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Retarding Mild Steel Corrosion using a Blend of Schiff Base Metal Complex and Neem Plant Extract

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ABSTRACT

Prepared inhibitor blend of synthesized Co (II) Schiff base complex and *Azadirachta indica* extract was applied as anti-corrosion agent to mild steel in acidic (0.5 M H_2SO_4) medium. A synergistic performance was the look-out of the study, with the green inhibitor as the synergistic additive. Inhibitors are characterized by their active functional groups, UV-visible profile and bioactive compounds. Surface characteristics of polished, corroded and coated mild steels were investigated using weight loss experiments. Results of phytochemical screening shows the presence of possible bioactive species, including glycoside, tannins and phenolic compounds, saponin, Steroids and Triterpenoids. Weight loss experiments at temperature range of 303 K to 323 K were performed. Inhibition efficiencies of the three systems demonstrated increments with increasing inhibitor concentration and decreases as the temperature rises, thus characterizes physi-sorption mechanism. The ethanol extract of *Azadirachta indica* leaves, cobalt (II) Schiff base complex and the blend in 0.5 M H_2SO_4 gives up to 46.88 %, 31.16 % and 59.69% inhibition efficiencies respectively at 323 K. The adsorption equilibrium data of these inhibitors on the surface of mild steel fits the Freundlich, Langmuir and Dubinin - Raduskevich isotherms at varying extent and the values of ΔG_{ads} for all the isotherms were below 20 kJ/mol, suggesting physical adsorption. The estimated thermodynamic parameters support process spontaneity. Generally, enhanced performance of blend inhibitor showed a synergistic effect (S_1> unity) and proved the effectiveness of derived blend as potent inhibitor of mild steel corrosion in acidic medium.

Keywords: Antagonistic, Blend, Complex, Inhibitor, Synergistic

INTRODUCTION

There is an increasing concern about the toxicity of corrosion inhibitors in the environment (especially in industry). Inorganic inhibitors are now gradually restricted by environmental legislatives because of their toxicity and challenges faced in their disposal especially in the marine industry, where aquatic life is at threat (Roy *et al*., 2014). The toxic Inorganic corrosion inhibitors are not only affecting living organisms but also poison the earth over time (Abo and Ashraf, 2015). It is known that organic coatings have many advantages for the protection of metals against corrosion (Adriana *et al.,* 2005). At present, there is much interest in the new anticorrosive pigments, called "green inhibitors", which have been shown to effectively replace the toxic anticorrosive coatings.
The surface of metals (except gold) is covered with oxide film when exposed to air. However, the oxide film so formed can dissolve when the metal is immersed in an aqueous solution. Almost all corrosion reactions are electrochemical in nature (Abo and Ashraf, 2015).

The disruption of protective layer comes with reactions (formation of oxide layers and diffusion of metal into coating matrix, pH changes and electrochemical potential) that alters the composition and properties of both metal surface and receiving environment (Ramya and Muralimohan, 2016). Inhibitor molecules retard the corrosion process by instituting an interaction with the metal surface.

Schiff bases (imine or azomethine) are important class of organic compounds. The inhibition of corrosion by Schiff bases can be attributed to its molecules with the –C=N-groups, an electron cloud on the aromatic ring, oxygen and sulphur atoms in the molecule, electronegative nitrogen which enhances adsorption (Chitra *et al.*, 2010). Schiff base compounds are easily synthesized from very cheap raw materials. The metal complexes of Schiff bases are attracting particular attentions owing to their diverse structures, attractive chemical and physical properties, wide range of biological importance and their industrial applications (Abuthahir *et al.*, 2013).

Many synthesized compounds have been very effective against corrosion (Patel *et al.*, 2013). Plant products are majorly organics with certain phytochemicals including tannins, flavonoids, saponins, organic and amino acids, alkaloids, and pigments which could be extracted by simple procedures (Fouda *et al.*, 2015; Nnanna *et al.*, 2016). In addition to being environmentally friendly and ecologically acceptable, plant products are readily available, relatively cheap, and renewable (Nnanna *et al.*, 2016). Plant extracts, obtained from different parts of plant have shown excellent corrosion inhibitory attributes in various corrosive media (Okafor *et al.*, 2008). To enhance the efficiency of corrosion inhibitors, extensive studies have been carried out on synergistic effect with additives (Ramya and Muralimohan, 2016).

Treatment of adsorption equilibrium data using a theoretical or empirical equation is useful for the interpretation of adsorption properties. Table 1 shows the isotherm models describing adsorption phenomenon in this study.

Table 1: Equations and plot axis of some isotherm models

Isotherm Model	Linear forms	plots	Reference
Langmuir:	$Qe = \frac{Qm\ KL\ Ce}{1 + KL\ Ce}$		(Dada *et al.*, 2012)
	$\frac{1}{Qe} = \frac{1}{Qm} + \frac{1}{Qm\ Kl\ Ce}$	$\frac{C_e}{q_e}\ vs\ C_e$	(Kumar and Kirthika, 2009)
	$\frac{C}{\theta} = \frac{1}{Kads} + C$	$\frac{C}{\theta}\ vs\ C$	
	$R_L = \frac{1}{1+KLCo}$	NA	(Wang *et al.*, 2010)
Freundlich	$ln\ Q_e = \frac{1}{n} lnC_e + l_n\ K_f$	$ln Q_e$ vs$ln C_e$	(Ho and Porter, 2002)
Dubinin-Rudushkevich	$ln\ q_e = ln\ q_D - B_{\varepsilon^2}$	$ln\ (q_e)\ vs\ \varepsilon^2$	(Kundu, 2006)
	$\varepsilon = RT \ln(1 + C_e)$	NA	(Kundu, 2006)
	$E = 1/(2B)^{1/2}$	NA	(Kundu, 2006)

NA-Not Applicable

Langmuir empirical model assumes monolayer adsorption at a fixed number of definite localized sites, that are identical and equivalent in its derivation; C is the concentration of inhibitor and K_{ads} is the equilibrium constant for the adsorption-desorption process. Generally, values of K_{ads} represent the adsorption power of the inhibitor molecule on the surface of the metal. The positive values indicate that the inhibitors adsorb well on the surface of the metal. θ is the degree of surface coverage. The values of R_L indicate the shape of the isotherm. When the value of $R_L > 1$, adsorption is unfavorable, when the values of R_L at different concentrations is between 0 and 1, the adsorption process is favorable, $R_L = 1$, adsorption is linear and $R_L = 0$, adsorption is irreversible. K_L (L/mg) and q_m are Langmuir isotherm constants (Dada *et al.*, 2012; Kumar and Kirthika, 2009; Wang *et al.*, 2010)

Freundlich model proposes heterogeneous energetic distribution of active sites; Q_e(mg/g) = adsorbate adsorbed per unit mass of the adsorbent and C_e(mg/L) = equilibrium concentration. Intercept, K_f is aconstant related to the adsorption capacity (Freundlian constant) and slope, n_f is an empirical parameter related to be adsorption intensity which varies with the heterogeneity of the materials (Ho and Porter, 2002).

Dubinin- Radushkevich isotherm gave Bas a constant related to the mean free energy of adsorption per mole of the adsorbate (mol^2/J^2) , R = universal gas constant (8.314J/molK), T= is absolute temperature (K). q_D = theoretical saturation capacity ($mg\ g^{-1}$), and ε =polanyi potential , E the mean sorption energy that predict whether an adsorption is physi-sorption or chemi-sorption (Kundu, 2006).

Azadirachta indica (commonly known as "Neem tree) has been widely documented for its excellent inhibition of corrosion, chemical and biological importance (Sharma *et al.*, 2015; Schaaf *et al.*, 2000; Koul *et al.*, 1990; Hossain *et al.*, 2013; Patel *et al.*, 2014 ; Okafor *et al.*, 2010). Kumar *et al.* (2014) synthesized and utilized 2-(5-Methoxy-2-Hydroxybenzylideneamino) Phenol Schiff Base ligand and its transition metal complexes in corrosion inhibition. It was found that the compounds had a promising inhibitory action against corrosion of mild steel in 0.1M HCl solution. This report is on synergistic study of blended synthesized Co (II) Schiff base complex and ethanol extract of *Azadirachta indica* leaves as corrosion inhibitor on mild steel in acidic medium.

MATERIALS AND METHODS

Analytical grade reagents (purity >98%), including methanol, ethanol, HCl, H_2SO_4, NH_4OH solution, glacial acetic acid, dichloromethane solution, diethylether, cobalt(II)chloride, aminophenol, 2 -hydroxy-5-mthoxybenzaldehyde, KOH, Mayer's reagent, ferric chloride, chloroform were used as received without further purification. Inhibitor characterization were based on the use of fourier transforms infrared spectrophotometer, UV-visible Spectroscopy and Gas Chromatography-Mass Spectrometry. Scanning electron microscopy was adopted for mild steel surface morphology.

Sampling and Sample treatment

The leaves of *Azadirachta indicia* were obtained from within Tombo community secondary school, Buruku, Benue state. The leaves were taken to the Department of Forestry and Wildlife, University of Agriculture Makurdi for identification. The *Azadirachta indicia* leaves were washed with distilled water, air dried for seven days at room temperature, ground into powder using mortar and pestle and used for the extraction (Yadav *et al*., 2014) of the green inhibitor.

Mild steel samples were sourced from modern market, Makurdi Benue state Nigeria. In order to conduct the weight loss experiment, coupons were prepared by mechanically cutting the mild steel sheet into small pieces with dimension of 3.0 cm×2.0 cm×0.2 cm. The test coupons were mechanically polished with emery paper. After polishing, each specimen was rinsed with distilled water followed by ethanol and acetone to remove grease. The samples were dried at room temperature and stored in a desiccator for future use (Nnanna *et al*., 2016).

Extraction and Concentration of Extract

The leaves extract was prepared by boiling 10 g of the powdered leaves of *Azadirachta indica* for 4 h, under reflux, in 150 mL of 98% ethanol solution. The resulting solution was immersed into a water bath at mild temperature (<80^0C) to evaporate all the ethanol and obtain the concentrate. The extract so obtained was stored in a desiccator from which inhibitor test solutions were prepared using 0.5M H_2SO_4 in the concentration range of 100 - 500 ppm (Oguzie, 2006).

Phytochemical Screening of Extract

The phytochemical screening of ethanolic extract of *A. indica* leaves was carried out to test for the presence of alkaloids (Prashanth and Krishnaiah 2014). Keller-Killiani test was adopted for cardiac glucosides (Singh and Chauhan, 2014), Froth test for saponins (Singh and Chauhan, 2014), Ferric chloride protocol was used for tannins and phenolic compounds while terpenes and steroids utilizes Salkowski's test (Prashanth and Krishnaiah 2014). Method documented by Itelima *et al*. (2016) was carefully followed for Tannins.

Synthesis of Schiff Base

In accordance with the method reported by Kumar *et al. (*2014), 2-Aminophenol (0.874 g) was dissolved in a 30 mL absolute ethanol with stirring. The mixture was added dropwise to a hot 2-Hydroxy-5-Methoxybenzaldehyde (1.22g) solution, which was dissolved in 30 mL of same solvent. To this mixture, 2 mL of glacial acetic acid was added followed by reflux at 80°C for 7h with stirring. The resulting red brown and clear solution was cooled at room temperature and transferred into ice-cooled water to precipitate out the Schiff base. The resulting colored precipitate was filtered and dried in vacuum oven at 80°C. The dried solid product was recrystallized from hot ethanol, washed with diethyl ether and then dried in a desiccator, made ready for use.

Synthesis of Metal Complexes

Schiff base metal complex was prepared with stoichiometric amount of ligand and metal salts in a 1:1 mole ratio. To a 25 mL of CH_2Cl_2 solution of Ligand (0.122 g), 20 mL of methanol solution of Co(II) chloride (0.0005 mole) was added drop wise. The mixture was refluxed with stirring for 2 h and then pH of the solution was adjusted to pH7 with NH_4OH solution. This was followed by further refluxing for 6 h at 50°C and allowed to stand overnight at room temperature to form a colored solid metal complex which was collected by filtration. Complex was washed with distilled water, diethyl ether followed by ethanol and oven dried to constant weight (Kumar *et al.,* 2014).

Preparation of Inhibitor Blends

Synergetic admixture (SA) concentrations (0.5 g/mL) were prepared by blending cobalt (II) Schiff base complex and *Azadirachta indica* in ratio 1:1, making up of the inorganic inhibitor on one part and the organic or green inhibitor on the other part. SA was characterized using UV- visible, FTIR and GC-MS following standard procedures.

Weight loss Experiment

The weight loss method involves weighing of the mild steel (MS) sample before immersion and then re-weighing after a pre-determined dwell time. In this study, polished and pre-weighed MS coupons were tied with thin threads to a retort stand and were completely immersed in a 100 mL beaker containing 70 mL test solution, with or without the addition of single or blend concentrations of *Azadirachta indica* extract and Schiff base complex for six hours in an aerated condition at temperatures of 303K, 308K, 313K, 318 and 323K. The temperature was regulated by a thermostatic water bath. The specimens were taken out of the test medium every 6 hours and rinsed in ammonium acetate solution to quench the reaction. They were then washed with double-distilled water, rinsed with ethanol and acetone, dried in a desicator and re-weighed (Loto *et al.*, 2011). Triplicate experiments were carried out in each set of the test and the mean values of the Weight Loss were reported (Patel *et al.*, 2013). The average weight loss of the mild steel coupon was taken as the difference between the initial weight (*Wo*) of the mild steel and final weight (*W*) after the immersion. This difference was used to determine the inhibition efficiency (IE %), surface coverage ($\emptyset$) and corrosion rate (CR) presented in equations 1,2 and 3.

$$\text{I.E} = 1 - \frac{(Wo - W)}{W} \text{ X } 100\% \qquad (1)$$

$$\emptyset = 1 - \frac{Wo - W}{W} \qquad (2)$$

$$\text{CR } (\text{mgcm}^{-2}\text{h}^{-1}) = \frac{\text{WL}}{\text{At}} \qquad (3)$$

Surface coverage ($\emptyset$) measures the interaction of inhibitor with mild steel surface, corrosion rate (CR) depicts the effectiveness of inhibitor and is directly related to weight loss in corrosive medium ($\text{mgcm}^{-2}\text{h}^{-1}$), WL is the weight loss in milligrams (mg), A is the surface area of coupon in cm^2 and t the immersion time, hrs (Gbertyo *et al.*, 2014). The same procedure was repeated for the control experiment using 0.5M H_2SO_4 (solution) without the introduction of inhibitor.

Adsorption Isotherm Experiments

Working solutions of five different concentrations (0.1-0.5 g/dm^{-3}) of each inhibitor were separately prepared. Those of the 1:1 inhibition blend were also prepared for adsorption study. Weight loss data generated from the effect of the initial inhibitor concentrations were used for isotherm study. Several adsorption isotherms were tested including Freundlich, Langmuir and Dubinin - Raduskevich to fit the experimental data (Khan *et al.*, 2015; Itodo *et al.*, 2014).

Thermodynamic Experiment

Effect of inhibitor on the corrosion of mild steel coupons in 0.5M H_2SO_4 solution at different temperatures was studied by weight loss measurements. 100 mL beaker containing both the mild steel and test solution were immersed in a thermostatic water bath and regulated at 303K, 308K, 313K, 318K and 323K for 360 minutes' immersion period. The relationship between the corrosion rate (CR) of Mild steel in the tested medium and temperature was expressed by the Arrhenius equations (4) and (5):

$$CR = A_{exp}{}^{(-\frac{Ea}{RT})} \qquad (4)$$

$$\ln CR = \ln A - \frac{E_a}{RT} \qquad (5)$$

$$CR = {}^{RT}\!/_{Nh} \exp \Delta S^0 \exp \left(-\Delta H^0 /_{RT}\right) \qquad (6)$$

$$\log CR = \log A - \frac{E_a}{2.303\, RT} \qquad (7)$$

Where, CR is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant (8.314 $\text{JK}^{-1}\text{mol}^{-1}$), T is the absolute temperature, and A is the pre-exponential factor (Ating *et al.*, 2010). Equation (6) is called transition state equation, where CR is the corrosion rate, h is the Plank's constant (6.626176×10^{-34} Js), N is the Avogadro's number (6.02252×10^{23} mol^{-1}), R is universal gas constant (Abbas *et al.*, 2015). The plot of log CR/T versus 1/T gives a straight line with slope of [$-\Delta H°/2.303R$] and intercept of [$\log R/Nh + \Delta S°/2.303R$] from which the values of ΔH° and ΔS° are calculated.

RESULTS AND DISCUSSION

Phytochemical Analysis

The results of qualitative phytochemical analysis of the ethanol leaves extract of *Azadirahtra indica* were presented in Table 2. The extract tested positive, indicating the presence of flavonoids, glycosides, tannins and phenolic compounds, saponins, steroids and triterpenoids. Alkaloid is absent. The presence of these bioactive phytoconstituents in the extract may have great influence on its corrosion inhibitive properties (Prashanth and Krishnaiah, 2014)

Table 2: Results of Qualitative Phytochemical Screening of *Azadirachta indicia* Leaves Extract

Constituents	**Test**	**Result**
Alkaloids	Mayer's reagent test	_
Glycosides	Keller-Killiani test	+
Tannins and Phenolic compounds	Ferric chloride test	+
Saponins	Froth test	+
Steroids and Triterpenoids	Salkowski's test	+

+ (presence); - (absence) of the constituent in the extract

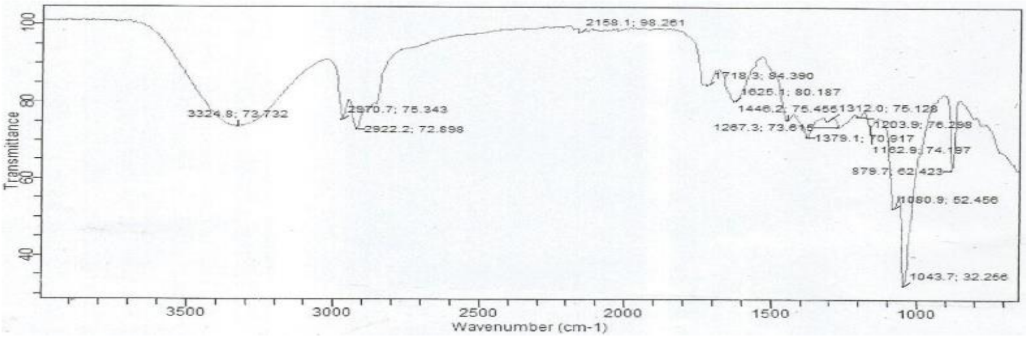

Figure 1: FTIR Spectrum of *Azadirachta indica* Leaves extract

Table 3: FTIR Spectral Characteristics of *Azadirachta indica* Leaves Extract

Vibrational Frequency (cm-^{1})	**Functional Group**	**Frequency of leaves extract (cm^{-1})**	**Assignment**
3400-3200	O-H Stretch	3324, 73.732	Alcohols, Phenols
3000-2850	C-H Stretch	2970.7, 75343	Alkanes
1640-1560	N-H bend	1625.1	Amines, amides
1565-1415	C-H bend	1446.2	Alkyl groups
1380-1370	C-H bend	1379.1	Methyl
1300-1150	C=O Stretch	1267.3	Acids,esters, anhydride
1050-675	C=O	1043.7	Alcohols
1200- 1070	C=O Stretch	488.97	Ethers

Figure 1 represents the FTIR spectrum of the *Azadirachta indica* Leaves extract, while the interpretation and spectral characteristics were shown in Table 3. Most of the functional groups assigned for the screened compounds (phenolic, Alcohols, Acids, esters, anhydride etc.) presented in Table 2 were further confirmed with FTIR analytical results in Table 3.

GC-MS Qualitative Analysis of Ethanolic Plant Extract

Figure 2 shows the chromatogram of *Azadirachta indica* and some predicted structures. The chromatogram for the leaves extract of *Azadirachta indica* presented twenty lines (Lines 1-20), depicting twenty compounds with major compounds having several suspected compounds (Hits) of variable similarity which are represented as similarity indices (% SI). Eight constituents were predominantly in the leaves extract of *Azadirachta indica* (Figure 2).

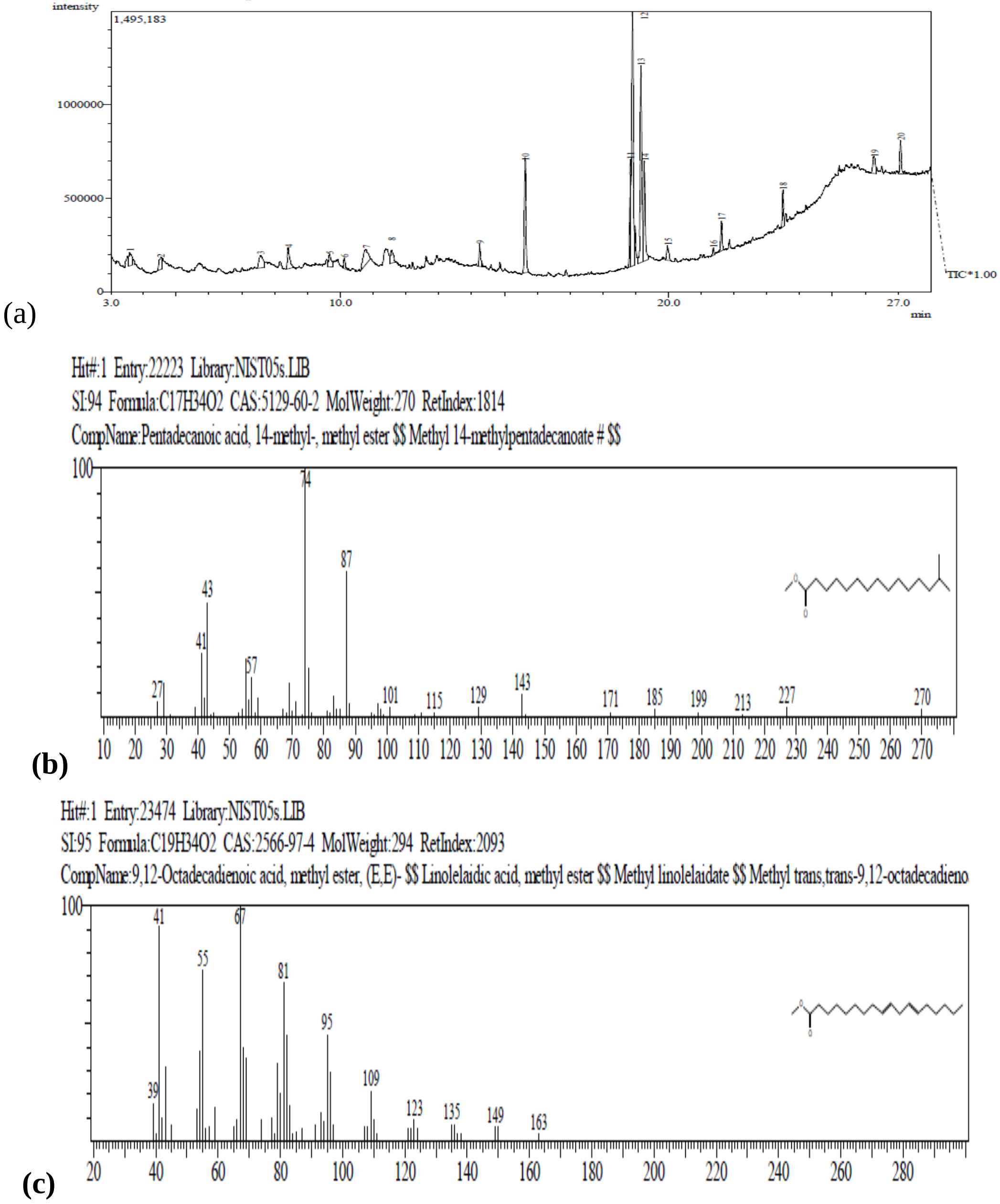

Figure 2: Chromatogram of *Azadirachta indica* (a) and some predicted structures (b and c)

Table 4: GC-MS Specification for Most Suspected Compounds with highest S.I (%) in the Leave Extract of *Azadirachta indica*

Line	S.I	Mol. Formular	Mol. Wt.	Name of Compounds
1	79	$C_4H_6O_2$	86	3-Hydroxybutanoic acid, .beta.-lactone
2	81	$C_4H_6O_3$		2-Hydroxy-gamma-butyrolactone
3	67	C_8H_8O	120	2,3-Dihydrobenzo Furan
4	84	$C_9H_{10}O_2$	150	2-Methoxy-4-vinyl Phenol
5	86	$C_{10}H_{16}$	136	(3E)-2,5,6-Trimethyl-1,3,6-heptatriene
6	85	$C_{12}H_{24}$	168	trans-3-Dodecene
7	77	$C_{10}H_{13}N_5O$	283	Guanosine
8	68	$C_{10}H_{12}O_3$	180	3-Hydroxy-2-Methyl isopropyl-5-benzo-1, 4-quinone

SI: Similarity index (Level of resemblance to suspected compounds)

The peak areas (or percentage compositions of the bioactive agents) are relative to other constituents within the crude extracts. The active components common to the inhibitors (Table 4) include 9-octadecenal, tetradecanoic acid, methyl ester, 7-hexadecanoic acid methyl ester, 6-octadecenoic acid, methyl ester, (Z)-9,12-octadecadienoic acid, methyl ester, (E,E)- tridecanoic acid, methyl ester , hexadecanoic acid, 15-methyl-, methyl ester, 1,2-dimethyl-3-nitro-4-nitroso-benzene and pentadecanoic acid, 14-methyl-, methyl ester. Most of these compounds have complicated molecular structures, large molecular weights and significant number of oxygen, sulphur and nitrogen atoms which are found in their structures. These compounds can adsorb on the surface of metal through the lone pairs of electrons present on their hetero atoms. The adsorption of such compounds on the metal surface creates a barrier leading to a decrease in the interaction between the metal and the corrodent. As a result, the corrosion rate of the metal is decreased. Thus the presence of the bioactive components containing Nitogen, Sulphur and Oxygen atoms in these compounds may have been responsible for the formation of a film layer which essentially blocks the Reduction of H+ from the acid to H_2 gas by the metal and reduce dissolution of metal ions (Okafor *et al*., 2010).

UV-visible Characterization of Extract

Figure 3 shows the UV- visible profile of the extract. A sharp band-edge absorption peak at 216 nm was observed in the UV-visible absorption spectrum of the leaves extract. This may be attributed to the presence of conjugated double bonds in the extract of *Azadirachta indica*. The ultraviolet-visible spectrophotometry technique was used to characterize the Schiff base and its metal complex, the extract as well as the blend of the extract and the complex.

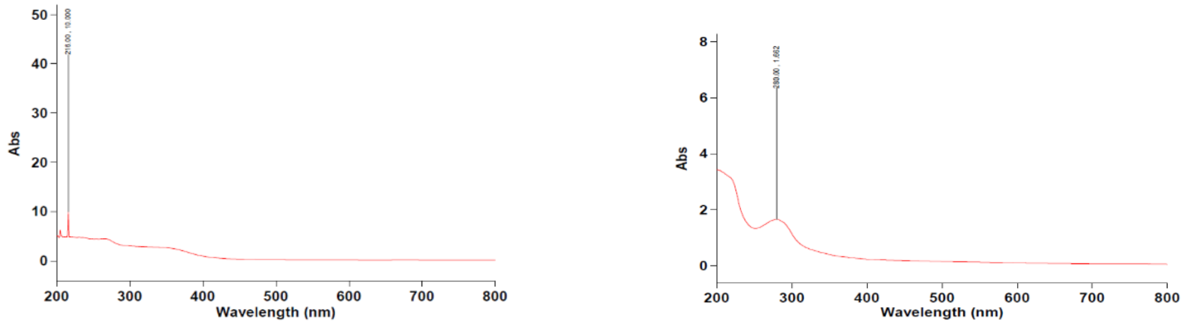

Figure 3: UV- visible Spectrum of *Azadirachta indica* Leaves (LHS; λ max 216 nm) and Extract-Cobalt (II) Schiff Base Complex in ratio 1:1 Blend (RHS; λ max 280 nm)

The ultraviolet-visible electronic spectra of the prepared Schiff base showed absorption band that could be attributed to π→π* electronic transitions; these transitions are assigned in relevance to the structure of the compound. Transitions between n - π* and π - π* common to unsaturated compounds; they require less energy and occur at longer wavelengths. The electronic spectrum of the blend shows a band at the wavelength 280 nm; this may be attributed to the π→π* electronic transitions of the aromatic system (Kumar *et al*., 2014; Abdulzahra and Ali, 2014).

Mild Steel Surface Characterization

The surface morphology of the mild steel coupons was studied by scanning electron microscopy. Plate 1a shows the SEM image of the corrosion product, while plate 1b is the SEM image of the mild steel coupon in the presence of the inhibitor at magnification of 1000x. Mild steel specimen dipped in 0.5 M H_2SO_4 solution in the absence of inhibitor appears to be very rough as the surface is eroded. This damage is due to dissolution of metal in the corrodent. However, the presence of 0.5 gdm^{-3} of all inhibitors suppressed rate of corrosion and surface damage was considerably reduced compared to the blank, suggesting formation of a protective film at the mild steel surface which in turn minimizes the attack of the aggressive medium on the metal. Similar to this is the report of Shivakumar and Mohana (2012).

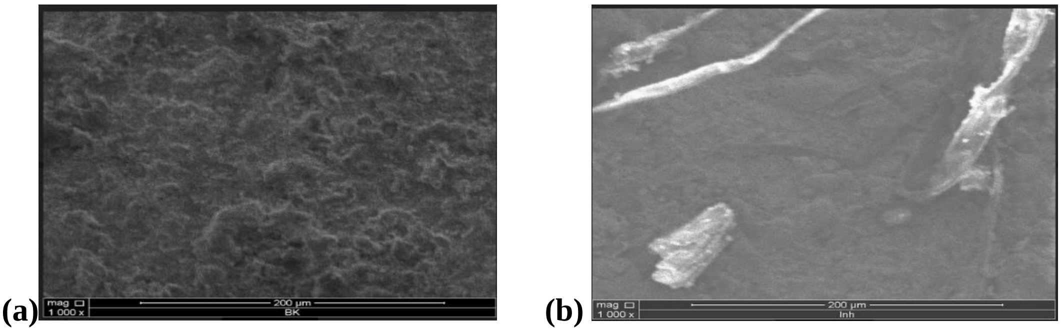

Plate 1: SEM Image of Mild Steel in 0.5 $moldm^{-3}$ H_2SO_4 Solution without Inhibitor (a) and with 0.5 gdm^{-3} Inhibitor (b) after 6h Immersion at 303K and 100X Magnification

Weight Loss Experiment

The data obtained from the weight losses, W_L, of the tested mild steel coupons were used to compute inhibition efficiency, % IE, corrosion rate, CR, and surface coverage, θ of all the inhibitors. The surface coverage at various concentrations and temperature were used to obtain plots which were used to calculate activation energy values for the corrosion inhibition process. Thermodynamic parameters and evaluated values of different linearized adsorption isotherms were also reported. Table 5 shows the Weight loss (g) of Mild steel in varying concentrations (g/dm^3) of the inhibitor and inhibition efficiency (I.E %) values were presented in parenthesis. Result shows that the leaves extract and the complex as well as the blend inhibited the corrosion of mild steel in acidic medium since there was a general decrease in weight loss when compared to the blank. It can be seen that the inhibitors minimized the loss in weight of mild steel coupons and the reduction in weight was depended on both the concentration of inhibitor and temperature. At each studied temperature, the weight loss of the metal without the inhibitor was highest. Similar result was documented by Ahile *et al*.(2014).

Table 5: Weight Loss (g) of Mild Steel in varying Concentrations (g/dm^3) of Leave Extract Inhibitor.

Conc.(g/dm) of inhibitor	Weight loss (g) at different temperatures				
	303K	308K	313K	318K	323K
Blank	0.680	0.543	0.758	1.067	1.444
0.1	0.372 (45.29)	0.378 (30.39)	0.593 (21.77)	0.882 (17.34)	1.210 (16.20)
0.2	0.297 (56.32)	0.331(39.04)	0.541(28.62)	0.789 (26.05)	1.076 (25.48)
0.3	0.246 (63.82)	0.289 (46.78)	0.477 (37.07)	0.696 (34.77)	0.953 (34.00)
0.4	0.199 (70.74)	0.240 (55.80)	0.387 (48.94)	0.637 (40.30)	0.876 (39.34)
0.5	0.147 (78.38)	0.209 (61.51)	0.372 (50.92)	0.536 (49.77)	0.767 (46.88)

Values of inhibition efficiency (IE %) in parenthesis

Table 6: Weight Loss (g) of Mild Steel in varying Concentrations (g/dm^3) of the Blend Inhibitor

Conc.(g/dm^3) of inhibitor	Weight loss (g) at different temperatures				
	303K	308K	313K	318K	323K
Blank	0.611	0.736	0.779	0.987	1.233
0.1	0.361 (40.92)	0.443 (39.81)	0.482 (38.13)	0.628 (36.37)	0.806 (34.63)
0.2	0.329 (46.15)	0.402 (45.38)	0.426 (45.31)	0.552 (44.07)	0.708 (42.58)
0.3	0.294 (51.88)	0.355 (51.77)	0.379 (51.35)	0.483 (51.06)	0.619 (49.80)
0.4	0.258 (57.77)	0.316 (57.07)	0.337 (56.74)	0.431 (56.06)	0.547 (55.64)
0.5	0.232 (62.03)	0.285 (61.28)	0.302 (61.23)	0.384 (61.09)	0.497 (59.69)

Values of inhibition efficiency (IE %) in parenthesis

Effect of temperature and inhibitor concentration on the corrosion of mild steel in 0.5 M H_2SO_4

Tables 5 and 6 also shows the effect of inhibitor concentration on mild steel corrosion in acidic medium. It was observed that the leaves extract of *Azadirachta indica* and the blends inhibit the corrosion of mild steel in H_2SO_4 solution, at all the concentrations used in the study. Maximum inhibition efficiency was recorded at 0.5 gdm^{-3} of inhibitors. It is evident from Tables 5 and 6 that the corrosion rates decreased on addition of 0.5 gdm^{-3} of inhibitors. From the results, it is evident that the inhibition efficiency increased with increase in the concentration of inhibitors and decreased as the temperature increases. This can also be seen in Figure 4. The increase in inhibition efficiency with increase in the concentration of inhibitors is due to increase in the surface coverage, as a result, metal dissolution (corrosion rate) is retarded (Samuel *et al.*, 2015). The inhibition efficiency was found to decrease as the temperature increases. The decrease in inhibition efficiency with increase in temperature suggests physical adsorption mechanism. This is similar to the report of Savita *et al.* (2015).

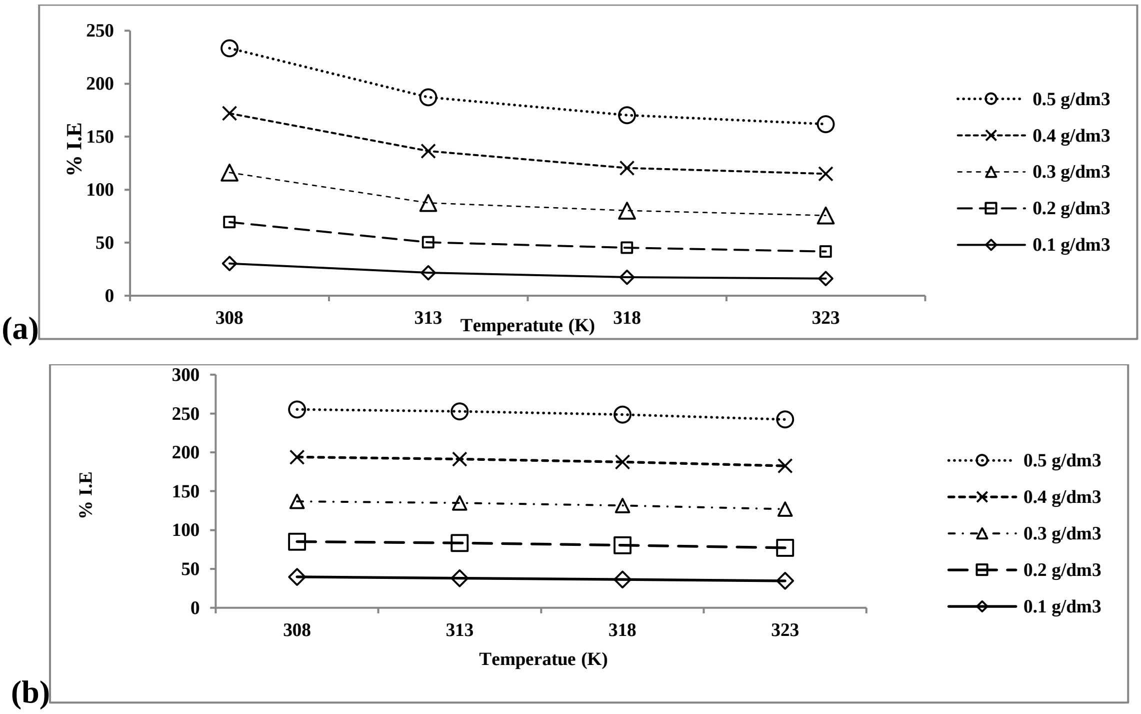

Figure 4: Effect of Temperature on I.E (%) of Mild Steel Immersed in 0.5 M H_2SO_4 solution in the presence of 0.1- 0.5 g/dm^3 Leaves Extract (a) and Blend (b) Inhibitors

ISOTHERM STUDIES

Isotherm plots for Langmuir and Freundlich models are presented in Figures 5 and 6 respectively. Only data (without plots) of Dubinin Raduskevick model is presented in Tables 7 and 8. Surface coverage (∅) was used to explain the interaction of inhibitor molecules with mild steel surface. When the inhibitor solution is transported towards the metal surface, Fe^{2+} - inhibitor complex is formed by all the inhibitors on the anodic sites of the metal surface since Fe and C are major components of steel. In this way, the anodic reactions are effectively controlled (Patrick *et al.*, 2013)

Good linearity and applicability of the Langmuir model was evidenced by high R^2 values (0.9002 - 0.9887 for the extract; 0.9424 – 0.9906 for the complex and 0.9960 – 0.9991 for the blend), as shown presented on Tables 7 and 8. The Langmuir constant, relating to the maximum adsorption capacity (qm) was also investigated. Extract of *Azadirachta indica* gave the highest value for maximum adsorption capacity (0.8040 - 1.1902 mgg^{-1}). This is in agreement with the high adsorption capacity values present by the extract inhibitor from the Freundlich constants (k_f = 1.009 – 1.370). In this work, it is evident that the maximum adsorption capacities of the studied inhibitors (obtained from the Langmuir relationship) are lower than their corresponding adsorption capacities values (kf) from the Freundlich isotherm, as shown in Table 7 and 8, comparing qm with (kf) values as; 0.8040 (1.009), 1.0232 (1.143), 1.1689(1.184), 1.1902 (1.278) and 1.0209 (1.370) for the extract inhibitor at 303 – 323K. The results also show similar results for the complex and the blend inhibitor respectively. Also revealed are values of the Langmuir constants, k_L (Lmg^{-1}) which directly affects the energy of adsorption. Inhibitors with high energy related value, k_L presented high adsorption intensity as it was deduced from the Freundlich constant on the same Table. The K_L and (k_f) values include 21.37 (1.009), 2.214 (2.023) and 5.086 (1.289) for the leaves extract of *Azadirachta indica*, complex and the blend inhibitors (at 303K) respectively. This research presented R_L values (0.0856 - 0.5433 for the extract, 0.4531 – 0.5862 for the complex and 0.2822 – 0.3151 for the blend), which justifies favorable adsorption ($0 < R_L < 1$). A confirmation of the fitness of experimental data into Langmuir isotherm model is an indication of the homogenous nature of the mild steel surface.

Freundlich isotherm was tested for all the inhibitors (extract and blend) at five different temperatures. In the Freundlich isotherm, a plot of $\log\theta$ versus $\log C$ gave a straight line with slope equal to 1/n 0.3561-0.6845) and intercept $\log K$. The data in Tables 7 and 8 were generated from Figures 5 and 6. The results show that the modeling of data generated using Freundlich model also gave a good linearity and applicability (R^2>0.8336) for all the studied inhibitors. Considering the mean of R^2 values,the trend of best fit follows the order; blend (0.9976) > Complex (0.9612) and extract (0.9440). The extent of applicability for the blend inhibitor is greater than those of the extract and complex inhibitors. It was also justified that the ranking based on the adsorption intensity (1/n) follows the same trend as in the applicability test displayed earlier by R^2. Thus, the adsorption intensity of the extract inhibitor (0.3258-0.3719) is least among the series. 1/n <1 is an indication of normal adsorption (Balarak *et al.*, 2017). The degree of heterogeneity of adsorption surface was also measured from the 1/n values. According to Balarak *et al.*, (2017) the slope (1/n), in the Freundlich equation (ranging between 0 and 1) is a measure of heterogeneity. The level of heterogeneity (Freundlich) is dominance over homogeneity (Langmuir) for the leaves extract surface coverage. Surface becomes more heterogeneous as 1/n values get closer to zero (Chatterjee *et al.*, 2009). Based on this, the extract and complex inhibitors blended together presented a more heterogeneous surface. The value of 1/n is always positive but not an integer, with a typical value of 0.60 (Adejo *et al.*, 2013).

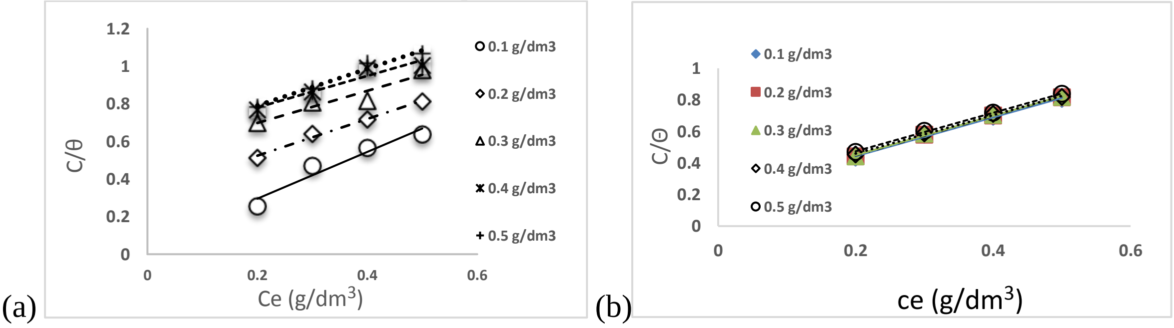

Figure 5: Langmuir Model Plot for the Extract (a) and Blend (b) at 303- 323K

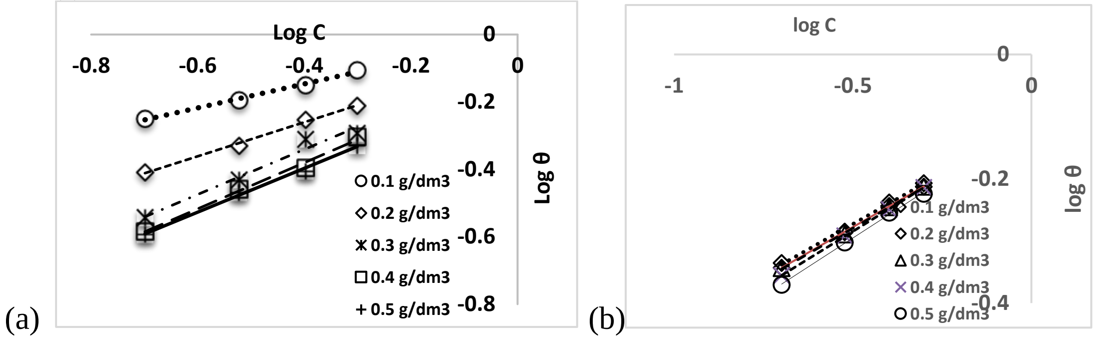

Figure 6: Freundlich Isotherm Plot for Leave Extract (a) and Blend (b) at 303- 323K

Dubinin – Radushkevich model was chosen to estimate the characteristic porosity of the adsorbent and the apparent energy of adsorption. A plot of ln qe against RT ln (1 + 1/Ce) ^{2} yielded straight lines and indicate a good fit of the isotherm to the experimental data. Another capacity parameter called theoretical adsorption capacity (q_D) was evaluated from the D- Radushkevich isotherm model, denoted as D-R model. The D-R model is known to be more general than both the Langmuir and Freundlich isotherm as its deviation is not based on ideal assumption. Just like the Langmuir maximum adsorption capacity (q_m), it was revealed that the Freundlich adsorption capacities (k_f) were also lower in magnitude than the theoretical adsorption capacity (q_D) from the D-R isotherm. Tables 7 and 8 presented a higher q_D values (1.325-1.348 mgg^{-1}) for the blend. This value is higher than its corresponding q_m value (0.8019 -0.8219 mgg^{-1}) for the same blend inhibitor.

Table 7: Isotherm Data of Corrosion Inhibition by Leaves Extract Inhibitor

Isotherm	Temperature (K)	Q_m (mg/g)	K_L (L/mg)	R_L	Linearity (R^2)
Langmuir	303	0.8040	21.37	0.0856	0.9331
	308	1.0232	3.04	0.3968	0.9887
	313	1.1689	1.896	0.5133	0.9002
	318	1.1902	1.632	0.5507	0.9244
	323	1.0209	1.681	0.5433	0.9735
Freundlich		1/n	n	K_f	(R^2)
	303	0.3561	2.81	1.009	0.9924
	308	0.5055	1.98	1.143	0.9956
	313	0.6685	1.50	1.184	0.9692
	318	0.6845	1.46	1.278	0.9911
	323	0.6505	1.54	1.370	0.9952
D-R		Q_D	B_D (mol^2/kJ^2	E_D (kJ/mol)	(R^2)
	303	1.049	3x10^{-8}	4.1x10^{-5}	0.9630
	308	1.203	4x10^{-8}	3.5x10^{-5}	0.9772
	313	1.259	5x10^{-8}	3.2x10^{-5}	0.9705
	318	1.370	5x10^{-8}	3.2x10^{-5}	0.9742
	323	1.459	5x10^{-8}	3.2x10^{-5}	0.9867

D-R = Dubinin - Raduskevick

Table 8: Isotherm Data of Corrosion Inhibition by the Blend in ratio 1:1

Isotherm model	**Temperature (K)**	**Q_m (mg/g)**	**K_L (L/mg)**	**R_L**	**Linearity (R^2)**
Langmuir	303	0.8119	5.086	0.2822	0.9960
	308	0.8019	5.056	0.2834	0.9981
	313	0.8023	4.985	0.2863	0.9968
	318	0.8219	4.617	0.3022	0.9978
	323	0.8193	4.348	0.3151	0.9991
Freundlich		1/n	n	K_f	(R^2)
	303	0.3258	3.07	1.289	0.9971
	308	0.3287	3.04	1.299	0.9999
	313	0.3292	3.04	1.303	0.9991
	318	0.3552	2.82	1.280	0.9998
	323	0.3719	2.69	1.287	0.9985
D-R		Q_D	B_D (mol^2/KJ^2	E_D (KJ/mol)	(R^2)
	303	1.333	$2x10^{-8}$	$5.0X10^{-5}$	0.9765
	308	1.341	$2x10^{-8}$	$5.0X10^{-5}$	0.9878
	313	1.348	$2x10^{-8}$	$5.0X10^{-5}$	0.9813
	318	1.325	$3x10^{-8}$	$4.1X10^{-5}$	0.9895
	323	1.333	$3x10^{-8}$	$4.1X10^{-5}$	0.9935

D-R = Dubinin - Raduskevick

The high values of q_D is an indication of high adsorption capacity. The quantitative trend of the 3 types of absorption capacities obtained from different isotherms in this analysis can be given as $q_D > k_f > q_m$. No known reference could make us conclude that the theoretical saturation capacity, q_D is always higher than the maximum adsorption capacity as evidenced in this research. The apparent energy (E) of adsorption from Dubinin-Radushkevich isotherm model is computed using the relation;

$$E_D = \sqrt{1/2B_D} \quad (8)$$

The estimated constant, B_D, related to adsorption energy was presented as $2.0x10^{-8}$ and $3.0x10^{-8}$ mol^{2}kJ^2. These values give an idea on the mean free energy which was valued as $E_D = 4.1x10^{-5} – 5.0x10^{-5}$ kJmol^{-1}. E_D is a parameter used in predicting the type of adsorption. An E_D value < 8 kJmol^{-1} is an indication of physi-sorption (Jain *et al.*, 2009).

Corrosion Rate and Surface Coverage

Tables 9 and 10 shows the calculated values of corrosion rates and surface coverage for leaves extract and blend of the leaves extract : complex (1:1) while Figure 7 is Arrhenius Plots for Mild Steel Immersed in 0.5 M H_2SO_4 solution in the presence of 0.1- 0.5 g/dm^3 leaves extract inhibitor (Figure 7a) and in 0.1- 0.5 g/dm^3 of Blend (ratio 1:1) inhibitor (Figure 7b). There is a relationship between the corrosion rate (CR) of Mild steel in the tested medium and temperature (Gbertyo *et al.*, 2014).

Table 9: Corrosion rate and Surface Coverage for Leave Extract

Conc. g/dm^3	Corrosion Rate (mgcm^{-2}h^{-1})					Surface coverage (θ)				
	303K	308K	313K	318K	323K	303K	308K	313K	318K	323K
Blank	0.0065	0.0081	0.0090	0.0127	0.0172	-	-	-	-	-
0.1	0.0044	0.0045	0.0071	0.0105	0.0144	0.4529	0.3039	0.2177	0.1734	0.1620
0.2	0.0035	0.0039	0.0064	0.0094	0.0128	0.5632	0.3904	0.2862	0.2605	0.2548
0.3	0.0029	0.0034	0.0057	0.0083	0.0113	0.6382	0.4678	0.3707	0.3477	0.3400
0.4	0.0024	0.0029	0.0046	0.0075	0.0104	0.7074	0.5580	0.4894	0.4030	0.3934
0.5	0.0018	0.0025	0.0044	0.0064	0.0091	0.7838	0.6151	0.5092	0.4977	0.4688

Table 10: Corrosion rate and Surface Coverage for the Blend in ratio 1:1

Conc. g/dm^3	Corrosion Rate (mgcm^{-2}h^{-1})					Surface coverage (θ)				
	303K	308K	313K	318K	323K	303K	308K	313K	318K	323K
Blank	0.0073	0.0088	0.0093	0.0118	0.0147	-	-	-	-	-
0.1	0.0043	0.0053	0.0057	0.0075	0.0096	0.4092	0.3981	0.3637	0.3637	0.3463
0.2	0.0039	0.0048	0.0051	0.0066	0.0084	0.4615	0.4538	0.4407	0.4407	0.4258
0.3	0.0035	0.0043	0.0045	0.0058	0.0074	0.5188	0.5177	0.5135	0.5106	0.4980
0.4	0.0031	0.0038	0.0040	0.0051	0.0065	0.5777	0.5707	0.5674	0.5633	0.5564
0.5	0.0028	0.0034	0.0036	0.0046	0.0059	0.6203	0.6128	0.6123	0.6109	0.5969

Corrosion and Corrosion Inhibition Thermodynamics

The effect of temperature on the inhibition action of leaves extract of *Azadirachta indica*, Cobalt (II) Schiff Base complex and the blend on the corrosion of mild steel in 0.5 M H_2SO_4 was determined at various concentrations and at the temperature ranges of 303 K to 323 K. Values of activation energy, enthalpy of adsorption, $\Delta H^*_{ads,}$ entropy change, ΔS^*_{ads} and free energy of adsorption, ΔG_{ads} as well as heat of adsorption, Q_{ads} for the leaves extract and the blend are represented in Tables 11 and 12. It is evident that the values of the apparent activation energy for the extract, complex and the blend were higher than those for the blank, which indicate that the dissolution of mild steel in the presence of inhibitor was decreased due to the formation of a thin film by the adsorption of the inhibitors which act as a barrier on the metal surface (Louadi *et al*., 2017).

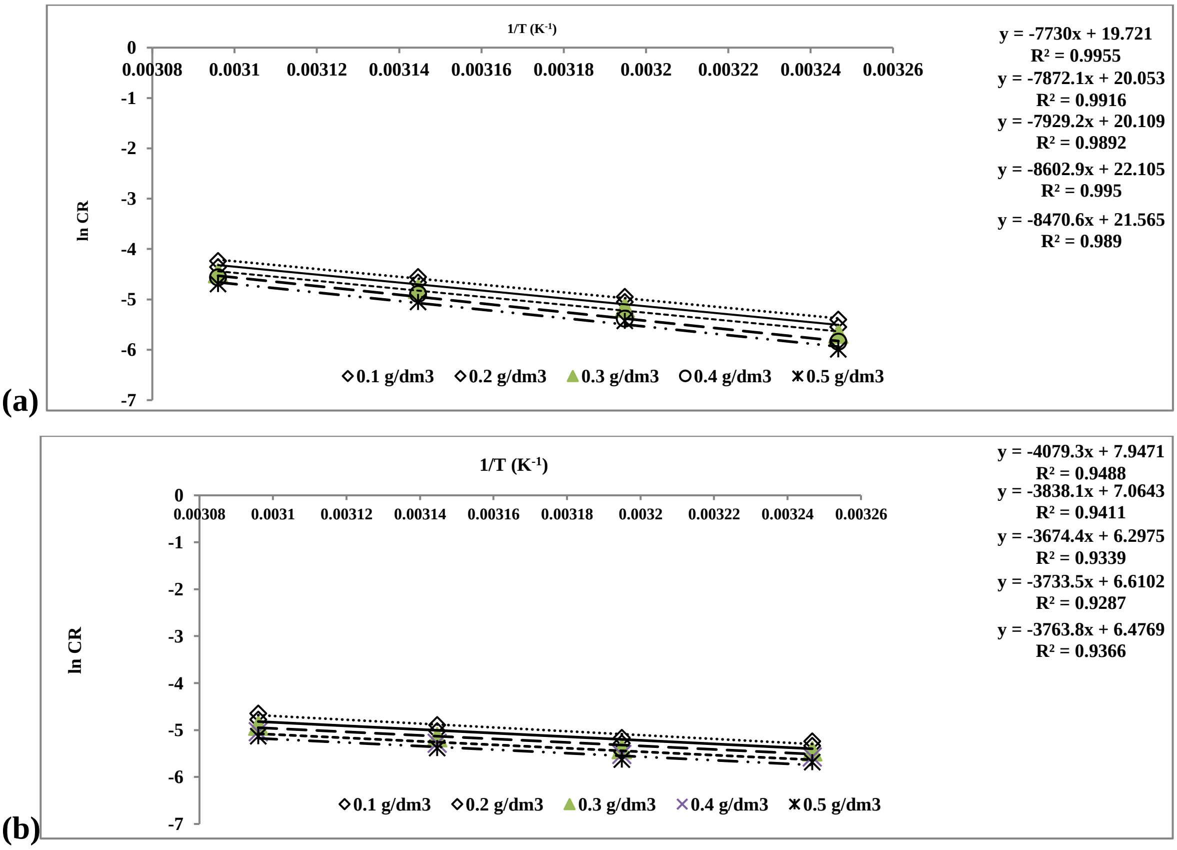

Figure 7: Arrhenius Plots for Mild Steel Immersed in 0.5 M H_2SO_4 Solution in the presence of 0.1- 0.5 g/dm^3 Leave Extract Inhibitor (a) and in 0.1- 0.5 g/dm^3 of Blend (ratio 1:1) Inhibitor (b)

The evaluated values of enthalpy of adsorption for the leaves extract, cobalt (II) Schiff Base complex and the blend are all positive and are higher than that of the blank respectively. The positive sign is an indication of the endothermic nature of the adsorption process. The values of E_a and ΔH^{*}_{ads} were found to increase in the presence of inhibitors, suggesting an increase in the energy barrier of the corrosion reaction, hence the dissolution of mild steel becomes difficult (Shukla *et al*., 2011). It has been shown that the inhibitor is more effective when values of activation energy are higher. We noted that the variations of activation energy E_a and the enthalpy of adsorption, ΔH^{*}_{ads} is similar to that of the concentration of the inhibitors, which satisfies the relationship between E_a and ΔH^{*}_{ads} as shown by equation 8 (Gharebaa and Omanovic, 2010; Adejo *et al*., 2013). The average difference in value of $E_a - \Delta H^{*}$(equation 8) for leaves extract was found to be 2.450 kJ/mol, almost near the value of RT (2.60 kJ/mol), the value for the complex was 2.450 kJ/mol, also equivalent to the value of RT (2.60 kJ/mol) and that for the blend was 2.450 kJ/mol, equivalent with the value of RT (2.60 kJ/mol) where T is the average of the temperatures (313 K) at which the work was carried out. This implies that the corrosion process of this metal in the acid medium is a unimolecular reaction (Gharebaa and Omanovic, 2010).

$$E_a - \Delta H^{*} = RT \tag{9}$$

The negative values of entropy of activation, ΔS^{*}_{ads}, as shown in Tables 11 and 12 for leaves extract, and blend respectively, indicated that the activated complex in the rate-determining step represented an association, rather than dissociation, that is a decrease in disorderliness in going from reactant to the activated complex (Adejo *et al*., 2013). The values were observed to decrease as the concentration increases showing a decrease in disorderliness in that direction. Heats of adsorption for both inhibitors were observed to be positive indicating that the processes were endothermic. The Free energy was calculated using the equation (10) (Adejo *et al*., 2014).

$$\Delta G_{ads=} -RTln\,(55.5K) \tag{10}$$

Where K = θ / [(1- θ) C], and is the equilibrium constant of adsorption, C is the concentration of the inhibitor, R is the universal gas constant, T is the absolute temperature and 55.5 is the molar concentration of water. The evaluated heat of adsorption, (Qads), ranged from 58.54 kJ/mol to 60.24 kJ/mol for the extract, 30.0 kJ/mol to 40.73 kJ/mol for the complex and from 35.68 kJ/mol to 42.25 kJ/mol for the blend. The positive values indicated that the adsorption of inhibitor onto the surface of the coupon was endothermic. The values of activation energy (Ea), ranged from 31.72 to 29.10 kJ/mol in the presence of the blend in ratio 1:1, which indicated physical adsorption. Values of enthalpy change of adsorption; (ΔH.ads) ranged from 29.22 kJ/mol to 26.63 kJ/mol in the presence of the blend and was higher than the uninhibited solution. The values of ΔGads were all negative an indication of the spontaneity of the adsorption process and were all below -20 kJ mol^{-1} which is consistent with physical adsorption process (Adejo *et al.*, 2014). On the contrary, values higher than 40 kJ mol^{-1} involves the sharing or transfer of charges from the inhibitor molecules to the surface of the metal to form a coordinate type of bond which suggests chemisorption.

Table 11: Thermodynamic Parameters of Corrosion Inhibition by Leaves Extract Inhibitor

Conc. g/dm^{-3}	**Ea (kJ/mol)**	**+Q$_{ads}$ (kJ/mol)**	**+ΔH$^{*}_{ads}$ (kJ/mol)**	**ΔS$^{*}_{ads}$ J/mol**	**ΔG$_{ads}$ (kJ/mol)**				
					303 K	308 K	313 K	318 K	323K
Blank	39.01	-	36.57	-166.65	-	-	-	-	-
0.1	52.19	58.54	49.62	-127.59	-15.44	-14.06	-13.12	-12.58	-12.56
0.2	56.39	53.52	54.0	-144.73	-14.81	-13.27	-12.26	-12.12	-12.23
0.3	58.69	57.31	56.29	-108.56	-14.58	-13.04	-12.21	-12.14	-12.24
0.4	63.12	61.45	60.67	-95.81	-14.65	-13.23	-12.73	-12.0	-12.08
0.5	68.03	60.24	65.58	-81.01	-15.11	-13.26	-12.35	-12.43	-12.31

Table 12: Thermodynamic Parameters of Corrosion Inhibition by Blends of *Azadirachta indica* and Cobalt(II) Schiff Base Complex

Conc. g/dm^{-3}	Ea (kJ/mol)	+Q_{ads} (kJ/mol)	+ΔH^{*}_{ads} (kJ/mol)	ΔS^{*}_{ads} J/mol	ΔG_{ads} (kJ/mol)				
					303 K	308 K	313 K	318 K	323K
Blank	27.50	-	24.98	-203.69	-	-	-	-	-
0.1	31.72	35.68	29.22	-194.15	-14.99	-15.12	-15.18	-15.23	-15.26
0.2	30.09	36.21	27.62	-200.2	-13.78	-13.93	-14.15	-14.24	-14.31
0.3	29.19	38.30	26.67	-204.23	-13.34	-13.55	-13.72	-13.91	-14-0
0.4	28.82	41.13	26.32	-206.40	-13.22	-13.36	-13.54	-13.71	-13.86
0.5	29.10	42.25	26.63	-206.24	-13.10	-13.24	-13.44	-13.64	-13.70

activation energy, Ea, heat of adsorption, Q_{ads}, enthalpy, ΔH^{*}_{ads}, entropy, ΔS^{*}_{ads} and free energy ΔG_{ads}

Synergistic Studies

Verifying the performance of blend inhibitory systems (extract and the complex) in synergy, statistical methods was used. From Figure 8, it was observed that at each studied temperature, the mean inhibition efficiency of the blend is higher than that of the individual inhibitors except at 303K. This generalization only holds for experimental runs with low inhibitor concentrations (0.1-0.3 g/dm^3). Whereas the inhibition efficiency of the extract is higher than that of the blend at higher inhibitor concentrations (0.4 and 0.5 g/dm^3). This implied that there could be a synergy between the green Extract-Schiff base complex inhibitor only at low to moderate concentrations on a 0.1-0.5 g/dm^3 scale. It is worth of note that Figure 8 also represent the trends of the mass lost data for the three system since IE% was deduced from mass lost.

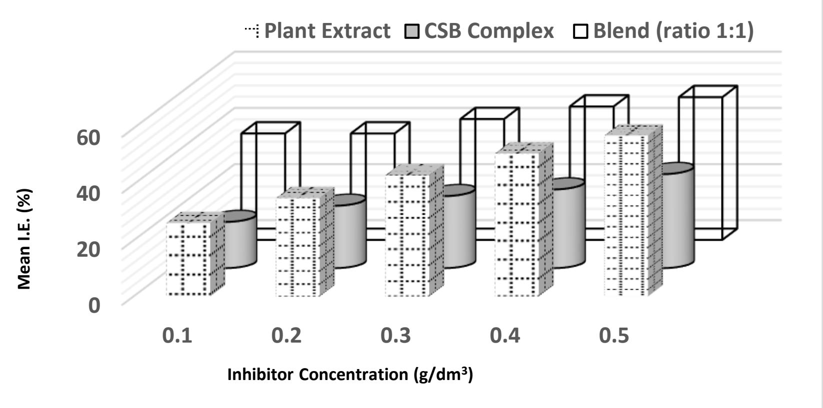

Figure 8: Comparative I E (%) of Mild Steel Corrosion by Leaves Extracts, Complex and Blend in varying Concentration of Inhibitor

Synergism or antagonism phenomenon between the Schiff base metal complex and the leaves extract of *Azadirachta indica,* was further estimated using the synergism parameter (S_1) from values obtained from the inhibition efficiencies of all the inhibitors, according to the following equations (Shu *et al.*, 2012).

$$S_1 = \frac{1- I_{1+2}}{1-I^{!}_{1+2}} \qquad (11)$$

$$I_{1+2} = I_1 + I_2 \qquad (12)$$

Where I_1 *and* I_2 is the inhibition efficiency of the complex and extract respectively. $I^{!}_{1+2}$ = inhibition efficiency of the blend. By implication, S_1 is equal to when combining the Schiff base metal complex and the leaves extract of *Azadirachta indica* has effect on each other and they are adsorbed at the metal/solution interface independently. Alternatively, synergistic effect exists among the blend when $S_1 > 1$ and antagonistic (contending) effect manifests at $S_1 < 1$.

Table 13: Synergism Parameters for the Relationship between Co (II) Schiff base metal complex, leaves extract of *Azadirachta indica* and their blend.

Temp.(K)	Inhibitor Conc. (g/dm^{-3})	Inhibition efficiency (IE %)				Synergism parameter (S_1)	Relationship
		I_1	I_2	I_{1+2}	$I^{!}_{1+2}$		
303	0.1	45.29	23.18	68.47	40.92	1.69013	Synergistic
	0.2	56.32	27.37	83.69	46.15	1.831451	Synergistic
	0.3	63.82	30.29	94.11	51.88	1.829992	Synergistic
	0.4	70.74	33.39	104.13	57.77	1.816629	Synergistic
	0.5	78.38	39.6	117.98	62.03	1.916762	Synergistic
308	0.1	30.39	15.38	45.77	39.81	1.153569	Synergistic
	0.2	39.04	23.75	62.79	45.38	1.392294	Synergistic
	0.3	46.78	25.25	72.03	51.77	1.399055	Synergistic
	0.4	55.8	28.26	84.06	57.07	1.481363	Synergistic
	0.5	61.51	32.78	94.29	61.28	1.547611	Synergistic
313	0.1	21.77	15.34	37.11	38.13	0.972529	Antagonistic
	0.2	28.62	21.13	49.75	45.31	1.100203	Synergistic
	0.3	37.07	24.87	61.94	51.35	1.210328	Synergistic
	0.4	48.94	27.32	76.26	56.74	1.350197	Synergistic
	0.5	50.92	32.73	83.65	61.23	1.37224	Synergistic
318	0.1	17.34	14.84	32.18	36.37	0.881538	Antagonistic
	0.2	26.05	20.32	46.37	44.07	1.053401	Synergistic
	0.3	34.77	24.64	59.41	51.06	1.1668	Synergistic
	0.4	40.3	27.31	67.61	56.06	1.209771	Synergistic
	0.5	49.77	31.67	81.44	61.09	1.338659	Synergistic
323	0.1	16.2	14.19	30.39	34.63	0.873922	Antagonistic
	0.2	25.48	18.89	44.37	42.58	1.04305	Synergistic
	0.3	34	23.59	57.59	49.8	1.159631	Synergistic
	0.4	39.34	27.23	66.57	55.64	1.200037	Synergistic
	0.5	46.88	31.16	78.04	59.69	1.31266	Synergistic

I_1 and I_2 - inhibition efficiency of the complex and extract respectively, $I^{!}_{1+2}$ = inhibition efficiency of the blend, S_1- Synergism parameter, $S_1<1$- Antagonistic, $S_1>1$- Synergistic

Table 13 presents a total of 25 experimental runs, investigating the roles of varying inhibitor concentrations and temperatures in the synergistic performance of the inhibitor blend. The synergistic parameter (S_1) for 22 experiments gave values of S1> 1 (greater than Unity), indicating a synergistic effect of combining the Co (II) Schiff base metal complex with the leaves extract of *Azadirachta indica* in the inhibitor of mild steel in 0.5 M H_2SO_4 solution. However, it is should be noteworthy that results at higher temperatures (313-323 K), are exceptions (S1<1), with contending or antagonistic effects.

CONCLUSIONS

Inhibition of corrosion of mild steel in acid solution by ethanol extract of leaves *Azadirachta indica*, Cobalt (II) Schiff base complex as well as their blend was studied using weight loss method. It was found that the inhibitors reduced the corrosion of the metal in 0.5 M H_2SO_4 solution. The inhibitive action of the inhibitors depends on both concentrations of the inhibitor and temperature. Results indicated that inhibition efficiency increased with increased inhibitor concentration but decreases with temperature rise, with the highest inhibition efficiency of 46.88% for leaves extract, 31.16% for the complex and 59.69 % for the ratio 1:1 blend in 0.5 g/dm^3 at 323 K. Evaluation based on the isotherm studied, indicated favorable adsorption. Model applicability trend based on highest applicability coefficient (R^2) follows; Freundlich > Langmuir > D-R. The adsorption capacities and intensities are also in agreement with those in literatures. Test of significance ($p<0.5$) between inhibition efficiency of extract and blend based on temperature shows no significant difference at 313 K, 0.1 and 0.2 g/dm^3 complex and extract concentrations but are significant at temperatures of 303 and 308 K respectively. Overall, Blends of *Azadirachta indica* leaves extract and cobalt (II) Schiff base complex indicated synergistic effect, enhancing the inhibition efficiency and can be used as cheap corrosion inhibitor for corrosion of mild steel in 0.5 M H_2SO_4. only at low inhibitor concentration.

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