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Corrosion Inhibitory Potential of Ethanol Extract of *Senna obtusifolia* on Mild Steel in 5M HCl

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Abstract
This study investigated the corrosion inhibition potential of *Senna obtusifolia* on electrochemical corrosion behavior of mild steel exposed to 5.0 M HCl. The results of the phytochemical screening revealed the presence of secondary metabolites such as flavonoid, tannins, anthraquinones, terpenoids, alkaloids, phenols and saponins. The FTIR result also revealed aromatics and functional groups such as R-OH, C=O, C-O and C-H which are attributes of good corrosion inhibitors. The effect of the extract as corrosion inhibitor was evaluated using gravimetric method at different concentrations of 0.1, 0.2, 0.3, 0.4, and 0.5 w/v respectively. The result revealed that *Senna obtusifolia* exhibits an inhibition efficiency of up to 87.64 % at extract concentration of 0.5 w/v. This could probably be due to the presence of the secondary metabolite and other functional groups revealed by both the phytochemical screening and FTIR spectrum that were present in the extract of *Senna obtusifolia*. Thermodynamics data generated suggested co-adsorption through a combination of both physisorption and chemisorption modes of interaction of the inhibitor. The negative free energy indicates that adsorption is spontaneous. The adsorption obeys both Langmuir and Freundlich adsorption isotherms. The degree of linearity is close to unity which indicates strong adsorption of the extracts on the mild steel.

Keywords: *Senna obtusifolia*, corrosion inhibition, mild steel, HCl

1.0 Introduction

Corrosion is a deterioration of a metal due to its interaction with the environment such as water, acid, alkaline, air *etc.* As a result of corrosion, many useful properties of metals such as malleability, ductility and electrical conductivity are lost. Metals are particularly prone to corrosion in the presence of hydrochloric and sulphuric acids that are in turn widely used for acid pickling, industrial acid cleaning, acid descaling and oil-well cleaning [1]

Corrosion is a natural process, and all natural processes tend toward the lowest possible energy states. Thus, for example, iron and steel have a natural tendency to combine with other chemical elements to return to their lowest energy states. In order to return to lower energy states, iron and steel frequently combine with oxygen and water, both of which are present in most natural environments, to form hydrated iron oxides (rust), similar in chemical composition to the original iron ore. Just as some chemical species, such as salts, promote corrosion, other chemical species inhibit corrosion. Chromates, silicates, and organic amines are common corrosion inhibitors [2]. The mechanisms of inhibition can be quite complex. In the case of the organic amines, the inhibitor is adsorbed on anodic and cathodic sites and stifles the corrosion current. Other inhibitors specifically affect either the anodic or cathodic process. Still others promote the formation of protective films on the metal surface. The use of inhibitors is favoured in closed systems where the necessary concentration of inhibitor is more readily maintained. The increased use of cooling towers stimulated the development of new inhibitor/water-treatment packages to control corrosion and biofouling. Inhibitors can be incorporated in a protective coating or in a primer for the coating. At a defect in the coating, the inhibitor leaches from the coating and controls the corrosion [2].

Mild steel have become relevant to the industries due to its properties such as hardness, malleability, ductile, weld ability and most

importantly, it is relatively cheap. Even though, mild steel possesses all the mentioned properties, it is still faced with the problem of galvanic and crevice corrosion, especially when used in aggressive environment such as acidic solution [3].

The prevention of corrosion has become most important area of research because of the growing need to implement effective and economical corrosion prevention methods. There are several methods of corrosion control and prevention such as material selection, coating, cathodic protection and the use of corrosion inhibitors among others. Apart from the high cost of inorganic inhibitors, most of the chemical substances used as corrosion inhibitors contaminate the environment after use and cause a lot of problems and destruction of plant and animal lives, therefore restrictions have been placed on the use of some of these chemical inhibitors because of their toxic nature. This is why attention has shifted to the use of environmentally friendly and ecologically acceptable, inexpensive, readily available and renewable plant products as green inhibitors. Synthetic organic inhibitors have also been extensively applied but their use is now being marred by their toxicity and high cost of manufacturing [4].

Natural plant extract as green corrosion inhibitor is an environmentally friendly, less toxic, very cheap and easily available alternative. Various plant extracts have been used for this purpose. Polar atoms such as S, N, O, P etc are present in the plant extracts. The lone pair of electrons present on these atoms is pumped on to the surface of metal, reducing loss of electrons from the surface of metal. Thus corrosion inhibition takes place because of the formation of protective film by the adsorption of polar groups from plant extracts on metal surface. Thus corrosion is controlled by these hetero atoms [5]. Many researchers have demonstrated the use of extracts of plant materials in the control of the corrosion of mild steel [6, 7, 8, 9]. The aim of this research is to investigate the corrosion inhibitory potential of ethanol extract of *Senna obtusifolia* leaves on mild steel in 5M HCl solution.

2.0 Material and Methods

Senna obtusifolia leaves were collected from Minna, Niger State, Nigeria. The leaf samples were washed with distilled water, dried at room temperature and milled to fine powder.

2.1 Preparation of Plant Extract

Senna obtusifolia powder (250 g) was transferred into 2000 cm^3 conical flask and 500 cm^3 of ethanol added, covered with stopper and left to stand for 48 hrs. After which it was filtered using Whatman No. 42 filter paper and the filtrate concentrated using rotary evaporator. The crude extract so obtained was used in preparing different concentrations, by dissolving 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5 g of the extract in 100 cm^3 of 5.0 mol/dm^3 HCl [1, 10].

2.2 Preparation of Mild Steel

Mild steel coupon (4.0 cm by 2.0 cm by 0.2 cm) was used. The composition (wt %) of the coupon were P(0.080), Mn (0.034), S (0.170), Cu (0.060), Cr (0.020), Ni (0.021), C (0.160) and Fe (99.509).

2.3 Gravimetric Method

The corrosion measurement by gravimetric method was carried out on the pre-weighed coupons at room temperature (25 . The coupons were washed with distilled water, degreased with ethanol and the surface was activated in 10% HNO_3. The concentration of the plant extract was varied from 0.0. 0.1, 0.2 to 0.5 g of the extracts in 100 cm^3 of 5.0 mole/dm^3 HCl. The pre-weighed coupons (w_1) were suspended by the aid of a thread into 250 cm^3 beaker containing a particular concentration. This was done for all the various concentrations and allowed to stand for three hours in an open air. After which the coupons were removed from the solution containing the acidic solution with and without inhibitor, rinsed with distilled water, ethanol and dried in acetone and then re-weighed (w_2). The average weight loss for each concentration was calculated. The degree of surface coverage area ( ), corrosion rate and inhibition efficiency (IE%) for all the concentration was calculated using the expression in equations 1 and 2 [12].

IE% = [1-—— (1)

[1-—— (2)

where w_1 and w are the values of the average weight losses without and with inhibitor, respectively.

The corrosion rate of the mild steel was also calculated using the method reported by Kavitha *et al.*, [13].

———— (3)

; = pre-weigh; = value of weight after 3hrs; D = density; A= Area of the mild steel; T = Time of exposure.

2.4 Thermal Stability

The pre-weighed coupons were immersed in 100 cm^3 of the various concentrations of the inhibitors/blank solution ranging from 0.1 to 0.5 g/100 cm^3 in 5 mol/dm^3 HCl and maintained at 303 K, 313 K, and 323 K in a thermostatic water bath for 3 hrs, after which it was retrieved, rinsed in distilled water, degreased in ethanol, dried in acetone and reweighed. The results obtained were fitted into different isotherms (such as Langmuir and Freundlich) and the thermodynamic parameters (such as activation energy, enthalpy change, entropy, and free energy) were calculated [14].

2.5 Surface Morphology

The surface morphology of the uninhibited and inhibited coupons was examined with Scanning Electron Microscopy (SEM) [15, 16].

2.6 FTIR Analysis

The FTIR analysis was also carried out on the *Senna obtusifolia* powder using standard procedures [15, 16].

2.7 Phytochemical screening

2.7.1 Determination of total phenol

The sample (2.0 g) was defatted with 100 cm^3 of diethyl ether using a soxhlet apparatus for 2 hr. The fat free sample was boiled with 50 cm^3 of petroleum ether for the extraction of the phenolic component for 15min. The extract (5 cm^3) was pipetted into a 50 cm^3 flask, and then 10 cm^3 of distilled water added. Ammonium hydroxide solution (2 cm^3) and 5 cm^3 of concentrated amyl alcohol were also added. The mixture was made up to mark and left to react for 30min for colour development. This was measured at 505 nm. Tannic acid was used to establish the calibration curve [17].

2.7.2 Determination of total flavonoid

Total flavonoid was determined using aluminum chloride colorimetric method. Quercetin was used to establish the calibration curve. Exactly 0.5 cm^3 of the diluted sample was added into test tube containing 1.5 cm^3 of methanol, unto which 0.1 cm^3 of 10% $AlCl_3$ solution and 0.1 cm^3 sodium acetate were added, followed by 2.8 cm^3 of distilled water. After incubation at room temperature for 30min, the absorbance of the reaction mixture was measured at 415 nm. The amount of 10% $AlCl_3$ was substituted by the same amount of distilled water in blank [18].

2.7.3 Determination of total alkaloids

To determine the total alkaloids, 0.5 g of the sample was dissolved in 96% ethanol - 20% H_2SO_4 (1:1). 1 cm^3 of the filtrate was added to 5 cm^3 of 60% tetraoxosulphate (VI) acid, and allowed to stand for 5 min, after which 5cm^3 of 0.5% formaldehyde was added and allowed to stand for 3h. The reading was taken at absorbance of 565 nm. The extinction coefficient (E296, ethanol {ETOH} = 15136 $M^{-1}cm^{-1}$) of vincristine was used as reference alkaloid [19].

2.7.4 Determination of saponins

The sample (0.5 g) was added to 20 cm^3 of 1N HCl and was boiled for 4 h. After cooling it was filtered and 50 cm^3 of petroleum ether was added to the filtrate for ether layer and evaporated to dryness. 5 cm^3 of 1:1 mixture of acetone and ethanol was then added to the residue. 0.4 cm^3 of each was taken into 3 different test tubes and 6 cm^3 of ferrous sulphate reagent was added into each of them followed by 2 cm^3 of concentrated H_2SO_4. It was thoroughly mixed after 10 min and the absorbance was taken at 490 nm [19].

2.7.5 Determination of tannins

Sample (0.2g) was measured into a 50 cm^3 beaker. 20 cm^3 of 50% methanol was added and covered with para film and placed in a water bath at 80^{O}C for 1hr. it was shaken thoroughly to ensure a uniform mixture. The extract was quantitatively filtered using a double layered whatman No.41 filter paper into a 100 cm^3 volumetric flask. To this was added 20 cm^3 of distilled water, 2.5 cm^3 Folin-Denis reagent and 10 cm^3 Na_2CO_3 and mixed properly. The mixture was made up to mark with distilled water, mixed well and allowed to stand for 20 min for the development of a bluish-green colour. The absorbance of the tannic acid standard solutions as well as samples were taken after colour development on a UV-spectrophotometer model 752 at a wavelength of 760 nm [20].

3.0 Results and Discussion

3.1 Phytochemical Constituents of *Senna obtusifolia*

Phytochemical screening of *Senna obtusifolia* leaf extract using qualitative methods revealed the presence of tannins, flavonoids, saponins, terpenoids, steroids, alkaloids and anthraquinone. While the quantitative phytochemical analysis, using UV-spectrophotometer, gave their concentrations as tannins (4.45 mg/g), alkaloid (0.034 mg/g), total phenol (14.39 mg/g), flavonoid (2.85 mg/g), and saponin (0.65 mg/g), as shown in Table 1.

Table 1: Phytochemical constituents of the leaf extract of *Senna obtusifolia*

Phytochemical constituents	Qualitative composition	Quantitative composition(mg/g)
Tannins	++	4.45
Flavonoid	++	2.85
Saponins	++	0.65
Terpenoid	++	N.D
Steroid	++	N.D
Alkaloid	+	0.034
Anthraquinone	+	N.D
Phenol	++	14.39

++ = strongly positive; + = positive
ND = not Determined

The chemical structure of the phyto-constituents contained electron rich bond or hetero atoms that facilitate their electron donating ability. Hence the inhibition of the corrosion of mild steel by ethanol extract of the plant can be attributed to the phyto-constituents of the extract. According to Nutan *et al* [21], compounds with bond generally exhibit good inhibitory properties due to interaction of π orbital with the surface of metal. Possession of π-electrons or suitable functional groups may facilitate the transfer of charge from the inhibitor's molecule to the charged metal surface (physical adsorption) or transfer of electron from the inhibitor's molecule to the vacant-orbital of the metal (chemical adsorption) [22].

Dargahi *et al*. [23], opined from their studies that tannins could act as a very good corrosion inhibitor of metals. The inhibitive properties of tannins have been attributed to the polyphenolic fraction of the tannins moieties, which ensures effective protection of the metal surfaces [24, 25]. Flavonoid has anti-oxidant activity, anti-allergic, anti-cancer, anti-inflammatory and anti-viral activities. Al-qudah [26] established in his study about 92% inhibitory efficiency using different flavonoids as corrosion inhibitors on metals. Terpenoids and other constituents also possess functional groups which are capable of chelating with metallic ions and thus facilitate strong coordination on the metal surface [27]. From the quantitative analysis carried out, as presented in Table 1, it could be concluded that *Senna obtusifolia* has the potential for inhibitory activities due to its high phytochemical constituent.

3.2: Corrosion inhibition analysis *Senna obtusifolia* leaf extract

Weight loss, percentage inhibition efficiency, corrosion rate and surface coverage in 5.0 mol/dm^3 HCl solution with different inhibitors of leaf extract are given in Table 2.

Table 2: Corrosion inhibitory efficiency of *Senna obtusifolia* leaf extract

Concentration (W/V)	Mass loss (mg)	Inhibition Efficiency (IE%)	Surface area (	Corrosion rate (mm/yr)
0.0	267.0	--------	-------	6.2073
0.1	150.0	43.820	0.4382	3.4872
0.2	133.0	50.187	0.5019	3.0920
0.3	83.0	68.914	0.6891	1.9296
0.4	50.0	81.273	0.8127	1.1624
0.5	33.0	87.640	0.8764	0.76063

Table 3: Thermal Stability (Temperature Variation)

Conc. (w/v)	Weight Loss (mg)			Corrosion Rate (mm/y)		
	30	40	50	30	40	50
0.0	750	1450	2250	16.10	22.54	48.31
0.1	350	800	1150	8.14	18.60	26.74
0.2	200	600	950	4.65	13.94	22.09
0.3	150	400	850	3.49	9.30	19.76
0.4	150	300	800	2.68	6.97	18.60
0.5	100	250	550	2.15	5.81	12.79

Table 4: Thermodynamics parameters for mild steel in 5mol/dm^3 HCl solution, in the absence and presence of inhibitor at different concentrations and temperatures

Concentration (w/v)	Ea (KJ/mol)	o ___	(KJ/mol) 30	50
0.0*	68.52	----	---	---
0.1	74.19	-110.89	-1.79	-1.04
0.2	97.18	-430.81	-1.84	-0.99
0.3	108.18	-553.44	-1.83	-0.95
0.4	104.40	-493.80	-1.75	-0.92
0.5	111.28	-463.63	-1.67	-0.97

* = Blank

Table 2 revealed that the inhibition efficiency increases with increasing concentration of the extract. The maximum inhibition efficiency (87.640%) was obtained at an extract concentration of 0.5 w/v in 5.0 mol/dm^3 HCl solution. It could also be observed that the surface coverage increases with increasing concentration of inhibitor (Table 2), due to the adsorption of the phyto constituents. This is in agreement with the findings of Abdulwahab *et al.* [28], Kenneth and Sunday [29] and Omotoyinbo *et al.* [30].

3.3 Effect of temperature on corrosion rate (Thermal Stability)

Corrosion rate is directly proportional to thermal stability of the inhibitor on the mild steel. From Table 3, it could be seen that as the temperature increased from 30^{o}C to 50^{o}C (303K to 323K) the rate of corrosion also increased which implied that the thermal stability also decreased. This could be attributed to desorption of the inhibitors on the mild steel. However, as the concentration of the inhibitor is increased, the corrosion rate decreases which make the thermal stability to improve this may be as a result of more adsorption of the inhibitor on the surface of the mild steel. The results obtained are in agreement with those of Ating *et al.* [31], Vijayalakshmi *et al.* [32], Ismail *et al.* [33], Okafor *et al.* [34] and Fadera *et al.* [3]. The rate of corrosion of mild steel increased as a result of increase in the average kinetic energy of the reacting molecules. However, the corrosion rate is much decreased for higher concentration of inhibited acid solution than the solution with low concentration of inhibitors as seen in Table 4. The decrease in the corrosion rate can be attributed to mitigating effect of the plant extract on the corrosion rate of the mild steel.

3.4 Thermodynamics Studies

The value of activation energy for uninhibited aqueous is 68.52 KJ/mol. The activation energy for *Senna obtusifolia* extract ranges from 74.19 KJ/mol to 111.28 KJ/mol with increasing concentration of the extract. From Table 4, it is found that activation energy values of the inhibited acidic solutions are higher than the uninhibited acidic solutions. It showed that the values of activated energy increase with an increase in the inhibitor concentrations from 0.1 w/v to 0.5 w/v is due to the deceleration of the corrosion rate of the mild steel. The result suggests that corrosion inhibition by *Senna obtusifolia* extract is brought about by the increasing its activation energy. There is an increase in activation energy as a result of adsorption of the constituents on the mild steel surface creating a barrier for mass and charge transfer.

According to Manimegalai and Manjula [35], the threshold for physical adsorption is < 80 KJ/mol and > 80 KJ/mol for chemical adsorption. The results obtained in this study (Table 4), show that adsorptions of the extracts on the mild steel surface are physisorption and chemisorptions. The higher activation energy implies a slow dissolution of the mild steel [36]. Table 4 also shows the results of the calculated heat of adsorption, *o* of ethanolic extract of *Senna obtusifolia* on the surface of mild steel. The values of *o* were negative and ranged from -110.89KJ/mol to -432.20KJ/mol indicating that the adsorption of the extracts is exothermic [1]. The negative value of is a suggestion that the adsorption of *Senna obtusifolia* leaf extracts onto the metal surface is a spontaneous process and the adsorbed layer is stable. According to Stephen *et al.* [37], the adsorption of free energy involved is a physical process, if is .

3.5 Adsorption Consideration

Langmuir adsorption isotherm: From the values of adsorption parameters deduced from Langmuir adsorption plot as seen in Figure 1, the values of degree of linearity (were found to be close to unity (R^2 = 0.8485, 0.9858 and 0.9932), indicating strong adherence of the adsorption of the extracts on the metal surface. This fits into Langmuir adsorption isotherm.

Freundlich isotherm: Freundlich adsorption isotherm is commonly used to describe the adsorption characteristics for the heterogeneous surface [38]. Figure 2 revealed Freundlich's adsorption isotherm of *Senna obtusifolia* extracts on the surface of the mild steel and is given by equations (4) and (5) and is in line with that reported by Sharma and Sharma [39].

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Log— –

The fraction — in equation (5) has been found to be approximate to the inhibition efficiency of the inhibitor, K and n are constant. Slope equal to − and intercept = logK. Therefore, from equation (5), a plot of log inhibition efficiency (IE%) versus log C produces a straight line that obeyed Freundlich adsorption isotherm.

3.6 Scanning Electron Microscopy

Plate I shows the micrograph of the micrograph of the mild steel immersed in 5 mol/dm^3 HCl solution in the absence of inhibitor for 5 hours. The surface of the treated coupon shows etching composed of white and dark areas [3, 40], the white areas represent the pearlite (mixture of ferrite and cementite (Fe_3C) in a lamellar form). It indicates clear disarrangement in the surface formation of the mild steel due to high metal dissolution rate and more active site available for corrosion [3]. The micrograph of the mild steel immersed in 5 mol/dm^3 HCl solution containing 0.1 w/v of extract (Plate II), shows that the surfaces were smoother when compared to the one without inhibitors. The plates show less extensive attack in the presence of the extract than in the uninhibited acid. This implies that the extracts components absorbed on the surface forming protective film over the surface of the mild steel thereby decreasing the dissolution in acidic medium. The protective film acts as a barrier between the steel and the aggressive environment and thus retards the corrosion reactions. This is in line with previous studies on plant extracts [3, 28].

3.7 FTIR Analysis

From Figure 3, the FTIR for *Senna obtusifolia* shows strong absorptions at 3272.6 cm^{-1} for OH stretching mode. The absorption at 2918.5 cm^{-1} is aromatic C-H band stretching mode. The peak at 1580.4 cm^{-1} corresponds to C=O stretching mode. The peaks at 1408.9 cm^{-1} and 1256.1 cm^{-1} indicate the presence of aryl OH. Finally, the absorption at 1028.7cm^{-1} shows the stretching mode of C-O.

4.0 Conclusion

The results obtained in this study showed that *Senna obtusifolia* is a good corrosion inhibitor which acts as a mixed type inhibitor in 5M HCl. The negative free energy of adsorption indicates strong and spontaneous adsorption of *Senna obtusifolia* on the mild steel surface. The increase in activation energy with increase in the extract concentration is an indication of decrease in corrosion rate and inhibition potential of *Senna obtusifolia* leaf extract on mild steel. FTIR spectra clearly reveal the functional group responsible for the inhibitory ability. Furthermore, SEM micrograph revealed that corrosion inhibition is due to the adsorption of *Senna obtusifolia* on the mild steel.

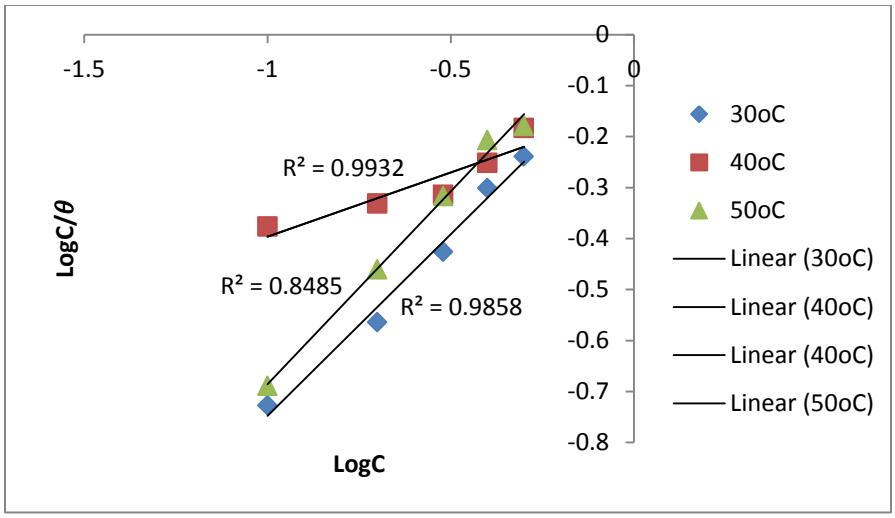

Figure 1: Langmuir isotherm of *Senna obtusifolia* extracts on mild steel in 5mol/dm^3 HCl at difference temperature

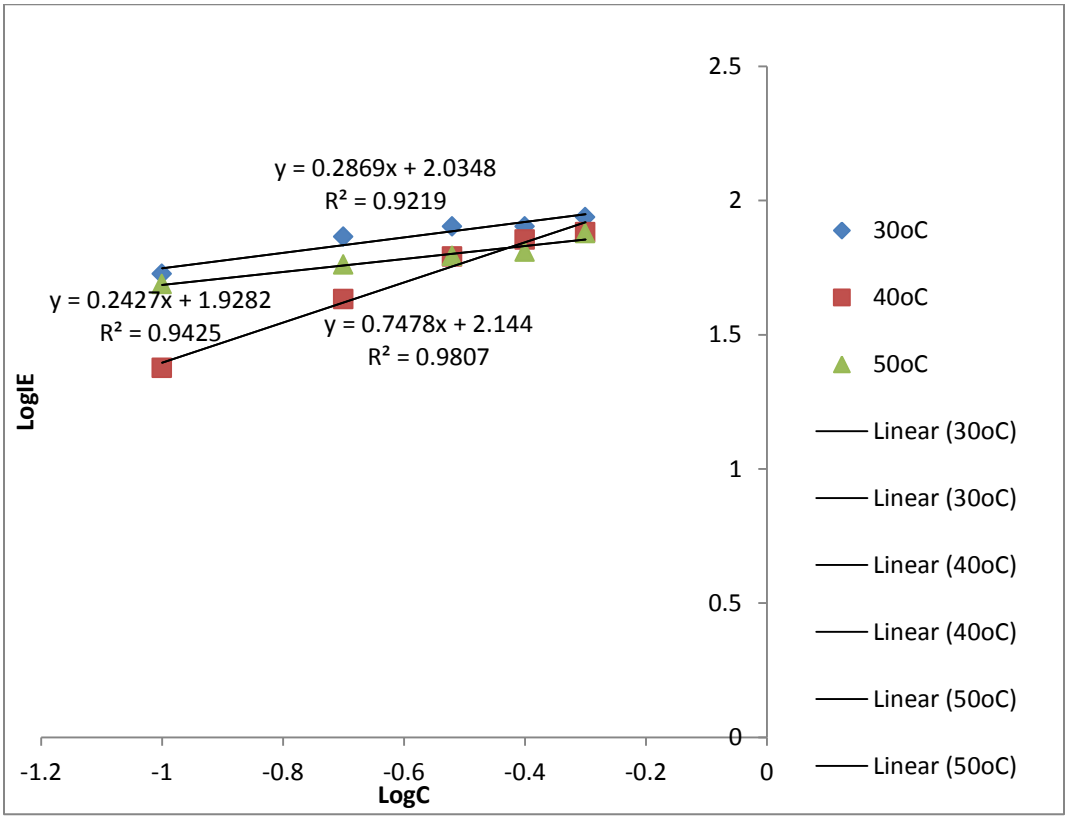

Figure 2: *Senna obtusifolia* Freundlich isotherm extracts on mild steel in 5mol/dm^3 HCl at difference temperature

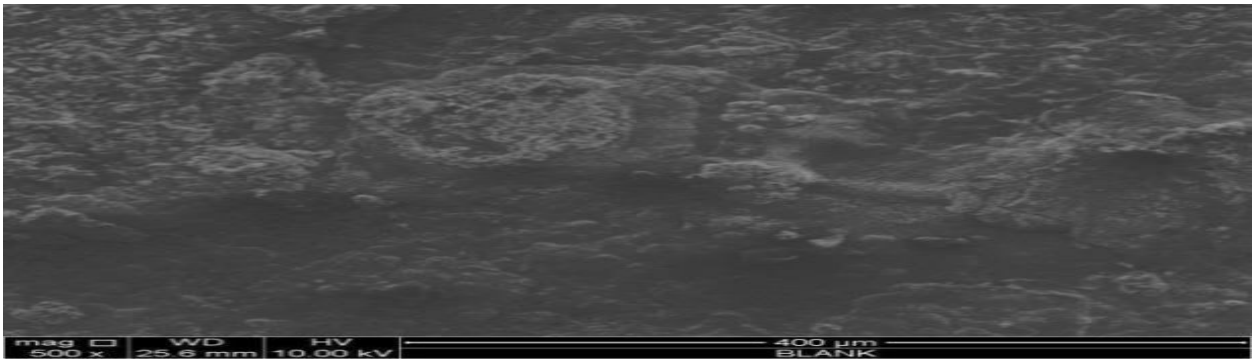

Plate I: SEM of the mild steel treated with 5mol/dm^3 HCl for 5h without inhibitor

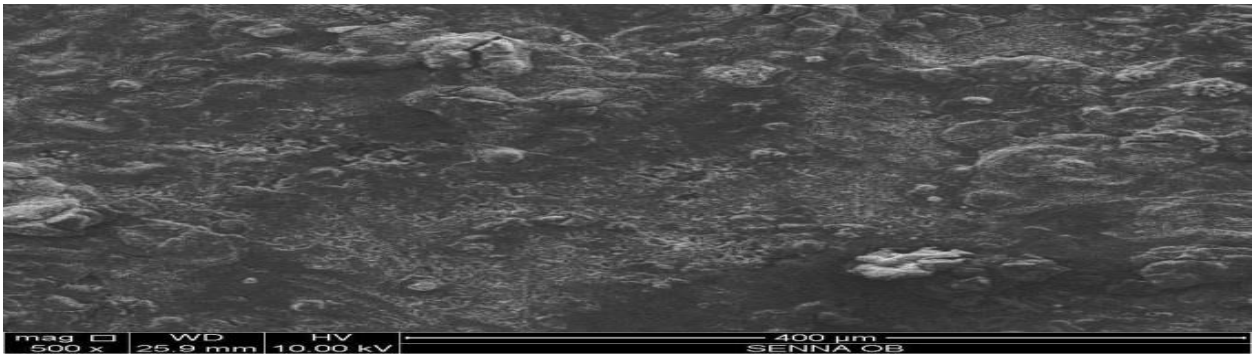

Plate II: SEM of the mild steel treated with 5mol/dm^3 HCl for 5h in the presence of 0.1%w/v of extract of *Senna obtusifolia* **inhibitor**

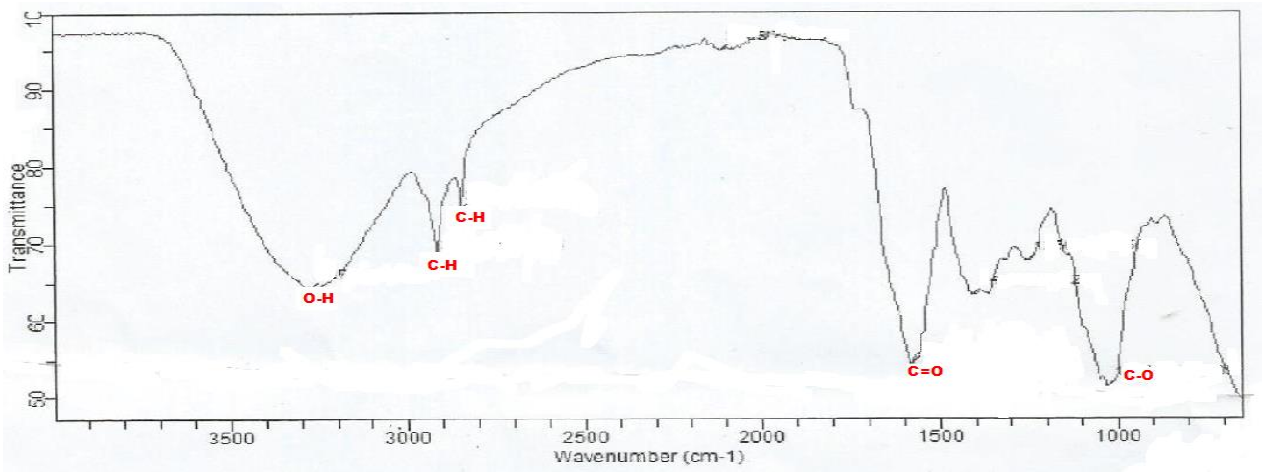

Figure 3: FTIR Spectrum of *Senna obtusifolia*

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