DISCOVERY

Inhibition of corrosion of low carbon steel in crude oil using the bark and root extracts of *Acacia nilotica*: Thermodynamic, electrochemical and phytochemical evaluation

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ABSTRACT

Corrosion inhibition of low carbon steel in crude oil was investigated in the absence and presence of extracts from the root and the bark of *Aacacia nilotica* as a friendly corrosion inhibitor. The effect of temperature and inhibitor concentration was studied using the weight loss method. The result shows that extracts act as an inhibitor for low carbon steel in crude oil and reduce the corrosion rate. The inhibition efficiency increased with an increase in inhibitor concentration at a given temperature. The highest inhibition efficiency was 95.58% at 1000ppm of inhibitor concentration at 313K. The adsorption of the root and bark of *Acacia nilotica* extracts was found to obey the Langmuir adsorption isotherm model. The free energy values of adsorption were more than 20 kJ/mol, which indicates mixed modes of physical and chemical adsorption.

Keywords: Corrosion, Low carbon steel, Phytochemical screening, corrosion inhibitor, crude oil

1. INTRODUCTION

Industrial processes, including acid cleaning, pickling, descaling, and drilling for oil and gas exploration, typically use acidic solutions; as a result, iron and steel vessels or surfaces used in these situations are prone to corrosion (Fiori-Bimbi et al., 2015). A metal's propensity to corrode can be affected by its grain structure, composition produced during alloying, or the temperature at which a single metal surface developed during manufacturing can deform. Avoiding corrosion rather than striving to eradicate it would be more practical. Given that the environment significantly impacts corrosion, the processes might vary as much as the settings to which a material is exposed.

Metal reactivity, the presence of impurities, the presence of oxygen, moisture, gases like sulphur dioxide and carbon dioxide, and the presence of electrolytes are all factors that contribute to corrosion. These issues are controlled via corrosion retardation and prevention (Sastri, 2014). One of the most effective ways to prevent corrosion, especially in acid solutions to stop metal dissolving and acid consumption, is to use inhibitors (Chauhan and Gunasekaran, 2007). Inhibitors interact with anodic or cathodic reaction sites to lessen the oxidation or reduction of corrosion processes by being adsorbed on the metal surface, providing a protective barrier (Singh et al., 2016).

Since they have -electrons in conjugated double or triple bonds and electronegative functional groups, the most well-known inhibitors are organic compounds that demonstrate good inhibitive capabilities by providing electrons through the orbitals (Yadav et al., 2016). Additionally, there is a unique interaction between the metal surface, which is crucial for inhibition, and functional groups comprising heteroatoms like nitrogen, sulfur, and oxygen that have a free lone pair of electrons and act as inhibitors. The combination of these two characteristics results in enhanced inhibition (Dutta et al., 2015).

The effectiveness of corrosion inhibitors in reducing the corrosion rate of metal surfaces in contact with hostile media has been extensively examined in various industries (Herrag et al., 2010; Okafor et al., 2009; Christov and Popova, 2004). Because of their toxicity and the challenges associated with disposing of them, many inorganic inhibitors, mainly those containing phosphate, chromate, and other heavy metals, are now being gradually restricted or banned by various environmental regulations, especially in the marine industry where aquatic life is at risk (Roy et al., 2014).

Although synthetic organic inhibitors have also been widely used, their effectiveness currently needs to be improved by their toxicity and high manufacturing costs, leading researchers to look into different areas in order to build green corrosion inhibitors that are affordable, biodegradable, and eco-friendly in order to replace inorganic and synthetic organic inhibitors. It has been found that natural items such as plant extract, amino acids, proteins, and biopolymers are practical corrosion inhibitors (Sigircik et al., 2016).

Plant-based products are readily available, affordable, and sustainable sources of resources. It has been observed that the extracts from these plants' leaves, barks, seeds, fruits, and roots contain organic compounds with nitrogen, sulphur, and oxygen atoms that can be used as metal corrosion inhibitors in a variety of situations (Rauscher et al., 1993; Ahmad, 2006; Ashassi-Sorkhabi and Asghari, 2008). Typically, the adsorption of organic materials onto the metal surface, which block active sites or even create a protective barrier, is blamed for the inhibitive impact of plant extract. Inhibitors made from natural substances, such as those found in herbal plants, and have recently been used to create novel cleaning agents that are environmentally friendly. Several studies have been reported on the use of natural products as corrosion inhibitors in different media (Al-Sehaibani, 2000).

The corrosion inhibitory effects of the extracts and their pure components of various plants, such as *Triticum aestivum* (Bhardwaj et al., 2021), *henna* (Hamdy and El-Gendy, 2013), *Aloe vera* (Abiola and James, 2010), *Gentiana olivieri* (Baran et al., 2017), *Dioscorea septemloba* (Emori et al., 2020), bamboo (Li et al., 2012), *Ficus hispida* (Muthukrishnan et al., 2019), *Aniba rosaeodora* (Chevalier et al., 2013), *Mansoa alliacea* (Suedile et al., 2014), *Sida acuta*, *Venonia Amagdalina* (Anafi and Obi, 2004), *neem, mahogony, cashew, locust* bean husk, and *acacia nilotica* (Yawas, 2005), *Gongronema latifolium* (Ikeuba and Okafor, 2018), *neem* oil and *locust* bean husk extract (Kuburi, 2011), *Vernonia amygdalina* (Ndibe et al., 2011) on carbon steel, cold rolled steel, stainless steel and zinc have been reported, with good results.

The inhibition performances of plant extracts are closely related to their chemical compositions, which take the form of tannins, alkaloids, carbohydrates, phenolics, and proteins. *Acacia nilotica* is an important plant recognized as a source of *tannin* ingredient (Gupta, 1970) and requires further investigation to identify its other potentials. *Acacia nilotica* is found in various parts of Nigeria spanning from the rainforest through the savanna up to the arid vegetation zones. It has been identified locally as a highly economic plant, useful in the medical and agricultural practices. It is a single stemmed plant which grows to 15-18 m in height and 2-3 m in diameter. The pods are 7-15 cm long, green when immature and greenish black when matured. A constriction between the seeds gives the pods a necklace appearance. The seeds are 8-12 per pod, compressed, ovoid, and dark brown, and shiny with hard testa (Al-Gohary and Mohamed, 2007).

It has bipinnate leaves at 3-10 pairs per pinnate. Each pinnate is 1.3-3.8 cm long, and 10-20 pairs of leaflets are 2 mm long (Beniwal et al., 1992). The flowers have globular heads, 1.2-1.5 cm in diameter, of a bright golden yellow colour. They develop either in an auxiliary or whorly pattern on peduncles 2-3 cm long at the branches' end (Bargal and Bargali, 2009). The Stems are usually dark to black in color, deep longitudinal fissured, grey-pinkish slash, exuding a reddish low-quality gum (Brenan, 1983). When young, the bark has a tinge of orange and green, but older trees have dark, rough bark and tend to lose their thorns (Khan et al., 2009). The root is generally brown colour in older regions and whitish in younger regions.

This study aims to evaluate the inhibitive effect of methanolic extracts of the bark and root of *acacia nilotica* for use as a green corrosion inhibitor on low carbon steel in crude oil. The low carbon steel test specimens were brought out of the test media of extract in crude oil at specific intervals, and corrosion rates were determined by computing the weight loss, inhibitor efficiency, attractive film power, activation energy, and *enthalpy* of adsorption of the inhibitors. Scanning electron microscopy (SEM) was used for its morphological studies, and the mechanical properties were evaluated. The roots and bark of this plant are not edible; hence, it is most appropriate to use this plant in the production of corrosion inhibitors which might complement existing organic and inorganic chemical corrosion inhibitors and replace those that are hazardous to humans and the environment.

2. EXPERIMENTAL

Preparation of specimens

Low carbon steel alloy specimens used in this investigation were cut from a new petroleum pipeline measuring 15 × 50 × 3 mm. The used Low carbon steel coupons have percent chemical composition (wt%) in Table 1, carried out at the extraction metallurgy assay laboratories in the University of Johannesburg in South Africa using the Spectral method. These coupons were polished with emery papers, washed with deionized water, degreased with acetone, washed with distilled water, dried, and weighed before experiments.

Table 1 Elemental composition of low carbon steel

Elements	C	Si	Mn	P	S	Cr	Mo	Ni	Cu
Composition (wt%)	0.215	3.350	1.316	0.102	<0.100	0.029	0.015	0.022	0.012
Elements	As	B	Ca	Co	Mg	N	Nb	Pb	Sn
Composition (wt%)	<0.0050	0.0041	~0.0072	0.0063	0.014	0.653	0.220	<0.100	<0.0020
Elements	V	W	Zn	Zr	Se	Fe	Al	Ti	
Composition (wt%)	<0.0050	<0.010	0.013	<0.0020	<0.020	93.65	0.130	0.0042	

Preparation of extracts

The bark and root of *Acacia nilotica* were obtained from the Nigerian Institute of Leather and Science Technology (NILEST) Zaria, Nigeria, rinsed with distilled water, shredded into pieces, sun-dried to remove the moisture content, ground to powder using a manual blender, and weighed on the analytical mass balance to 700g using the method developed by Loto et al., (2012). A Soxhlet apparatus (available at NILEST Zaria) was used for the extraction (Plate 1).

Plate 1 Soxhlet extractor (NILEST Zaria)

The soxhlet extractor consists of a primary extractor and a reflux condenser. The powdered samples were placed in a thimble made of paper and inserted into a wide central tube of the extractor solvent (methanol) was placed in the flask and boiled, its vapour rising into the large right-hand tube onto the central space above the sample and thence to the condenser. The condensate then drops back into the raw material through which it percolates, leaching the solute. When a sufficient quantity of the solution has been collected to raise its level to that of the top of the siphon tubes, the whole of the percolates siphons lower into the flask.

The suction effect of the siphoning assists the permeation of solvent through the raw materials. A limited amount of hot solvent was thus made to percolate repeatedly through the raw material, the solute from which was transferred to the flask until the required extract quantity was obtained. The inhibitors test solution of concentration: 400, 600, 800, and 1000 ppm were prepared using the formula:

$$Concentration(ppm) = \frac{mass\ in\ milligrams}{volume\ in\ litres} \quad (1)$$

Phytochemical screening

Phytochemical screening is the application of chemical tests to detect the presence of accumulated natural products referred to as secondary metabolites and is responsible for the therapeutic properties of plants (Yawas, 2005). Phyto-chemical analysis for the extracts was carried out in the Department of Pharmacognosy, Ahmadu Bello University Zaria, Nigeria. The procedure for the analysis is in (Table 2).

Table 2 Procedure for Phytochemical Screening

Phytochemical	Test	Observation	Inference
Cardiac Glycosides	The extract was dissolved in glacia acetic acid containing traces of ferric chloride. The test tube was held at an angle of 45 degrees, 1ml of concentrated sulphuric acid was added down the side	A purple ring colour was formed at the interface	Indicates the presence of cardiac glycosides
Flavonoids	A few drops of aqueous NaOH were added to 5ml of extract.	Yellow colouration is observed	Indicates the presence of flavonoid
Tannins	About 0.5ml of the extract was dissolved in 10ml of distilled water, and then filtrated.	A blue-black precipitate is formed	Indicate the presence of tannin
Alkaloids			
(a)	A few drops of Mayer's reagent were added to a sample of the extract in a test tube	The cream precipitate is formed	Indicate the presence of alkaloids
(b)	A few drops of Dragendorff's reagent were added to the extract		Indicate the presence of alkaloids
(c)	A few drops of Wagner's were added to a small extract		Indicate the presence of alkaloids
Steroid and Triterpenes	An equal volume of acetic anhydride was added to the extract. 1ml of concentrated sulphuric acid was added downside the tube.	The red, pink, or purple colour was observed, and a blue-green or blue was also observed.	Red, pink, and purple Indicates the presence of triterpenes and while blue or blue-green indicates the presence of steroid

Weight Loss Measurements

The test medium was prepared with varying concentrations of 400 ppm, 600 ppm, 800 ppm, 1000 ppm of each extract, and a control medium without inhibitor was also provided according to ASTM G1-03 (2017) (Standard practice for preparing, cleaning and evaluating corrosion test specimens). The carbon steel test specimens were weighed, suspended with rubber threads and fully immersed in each test medium in a 250 ml beaker at various temperatures (303, 313, 323, and 333K) for 33 days. The carbon steel test specimens were retrieved after the first five days, then at seven days intervals, washed thoroughly with distilled water, dried with acetone, and re-weighed. The experimental setup is in (Plate 2).

The weight loss (Δw), corrosion rate (CR), degree of surface coverage (θ), and inhibition efficiency (IE) were calculated using equations 2 - 5:

$$\Delta w = w_i - w_f \quad (2)$$

$$CR = \frac{\text{weight loss (g)}}{\text{area } (m^2) \text{ of the specimen} \times \text{immersion time(day)}} \quad (3)$$

$$\theta = \frac{\text{weight loss } (w_i - w_f)}{w_i} \quad (4)$$

$$IE = \frac{\text{weight loss } (w_i - w_f)}{w_i} \times 100 \quad (5)$$

Where w_i and wf are the initial and final weights of the low carbon steel coupon.

Plate 2 Experimental setup

Scanning Electron Microscopy (SEM) analysis

The surface morphology of low carbon steel specimens in crude oil in the absence and presence of extracts from bark and root of *Acacia nilotica* for 33 days was examined using a scanning electron microscope (SEM) at the Nigerian Institute of Leather and Science Technology (NILEST), Zaria, Nigeria.

3. RESULTS AND DISCUSSION

Phytochemical Analysis of the Extracts

The phytochemical constituents of the methanol extract of *Acacia nilotica* are in (Table 3). The result indicates that Alkaloids, Cardiac glycosides, saponins, Flavonoids, Tannins, Anthraquinone, steroids, and triterpenes are all present in the bark, while the root extract contains no Anthraquinone content.

Table 3 Phytochemical Screening of Extracts

Chemical Constituent	Root	Bark
Carbohydrates	+	+
Anthraquinone	-	+
Cardiac glycoside	+	+
Saponins	+	+
Steroid	+	+
Triterpene	+	+
Tannins	+	+
Flavonoid	+	+
Alkaloid	+	+

+ indicates presence; - indicates absence

Tannins, an ingredient known to be commonly used for dye, are the most active ingredient in inhibiting corrosion in steel. To inhibit the corrosion of the steel, a thin film is usually formed on the surface of the metal, which then isolates the metal surface from the environment causing a reduction in corrosion rate.

Effect of exposure time on Corrosion Rate

Figure 1-4 show the effect of the inhibitor on the exposure time of low carbon steel in crude oil at concentrations of 400, 600, 800, and 1000 ppm at ambient temperature. The result showed a higher corrosion rate in the separate uninhibited medium than the inhibited medium and decreased with an increase in the number of days viz: From 5 days – 33 days. This behaviour is attributed to the high adsorption level of active ingredients by the plant extract on the metal surface to reduce attack on the metal from the crude oil environment, thereby lowering the metal's weight loss.

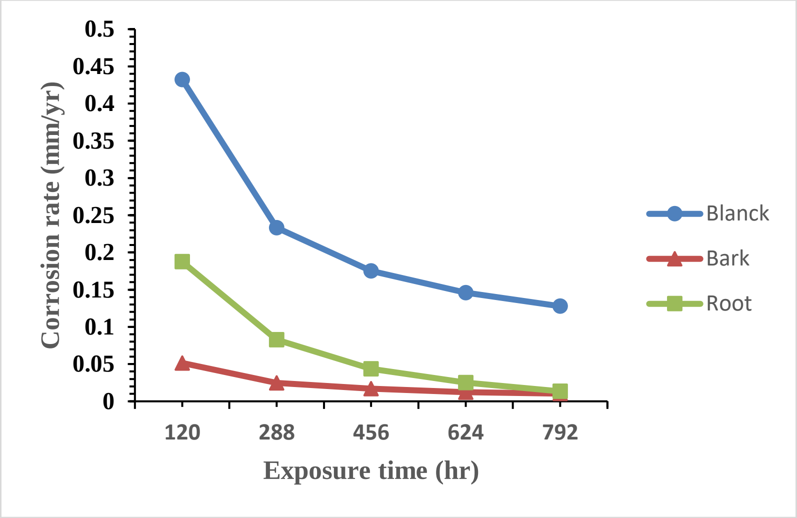


Figure 1 Variation of corrosion rate with respect to exposure time for corrosion of low carbon steel in crude oil in the absence (Blanck) and presence of 400 ppm concentration of crude extract

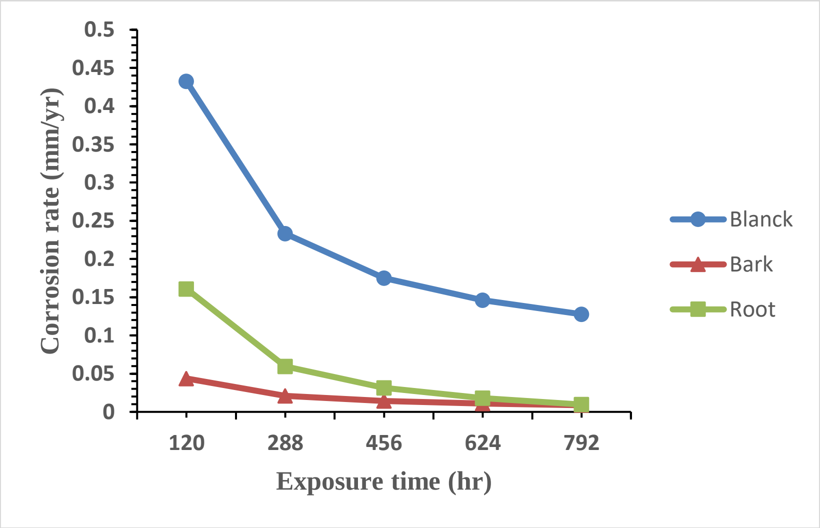


Figure 2 Variation of corrosion rate with respect to exposure time for corrosion of low carbon steel in crude oil in the absence (Blank) and presence of 600 ppm concentration of crude extract

Effects of Concentration on inhibition efficiency

Figures 5-9 show the variation of extract concentration on the inhibition efficiency. It is generally observed that there is a direct proportionality between the two variables. The plots indicate an increase in inhibition efficiency at higher inhibitor concentrations for the two extracts, with the root and the bark having efficiencies of 94.67% and 95.58%, respectively, at the concentration of 1000ppm. Yawas, (2005) and Kuburi, (2011) obtained similar results.

Thermodynamic consideration

Thermodynamic parameters of the corrosion reaction, namely activation energy E_a, entropy ΔS_{act}, and enthalpy ΔH_{act} which provide valuable insights when discussing the corrosion behaviour of different systems (Ikeuba and Okafor, 2018) were calculated using Arrhenius equation (Eq. 6) and transition state theory (Eq. 7) (Khadom et al., 2017; Umoren et al., 2007).

$$CR = A \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S_{act}}{R}\right) \exp\left(-\frac{\Delta H_{act}}{RT}\right) \quad (7)$$

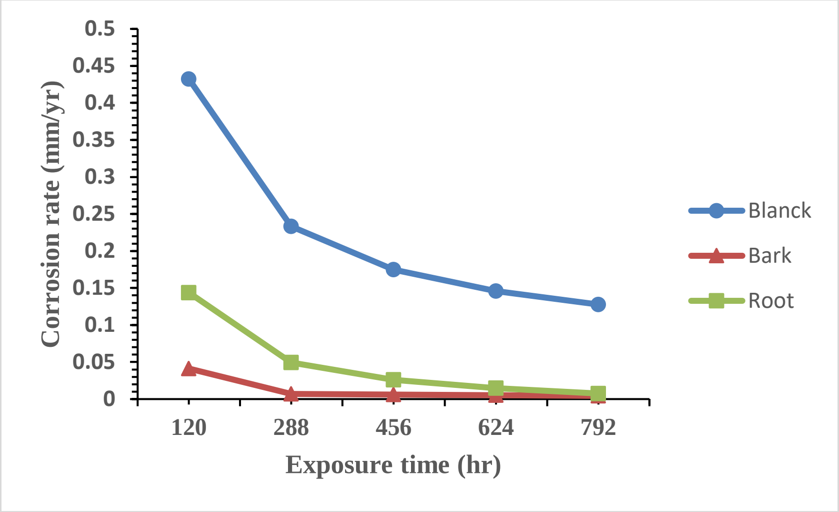


Figure 3 Variation of corrosion rate with respect to exposure time for corrosion of low carbon steel in crude oil in the absence (Blanck) and presence of 800 ppm concentration of crude extract

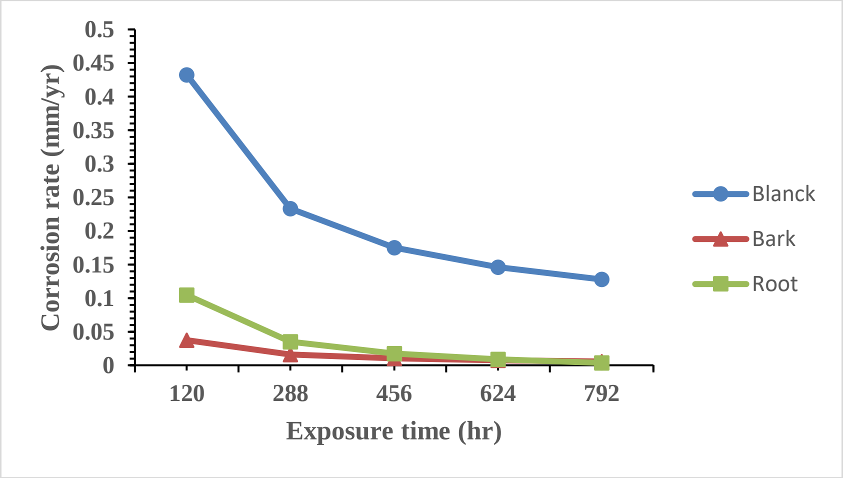


Figure 4 Variation of corrosion rate with respect to exposure time for corrosion of low carbon steel in crude oil in the absence (Blanck) and presence of 1000 ppm concentration of crude extract

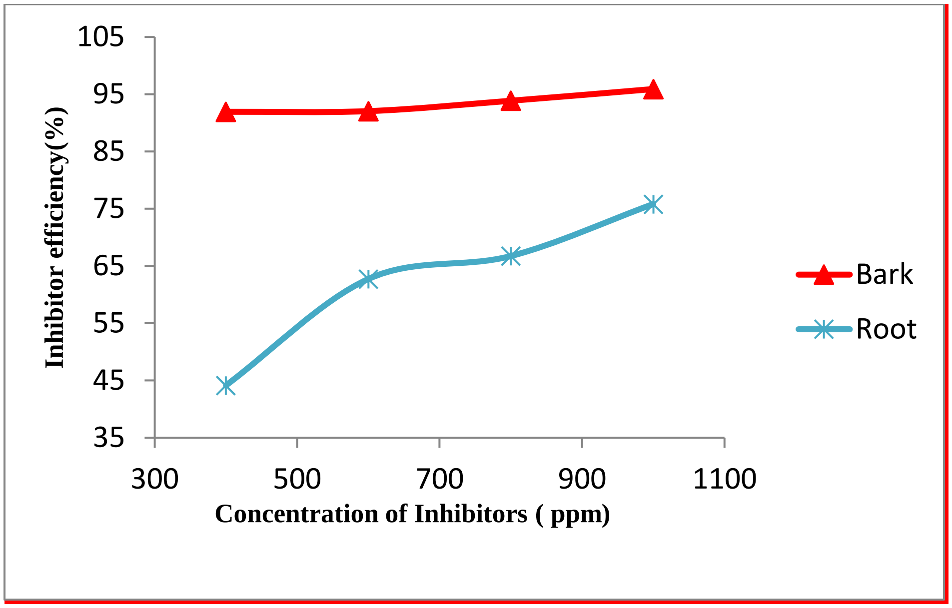


Figure 5 Variation of inhibitor Efficiency with inhibitor concentration of low carbon steel in crude oil after five days at ambient temperature

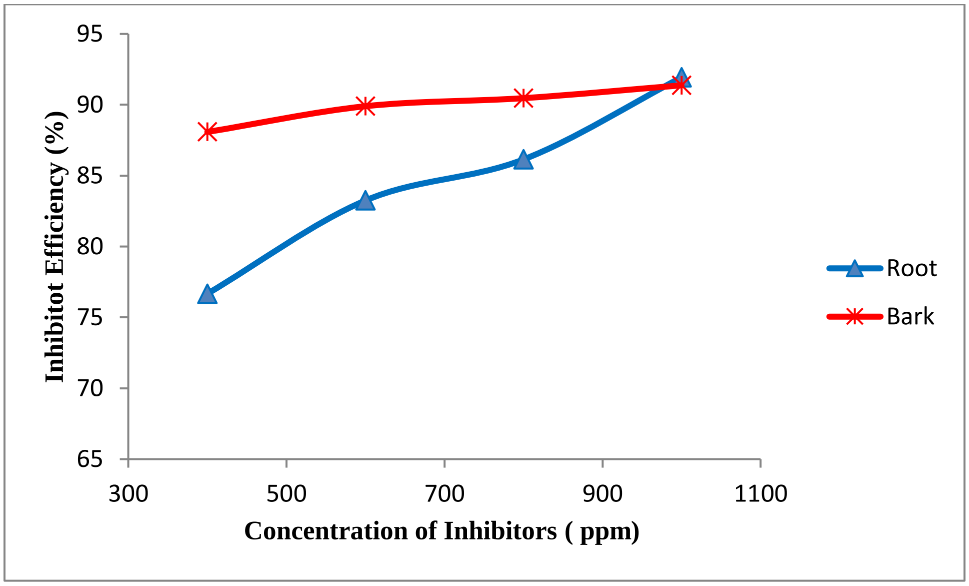


Figure 6 Variation of inhibitor Efficiency with inhibitor concentration of low carbon steel in crude oil after 12 days at ambient temperature

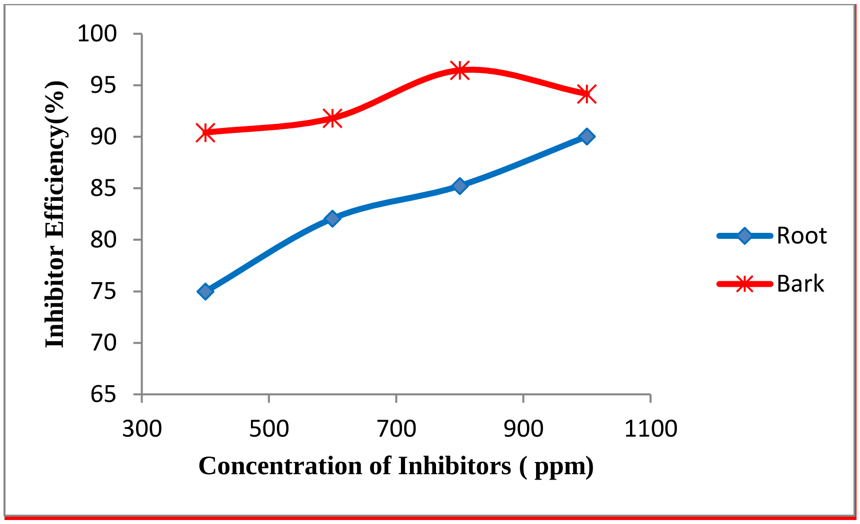


Figure 7 Variation of inhibitor Efficiency with inhibitor concentration of low carbon steel in crude oil after 19 days at ambient temperature

where A is the frequency factor, T is the absolute temperature, R is the universal gas constant, N Avogadro's number ($6.022 \times 10^{23}\ molecule\ mol^{-1}$), and h Plank's constant ($6.626 \times 10^{-34} J\ s.molecule^{-1}$). Eq. (6) can be plotted as $\ln CR$ against ${}^{1}/_{T}$ for the root and bark extracts, as in (Figure 10, 11). Slope and intercept yield the values of A and E_a. All the values are lower than the threshold value of 80 kJ/mol (Eddy and Odoemelam, 2009), which supports the physical adsorption mechanism (physisorption). Higher values of E_a in the presence of an inhibitor indicate that the extract increased the energy barrier for the corrosion process.

Eq. (4) can be plotted as $ln({}^{CR}/_{T})$ against ${}^{1}/_{T}$, as in (Figure 6, 7, 8). The plots gave a linear graph with a slope equal to $-{}^{\Delta H_{act}}/_{2.303\ R}$ and an intercept equal $[log\ ({}^{R}/_{Nh}) + {}^{\Delta S_{act}}/_{2.303\ R}]$. The entropy of activation is positive in both the absence and presence of inhibitor; the increase in entropy implies that disordering occurred on going from reactants to the activated complex. The positive sign of enthalpy of activation reflects the endothermic nature of the steel dissolution process, meaning that the dissolution of steel is challenging and controlled by the activation complex.

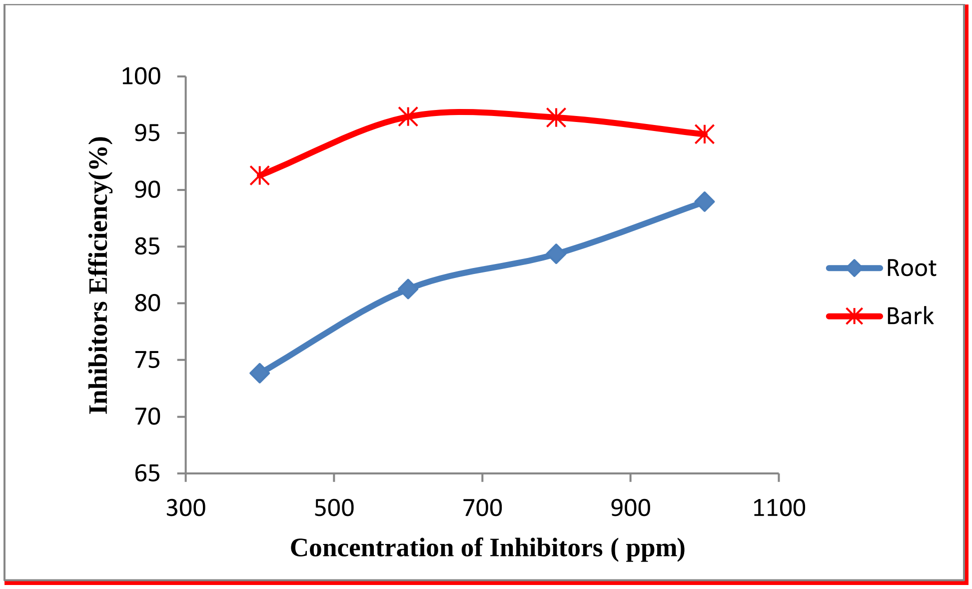


Figure 8 Variation of inhibitor Efficiency with inhibitor concentration of low carbon steel in crude oil after 26 days at ambient temperature

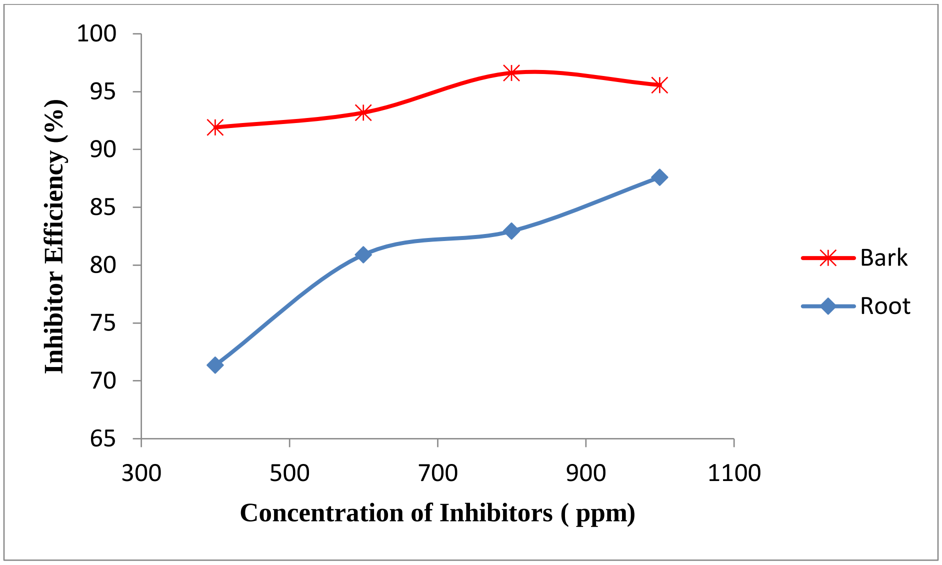


Figure 9 Variation of inhibitor Efficiency with inhibitor concentration of low carbon steel in crude oil after 33 days at ambient temperature

An increase in the corrosion reaction's energy barrier explains the increase of E_a and ΔH_{act} accompanying the increase in the inhibitor concentration. The high activation energy in the inhibitors' presence further supports the proposed physisorption mechanism. The activation energy (E_a), enthalpy of activation ($-\Delta H_{act}$)and the entropy of activation (ΔS_{act}) were calculated (Table 4).

Langmuir adsorption isotherm

The adsorption isotherm is used to describe the interaction between the inhibitor and the metal surface. The inhibition mechanism is generally attributed to the adsorption of the inhibitor species onto the metallic surface. The molecules of the inhibitor on metal are influenced by the nature and charge of the metal, chemical structure of the inhibitor and the type of electrolyte (Umoren et al., 2007; Fouda and Wahed, 2016). The Langmuir theory allows the most basic presentation of adsorption on an ideal surface. The Langmuir adsorption isotherm can be represented by Equation 8 (Nataraja et al., 2011; Ameer et al., 2010; Fouda and Wahed, 2016).

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (8)$$

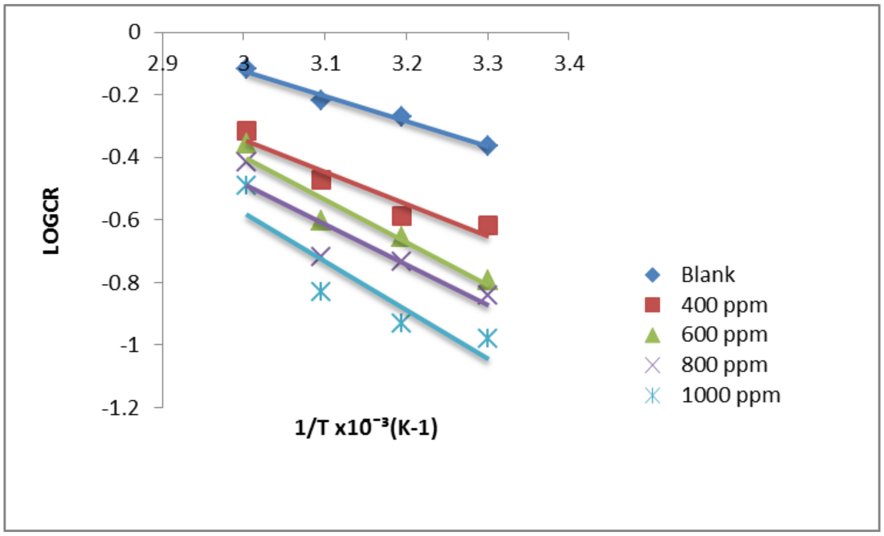


Figure 10 Arrhenius plot for low carbon steel in crude oil in the blank and presence of various concentrations of root extract

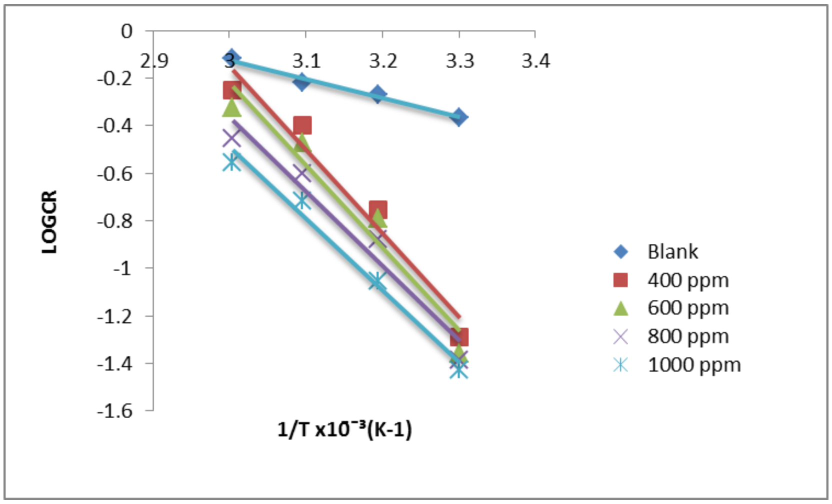


Figure 11 Arrhenius plot for low carbon steel in crude oil in the blank and presence of various concentrations of bark extract

Table 4 Values of activation energy, enthalpy of activation, and entropy of activation for the two inhibitors in the crude oil environment

Concentration (ppm)	Root			Bark		
	E_a (kJ/mol)	ΔH_{act} (kJ/mol)	ΔS_{act} (J/mol)	E_a (kJ/mol)	ΔH_{act} (kJ/mol)	ΔS_{act} (J/mol)
Blank	35.49	35.47	1160.185	35.49	35.47	1160.185
400ppm	67.55	67.52	1253.324	37.82	35.14	1193.353
600ppm	69.94	69.91	1259.2	44.64	41.96	1180.718
800ppm	71.54	71.52	1262.526	47.29	44.61	1166.689
1000ppm	73.29	73.89	1268.058	53.52	50.83	1187.379

Where C is the concentration of the inhibitor, K is the equilibrium adsorption constant, and θ is the surface coverage (Ikeuba, 2019; Okafor, 2010). The plot of $^{C}/_{\theta}$ against C gives a linear behaviour at all temperatures studied for inhibitor extracts, as in (Figure 12, 13).

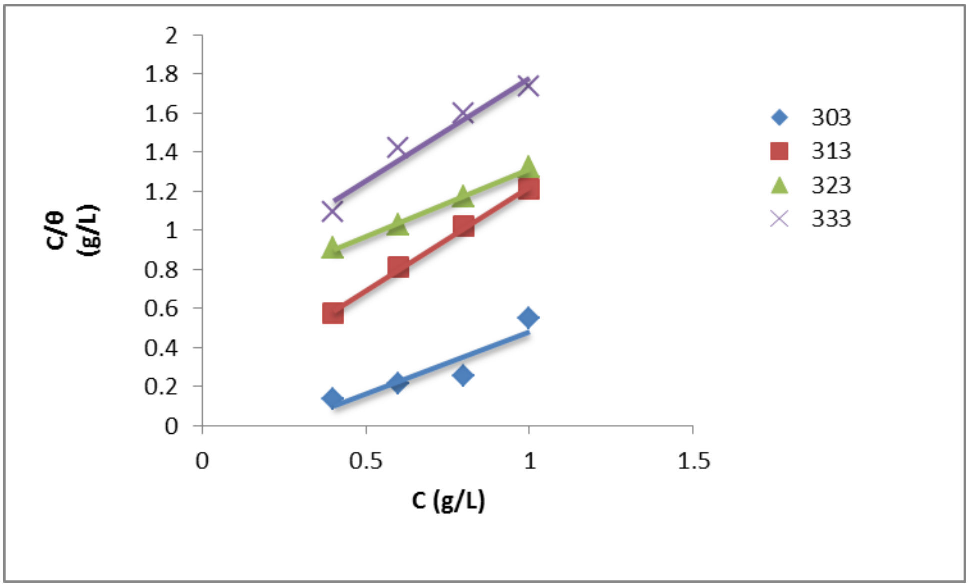


Figure 12 Plot of C/θ against C for corrosion of low carbon steel in crude oil at different concentrations of root extract

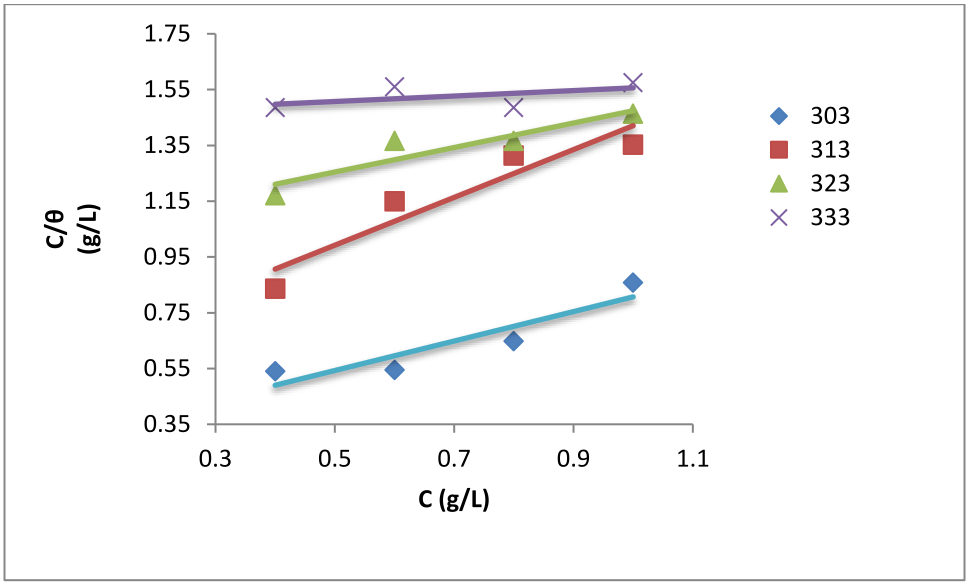


Figure 13 Plot of C/θ against C for corrosion of low carbon steel in crude oil at different concentrations of bark extract

The reciprocal of the slope K_{ads} is the adsorptive equilibrium constant representing the degree of absorption. The high values of K_{ads} indicate that inhibitors are strongly adsorbed on the metal surface. The adsorption rate constant $K_{ads\,values}$ from the isotherm for the two inhibitors, Gibbs free energy G_{ads}, and the correlation factors R^2 were also obtained from the plot and in (Table 5). From the K_{ads} values, the standard adsorption free energy ΔG_{ads} values shown in the Table were obtained using equation 9:

$$K_{ads} = \frac{1}{55.5}\exp\left(-\frac{\Delta\, G^0_{ads}}{RT}\right) \qquad (9)$$

The constant value of 55.5 is the water concentration in solution (mol/l). The adsorption parameters are listed in Table 5 and show the higher correlation coefficients (R^2) obtained using Langmuir adsorption isotherm. Generally, a higher value of K_{ads} encourages adsorption on low carbon steel surfaces. On the other hand, it was observed to increase with an increase in temperature. The K_{ads} values may be taken as an indication of the strength of the adsorption forces between the inhibitor molecules and the low carbon steel surface (Fekry and Ameer, 2010), leading to the improvement of the adsorption process at elevated temperatures.

The negative values of ΔG_{ads} mean that the adsorption of the inhibitors on the low carbon steel surface is a spontaneous process and also indicates a strong interaction of the inhibitor molecule onto the low carbon steel surface, as earlier shown by Zarrouk et al., (2011). Generally, ΔG_{ads} around $-20kJ/mol$ or lower values are constant with the electrostatic interaction between the charged molecules and the charged metal (physisorption). Those more negative than -40KJ/mol involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (Chemisorption) as established by Zarrouk et al., (2011).

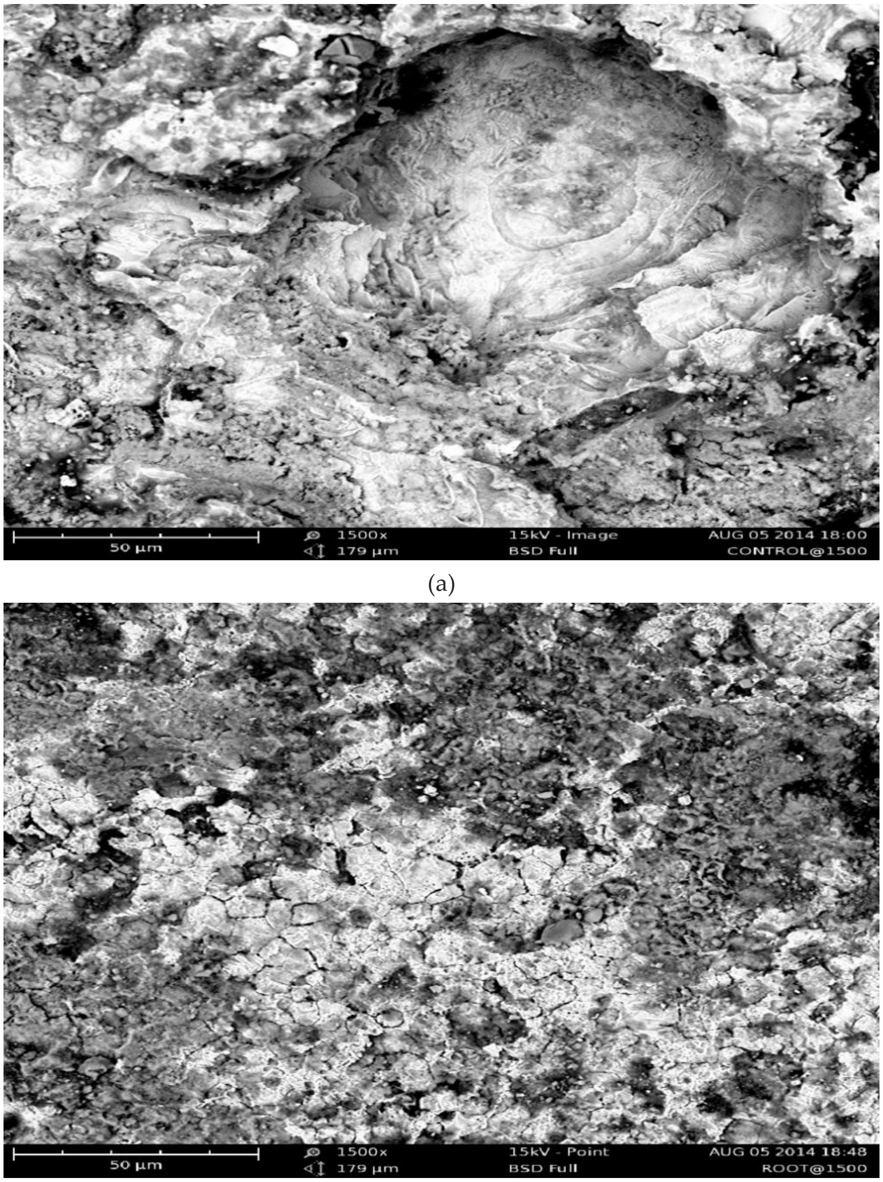
The calculated values of ΔG_{ads} are more significant than $-20kJ/mol$ but less than $-40kJ/mol$ indicating that the adsorption mechanism of inhibition on low carbon steel by crude oil at the studied temperatures might be a combination of both physisorption and chemisorption (comprehensive adsorption) as posited by Zarrouk et al., (2011). However, physisorption was the major contributor, while chemisorption slightly contributed to the adsorption mechanism judging from the decrease of inhibitor efficiency (IE) with an increase in temperature and the higher values of E_a obtained in the presence of inhibitor.

Table 5 Langmuir adsorption isotherm for the two inhibitors in Crude oil on low carbon steel samples at different temperature

	Root			Bark		
Temperature (K)	K_{ads} (mol^{-1})	$\Delta\, G^0_{ads}$ (kJ/mol)	Linear regression coefficient (R^2)	K_{ads} (mol^{-1})	$\Delta\, G^0_{ads}$ (kJ/mol)	Linear regression coefficient (R^2)
303	646.83	26.42	0.8391	771.46	26.87	0.8858
313	944.73	-28.287	0.996	857	-28.033	0.9415
323	1448.44	-30.338	0.9974	2276.35	-31.552	0.9537
333	953.47	-30.120	0.9587	10214.5	-36.687	0.9815

Scanning electron microscopy consideration

The scanning electron microscope (SEM) was used to evaluate the conditions of the low carbon steel surface in the absence and presence of extracts from *acacia nilotica* (the root and bark) in the crude oil environment for 33 days. The images are in (Figure 14a-c). These figures show that surface corrosion of low carbon steel decreased noticeably in the presence of extracts. Examinations of the scans expose severe damage, clear pits, and cavities on low carbon steel surfaces in the absence of inhibitor (Figure 14a) than in its presence (Figure 14b, 14c). There are fewer pits and cracks observed on the inhibited surface. It confirms that the metal surface is covered with the molecules from the extracts, and a protective inhibitor layer was formed, evident from the results obtained from the weight loss analysis.



(b)

(c)

Figure 14 SEM micrograph of low carbon steel in (a) crude oil at 50µm magnification (b) crude oil + 1000ppm of root extract at 50µm magnification (c) crude oil + 1000ppm of bark extract at 50µm magnification

4. CONCLUSION

Acacia nilotica extracts (root and bark) act as excellent and efficient anti-corrosion material for low carbon steel in crude oil. The phytochemical analyses show that all the two extracts contain tannin and other constituents responsible for inhibiting corrosion in low carbon steel. The inhibition efficiency increases with inhibitor concentration, and maximum inhibition efficiency for the extract was found to be 95.58% at the optimum concentration of 1000ppm. The adsorption of different concentrations of the plant extracts obeyed Langmuir's adsorption isotherm.

As the inhibitor concentration increased, higher activation energy, enthalpy of activation, and entropy of activation were obtained, which suggests a physical mechanism of adsorption (physisorption). The negative sign of the free energy of adsorption indicates that the adsorption of the extracts on the metal surface was a spontaneous process and was found to be a combination of physical and chemical adsorption. Investigations of the SEM figures show severe damage on low carbon steel surfaces in the absence of an inhibitor. There are fewer pits and cracks observed in the inhibited surface. It confirms that the metal surface is covered with the *acacia nilotica* molecules, and a protective inhibitor layer was formed.

Informed consent
Not applicable.

Ethical approval
Not applicable.

Conflicts of interests
The authors declare that there are no conflicts of interests.

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Data and materials availability
All data associated with this study are present in the paper.

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