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Green corrosion inhibitor: inhibitive action of aqueous extract of *Anacyclus pyrethrum* L. for the corrosion of mild steel in 0.5 M H_2SO_4

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Abstract

The efficacy of an aqueous extract of the leaves and stems of Anacyclus pyrethrum L (LS-AP) as corrosion inhibitor for mild steel in 0.5 M sulphuric acid medium was carried out using the electrochemical methods. Experiments are performed by concentration of the inhibitor, temperature, synergism effect and varying immersion period. The results showed variation in inhibition performance of the inhibitor with varying concentration, temperature, iodide concentration and immersion time. Langmuir model was tested to describe the adsorption behaviour of inhibitor on the mild steel surface for all temperatures. Some thermodynamic functions of dissolution and adsorption processes were also determined.

Keywords: alloys, corrosion test, electrochemical techniques, adsorption.

1. Introduction

Use of inhibitors is one of the most practical methods for protection against corrosion especially in acid solutions to prevent unexpected metal dissolution and acid consumption [1-3].
Different organic and inorganic compounds have been studied as inhibitors to protect metals from corrosion attack. Usually, organic compounds exert a significant influence on the extent of adsorption on the metal surface and therefore can be used as effective corrosion inhibitors. The efficiency of these organic corrosion inhibitors is related to the presence of polar functions with S, O or N atoms in the molecule, heterocyclic compounds and p electrons [4-7]. The polar function is usually regarded as the reaction center for the establishment of the adsorption process [8-10]. The known hazardous effects of most synthetic organic inhibitors and restrictive environmental regulations have now made researchers to focus on the need to develop cheap and environmentally benign natural products as corrosion inhibitors. These natural organic compounds are either synthesized or extracted from aromatic herbs, spices and medicinal plants. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost and are biodegradable in nature. The use of these natural

products such as extracted compounds from leaves or seeds as corrosion inhibitors have been widely reported by several authors [2, 11–19].

Anacyclus pyrethrum L. (Link) (Compositae, Asteraceae), commonly known as ‘‘African Pyrethrum” and referred to as ‘Tigenthast’, is a perennial, procumbent herb, which is native from the North of the Africa and is cultivated in the Mediterranean [20].

The plant grows to about 30 to 50 cm high and has tough double-pinnate leaves.The stems are numerous, procumbent and somewhat branched. The root which represents the medicinal part of the plant is almost cylindrical, long, thick, fibrous, rough, brown outside and white inside [21].

Anacyclus pyrethrum L. is being widely used in the local traditional medicinal treatment system to several diseases: it is used in the treatment of some rheumatic and neuralgic affection of the head, the tooth and face**.** A local ethnobotanical survey carried out showed its possible anti-diabetic activity [22].

Previous chemical studies indicate that the plant possesses immunomodulatory properties [23-24].

Everywhere in Algeria, the root is used as sternutatory, sialagogue and diaphoretic. It is regarded as a tonic to the nervous system. It is also used in respiratory infections and in the treatment of liver disease [20, 23]. In some other countries, the roots are also considered aphrodisiac and sexual stimulant. In Indian medicine, the plant is widely recognized as tonic and rejuvenator [25]. It has been reported that the *Anacyclus pyrethrum* root has antibacterial and anti-inflammatory activities and is known for its insecticidal properties [20].

This study aims to gain some insight into the corrosion of mild steel in 0.5 M H_2SO_4 in the presence of the aerial parts (Leaves and Stems) of *Anacyclus pyrethrum* L. (LS-AP) extract as a corrosion inhibitor. The inhibitor effect of this naturally occurring biological molecule on the corrosion of mild steel in 0.5M H_2SO_4 was investigated by potentiodynamic polarization and electrochemical impedance methods. Thermodynamic parameters such as adsorption heat, adsorption entropy and adsorption free energy can be obtained from experimental data of the studies of the inhibition process at different temperatures. The kinetic data such as apparent activation energy and pre-exponential factor at different inhibitor concentrations are calculated and discussed. The synergism effect of LS-AP extract and iodide anion and influence of immersion time were also studied.

2. Experimental

2. 1. Plant material

The aerial parts (Leaves and Stems) of *Anacyclus pyrethrum* L. were harvested from the mounts of Tlemcen (north-west of Algeria), in April 2009. The authenticity and the botanical identification of the species were confirmed, according to the ‘‘Nouvelle Flore de l’Algérie” [21] by Pr. Noury Benabadji, “Laboratoire d’Ecologie et Gestion des Ecosystèmes”, University of Tlemcen (Algeria). A voucher specimen was deposited in this laboratory.

2. 2. Preparation of the extract

Fresh leaves and stems were dried at room temperature. Aqueous extract was obtained as follows. In brief, 100 g of dried leaves and stems were extracted by refluxing with distilled water for one hour. Thereafter, it was decanted and filtered with filter paper and followed by centrifugation for 30 min at 5000 rpm. The supernatant was filtered to eliminate any residues. The filtrate was dried in the oven at 40 °C to make a powder yielding 3.6 % (w/w). The solid residue was stored in dessicator prior use for subsequent experiments.

2. 3. Phytochemical screening

Phytochemical screening was carried out on the aqueous extract freshly prepared according to the common phytochemical methods described by Harborne [26]. The different chemical constituents tested, included reducing sugars, gallic and catechol tannins, saponins, alkaloids, sterols and triterpenes, anthraquinones and flavonoids.

2. 4. Solution and material

A 0.5 M H_2SO_4 solution was prepared from an analytical reagent grade of H_2SO_4 98% and distilled water and was used as corrosion media in the studies.

For the electrochemical measurements, the experiments were carried out in solution of 0.5 M sulfuric acid (uninhibited and inhibited) on mild steel of composition (wt%) : C $\leq$ 0.1%, Si$\leq$ 0.03%, Mn$\leq$ 0.2%, P$\leq$ 0.02%, Cr$\leq$ 0.05%, Ni$\leq$ 0.05%, Al $\leq$0.03% and the remainder iron. Specimens in the form of disc were abraded successively with different grades of emery paper up 1200 grade.

2. 5. Electrochemical measurements

Electrochemical experiments were carried out in a glass cell (CEC/TH-Radiometer) with a capacity of 500 ml. A platinum electrode (1cm^2) and a saturated calomel electrode (SCE) were used as a counter electrode and a reference electrode, respectively. The working electrode (WE) was in the form of a disc cut from mild steel under investigation and was embedded in a Teflon rod with an exposed area of 0.5 cm^2.
Electrochemical impedance spectroscopy (EIS), potentiodynamic and linear polarization tests were conducted in an electrochemical measurement system (VoltaLab40) which comprises a PGZ301 potentiostat, a personal computer and VoltaMaster 4 and Zview software. The potentiodynamic current–potential curves were recorded by changing the electrode potential automatically from –750 to –300 mV with scanning rate of 0.5 mV s^{-1}. The polarization resistance measurements were performed by applying a controlled potential scan over a small range typically 20 mV with respect to E_{corr}. The resulting current is linearly plotted against potential, the slope of this plot at E_{corr} being the polarization resistance (Rp). All experiments were carried out in freshly prepared solution at constant temperatures, 25, 30, 35 and 40 ± 0.1 °C using a thermostat.
The ac impedance measurements were performed at corrosion potentials (E_{corr}) over a frequency range of 10 kHz – 100 mHz, with a signal amplitude perturbation of 10 mV. Nyquist plots were obtained.
From the measured polarization resistance value, the inhibition efficiency has been calculated using the relationship:

$$IE\ (\%) = (1 - R_{0p}/R_{ip}) \times 100 \qquad (1)$$

where R_{0p} and R_{ip} are the polarization resistance in absence and in presence of inhibitor, respectively.
The inhibition efficiency was evaluated from the measured I_{corr} values using the relationship:

$$IE\ (\%) = (1 - i_{icorr}/i_{0corr}) \times 100 \qquad (2)$$

where i_{0corr} and i_{icorr} are the corrosion current density in absence and in presence of inhibitor, respectively.
The inhibition efficiency of the inhibitor has been found out from the charge transfer resistance values using the following equation:

$$IE\ (\%) = (1 - R_{0t}/R_{it}) \times 100 \qquad (3)$$

where R_{0t} and R_{it} are the charge transfer resistance in absence and in presence of inhibitor, respectively.

2. 6. Scanning electron microscopy (SEM) analysis

The scanning electron microscope images of the samples were recorded using HITACHI TM 1000 analytical scanning electron microscope.

3. Results and discussion

3. 1. Phytochemical screening

The findings of the phytochemical screening of the aerial parts of plant's aqueous extract are shown in Table 1. The results of the phytochemical analysis showed that the aqueous extract contained flavonoids, sterols and triterpenes, catechol tannins, reducing sugars, saponins and alkaloids. The number of positive signs is proportional to the intensity of the reactions that reflects the available quantity. The assays for gallic tannins and anthraquinones gave negative results.

Table 1. Phytochemical screening of extract of the aerial parts (Leaves and Stems) of *Anacyclus pyrethrum* L

Chemical constituent	**Screening**
Reducing sugars	++
Gallic tannins	-
Catechol tannins	++
Saponins	+
Alkaloids	+
Sterols and triterpenes	+++
Anthraquinones	-
Flavonoids	+++

−, Negative test, +, slightly positive test; ++, positive test and +++, very positive test .

3. 2. Polarization measurements

Potentiodynamic anodic and cathodic polarization scans were carried out at 30±0.1 °C in 0.5 M H_2SO_4 with different concentrations of LS-AP extract.

Anodic and cathodic polarization curves in the absence and in the presence of inhibitor at different concentrations after 1 h of immersion are shown in Figure 1.

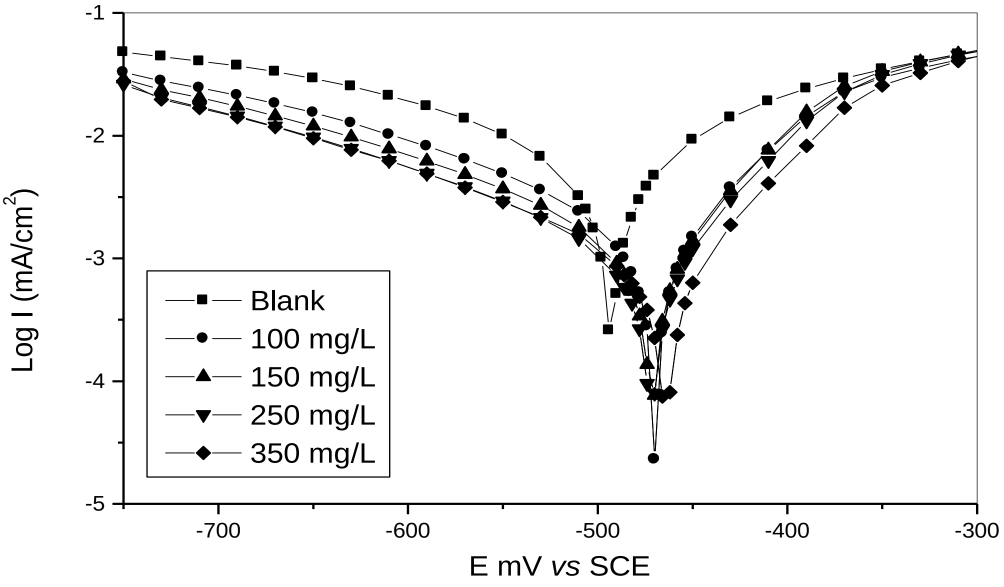


Figure 1. Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 containing different concentrations of LS-AP extract at 30 °C.

From this figure, it can be seen that with the increase of LS-AP extract concentrations, both anodic and cathodic currents were inhibited. This result shows that the addition of LS-AP extract inhibitor reduces anodic dissolution and also retards the hydrogen evolution reaction.

Table 2 gives the values of kinetic corrosion parameters as the corrosion potential E_{corr}, corrosion current density I_{corr}, Tafel slope b_c, R_p values and inhibition efficiency for the corrosion of mild steel in 0.5 M H_2SO_4 with different concentrations of LS-AP extract. The corrosion current densities were estimated by Tafel extrapolation of the cathodic curves to the open circuit corrosion potential.

From this table, it can be concluded that:

- The I_{corr} values decrease with increasing inhibitor concentration.
- The cathodic Tafel slopes were found to vary over a range of 285 - 222 mV dec^{-1}. Therefore, the cathodic slope value was found to change with increasing concentration of LS-AP extract in 0.5 M H_2SO_4. This result indicates the influence of the inhibitor on the kinetics of the hydrogen evolution reaction [8].
- The values of inhibition efficiency (P %) increase with inhibitor concentration reaching a maximum value (82%) at 350 mg /L.
- The LS-AP extract is a mixed inhibitor with small shift in anodic values.

Table 2. Electrochemical parameters and the corresponding corrosion inhibition efficiencies for the corrosion of mild steel in 0.5 M H_2SO_4 containing different concentrations of AP-LS extract at 30 °C.

Conc. (mg/L)	**E_{corr} (mV vs CSE)**	**I_{corr} (mA /cm^2)**	**R_p (Ω. Cm^2)**	**b_c (mV/dec)**	**P% (I_{corr})**	**P% (R_p)**
Blank	-494	8.22	6.35	285.00	---	---
100	-470	2.63	14.39	232.60	68.00	55.87
150	-470	2.04	19.54	234.70	75.20	67.50
250	-469	1.51	24.13	222.20	81.64	73.68
350	-469	1.48	26.60	229.30	82.00	76.13

3.3. Electrochemical impedance spectroscopy measurements

Nyquist plots of mild steel in 0.5 M H_2SO_4 in the presence and absence of different concentrations of LS-AP extract at 30°C and after 1 h of immersion are given in Figure 2. All the plots display a single capacitive loop [27]. Impedance parameters derived from the Nyquist plots and percent inhibition efficiencies are given in Table 3.

The circuit consists of a constant phase element (CPE) Q, in parallel with a resistor R_t The use of CPE-type impedance has been extensively described [28–30]:

$$Z_{CPE} = [Q(jw)^n]^{-1} \tag{4}$$

The above equation provides information about the degree of non-ideality in capacitance behavior. Its value makes it possible to differentiate between the behavior of an ideal capacitor (n = 1) and of a CPE (n < 1).

Considering that a CPE may be considered as a parallel combination of a pure capacitor and a resistor that is inversely proportional to the angular frequency,

the value of capacitance, C_{dl}, can thus be calculated for a parallel circuit composed of a CPE (Q) and a resistor (R_t), according to the following formula [31, 32]:

$$Q = (C_{dl}R_t)^n/R_t \tag{5}$$

The impedance spectra of mild steel in 0.5 M H_2SO_4 with and without inhibitor were analyzed by using the circuit in Figure 3, and the double layer capacitance (C_{dl}) was calculated in terms of Eq. 5. Values of elements of the circuit corresponding to different corrosion systems, including values of C_{dl}, are listed in Table 3.

As can be seen from Table 3, the increase in resistance in the presence of LS-AP extract compared to H_2SO_4 alone is related to the corrosion protection effect of the phytochemical constituents. The value of C_{dl} decreases in the presence of LS-AP extract, suggesting that the extract plant molecules function by adsorption at the metal solution/interface. It is important to point out that n reaches approximately the same value of 0.80. This result can be interpreted as an indication of the degree of heterogeneity of the metal surface, corresponding to a small depression of the double layer capacitance semicircle [9]. The values of inhibition efficiency increase with inhibitor concentration at a maximum value (87%) at 350 mg /L.

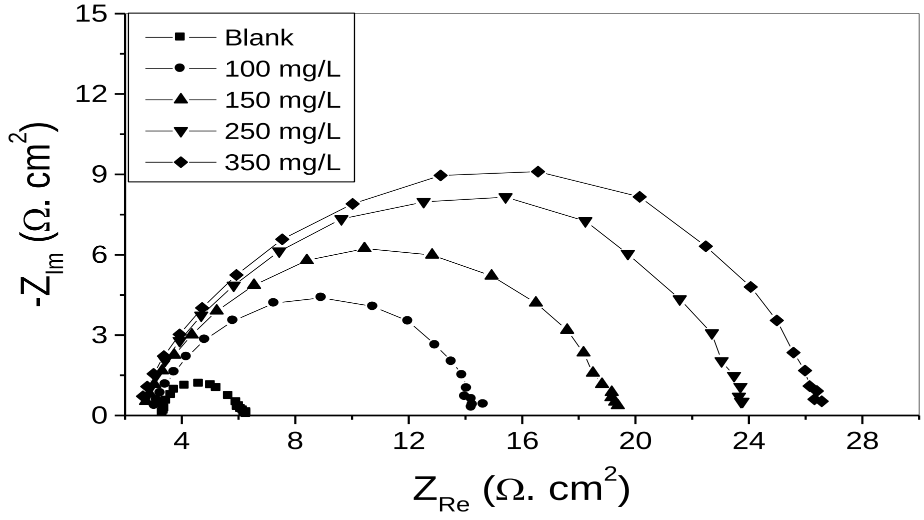


Figure 2. Complex plane plots for mild steel in 0.5 M H_2SO_4 solution in the absence and in the presence of different concentrations of LS-AP extract at 30°C.

Table 3 . Impedance parameters and inhibition efficiency for the corrosion of mild steel in 0.5 M H_2SO_4 containing different concentrations of AP-LS extract at 30°C

Conc. (mg/ L)	Q ($s^n\Omega^{-1}.cm^{-2}$)	n	R_t ($\Omega.cm^2$)	C_{dl} (μ F cm^{-2})	P (%)
Blank	0.00100	0.81	3.13	259	-----
100	0.00030	0.81	11.69	80	73.22
150	0.00028	0.78	17.08	62	81.67
250	0.00021	0.79	21.65	50	85.54
350	0.00021	0.78	24.11	47.28	87.01

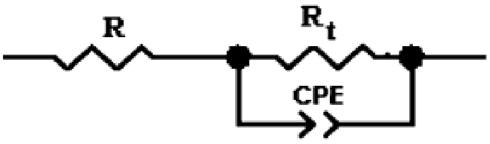


Figure 3. The equivalent circuit of the impedance spectra obtained for LS-AP extract.

3.4. Effect of temperature

To investigate the mechanism of inhibition and to calculate the activation energies of the corrosion process, polarization measurements were taken at various temperatures in the absence and the presence of different concentrations of LS-AP extract. Corresponding data are given in Table 4. In the studied temperature range (25 - 40 °C) the corrosion current density increases with increasing temperature both in uninhibited and inhibited solutions and the values of the inhibition efficiency of LS-AP extract increases with the temperature. The corrosion current density of steel increases more rapidly with temperature in the absence of the inhibitor, these results confirm that LS-AP extract acts as an efficient inhibitor in the range of temperature studied.

The activation parameters for the corrosion process were calculated from Arrhenius type plot according to the following equation [3]:

$$\log \mathrm{I} = -\frac{\mathrm{E_a}}{2.303\,RT} + \log A \qquad (6)$$

and from transition state plot according to the following equation[3]:

$$\log \frac{\mathrm{I}}{\mathrm{T}} = -\frac{\Delta \mathrm{H}_a^0}{2.303\ \mathrm{R\,T}} + \mathrm{B} \qquad (7)$$

where E_a is the apparent activation energy, A the pre-exponential factor, R the universal gas constant, ΔH_a the enthalpy of activation and T the absolute temperature.
The variations of logarithm of the corrosion rate of mild steel (log I) in sulphuric acid containing various concentrations of LS-AP extract used and log (I/T) with reciprocal of the absolute temperature are presented in Figs. 4 and 5, respectively. Straight lines with coefficients of correlation (c. c) of 0.99 are obtained.

The E_A and ΔH_a values were determined from the slopes of these plots. The calculated values of E_a and ΔH_a in the absence and the presence of different concentrations of LS-AP extract are given in Table 5. Inspection of these data reveal that the apparent activation energy E_a and pre-exponential factor (A) in 0.5 M H_2SO_4 in absence of LS-AP extract was 48.63 kJ/mol and $1.84\text{x}10^{10}$ mA.cm^2, respectively. The addition of LS-AP extract to the acid solution decreases the activation energy and exponential factor (A) and the extent of the decrease is very pronounced at 350 mg/L. Note that the reduction of the activation energy in the presence of LS-AP extract may be attributed to the chemisorption of the LS-AP extract inhibitor on mild steel surface [33, 34].

Table 4. Effect of temperature on the inhibition efficiency and electrochemical parameters of the mild steel in 0.5 M H_2SO_4 with and without LS-AP extract at different concentrations

Conc. (mg/L)	Temp. (°C)	E_{corr} *vs*SCE/ mV	I_{corr} (µA cm^{-2})	P (%)
Blank	25	-497	5.01	----
	30	-494	8.22	----
	35	-490	10.92	----
	40	-490	13.49	----
100	25	-469	1.65	67.07
	30	-470	2.63	68.00
	35	-474	3.02	72.34
	40	-470	3.80	71.83
150	25	-470	1.55	69.06
	30	-470	2.04	75.20
	35	-474	2.45	77.56
	40	-470	2.69	80.06
250	25	-474	1.15	77.05
	30	-469	1.51	81.64
	35	-474	1.82	83.33
	40	-470	2.04	84.88
350	25	-474	1.10	78.08
	30	-469	1.48	82.00
	35	-474	1.63	85.07
	40	-486	1.77	86.88

The lower Ea value obtained in the presence of LS-AP extract when compared to that in its absence indicates chemisorption of the corrosion inhibitor [19]. According to Radovici, cited by Popova et al. [35], lower Ea values in solutions containing inhibitor indicate a specific type of adsorption of the inhibitors, while Szauer and Brandt [36] associate this behavior with the chemisorption of the inhibitor to the metal surface and Machu, cited in reference [19, 35], to the action of powerful corrosion inhibitors.

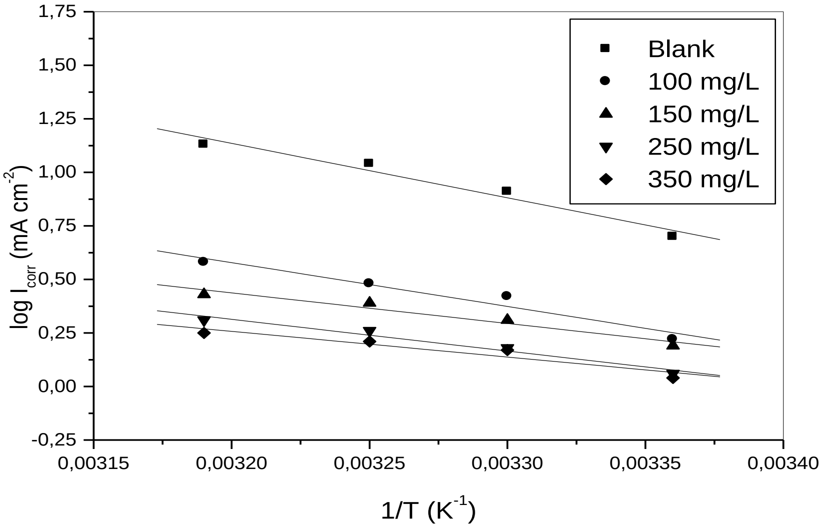


Figure 4. log I_{corr} *vs* T for mild steel dissolution in in 0.5 M H_2SO_4 in the absence and the presence of different concentrations of LS-AP extract.

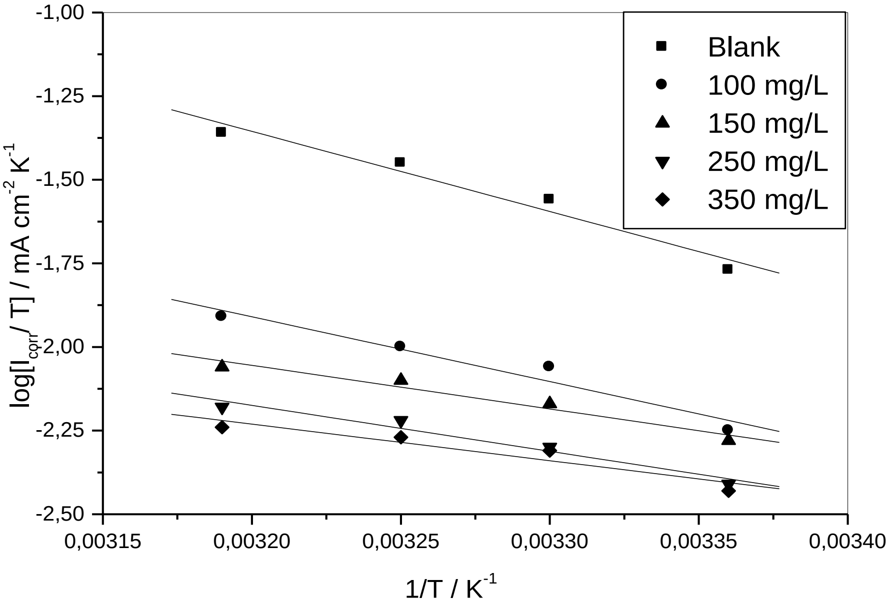


Figure 5. log I_{corr} *vs* 1/T for mild steel dissolution in in 0.5 M H_2SO_4 in the absence and the presence of different concentrations of LS-AP extract.

Taking into consideration these references and the E_a value calculated from Arrhenius plots, the action of LS-AP extract as a corrosion inhibitor for mild steel in acid solution can be attributed to a strong adsorption bond which is of a chemiosorptive nature, involving charge sharing or charge transfer from the molecules of LS-AP extract to the mild steel surface to form a coordinate-type bond.

Table 5. The apparent activation energy E_a and the activation enthalpy $\Delta H°_a$ of dissolution of mild steel in 0.5 M H_2SO_4 in the absence and presence of different concentrations of LS-AP extract.

Conc. (mg/L)	E_a (kJ.mol^{-1})	Pre-exponential Factor (A) (mA.cm^2)	$\Delta H°_a$ (kJ mol^{-1})	$\Delta H°_a$ (kJ mol^{-1}) (from equation (8))
Blank	48.63	$1.84x10^{10}$	45.85	46.11
100	39.14	$1.30x10^{7}$	37.07	36.62
150	27.32	$1.00x10^{5}$	24.94	24.80
250	28.33	$1.12x10^{5}$	26.27	25.81
350	22.98	$1.25x10^{4}$	20.91	20.46

Moreover one remark that the ΔH_a values obtained from the slopes of plots log (I_{corr}/ T) *vs* f (1/T) and those determined from the equation (8) are in good agreement:

$$\Delta H_a = E_a - RT \quad (8)$$

3.5. Adsorption

Basic information on the interaction between the inhibitor and the mild steel can be provided by the adsorption isotherm. The adsorption of the organic compounds can be described by two main types of interaction: physical adsorption and chemisorption. These are influenced by the chemical structure of the inhibitor, the type of the electrolyte and the charge and nature of the metal. The surface coverage θ of the metal surface by the adsorbed inhibitor was calculated [30] assuming no change in mechanism of the cathodic reaction using the equation:

$$\theta = (I_{0corr} - I_{icorr})/I_{0corr} \quad (9)$$

where I_{0corr} and I_{icorr} are the currents densities in the presence and absence of the inhibitor.

The θ values for different inhibitor concentrations at different temperatures were tested by fitting to various isotherms. By far the best fit was obtained with the Langmiur isotherm. According to this isotherm θ is related to concentration inhibitor C via

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (10)$$

where K is the adsorptive equilibrium constant.

The obtained values of adsorption constant, slope and regression factors are given in Table 6.

Table 6. Thermodynamic parameters for of mild steel in 0.5 M H_2SO_4 in the absence and presence of different concentrations of LS-AP extract.

T (K)	**K (L/mg)**	**slope**	**R**
298	2.92×10^4	1.17	0.999
303	3.05×10^4	1.11	0.999
308	3.45×10^4	1.08	0.999
313	3.30×10^4	1.06	0.999

3. 6. Synergistic consideration

Halides ions have been widely reported to synergistically increase the inhibition of the corrosion of metals in acidic medium by organic compounds [4, 37-42]. The enhanced corrosion inhibition on addition of the halides was attributed to promotion of the adsorption of the organic molecules on the metal surface. The effect of KI on the inhibition efficiency of LS-AP extract was investigated in the present work at 30°C. Figure 6 shows the plot of different values of R_t for all concentration of LS-AP extract in the absence and presence of 0.2% KI at 30°C after one hour of immersion.

Similarly, Figure 7 shows the plot of R_t values vs. KI concentration added to a fixed extracts' concentration (350 mg/L) for LS-AP extract at 30°C after one hour of immersion.

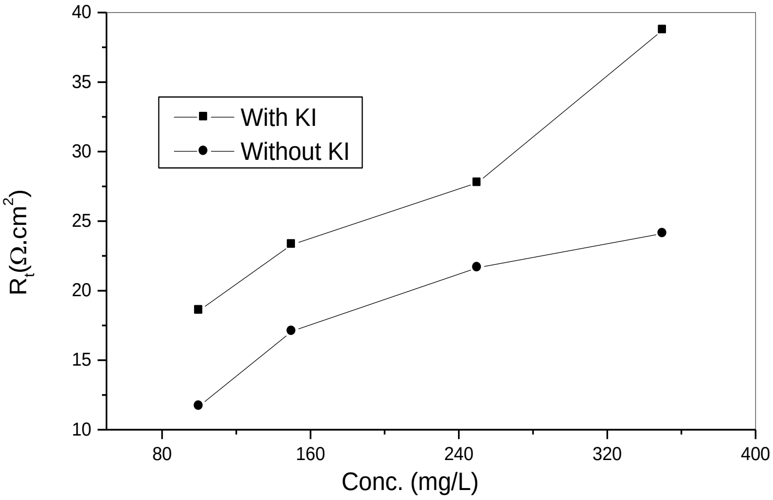


Figure 6. R_t values in the absence and presence of 0.2% KI for different concentrations of LS-AP extract.

Figs. 6 and 7 clearly reveals the existence of synergism phenomenon between iodide ions and the LS-AP extract considering that R_t was increased on addition of the iodide ions to the extracts in comparison to the extract alone.

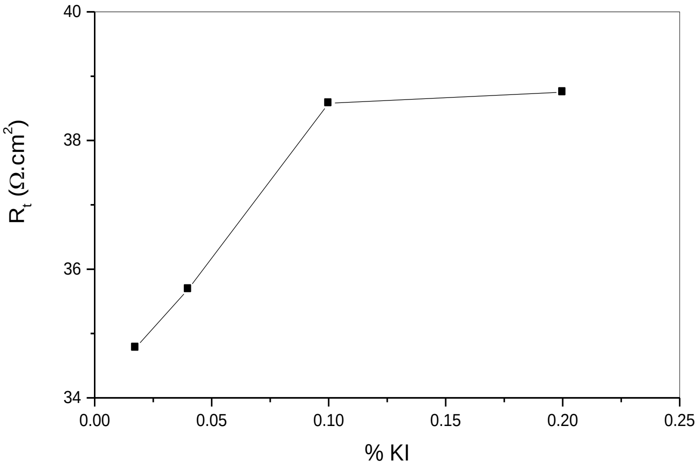


Figure 7. The plot of Rt values vs. % KI for LS-AP extract at 350 mg/L.

To further confirm whether synergism is taking place, one has to determine the synergism parameter (s), the synergism parameters were calculated using the relationship proposed by Aramaki and Hackerman [43]:

$$S = \frac{1 - P_{1+2}}{1 - P'_{1+2}} \tag{11}$$

where $P_{1+2} = (P_1+P_2) - (P_1 \times P_2)$; P_1 is the inhibition efficiency (no exprimed in percent) of substance 1 (LS-AP extract), P_2 is the inhibition efficiency of substance 2 (KI), P'_{1+2} is the measured inhibition efficiency for substance 2 in combination with substance 1. Here, P that is equal to % P/100 is determined from impedance measurements. S approaches 1 when no interaction between the inhibitor compounds exists, while S > 1 points to a synergistic effect. In the case of S < 1, the adsorption of each compound antagonizes the others adsorption. Values of S are given in Table 7. It can be seen from this table that most of values are greater than unity. This result suggests that the improvement of inhibition efficiency generated by the addition of KI to LS-AP extract is generally due to a synergistic effect, exceptionally for 250 mg /L.

Table 7. Values of synergisms parameter (S) for different concentrations of LS-AP extract

Conc. (mg/ L)	S
100	1.21
150	1.04
250	0.97
350	1.22

2. 7. Immersion time

The impedance spectra of mild steel in 0.5 M H_2SO_4 with and without 350 mg/L of LS-AP extract are shown in Figs 8a and 8b. The Nyquist plots were recorded after different immersion periods and each spectrum is characterized by a single full semi–circle.

The calculated values of R_t and C_{dl} for mild steel immersed in the inhibited H_2SO_4 solution at different exposure times are shown in Table 8.

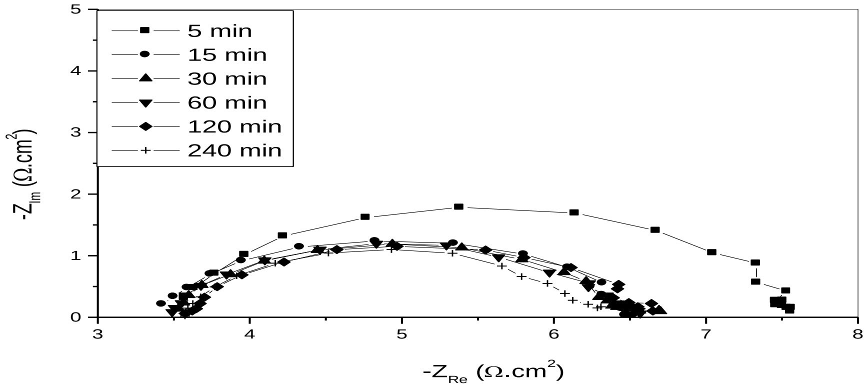


Figure 8a. Effect of immersion time on Nyquist plots of mild steel in 0.5M H_2SO_4 in absence of LS-AP extract.

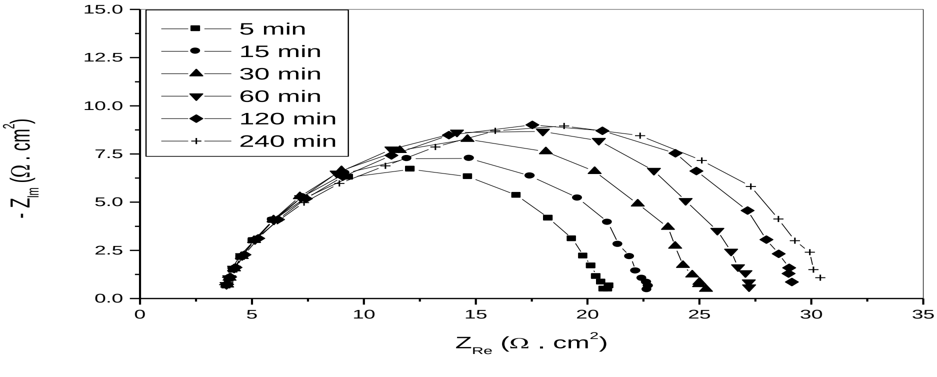


Figure 8b. Effect of immersion time on Nyquist plots of mild steel in 0.5M H_2SO_4 in presence of 350mg/L of LS-AP extract.

Table 8 . Effect of immersion time on R_t, C_{dl} and inhibition efficiency for mild steel in 0.5M H_2SO_4 with and without 350mg/L of AP-LS extract

Immersion time (min)		R_t(ohm cm^2)	C_{dl} (µF cm^{-2})	P (%)
5	Blank	4.11	63.11	---
	350mg/L	17.36	35.46	76.32
15	Blank	3.09	89.81	-----
	350mg/L	19.24	37.94	83.94
30	Blank	2.97	164.20	-----
	350mg/L	21.84	40.93	86.40
60	Blank	3.13	259	----
	350mg/L	24.11	47.28	87.01
120	Blank	3.10	373.93	-----
	350mg/L	26.45	52.38	88.23
240	Blank	2.74	594.27	-----
	350mg/L	28.74	24.68	90.46

As can be seen from Table 8, we notice that as when the immersion time increases the difference between the double-layer capacity of mild steel immersed in acid alone and those in the presence of 350 mg/L of LS-AP extract increases, this phenomenon is attributed to the film formed by the protective molecule inhibitors is thicker when the immersion time increases. In addition, we note that the inhibition efficiency increases from 76% to 91% after 4 hours of immersion.

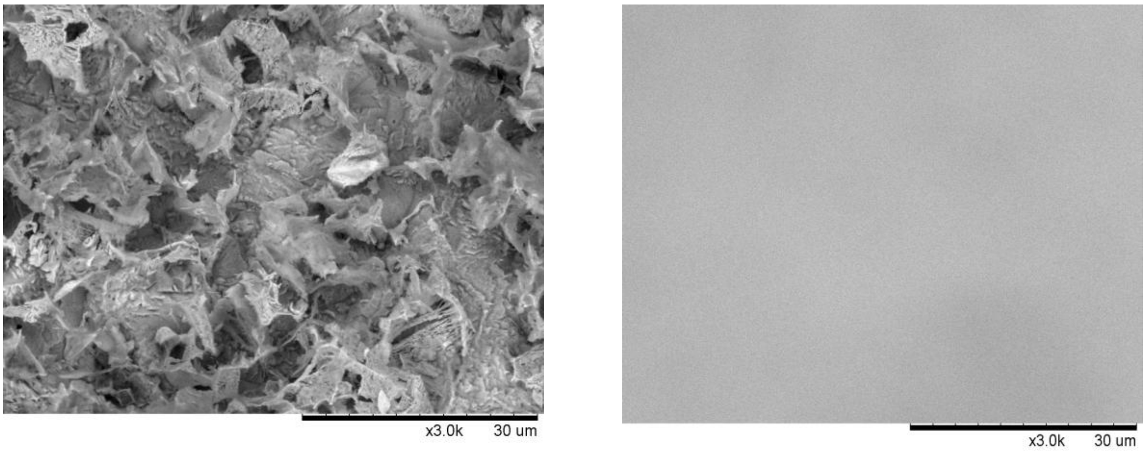
As the thickness (d) of the protective film can be related to the film's capacitance (C) by the expression [8]:

$$d = \frac{\varepsilon_0 \varepsilon_r A}{C_{dl}} \tag{12}$$

where ε_0 , vacuum permeability; ε_r , dielectric constant of the film ; A , area of electrode , it can be assumed that film thickness increases with decrease in C_{dl} .

2. 8. Scanning Electron Microscopy

In order to evaluate the surface morphology of the composite surface in contact with sulphuric solution, a superficial analysis was carried out.



(a) (b)

Figure 10. SEM image of the surface of mild steel after immersion for 6 h in 0.5 M H_2SO_4 solution at 30 ^oC (a) in the absence of inhibitor (b) in the presence of 350 mg/L of LS-AP extract

The SEM micrograph of the corroded specimen after 6 hour of immersion in 0.5 M H_2SO_4 solution is shown in Fig 9(a).The faceting seen in the figure is due to the attack of aggressive solution on the composite sample, causing more or less uniform corrosion. Fig 9(b) depicts the SEM of the specimen after 6 hour of immersion in 0.5 M H_2SO_4 solution in the presence of 350 ppm of LS-AP extract. It can be seen that the flakes on the surface of the specimen are reduced when compared with the micrograph given in Fig 9(a). The specimen surface can be observed to be covered with a thin layer of the inhibitor molecules, giving protection against corrosion.

Conclusion

The results obtained show that LS-AP extract is a good corrosion inhibitor for mild steel under acidic conditions. The maximum inhibition efficiency was 87%. Good agreement between the inhibition efficiencies calculated using different techniques was obtained. The adsorption of the organic inhibitor onto the mild steel surface was characterized by the decrease in (i) the cathodic and anodic current densities observed in the potentiodynamic polarization curves carried out in the presence of LS-AP extract, (ii) the polarization resistance in the solutions containing the inhibitor, (iii) the double-layer capacitance computed from electrochemical impedance spectroscopy experiments. Also, the components of the inhibitor acts by blocking the cathodic and anodic surface sites and by modifying activation energy of the both cathodic and anodic reaction. The chemisorption aspect of the adsorption process was well-established by the values of ΔG^0_{ads} calculated from the slope of the Langmuir isotherm at different temperatures, which best fitted the experimental data of the relationship between LS-AP extract concentration and surface coverage. The lower activation energy of the corrosion process in the presence of the corrosion inhibitor, when compared to that in its absence, also demonstrated the chemisorptive nature of the adsorption. The synergism parameter (S) evaluated for 0.2% KI was found to be greater than unity showing that the enhanced inhibition efficiency of LS-AP extract on the addition of iodide ions was due to synergistic effect. The values of the inhibition efficiency increased with the immersion time and leads to the formation of a protective film which grows with increasing exposure time.

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