



Inhibitive Behaviour of *Acacia senegalensis* on Corrosion Resistance of Mild Steel-Acidic Environment

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The ethanolic extract of *Acacia senegalensis* (gum arabic) stem was used as corrosion inhibitor for mild steel in 0.5 M H₂SO₄ using gravimetric-weight loss and potentiodynamic polarization. The characterization of the coupon before and after the corrosion test was done using scanning electron microscopy equipped with energy dispersive X-ray spectroscopy (SEM/EDS). The temperature, inhibitor concentration and time were varied in the range of 30-70 °C at 20 °C interval, 0-10 % v/v at 2 % v/v interval and 45 to 270 min at 45 min interval, respectively. The synergetic effect of the inhibitor was evaluated by addition of halide ion (KI). Corrosion rate increased with increase in temperature and decreased with increase in both inhibitor concentration and time. Inhibition efficiency was found to increase with increase in concentration of the extract and the maximum inhibition efficiency was found to be 94.16 %, maximum inhibition efficiency in the presence of KI was 99.62 % and was assumed to occur *via* adsorption of the inhibitor molecules on the metal surface. The adsorption of the molecules of the extract on the mild steel surface obey Langmuir adsorption isotherm. The potentiodynamic polarization results revealed that the extract acts as mixed type inhibitors.

Keywords: *Acacia senegalensis*, Adsorption isotherm, Thin film, Halide ions.

INTRODUCTION

Metals in service often give a superficial impression of permanence, but all except gold are chemically unstable in air and air-saturated water at ambient temperatures and most are also unstable in air-free water. Hence almost all of the environments in which metals serve are potentially hostile and their successful use in engineering and commercial applications depends on protective mechanisms [1]. Mild steel finds application in many industries due to its easy availability, ease of fabrication, low cost and good tensile strength besides various other desirable properties. It suffers from severe corrosion when it comes in contact with acid solutions during acid cleaning, transportation of acid, de-scaling, storage of acids and other chemical processes [2,3]. Corrosion plays a very important role in diverse fields of industry and, consequently, in economics. The protection of metals and alloys is thus of particular interest. The goal of studying the processes of corrosion is to find methods of minimizing or preventing it. One approach is the use of corrosion inhibitors. Inorganic compounds like chromates are costly, some of them are not easily biodegradable and their disposal creates pollution problems which make them harmful to environment [4].

Organic compounds have become widely accepted as effective corrosion inhibitors in various media. Most of the organic inhibitors containing nitrogen, oxygen, sulfur atoms and multiple bonds in their molecules facilitate adsorption on the metal surface [5]. A variety of organic compounds containing heteroatom like nitrogen, sulphur and oxygen had been investigated as corrosion inhibitors [6,7]. Natural inhibitors like plant extracts are environment friendly, bio-degradable, non-toxic, easily available and of potentially low cost. They are safe and can be extracted by simple procedures and works had been carried out using different plant extracts for corrosion inhibition in different media [8-10]. It has been established that the initial step in any corrosion inhibition process is the adsorption of the inhibitor on the surface of the metal. Although, the stability of this inhibitor film formed over the metal surface depends on some physicochemical properties of the molecule related to its functional groups such as aromaticity, type of the corrosive medium and nature of the interaction between the inhibitors with the *d*-orbital vacant of iron [11,12]. The present study examines the potential of *Acacia senegalensis* as eco-friendly inhibitor for corrosion control of mild steel in 0.5 M H₂SO₄ using weight loss and potentiodynamic polarization method.

TABLE-1
CHEMICAL COMPOSITION OF MILD STEEL USED

Element	Fe	C	Si	Mn	P	S	Co	Mo	Ni	Al	Cu
% Wt.	99.00	0.17	0.033	0.423	0.018	0.014	0.05	0.014	0.19	0.002	0.015

EXPERIMENTAL

The chemical composition of mild steel used is given in Table-1 for both weight loss and potentiodynamic polarization method.

Preparation of inhibitor: The plants were washed with tap water two times to remove dust particles and cut into small pieces. These were then kept in an open place to dry at room temperature (30 °C). The dried plants were then grounded into fine powder using mortar and pestle. 100 g of ground sample was extracted in 1.5 L of 70 % ethanol and 30 % distilled water were used as solvent using maceration method by separating funnel. The concentrations of the extract were obtained.

Gas chromatography-mass spectrometry (GC-MS):

About 1 mL of each of the concentration of the extract was analyzed by GC-MS using QP 2010 Plus Schmadzu Product equipped with two fused-silica capillary columns (60 m × 0.22 mm), film thickness at National Research Institute for Chemical Technology, Zaria. Conditions under which was carried out are: column oven temperature 80 °C, injection temperature 250 °C, injection mode: split flow control mode: linear velocity, pressure: 108.0 kPa, total flow: 6.2 mL/min column flow: 1.58 mL/min, linear velocity: 46.3 cm/s, split ratio: 1.0.

Gravimetric measurements and electrochemical measurements: The sample was mechanically machined into 10 mm in diameter and length of 20 mm (7.86 cm²) into coupons for weight loss and 10 mm × 10 mm coupons for electrochemical method. The specimens were abraded with various grades of wax coated emery papers from 600 to 1800 grit and degreased in absolute ethanol, dried in acetone, weighed and stored in moisture-free desiccators prior to use to avoid reaction with atmospheric air. The metal coupons were then suspended with the help of glass hooks into beakers containing 100 mL of corrosive electrolyte for complete immersion test. The solution of 0.5 M H₂SO₄ were prepared using double distilled water. The corrosion rate of each specimen in mpy, inhibition efficiency and surface coverage were determined according to the method reported [13,14].

$$\text{mpy} = \frac{534W}{\text{DAT}} \quad (1)$$

where W, D, A and t will be in units of milligrams, grams per cubic centimeter, square inches and hours, respectively.

Inhibition efficiency (IE %) and surface coverage (θ) were calculated from the following equations:

$$\text{IE (\%)} = \frac{\text{CR}_o - \text{CR}_i}{\text{CR}_o} \quad (2)$$

$$\theta = \frac{\text{CR}_o - \text{CR}_i}{\text{CR}_o} \quad (3)$$

where CR_o and CR_i are corrosion rates in the absence and presence of inhibitors, respectively.

The specimens were embedded in epoxy resin leaving a working area of 1.33 cm². The working surface was subsequently ground with grinding papers from 600 down to 1800 grit, cleaned by distilled water and ethanol. The solutions of 0.5 M H₂SO₄ were prepared by dilution of an analytical reagent grade 98.3 % H₂SO₄ with doubly distilled water. Potentiodynamic polarization measurements were done using an Autolab potentiostat (PGSTAT30 computer controlled) with the General Purpose Electrochemical Software (GPES) package version 4.9. Potentiodynamic anodic and cathodic polarization curves were obtained with a scan rate of 2 mV/s in the potential range from -0.2 to -0.8 mV relative to the corrosion potential (E_{corr}). Values of the corrosion current density (I_{corr}) were obtained by extrapolation of the cathodic branch of the polarization curve back to E_{corr}. From the polarization curves, Tafel slopes, corrosion potential and corrosion current were calculated. All the tests were performed at ambient temperature (30 °C) in a static solution. The inhibitor efficiency was calculated according to eqn. 4 as reported elsewhere [14].

$$\text{IE (\%)} = \frac{I_{\text{corr}} - I_{\text{corr}}^*}{I_{\text{corr}}} \times 100 \quad (4)$$

Characterization of the coupons: A Philips model XL30SFEG high resolution field emission scanning electron microscope equipped with energy dispersive X-ray analyzer was used in this study. The surface morphology of the coupons before and after corrosion were analyzed [15].

RESULTS AND DISCUSSION

Gas chromatograph and mass spectroscopy: The results obtained from the GC-MS analysis are shown in Fig. 1, while GC-MS data of *Acacia senegalensis* ethanolic extract and hydroxyl aromatic compounds are presented in Table-2.

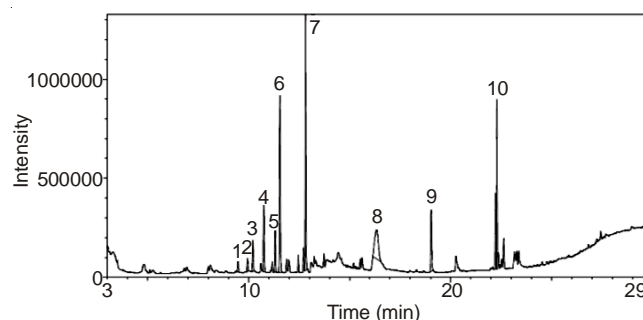


Fig. 1. Chromatogram and corresponding mass spectra of *Acacia senegalensis* extract showing the peaks of the compounds

Effect of concentration of *Acacia senegalensis* on mild steel corrosion: The variation of corrosion rates, inhibition efficiency and surface coverage for the corrosion of mild steel in 0.5 M H₂SO₄ (containing various concentrations of *Acacia senegalensis*) at 30 °C were presented in Table-3 and Fig. 2. The extract shows maximum inhibition efficiency of 94.19 %

TABLE-2
GC-MS DATA OF *Acacia senegalensis* EXTRACT

Peaks	Compounds name	m.f.	m.w. (g/mol)	R. time	I. time	F. time	Peak report TIC				A/H
							Area	Area (%)	Height	Height (%)	
1	Cyclohexene or 3-methyl-6-(1-methylethylidene)-	C ₁₀ H ₁₆	136	9.471	9.425	9.525	149655	1.16	50286	1.16	2.98
2	6-Octen-1-ol, 3,7-dimethyl-, acetate	C ₁₂ H ₂₂ O ₂	198	9.942	9.900	10.000	187609	1.45	67655	1.56	2.77
3	2,6-Octadien-1-ol, 3,7-dimethyl-, acetate,	C ₁₂ H ₂₀ O ₂	196	10.210	10.158	10.283	423848	3.29	158441	3.66	2.68
4	Cyclohexane, 1-ethenyl-1-methyl-2	C ₁₅ H ₂₄	204	10.755	10.708	10.825	924520	7.17	337204	7.79	2.74
5	Bicyclo 4,11,11-trimethyl-8-methylene-, [C ₁₅ H ₂₄	204	11.313	11.258	11.375	550400	4.27	209953	4.85	2.62
6	Bicyclo[3.1.1]hept-2-ene, 2, 2-Norpinene	C ₁₅ H ₂₄	204	11.553	11.375	11.650	2388362	18.52	893753	20.65	2.67
7	Cyclohexene, 1,5-Heptadiene,	C ₁₅ H ₂₄	204	12.822	12.775	12.908	3062007	23.74	1293754	29.90	2.37
8	α -d-annofuranoside, methyl	C ₇ H ₁₄ O ₆	194	16.337	16.150	16.550	1902646	14.75	146573	3.39	12.98
9	Hexadecanoic acid, methyl ester	C ₁₇ H ₃₄ O ₂	270	19.034	18.967	19.125	1027047	7.96	310804	7.18	3.30
10	11-Octadecenoic acid, methyl ester	C ₁₉ H ₃₆ O ₂	296	22.279	22.242	22.333	2280833	17.69	858842	19.85	2.66
							12896927	100.00	4327265	100.00	

TABLE-3
CORROSION PARAMETERS FOR MILD STEEL IN AQUEOUS
SOLUTION OF 0.5 M H₂SO₄ IN PRESENCE AND ABSENCE
OF DIFFERENT CONCENTRATIONS OF *Acacia senegalensis*
EXTRACT FROM CORROSION RATE AT 30 °C FOR 270 min

Inhibitor conc. (% v/v)	Inhibition efficiency (%)	Surface cov. (θ)
Blank	—	—
2	68.48	0.68
4	71.31	0.71
6	94.16	0.94
8	88.10	0.88
10	88.11	0.88

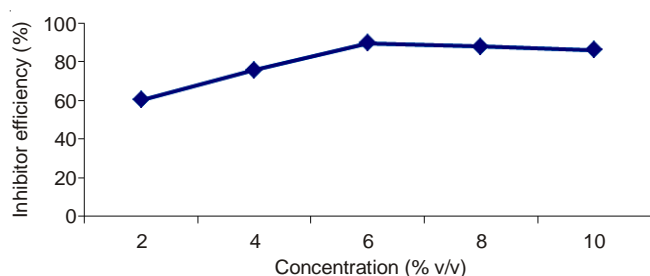


Fig. 2. Inhibitor efficiencies (IE %) of steel in absence and presence of *Acacia senegalensis* in 0.5 M H₂SO₄ at 30 °C

in H₂SO₄ and at optimum concentration of 6 % v/v. Further increase in extract concentration did not cause any significant change in the performance of the extract. The corrosion rates of mild steel for the blank solutions are higher than those obtained for solutions containing various concentrations of *Acacia senegalensis*. The result also indicates that corrosion rates of mild steel decreases with increasing concentration of *Acacia senegalensis*, but increases with increasing temperature. These also imply that the rate of corrosion of mild steel in H₂SO₄ is retarded by *Acacia senegalensis* and that the inhibition

efficiency increases with increasing concentrations, but decreases with increasing temperature meaning that *Acacia senegalensis* is temperature dependent. This observation is in agreement with previous work [16,17].

Effect of immersion time: In order to assess the stability of inhibitive behaviour of the extract on a time scale, weight loss measurements were performed in 0.5 M H₂SO₄ in the absence and presence of the extract at 2-10 % v/v concentration. The effect of immersion period on mild steel corrosion inhibition by *Acacia senegalensis* (AS) was studied for 45, 90, 135, 180, 225 and 270 min (4.5 h) immersion time in 0.5M H₂SO₄ at 30 °C. The values of percentage inhibition efficiency (IE %), corrosion rate and surface coverage obtained from weight loss measurements after 45, 90, 135, 180, 225 and 270 min immersion time in 0.5 M H₂SO₄ at 30 °C are summarized in Table-4. The inhibition efficiencies against immersion time and temperatures (30-70 °C) can be found in Figs. 3 and 4. It shows that inhibition efficiency of the extract increased with increasing immersion time from 45 to 270 min and decrease with increase in temperature. The increase in inhibition efficiency up to 270 min reflects the strong adsorption of constituents present in the extract (functional groups, hydroxyl aromatic compounds), resulting in a more protective layer

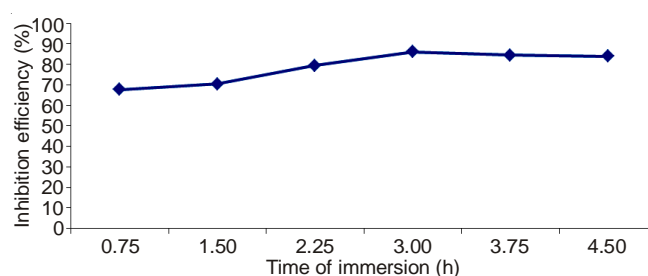


Fig. 3. Variation of inhibition efficiency of *Acacia senegalensis* (gum arabic) extracts in 0.5 M H₂SO₄ with immersion time of the solution

TABLE-4
EFFECT OF IMMERSION TIME ON PERCENTAGE INHIBITION EFFICIENCY OF MILD STEEL IN
0.5 M H₂SO₄ AT 30 °C IN THE PRESENCE OF OPTIMUM CONCENTRATIONS OF THE EXTRACT

Plant extract with optimum concentration	Time (min)					
	45	90	135	180	225	270
6 % v/v of <i>Acacia senegalensis</i>	Inhibition efficiency (%)					
	60.67	65.71	70.11	94.16	88.71	88.10

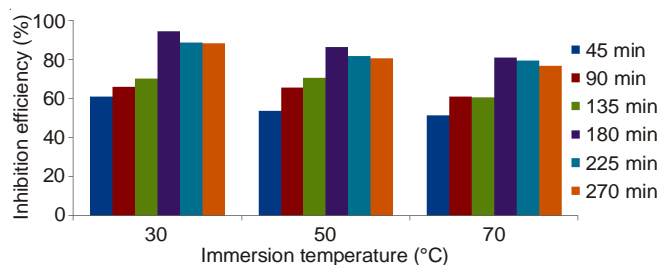


Fig. 4. Variation of inhibitor efficiency (IE %) with immersion temperature at different immersion time for 6 % v/v of *Acacia senegalensis* inhibitor concentration

formed at mild steel-sulphuric acid solution interface [18]. Thus, the extract effectively inhibits the samples in 0.5 M sulphuric acid solution.

Effect of temperature: The results obtained from temperature studies of the corrosion of mild steel in 0.5 M H₂SO₄ in the absence and presence of *Acacia senegalensis* in the temperature range of 30-70 °C revealed that increasing temperature increases corrosion rate and decreases inhibition efficiency at all the concentrations studied (Fig. 4). It is evident that inhibition efficiency decreases with increasing temperature. This is due to increased rate of dissolution process of mild steel and partial desorption of the inhibitor from the metal surface with temperature [19]. In an acidic solution the corrosion rate is related to temperature by the Arrhenius equation. The log of corrosion rate is a linear function of temperature (Arrhenius equation) [20]:

$$\log CR = \log A - E_a/2.303RT \quad (5)$$

where E_a is the apparent effective activation energy, R is the general gas constant and A is Arrhenius pre-exponential factor. A plot of log of corrosion rate obtained by weight loss measurement versus $1/T$ gave a straight line with a slope of $-E_a/2.303R$. The values of activation energy corresponding to the extract concentrations are presented in Table-5. It is apparent that activation energy is higher in the presence of inhibitor than in the absence. The increase in apparent activation energy for mild steel dissolution in the inhibited solution may be interpreted as physical adsorption that occurs in the first stage [21] and can be attributed to an appreciable decrease in adsorption of the inhibitor on the mild steel surface with increase in temperature. An alternative formulation of Arrhenius equation is given by Saratha and Vasudha [2].

$$CR = \frac{RT}{Nh} \exp\left\{\frac{\Delta S_{ads}}{R}\right\} \exp\left\{\frac{-\Delta H_{ads}}{RT}\right\} \quad (6)$$

System/concentration	E_a (kJ mol ⁻¹)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (J/mol k)
Blank	6.89	-10.68	-19.65
2 % v/v <i>Acacia senegalensis</i>	8.18	-11.71	-18.91
4 % v/v <i>Acacia senegalensis</i>	14.55	-13.29	-18.62
6 % v/v <i>Acacia senegalensis</i>	15.24	-13.84	-17.97
8 % v/v <i>Acacia senegalensis</i>	19.63	14.90	-17.52
10 % v/v <i>Acacia senegalensis</i>	21.29	-15.23	-16.81

where CR is the corrosion rate of mild steel, R is the gas constant, N is the Avogadro's number (6.022×10^{23} mol), h is the Planck constant (6.6261×10^{-34} Js), T is the temperature, ΔS_{ads} and ΔH_{ads} are the entropy and enthalpy of adsorption of the inhibitor on mild steel surface respectively.

Transforming (eqn. 6) into a linear form by taking the logarithm of both sides [22]: to obtain eqn. 7:

$$\log (CR/T) = \log (R/Nh) + \Delta S_{ads}/2.303R - \Delta H_{ads}/2.303RT \quad (7)$$

From eqn. 7, a plot of $\log (CR/T)$ versus $1/T$ is expected to yield a straight line with slope and intercept equal to $\Delta H_{ads}/2.303R$ and $(\log(R/Nh) + \Delta S_{ads}/2.303R)$ from which the values of ΔS_{ads} and ΔH_{ads} were calculated as given elsewhere [13,23]. The calculated values of activation energy, enthalpy and entropy (E_a , ΔH , ΔS) for the extract in 0.5 M H₂SO₄ is shown in Table-5.

Adsorption isotherms: Adsorption isotherms are very important for understanding the mechanism of organo-electrochemical reactions [18]. In discussing adsorption isotherms, the degree of surface coverage values were obtained from weight loss measurements using the equation [23]. Attempts were made to fit (θ) values to the thermodynamic-kinetic models of El-Awady, Freundlich, Temkin and Langmuir isotherms as described elsewhere [17] and the correlation coefficient (R^2) values were used to determine the best fit isotherm. By far, best results were obtained for the Langmuir adsorption isotherms model, which have the forms [20,23].

$$\theta/(1-\theta) = K_{ads}C \text{ or } C/\theta = 1/K_{ads} + C \quad (8)$$

where θ is the degree of surface coverage, ' K ' is equilibrium constant of adsorption process and ' C ' is the concentration of the inhibitor. A plot of C/θ against C was linear for the inhibitor suggesting that the adsorption of the compounds on the mild steel surface follows the Langmuir adsorption isotherm. The isotherm assumes that the solid surface contains a fixed number of adsorption sites and each site of metal surface holds one adsorbed species [20]. Therefore, one adsorbed H₂O molecule was replaced by one molecule of the inhibitor adsorbate on the mild steel surface.

The free energy of adsorption is related to the equilibrium constant of adsorption, K by the following equation:

$$K = \frac{1}{55.5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right) \quad (9)$$

The values of free energy of adsorption (ΔG_{ads}), K_{ads} , slope and R^2 for *Acacia senegalensis* in the temperature range of 30-70 °C are shown in Table-6. The negative values indicate spontaneous adsorption of the inhibitor on the metal surface [8]. The results in general indicate that *Acacia senegalensis* was physically adsorbed on the metal surface.

Temp. (°C)	ΔG_{ads} (KJ/mol)	Slope	R^2	K_{ads}
30	-11.278	1.223	0.989	1.585
50	-11.767	1.175	0.996	1.441
70	-12.166	1.097	0.998	1.284

Potentiodynamic polarization: Electrochemical corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion

current (I_{corr}), anodic and cathodic Tafel slopes (b_a and b_c) and percentage efficiency (IE) for the corrosion of mild steel in 0.5 M H_2SO_4 at 30 °C in the absence and presence of different concentrations of the plant extract were given in Table-7 and its corresponding polarization curves are shown in Fig. 5. Potentiodynamic polarization studies revealed that the corrosion current density (I_{corr}) markedly decreased with the addition of the extract and the corrosion potential shifts to less negative values upon addition of the plant extract. Moreover, the values of anodic and cathodic Tafel slopes (b_a and b_c) are slightly changed indicating that this behaviour reflects the plant extracts ability to inhibit the corrosion of mild steel in 0.5M H_2SO_4 solution *via* the adsorption of its molecules on both anodic and cathodic sites and consequently, the extracts act through mixed mode of inhibition. This is similar to the report [17]. It was observed that with increase in concentration of the plant extract from 2 to 10 %, the maximum inhibition efficiency of 90.60 % was observed for *Acacia senegalensis*.

<i>Acacia senegalensis</i> (% v/v)	E_{corr} (SCE) (mV)	I_{corr} (mA/cm ²)	Tafel slopes (mV/decade)		Inhibition efficiency (%)
			b_a	b_c	
Control	-0.502	9.86	62	87	—
2.0	-0.510	3.08	65	86	68.70
4.00	-0.510	2.76	68	118	71.90
6.00	-0.506	1.50	65	126	88.84
8.00	-0.505	1.49	68	130	89.52
10.00	-0.508	1.05	73	128	90.60

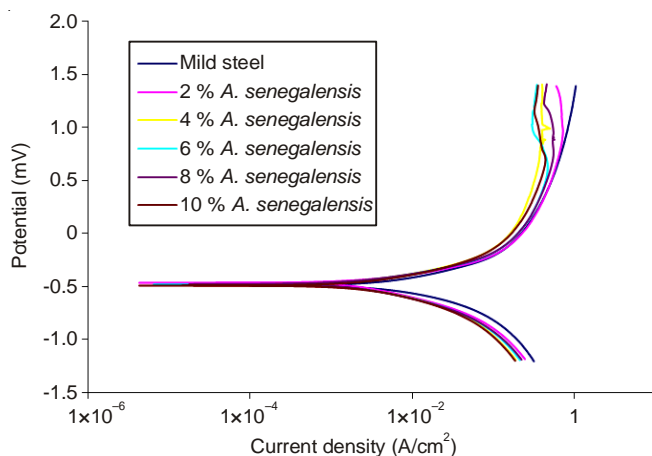


Fig. 5. Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 solution in the absence and presence of various concentrations of the plant extract of *Acacia senegalensis* at 30 °C

SEM/EDS studies on mild steel surface: Figs. 6-8 show different morphologies structures of the coupons of polished, without and with inhibitor. The morphology of the uninhibited surface was altered during corrosion and as expected rough, uneven surface covered, pits and cracks were seen in Fig. 7. However, no pits and cracks were observed in the morphology of sample with inhibitor as shown in Fig. 8. The protective film formed on the surface of the mild steel was confirmed by SEM studies. Whereas in the presence of the optimum extract,

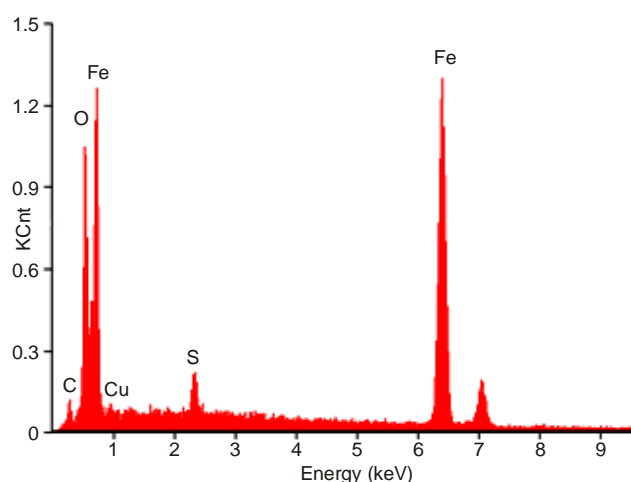
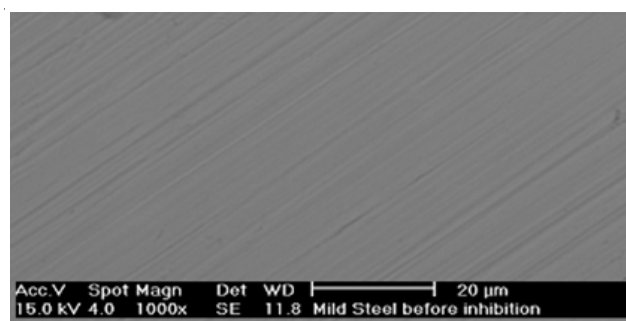


Fig. 6. SEM microstructure and EDS spectrum of mild steel as-received

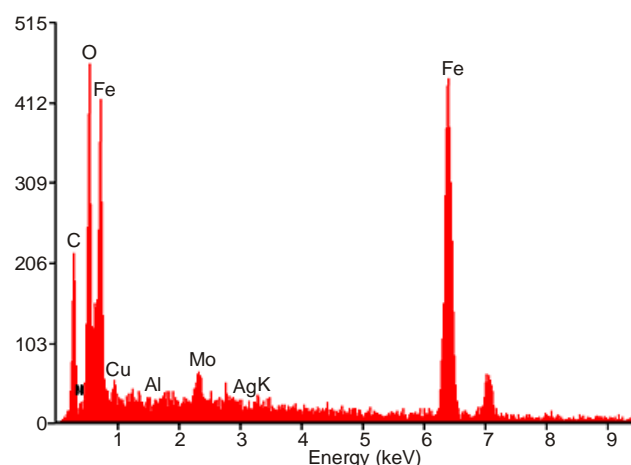
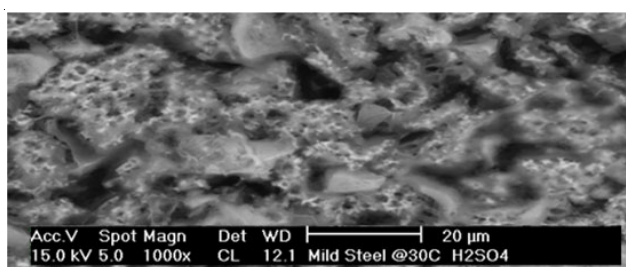


Fig. 7. SEM microstructure and EDS spectrum of mild steel immersed in 0.5 M H_2SO_4 at 30 °C without extracts (control)

mild steel immersed in acidic medium-plant extract indicates evident of a protective film and smooth surfaces. This shows that the extract inhibits corrosion of mild steel in acidic solution. This is in agreement with earlier work [14,21].

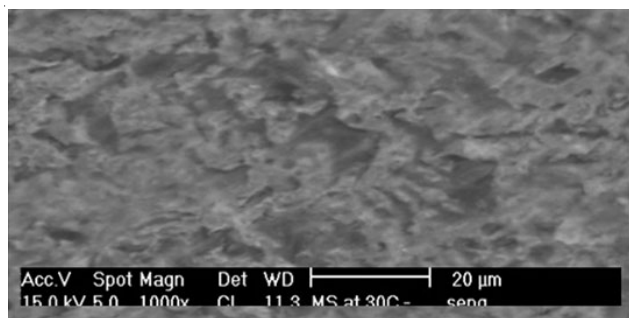


Fig. 8. SEM microstructure and EDS spectrum of mild steel immersed in 0.5 M H_2SO_4 at 30 °C in the presence of optimum extract of *Acacia senegalensis*

Synergism effect of halide ion: Synergism variables obtained are indications of synergistic effect existing between the inhibitor and the halide ions [7,24]. In the actual practical application of corrosion inhibitors, single compound is rarely used, rather formulations of two or more inhibitors are usually employed. Fig. 9 and Table-8 show the results of synergy between inhibitor and halide ion (KI). The synergy of the extracts show that their efficiencies decrease with increase in temperature from 30-70 °C. All the calculated synergy values are more than unity and that the enhanced inhibition efficiency caused by the addition of iodide ion to the extract is only due to synergistic effects. This agrees with the claims [2]. Previous report [25] indicated that the inhibitive effects of halide ions increase in the order of $\text{Cl}^- < \text{Br}^- < \text{I}^-$ and that the observed synergistic effect results from increased surface coverage arising from ion-pair interaction between I^- anion and the extracts present in the medium [25]. This agrees with the previous report [26].

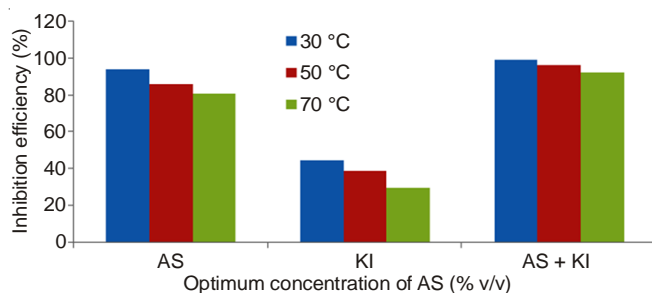


Fig. 9. Influence of halide additive (0.5 M) on the inhibition efficiency of optimum concentrations (6 % v/v) of *Acacia senegalensis* (AS) at different temperatures

TABLE-8
SYNERGISTIC PARAMETERS (S_p) FOR DIFFERENT
CONCENTRATIONS OF *Acacia senegalensis* EXTRACT
AT 30, 50 AND 70 °C IN 0.5 M H_2SO_4

Conc. of inhibitor (% v/v)	S_p		
	30 °C	50 °C	70 °C
2	1.53215	1.42356	1.39032
4	1.83457	1.82389	1.79654
6	1.97654	1.95483	1.93482
8	2.09456	2.00529	1.96432
10	2.26543	2.14567	2.07894

Mechanism of corrosion inhibition: In acidic solution, transition of the metal/solution interface is attributed to the adsorption of the inhibitor molecules at the metal/solution interface, forming a protective film. The rate of adsorption is usually rapid and hence, the reactive metal surface is shielded from the acid solutions [18]. The adsorption of any inhibitor depends on its chemical structure, its molecular size, the nature and charged surface of the metal and distribution of charge over the whole inhibitor molecule. In fact, adsorption process can occur through the replacement of solvent molecules from the metal surface by ions and molecules accumulated near the metal/solution interface [27]. Ions can be accumulated at the metal/solution interface in excess of those required to balance the charge on the metal at the operating potential. These ions replace solvent molecules from the metal surface and their centers reside at the inner Helmholtz plane. This phenomenon is termed as specific adsorption or contact adsorption. The anions are adsorbed when the metal surface has an excess positive charge in an amount greater than that required to balance the charge corresponding to the applied potential. The exact nature of the interactions between a metal surface and an aromatic molecule depends on the relative coordinating strength towards the given metal of the particular group present [1].

The polar nitrogen groups attached to a hydrocarbon chain donate electrons to the metal surface and form a physisorption bond. The strength of protection depends on this bond. The hydrocarbon portion of the inhibitor is oil soluble and it is water repellent. The large hydrocarbon chain orients towards the solution and forms a hydrophobic network (repels water from the metal surface). The water molecules are desorbed and replaced by organic molecules [$\text{Org (soln)} + n\text{H}_2\text{O (ads)} \rightarrow \text{Org (ads)} + n\text{H}_2\text{O (soln)}$]. Water molecules, which are the main source of corrosion, are thus eliminated.

Generally, two modes of adsorption were considered. In one mode, the neutral molecules of extract can be adsorbed on the surface of mild steel through the chemisorptions mechanism, involving the displacement of water molecules from the mild steel surface and the sharing of electrons between the heteroatoms and iron. The inhibitor molecules can also adsorb on the mild steel surface based on donor-acceptor interactions between π -electrons of the aromatic/heterocyclic ring and vacant d -orbital's of surface iron. In another mode, since it is well known that the steel surface bears positive charge in acidic solutions [14], so it is difficult for the protonated extract to approach the positively charged sample surface ($\text{H}_3\text{O}^+/\text{metal interface}$) due to the electrostatic repulsion. Since sulphide ions have a smaller degree of hydration, thus they could bring excess negative charges

in the vicinity of the interface and favours more adsorption of the positively charged inhibitor molecules. The protonated extract adsorbed through electrostatic interactions between the positively charged molecules and the negatively charged metal surface. Since all the different parts of extract possess several heteroatoms containing active constituents, there may be a synergism between the molecules accounting for the good inhibition efficiencies [13,14].

Conclusions

- Maximum inhibition efficiency for *Acacia senegalensis* extract was found to be 94.16 % at the optimum concentration of 6 % in v/v and 99.62 % in the presence of KI⁻ and occurred at 180 min of immersion time at 30 °C and was sufficient for pickling process. The high IE % was attributed to the presence of hydroxyl groups and aromatic compounds revealed by the GC-MS analysis of the extract.

- Potentiodynamic polarization studies revealed that the extracts act through mixed modes of inhibition and the adsorption of different concentrations of the extract on the surface of mild steel in 0.5 M H₂SO₄ acid and followed Langmuir adsorption isotherm.

- The value of activation energy E_a revealed that the adsorbed organic matter provided a physical barrier to charge and mass transfer leading to reduction in corrosion rate. The negative sign of free energy of adsorption indicates that the adsorption of the inhibitor on mild steel surface was a spontaneous process and was found to be physisorption. The positive value of enthalpy of adsorption (ΔH) suggests that the reaction was endothermic and the adsorption of the inhibitors on the metal surface takes place and positive value of entropy of adsorption (ΔS) indicates that the reaction was spontaneous and feasible.

- SEM morphology of the adsorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the extract.

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