Anticorrosion Potential of *Kola nitida* Testa Extract on Mild Steel in Acidic Environment

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Abstract-The inhibitive effects of ethanolic extracts of *Kola nitida* testa (KNT) on the corrosion of mild steel in hydrochloric acid solution was investigated using gravimetric method. Experiments were performed by varying immersion period, concentration of the inhibitors and the temperature of study. The results revealed that ethanolic extract of KNT acts as a potential inhibitor for mild steel corrosion in acid media. Inhibition efficiency increased with increasing concentration of the extract and temperature. Thermodynamic studies revealed that corrosion inhibition may be due to the spontaneous chemical adsorption of the plant constituents on the surface of mild steel. Langmuir adsorption isotherm is the best adsorption model applicable to the adsorption of KNT extract on mild steel. Activation parameters such as activation energies (E_a), activation enthalpy (ΔH^o) and activation entropy (ΔS^o) were evaluated from the effect of temperature on the corrosion and inhibition process. There was an indication of synergism when potassium halide was introduced with the extract to inhibit corrosion of mild steel in the acid media.

Keywords: corrosion, mild steel, inhibitor, *kola nitida*, inhibition efficiency, Langmuir.

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1   INTRODUCTION

MILD steel is an important category of materials due to its wide range of industrial applications. It is used in many industries due to its excellent mechanical properties as pipelines for petroleum industries, storage tanks, reaction vessels and chemical batteries [1]. However, it is highly susceptible to corrosion attacks [2].

Several mineral acid solutions are widely used for various treatments of materials in industry such as pickling, descaling, acid cleaning and oil-well acidizing, thus the presence of corrosion inhibitors is very important to keep the surface of steel intact and reduce their corrosion rates. The highly corrosive nature of aqueous mineral acids on most metals requires degree of restraint to achieve economic maintenance, operation of equipment, minimum loss of chemical product and maximum safety condition [3].

Use of inhibitors is one of the most practical methods for protection of mild steel against corrosion, especially in acid solutions to prevent unexpected metal dissolution and acid consumption [4]. Meanwhile, the most common type of corrosion inhibitors are organic compounds. Their inhibition property is dependent upon their functional group, which adsorb on the metal surface forming a protective barrier [5]. The efficiency of these organic corrosion inhibitors is related to the presence of polar functions with S, O or N atoms in the molecule, heterocyclic compounds and π electrons [6], [7]. The polar function is usually regarded as the reaction centre for the establishment of the adsorption process [8], [9].

A large number of organic compounds have been used as corrosion inhibitors for mild steel and most of them are highly toxic to both human beings and environment. Due to the increasing environmental awareness and the negative effects of some chemicals, research activities in recent times are geared towards environmentally safe corrosion inhibitors [9].

The exploration of natural products of plant origin as inexpensive, eco-friendly corrosion inhibitors is an essential field of study [10]. In addition to being environmentally friendly and ecologically acceptable, plant products are low-cost, readily available and renewable sources of materials [11], [12], [13]. The inhibition performance of plant extract is normally ascribed to the presence of complex organic species including tannins, alkaloids and nitrogen bases, carbohydrates and proteins as well as hydrolysis products. These organic compounds usually contain polar functions with nitrogen, sulphur, or oxygen atoms as well as those with triple or conjugated double bonds or aromatic rings in their molecular structures, which are the major adsorption centres [13]. Some have been reported to function as effective inhibitors of metal and alloy corrosion in different aggressive environments [8], [14], [15].

2   Materials and Method

2.1   Material Preparation

The mild steel used for this experiment was obtained in the form of a square rod. A spectrometric analysis of the steel gave its chemical composition as: 0.122% C, 0.172% Si, 0.56% Mn, 0.021% P, 0.032% S, 0.085% Cr, 0.114% Ni, 0.0068% Mo, 0.0022% Zr, 0.0009% Al, 0.280% Cu, 0.0069% Co, 0.0008% Ti, 0.0062% Nb, 0.0013% V, 0.012% W, 0.0023% Pb, 0.0006% La, 0.0011% B, 0.011% Sn, 0.0022% Zn, 0.0009% As, 0.0009% Bi, 0.0008 % Ca, 0.0038% Ce, 98.6% Fe. The coupons were pressed cut into 14 mm ×11mm ×11mm and their surfaces abraded with emery papers, washed with water and air-dried. Subsequently, the initial weights of the coupons were measured on a Metler balance up to 0.0001g accuracy. Immediately afterwards, the coupons were immersed completely in the freshly prepared corrosion media. Analytical grade Hydrochloric acid and distilled water were used to prepare 1M HCl for the experiments. Ethanol was used in obtaining the aqueous extracts of

the *Kola nitida* testa (KNT). The agricultural waste was collected from a farm, washed and sun-dried. It was then blended and sieved into fine particles. Ethanol extract of the fine particles was obtained by soaking 100 g of the sample in 1000 mL of ethanol for 72 hours at room temperature, after which the mixture was filtered. The filtrate was further subjected to evaporation over a boiling water bath and finally, a solid residue was obtained and preserved in a desiccator.

The corrosion media were prepared with 1M HCl having different inhibitor concentrations (g/v): viz., 0%, 0.5%, 1.0%, 1.5% and 2.0% of KNT extracts. Pre-weighed coupons were immersed in the corrosion media and after completion of each exposure test, the coupons were removed, rinsed under running tap, further rinsed with distilled water and in acetone, dried and weighed to determine weight losses due to corrosion.

2.2. Characterization of the extract

Phytochemical analysis of the extract, carried out according to the method described by AOAC [16], showed that the extract contains tannin, cardiac glycoside, steroid, flavonoids, saponin and terpenoid, the presence of which has been identified to be responsible for inhibition of corrosion on metal surface in some plants extracts [17], [18], [19] and [20]. Infrared spectroscopy of the extracts was carried out using FTIR spectrophotometer (spectrum bx, Perkin Elmer) to elucidate the functional groups of the active constituents responsible for the inhibitive properties of the extract.

2.3. Weight Loss Studies

Mild Steel samples were immersed in 1 M HCl solution containing different concentrations of inhibitor for two hours. Samples were weighed before and after immersion after which the weight difference was determined. The corrosion rate, percentage inhibition efficiency and degree of surface coverage (θ) were calculated from the following equations:

$$\text{Corrosion rate } C_R = \frac{\Delta w}{At} \qquad (1)$$

Inhibition Efficiency

$$(\text{I.E\%}) \quad = 1 - \left[\frac{C_{R2}}{C_{R1}}\right] \times 100 \qquad (2)$$

$$\text{Surface coverage } (\theta) = \frac{\% \text{ I.E}}{100} \qquad (3)$$

where Δw is the weight loss in grammes, C_{R1} and C_{R2} are the corrosion rates of the mild steel strip coupons in absence and presence of inhibitor, A is the cross-sectional area in cm^2 and t is the exposure time in hours.

3.0   Results and Discussion
3.1   Effect of extract concentration on Corrosion Rate and Inhibition Efficiency

The effect of extract concentration on the corrosion rate of the mild steel and inhibition efficiency of the extract is shown in Figures 1a and 1b, respectively. The corrosion rate of the mild steel in the presence of the extract decreases with increasing concentration of the extract. However, the inhibition efficiency of the extract increases monotonically as the concentration of the extract increases. Maximum inhibition efficiency of 91.14 % was achieved with 2% of KNT extract at 2 hours of immersion at room temperature.

In accounting for the observed protective effect, it should be noted that the extract comprises a mixture of organic and resinous matters as revealed by the phytochemical screening, some of which are known to exhibit good corrosion inhibiting abilities. The complex chemical composition makes it rather difficult to assign the inhibiting action to a particular constituent due to higher degree of surface coverage resulting from enhanced adsorption of the extract organic matter [21]. However, we are currently carrying out active research on the isolation and characterization of the constituents with a view to understanding the particular constituent in KNT which is most responsible for the inhibition of mild steel.

The inhibitive properties of tannins have been attributed to the reaction of the polyphenolic fraction of the tannin molecule with ferric ions, thereby forming a highly cross-linked network of ferric tannate moieties which ensures effective protection of the metal surface. The triterpenoid and other constituents also possess functional groups which are capable of chelating with ferric ions and thus facilitate strong coordination on the steel surface. The resulting Fe-extract complexes depending on their relative solubility, inhibit or even catalyse further metal dissolution. The present result indicates a pervasiveness of the inhibiting effect, which implies that the Fe-extract complexes formed an insoluble surface layer which isolated the metal surface from the corroding medium. The integrity of this protective film has been shown to be quite sensitive to the extract concentration [10]. Possible synergistic interactions between the different adsorbed constituents could also contribute to the high inhibition efficiencies observed.
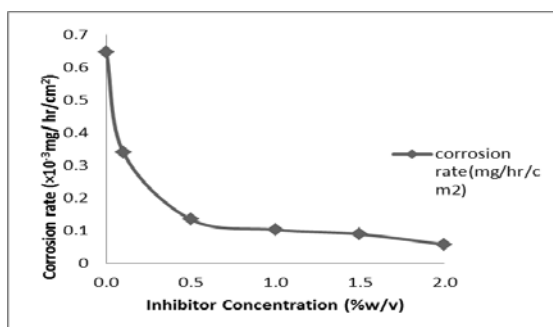
Fig. 1a Effect of extract concentration on corrosion rate of mild steel at room temperature
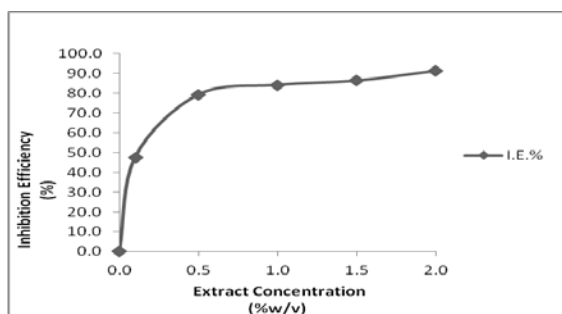

Fig. 1b Effect of extract concentration on inhibition efficiency of mild steel at room temperature

3.2 Effect of Immersion Time

In order to assess the stability of inhibitive behaviour of the extract on a time scale, weight loss measurement was performed in 1M HCl in absence and presence of the extract at 0.5, 1.0, 1.5 and 2.0% (w/v) concentration for 24 to 120 hours at room temperature. The plot of weight loss against time (Fig. 2) shows that increase in concentration of extract reduces the corrosion rate. The graph of logarithm of weight of the metal after immersion was plotted against time to obtain the rate constant (k).

$$\ln (W_i - \Delta W) = -kt + \ln W_i \qquad (4)$$

The half life of the inhibitor was determined using the following equation:

$$t_{1/2} = \frac{0.693}{k} \qquad (5)$$

where k is the rate constant. The values of the rate constant and half-lives are listed in Table 1. A logarithmic plot of the weight of the metal against time using equation 4 revealed that the reaction follows a first order reaction (Fig. 3) and the half-lives of the mild steel increase as the concentration of the extract increases suggesting that inhibition efficiency increases with increase in the concentration of the extract.

Table 1:   The values of rate constant (k) and half-life ($t_{1/2}$) for mild steel in 1M HCl with and without different concentration of KNT extract.

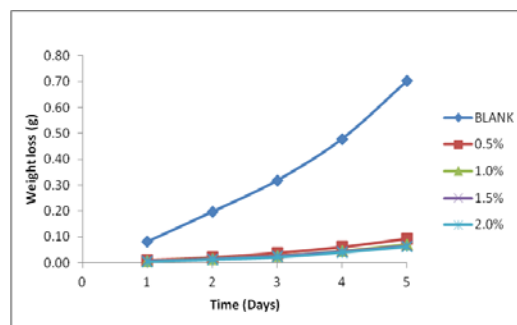| Extract Concentration (g/v)	Rate Constant day^{-1} ($\times 10^{-3}$)	Half-lives (days)
Blank	11.04	62
0.5	2.17	498
1.0	1.35	644
1.5	1.05	662
2.0	0.99	700

Fig. 2   Variation of weight loss against time for the corrosion of mild steel in 1M HCl with and without the extract
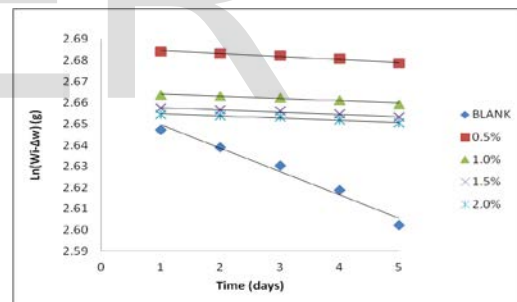

Fig. 3   A plot of ln (W_i-ΔW) against Time for the adsorption of ethanolic extract of *Kola nitida* testa on Mild Steel at room temperature

3.3 Effect of Temperature

Two main types of interaction often describe adsorption of organic inhibitors on a corroding metal surface viz: chemical adsorption and physical adsorption. It has been suggested that physisorbed molecules are attached to the metal at local cathodes and essentially retard metal dissolution by stifling the cathodic reaction whereas chemisorbed molecules protect anodic areas and reduce the inherent reactivity of the metal at the sites where they are attached [8]. The more efficient inhibitors appear to protect anodic areas preferentially by chemisorptions [21].

In this study, temperature variation from 303K-333K was carried out in absence and presence of varying concentration of the extract. Results thus obtained are shown in Fig. 4. Inhibition Efficiency values were found to increase with increase in concentration of the extract and temperature. Inhibition efficiency of 90.72% was obtained with extract concentration of 2% (w/v) at 333K.
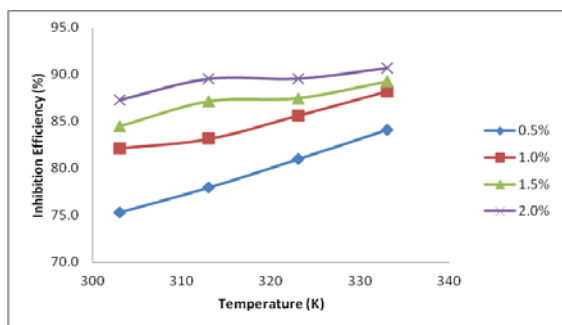

Fig. 4 Variation of Inhibition Efficiencies of ethanolic extract of *Kola nitida* testa with temperature on Mild Steel in 1M HCl.

Analysis of the temperature dependence of inhibition efficiency as well as comparison of corrosion activation energies in absence and presence of inhibitor gives some insight into the possible mechanism of inhibitor adsorption.

A decrease in inhibition efficiency with rise in temperature, with analogous increase in corrosion activation energy in the presence of inhibitor compared to its absence, is frequently interpreted as being suggestive of formation of an adsorption film of physical (electrostatic) nature. The reverse effect, corresponding to an increase in inhibition efficiency with rise in temperature and lower activation energy in the presence of inhibitor, suggests a chemisorption mechanism [21].

Fig. 5 shows Arrhenius plots for the mild steel in 1 M HCl solutions in the absence and presence of the extract. The activation energy (E_a) can be expressed by the Arrhenius equation:

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

where T is the absolute temperature, A is the Arrhenius constant and R is the universal gas constant. The values of k were taken to be equal to the corrosion rate of the mild steel. The activation energies are given in Table 2.

The enthalpy ($-\Delta H^o$) and entropy (ΔS^o) values were obtained from the Erying Transition State equation denoted by:

$$C_R = \left[\frac{RT}{Nh}\right] \exp\left[\frac{\Delta S^o}{R}\right] \exp\left[\frac{-\Delta H^o}{RT}\right] \qquad (7)$$

where h is the Plank's constant, N is the Avogadro's number, T is the absolute temperature, R is the universal gas constant, ΔS^0 is the entropy of activation and ΔH^0 is the enthalpy of activation. A plot of Log (C_R/T) against $1/T$ (Fig. 6) gave straight lines with slopes of ($-\Delta H^0/$ 2.303R) and intercept of Log R/N h + $\Delta S^0/2.303R$, from which the values of ΔS^0 and ΔH^0 were calculated.

Table 2 Calculated values of activation parameters for mild steel corrosion in 1M HCl in the absence and presence of different concentrations of *K. nitida* testa extract.

Concentrations (w/v)	Ea (kJmol⁻¹)	ΔH (kJmol⁻¹)	ΔS (kJmol⁻¹K⁻¹)
BLANK(1M HCl)	73.2785	70.6386	-75.8557
0.5%	61.0560	58.4162	-127.6596
1.0%	61.5940	58.9541	-128.4108
1.5%	63.8372	61.1973	-122.6674
2.0%	65.2889	62.6491	-119.6322

From the above Table, it is evident that E_a values in the presence of the different concentrations of the extract are lower than in their absence. The activation energy increased from 61.06 kJ/mol to 65.29 kJ/mol with increase of bio-inhibitor concentration. The average value of Ea obtained from blank (73.28 kJ/mol) is higher than that of the values obtained for a system containing various concentrations of the extract. The decrease in apparent activation energy in the presence of the extract denotes chemical adsorption while the reverse is usually attributed to physical adsorption [21], [22]. This conclusion is proven by the increase in inhibition efficiency with increasing temperature as shown in Fig. 4. Similar result has been reported by Okafor et al. [14]. This result indicated that the *Kola nitida* testa extract is adsorbed on the surface of mild steel by chemical adsorption [22], [23].

The positive values of ΔH both in the absence and presence of the extract reflect the endothermic nature of the mild steel dissolution process. It is also clear that the activation enthalpies vary in the same manner as the activation energies.

The shift towards negative values of entropies (ΔS) implies that the activated complex in the rate determining step represents association rather than dissociation, meaning that disordering reduces on going from reactant to activated complex. Similar observation has been reported in literature [24].
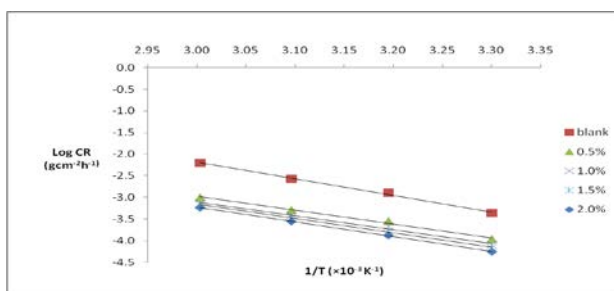
Fig. 5 Arrhenius plot for mild steel in 1 M HCl in absence (blank) and presence of ethanolic extract of *Kola nitida* testa
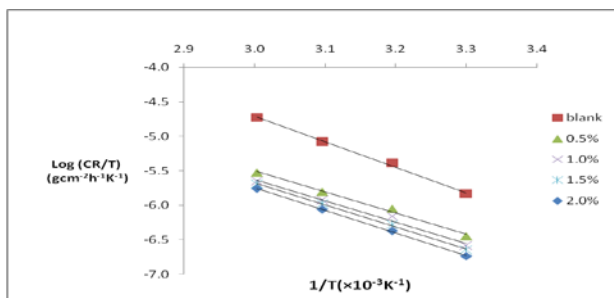

Fig. 6 Eyring transition state plot for mild steel in 1M HCl in the absence (blank) and presence of ethanolic extract of *Kola nitida* testa

3.4 Adsorption Studies

Adsorption isotherms provide basic information on the interaction between the inhibitor and the mild steel surface. For this purpose, the values of surface coverage (θ) at different concentrations of *Kola nitida* testa extract in HCl medium in the temperature range (303-333K) have been used to explain the best isotherm to determine the adsorption process. Attempts were made to fit these θ values to various isotherm including Langmuir, Temkin and Freundlich. According to these isotherms; θ is related to the inhibitor concentration C_{inh} via:

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

Langmuir isotherm

$$\exp(-2a\theta) = KC_{inh} \qquad (9)$$

(Temkin isotherm)

$$\text{Log } \theta = \text{Log } K + 1/n \text{ Log } C_{inh} \qquad (10)$$

(Freundlich isotherm)

where "K" is the binding constant of the adsorption reaction and "a" is the lateral interaction term describing the molecular interactions in the adsorption layer and the heterogeneity of the surface. By far, the best fit was obtained with Langmuir isotherm (with strong correlation coefficient $R^2 \approx 1$ at all the temperatures of study). The plots of C_{inh}/θ vs. C_{inh} yielded a straight line (Fig. 7). This indicates that the adsorbing *Kola nitida* testa extract occupies typical adsorption site at the metal/solution interface. As can be seen by the good fit, ethanolic extract of *Kola nitida* testa (EEKNT) as corrosion inhibitor was found to best fit Langmuir adsorption isotherm. The values of K_{ads} (Table 3) revealed that adsorption coefficient increases with increase in temperature.

Table 3 Calculated parameters from Langmuir adsorption Isotherm

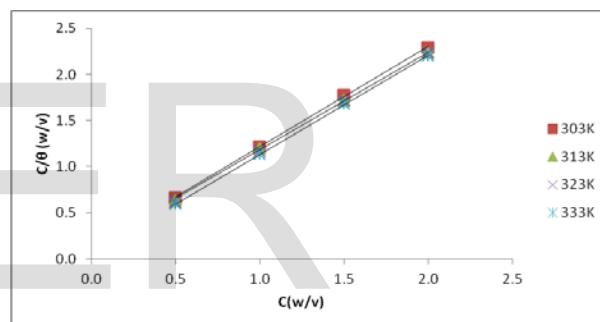| Temperature (K)	Slope	R² value	Adsorption constant (K_{ads})
303	1.0884	0.99969	7.9019
313	1.0590	0.99953	7.9368
323	1.0787	0.99980	11.7695
333	1.0755	0.99992	16.9115

Fig. 7 Langmuir adsorption isotherm plot for Mild Steel corrosion in 1M HCl for ethanolic extract of *Kola nitida* testa at different temperatures.

K_{ads} is related to the free energy of adsorption by the equation:

$$K_{ads} = \frac{1}{55.5} \exp\left[\frac{-\Delta G^\circ_{ads}}{RT}\right] \qquad (11)$$

This equation can also be expressed in the form as follows:

$$\Delta G^\circ_{ads} = -2.303RT \text{ Log } (55.5K_{ads}) \qquad (12)$$

where θ is the degree of surface coverage, ΔG°_{ads} is Gibbs free energy of adsorption, T is the temperature in Kelvin and K_{ads} is the equilibrium constant for the adsorption process and 55.5 is the molar concentration of water in solution. K_{ads} value was calculated from the intercept of Fig. 7 and presented in Table 3.

The free energy of adsorption values, ΔG°_{ads}, was obtained from Equation (12) above. The values obtained are presented in Table 4. Results presented in the table indicate

that the values of ΔG°ads are negative in all cases and ranged between -15.33 and -18.95 KJmol[-1]. The negative values of ΔG°ads indicate a spontaneous adsorption of the inhibitor molecules.

The values of ΔG°ads below -40 KJ/mol indicate that the inhibitor function by physically adsorbing on the surface of the metal. Generally, ΔG°ads less than 20 kJmol[-1] imply that coulombic electrostatic interactions exist between the charged molecules and the charged metal surface (which indicates physical adsorption) while those more negative than -40KJ/mol involves charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond which indicates chemisorptions [21], [25].

Results of the present study have shown that *Kola nitida* testa extract inhibits the acid induced corrosion of mild steel by virtue of adsorption of its components onto the metal surface. The inhibition process is a function of the metal, inhibitor concentration, temperature as well as inhibitor adsorption abilities which is so much dependent on the number of adsorption sites.

The mode of adsorption (physisorption and chemisorption) observed could be attributed to the fact that *Kola nitida* testa contains many different chemical compounds, some of which can be adsorbed chemically and others adsorbed physically. This observation may be attributed to the fact that adsorbed organic molecules can influence the behavior of electrochemical reactions involved in corrosion processes in several ways.

The action of organic inhibitors depends on the type of interactions between the substance and the metallic surface. The interactions can bring about a change either in electrochemical mechanism or in the surface available for the processes [18].

Table 4 The values of equilibrium constant and energy of adsorption for mild steel corrosion in 1M HCl for *K. nitida* testa extract at different temperatures.

Temperature (K)	K_{ads}	ΔG_{ads} (KJmol[-1])
303	7.9019	-15.3288
313	7.9368	-15.8462
323	11.7695	-17.4107
333	16.9115	-18.9536

3.5 Synergetic Influence of Potassium Iodide.

Inhibition efficiency of KNT on mild steel was observed in the presence of various concentration of KI (0.025M, 0.050M and 0.075M). The results showed that there was an increment in the inhibition efficiency of the extract on

addition of KI compared to the inhibitive effect of extract only as shown in Fig. 8.

It is generally believed that the presence of halide ions in acidic media synergistically increases the inhibition efficiency of some organic compounds. It is thought that the halide ions are able to improve adsorption of the organic cations by forming intermediate bridges between the positively charged metal surface and the positive end of the inhibitor. According to Oguzie *et al.* [26], corrosion inhibition synergism is as a result of increased surface coverage arising from ion-pair interactions between the organic cations and the anions.
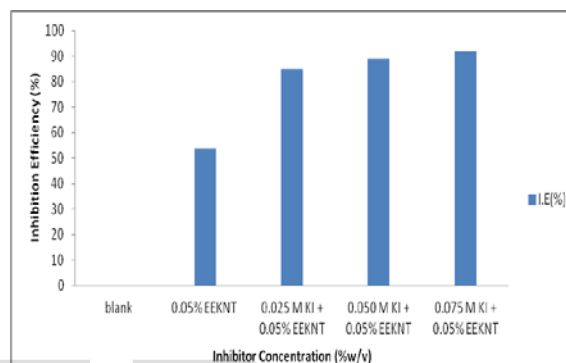

Fig. 8 Bar Chart showing the synergetic influence of Potassium Iodide on EEKNT

3.6 FT- Infra Red Spectroscopy.

FT-IR spectra of ethanolic extract of *Kola nitida* testa (EEKNT) and the corrosion product on the surface of mild steel in the presence of the inhibitors are represented by Figures 9 and 10, respectively. Fig. 9 shows the various adsorption bands of the phytochemicals present in EEKNT. Absorption bands were observed at 3399.00cm^{-1} strong peak corresponding to hydroxyl group, 1626.00 cm^{-1} corresponding to C=O (carbonyl groups), 1441.00 cm^{-1}, 1247.66 cm^{-1}, 1058.61 cm^{-1} corresponding to C=C stretch in alkenes, and 609.32 cm^{-1} which corresponds to the finger-print region of the adsorption band. Two intermediate peaks occur between 3399.00cm^{-1} and 1626.00cm^{-1}.

Fig. 10 reveals the various peaks of adsorption of the phytochemicals present in EEKNT on mild steel. Absorption bands were observed at 3754.28cm^{-1}, 3419.00cm^{-1}, 2365.71cm^{-1}, 1635.23cm^{-1}, 1016.83cm^{-1}, 676.00cm^{-1}, 444.04cm^{-1} and 369.94 cm^{-1}.

On comparing both spectra, for the -OH stretching of EEKNT, there was forward shift from 3399.00cm^{-1} (sharp) to 3419.00cm[-1](broad). This –OH stretching may suggest that there is an interaction between the extract and metal surface. Also, the stretching frequency of C=O and C-O

shift from 1626.00cm^{-1} to 1635.23 cm^{-1} could be due to electron cloud density shift from O atoms to co-ordinate with Fe^{2+} to form Iron-extract complex [10].

The band at 3754.28cm^{-1} is attributed to N–H or O–H stretching. The strong band at 1635.23 cm^{-1} could be assigned to C=C and C=N stretching vibration. Besides these, there is an absorption band at 1016.83 cm^{-1}, which can be assigned to the C–N or C–O stretching vibration. The absorption bands below 1000 cm^{-1} corresponds to aliphatic and aromatic C–H group. This result indicates that KNT contains oxygen and nitrogen atoms in functional groups (O–H, N–H, C=C, C=O, C=N, C–N, C–O), which meets the general consideration of typical corrosion inhibitors.
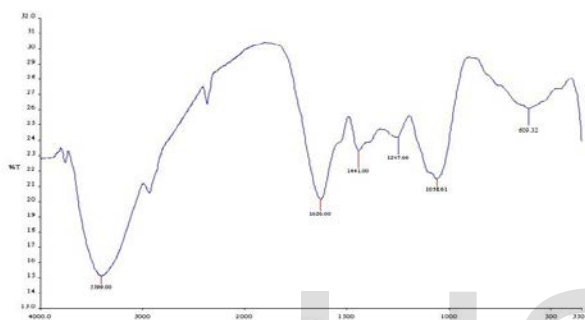

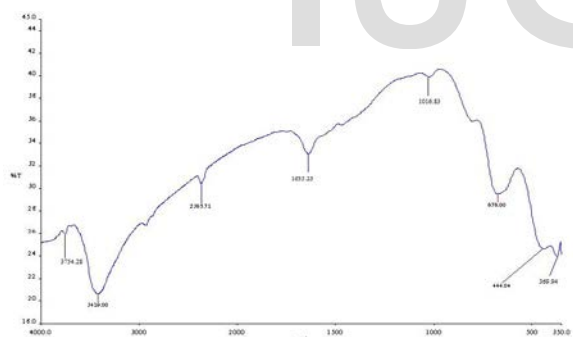**Fig. 9   FT-IR spectrum of ethanolic extract of *Kola nitida* Testa (EEKNT)**

Fig. 10   FT-IR spectrum of dried solid adsorption product of ethanolic extract of *Kola nitida* Testa (EEKNT) on Mild Steel.

4   Conclusion

The crude extract of *Kola nitida* testa acts as inhibitor for mild steel corrosion in acidic medium. Inhibition efficiency of the extract increases with increase in concentration of the inhibitor and also with increase in temperature. The corrosion inhibition is probably due to the adsorption of the phytochemical constituents of the extract on the metal surface thereby blocking its active sites by phenomenon of chemical adsorption. The extract was found to best obey Langmuir adsorption isotherm from the fit of the experimental data at all the concentrations and temperatures studied. The FT-IR spectra indicate that the extract contains O, and N atoms in functional groups (O-H, N-H, C-O, C=O, C-H) and aromatic rings which meet the general consideration of a typical corrosion inhibitor. The values of E_a obtained in the presence of the extract were lower compared to the blank acid solution which further support the chemical adsorption proposed. The values of $\Delta G°_{ads}$ obtained are low and negative, which reveals the spontaneity of the adsorption process. Kinetics of the inhibition process followed a first order reaction.

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