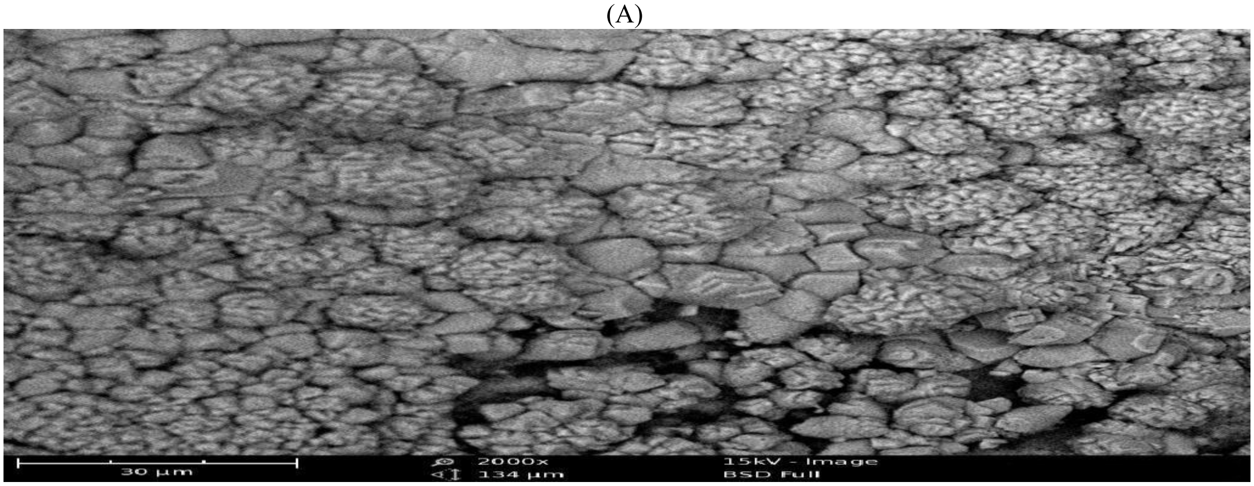
3.5. Morphological Studies

The surface morphology of the polished zinc coupons in the absence and presence of the inhibitor was studied using scanning electron microscopy. The scanning electron micrographs obtained from the study are presented in Figure 12a, 12b and 12c. The micrograph obtained for the polished zinc metal (Figures 12 a) shows that the metal coupon surface is smooth which is an indication that the zinc used in the study was not corroded prior to immersion in aggressive media. From Figures 12 b, the micro-flakes are clearly visible depicting dissolution of metal surfaces which also indicates that the surface is strongly and uniformly damaged by corrosion due to aggressive media.

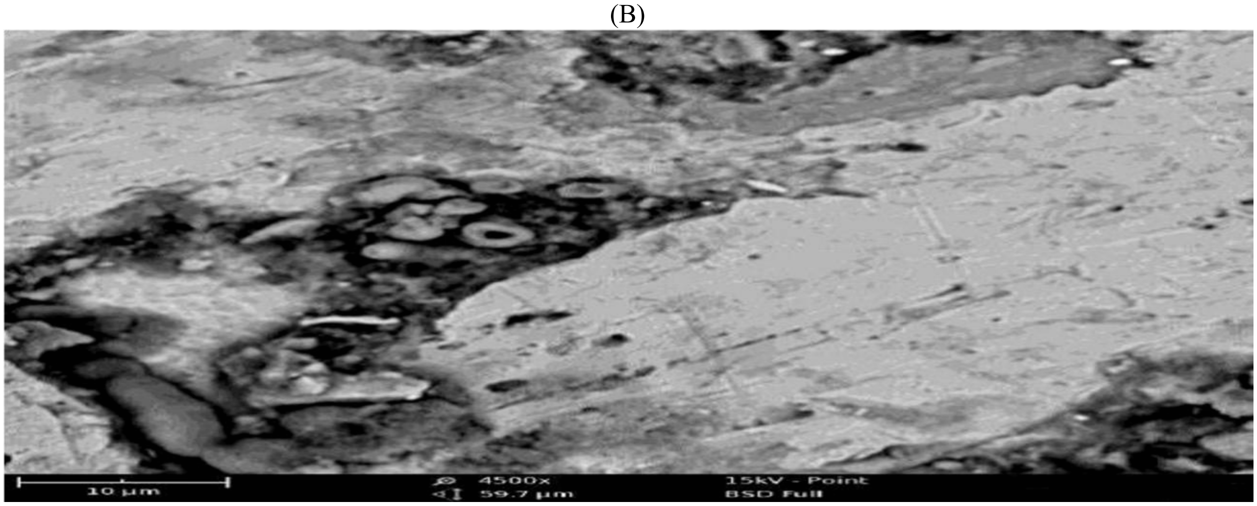
However, Figures 12c reveals that the surface of the metal in the presence of the inhibitor was smother than when inhibitor was absent which is an indication that a good protective adsorbed film is formed on the samples [4].



(A)



(B)

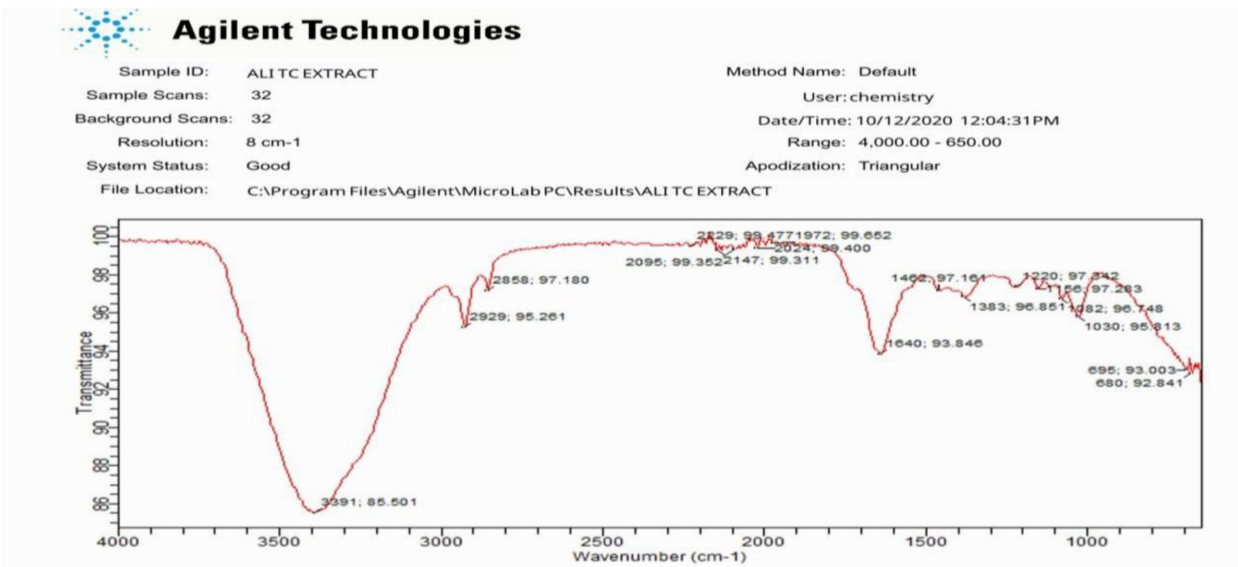


(C)

Figure 12: Scanning electron micrographs of zinc (A) alone (B) in 0.1 M HNO_3 solution (C) in 0.1 M HNO_3 solution plus 0.5 g/L Citrus Limonum

3.6. FTIR study

The FTIR spectrum obtained for *Citrus Limonum* extract is as presented in Figure 13a while that the FTIR spectrum of the corrosion product of zinc when the extract was used as an inhibitor is given in Figure 13b. Frequencies and peaks of IR adsorption for both cases are presented in Table 6. From the results obtained, it can be seen that the = C – H bend at 680 cm^{-1} is shifted to 672 cm^{-1}, the C-H "oop" at 695 cm^{-1} is shifted to 709 cm^{-1}, the -C ≡ C stre*Citrus limonum*h at 1972 cm^{-1} is shifted to 1935 cm^{-1}, the - C = C stre*Citrus limonum*h at 1640 cm^{-1} is shifted to 1644 cm^{-1} and the H - C = O stre*Citrus limonum*h at 2858 cm^{-1} was shifted to 2854 cm^{-1}. These shifts indicate that there is interaction between the zinc metal and some molecules in the inhibitor (Ameh et al 2012b, Eddy, 2009). Also the C-N stre*Citrus limonum*h C-O stre*Citrus limonum*h , O-H stre*Citrus limonum*h and - C – H bend and scissoring were missing in the spectrum of the corrosion product indicating that these bond might have been used for bonding between the inhibitor's molecules and the metal.



(A)

(B)

Figure 13: FTIR spectrum of (A) Citrus Limonum extract (B) the corrosion product of zinc in 0.1 M HNO$_3$ when Citrus Limonum was used as an inhibitor

Table 6: Polarization data for the corrosion of zinc in 0.1 M HNO$_3$ in the absence and presence of TC at 303 K

Concentration (g/L)	β_a (mVdec^{-1})	β_c (mVdec^{-1})	E_{corr} (mV)	I_{corr} (µA)	I %
Blank	119.3	122.1	- 606.2	141.16	
0.1	98.4	111.3	-547.3	35.61	74.78
0.3	96.7	108.5	- 545.2	24.22	82.83
0.5	95.2	107.7	-543.7	20.48	85.48

4. Conclusions

From the results and findings of the study, the following conclusions are made:

- The corrosion of zinc in HNO_3 is a function of temperature, concentration of the acid, concentration of the inhibitor and the period of contact with the aggressive medium.
- *Citrus limonum* leaves are a good inhibitor for the corrosion of zinc in HNO_3. The inhibitor is an adsorption inhibitor in that their inhibition efficiencies increased with increase in the concentration of the inhibitor.
- The adsorption of the inhibitor on the surface of zinc metal is spontaneous, exothermic and is consistent with the assumption of Langmuir adsorption isotherm.
- Based on the variation of the inhibition efficiencies of the inhibitor with temperature, values of activation energies and free energies of adsorption, the mechanism of adsorption of the inhibitor points towards physical adsorption.
- Some functional groups of the inhibitor have been used in the formation of bonds and adsorption layer between Zn and the inhibitor which indicates that there is interaction between the inhibitor and the studied metal.

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