

## Electrochemical study on the Effectively of Cyperus Articulates extract as a green Inhibitor for Corrosion of C Steel in 0.5MH<sub>2</sub>SO<sub>4</sub>

A.S.Fouda, H. Gado, W.Aboelmaaty and M.Omar

Department of Chemistry, University of El-Mansoura, Faculty of Science, 35516, Egypt.

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### ABSTRACT

Cyperus Articulates extract (CA), was investigated as a green corrosion inhibitor for C steel in 0.5 MH<sub>2</sub>SO<sub>4</sub> solution using mass loss, electrochemical frequency modulation (EFM), potentiodynamic polarization, and (EIS)electrochemical impedance spectroscopy techniques. The temperature effect on corrosion behavior with addition of various concentrations was done in the temperature range of 25-45 °C by weight loss. Polarization diagram given that the investigated extract is a cathodic behavior. The inhibition efficiency was found to rise with increase in the investigated extract concentration and lower with increase in solution temperature. Adsorption of inhibitor on metal surface found obeyed the adsorption isotherm Langmuir's. The activation and adsorption parameters were measured and illustrated. The data from electrochemical and chemical methods are a good agreement.

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### Introduction

Corrosion is a main process that plays an vital role in safety' and economics respect for metals. The utilized of inhibitors is the best labor expermental for protection versus corrosion, especially in acidic solution[1]. The most acid inhibitors are organic compounds with N, O, and Satoms. The advantages of organic inhibitors are easy production, and high inhibition efficiency [2-5]. Heterocyclic organic compounds have been utilized for the inhibition of C steel corrosion [6-9], aluminum [10], iron[11-13]and other metals[14-15]in various with media. Although many of organic have high inhibition efficiencies, several have undesirable side effects, even in very small concentrations, due to high-cost,their toxicity to humans, and deleterious environmental effects [16].

Plant extract is environmental safe and low-cost, so the advantages of utilized plant extracts as corrosion inhibitor are safe environment and economic. many plant extracts have been utilized as effective corrosion inhibitors for C steel in acid, such as: Azadirachta Indica[17], Zenthoxylumalatum[18], Cannabis[19]caffeine[20]. "The inhibition performance of plant extract is normally ascribed to the found of complex organic types, containing nitrogen ,tannins, and alkaloids bases, proteins and carbohydrates as well as hydrolysis results in their composition, these organic compounds usually contain polar functions with nitrogen, sulfur, or oxygen atoms and have triple or conjugated double bonds with aromatic rings in their molecular structures, which are the major adsorption centers".Cyperus articulates is a species of sedge known by the common names jointed flats edge and priproica. It is widespread across tropical and subtropical regions in Africa, southern Asia, northern Australia, the southeastern United States, the West Indies, and Latin America.<sup>[21]</sup>It is used by the cosmetic industry, and increasingly as a flavoring for food.[22]

The present study was done to given the inhibitory action of Cyperus Articulates for C steel corrosion in 0.5 MH<sub>2</sub>SO<sub>4</sub>utilizedmass loss electrochemical impedance spectroscopy (EIS), electrochemical frequency modulation (EFM) and potentiodynamic polarization measurements technique, and morphology of surface was measured utilized scanning electron microscope (SEM).

### Materials and Methods

#### Specimen preparation

Experiments were performed using C steel specimens (99.98%) were mounted in Teflon. The chemical composition of the material (weight %) is as follows; Carbon (0.17-0.20), Manganese(0.35),Phosphorus(0.025),Silicon(0.003)andFerest. Thesamples were firs tmechanically cut and prepared into seven coupons each of dimensions, 20 x20x1 mm.

#### Solution preparation

The test solution was 0.5M96% H<sub>2</sub>SO<sub>4</sub>. The sulfuric acid was purchased from Al-GomhoriaCo.forchemicals, in Egypt.Avolumeof100ml ofHCl solutionswas utilized as test solution and prepared for each experiment. In the present work, Analar grade reagents and bi-distilled water were used for the acid solution preparing. The solution stock (500 ppm) of CA was utilized to prepare the wanted concentrations by bidistilled water dilution. The range of concentration for CA extract utilized was 25-150 ppm.

#### Plant extracts preparation

Fresh aerial parts of CA sample were air-dried crushed down to small pieces to produce fine powder. The powdered samples (225 g) were mixedwith150 ml of dichloromethane for four days and then given extraction with 5× 25 ml until yield of plant samples. The extracts given were then concentrated under decrease pressure utilized rotary evaporator at temperature down25°C. The evaporated of

solvent yield solid extract was done for application as corrosion inhibitor.

Chemical studies have demonstrated that the CA contains many alkaloids as Hyoscyne, Atropine and Hyoscyanine as the major compounds [23].

#### Mass loss measurements

The surface of carbon steel specimens were handy paper dusting different series of sand paper starting with coarser type 80 to finer one 1200, remove with acetone, washed with bi-distilled water and gently dried using filter papers. The procedure of the experiment was as follows; first, the mass of specimens was measured precisely to 0.0001 digits by using a high sensitive electronic balance, and then the specimens were immersed into a solution of a volume 100 ml of 0.5 M H<sub>2</sub>SO<sub>4</sub> in the without and with various concentrations of CA sample at 25°C. For weight reduction experiment, the immersion time intervals were (30 min until 180 min). After each interval time, the tested specimens were obtaining of the solution, rinsed with bi-distilled water, thoroughly dried and the mass after immersion is precisely reweighed and recorded. All the aggressive acid solutions were open to air. After 180 minutes, the specimens were taken out, washed, dried, The corrosion rate (CR) in mg cm<sup>-2</sup> min<sup>-1</sup> was calculated from the value of mass loss divided by the total surface area (cm<sup>2</sup>) and immersion time (min). The degree of surface coverage  $\theta$  and The inhibition efficiency (IE%) of CA for the corrosion of C steel were calculated as follows [24],

$$IE \% = \theta \times 50 = \left[ 1 - \frac{W}{W^0} \right] \times 50 \quad (1)$$

where W<sup>0</sup> and W are the data of the mean mass loss with and without appending of the inhibitor, respectively.

#### Electrochemical Techniques

Three different electrochemical techniques were conducted using three electrode system arranged in a glass cell as follows; carbon steel specimen as working electrode (1cm<sup>2</sup>), saturated calomel electrode (SCE) acts a reference electrode, and platinum wire serves as an auxiliary electrode. In the present work, the working electrode was made of square specimen of carbon steel welded with copper rod from one side and totally encapsulated into a glass rod, of larger diameter (5 mm) so that only one face of the carbon steel specimen, of dimension (1cm × 1cm), was left to be exposed to the test solution. The electrode reference was related to a Luggin capillary and the tip of the capillary is set to be very near to the surface of the electrode working in order to partially eliminate error originated from IR drop. All the measurements were performed under stagnant conditions. Before starting electrochemical experiments, the working electrode was prepared in the same manner of sample preparation for mass loss method and the electrode potential was stabilized for 20 min. All results from electrochemical were utilized by Gamry Instrument (PCI4/750) with a Gamry system depend on the ESA400 and computerized frameworks contain DC105 software for potentiodynamic polarization measurements, EIS300 software for electrochemical impedance (ac) spectroscopy, and EFM140 software for electrochemical frequency modulation techniques. In addition, Echem Analyst 6.03 software was used for data fitting, graphing and plotting.

#### Potentiodynamic Polarization

Tafel curves obtained from potential polarization scan by automatically sweeping the working electrode potential from (-0.7 to 0.7 V vs. SCE) [25], utilized for calculated The current

corrosion by extrapolation of cathodic and anodic Tafel solp ( $\beta_a$  and  $\beta_c$ ) to gives  $\log i_{corr}$  and potential of corrosion (E<sub>corr</sub>) for acid free with each concentration of the investigated plant extract. The inhibition efficiency (%IE) and surface coverage ( $\theta$ ) were calculated using the obtained values of  $i_{corr}$ . Then ( $i_{corr}$ ) was utilized for measured of (IE %) and ( $\theta$ ) as in equation 2:

$$IE \% = \theta \times 50 = \left[ 1 - \frac{i_{corr(inh)}}{i_{corr(free)}} \right] \times 50 \quad (2)$$

Where

$i_{corr(free)}$  = corrosion current densities without inhibitor,

$i_{corr(inh)}$  = corrosion current densities with of inhibitor.

#### Electrochemical impedance spectroscopy (EIS)

At open circuit potential, alternative current signals, in range of frequency from 100 kHz to 0.5 Hz, were applied to measure the impedance of the corrosion process. An equivalent electrical circuit was tested to analyze and explain the impedance. The coverage surface ( $\theta$ ) and inhibition efficiencies given from the impedance results are measured from equation 3:

$$IE \% = \theta \times 50 = \left[ 1 - \left( \frac{R_{ct}^0}{R_{ct}} \right) \right] \times 50 \quad (3)$$

Where

$R_{ct}^0$  = the charge transfer resistance without inhibitors.

$R_{ct}$  = charge transfer resistance with inhibitor.

#### Electrochemical frequency modulation (EFM)

Two different frequencies 2 : 5 Hz with frequency base equals to 0.1 Hz were applied to obtain the intermodulation spectra of the electrochemical frequency modulation. It is necessary for the value of lower frequency to be not greater than a half of the higher frequency. The current responses, obtained from EFM spectra, assigned for intermodulation and harmonically current peaks. The biggest peaks were utilizes to measure the Tafel slopes ( $\beta_a$  and  $\beta_c$ ), the current density for corrosion ( $i_{corr}$ ), and the causality factors CF-2&CF-3 [26].

### Results and Discussion

#### Mass reduction measurements

Mass loss in mg per cm<sup>2</sup> was determined in laboratory after equal time interval of immersion into attest solution of 0.5 M H<sub>2</sub>SO<sub>4</sub> without and with treatment of various concentrations of the investigated additive. As shown in Figure (1), curves for additive-containing systems fall below of the free acid. This suggests that the weight loss of carbon steel is a function of both the type and the concentration of the additive. The surface coverage, likewise, the inhibition efficiency increases when the additive bulk concentration rises as indicated by the drop of current in weight loss per cm<sup>2</sup> and lower with temperature raising from 25-45°C.

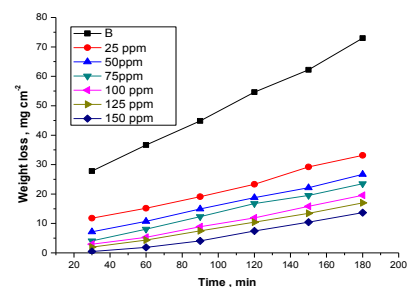


Figure 1. Plots of mass loss vs. immersion time for carbon steel corrosion in 0.5 M H<sub>2</sub>SO<sub>4</sub> without and with the treatment of CA at 25°C

Table(1, 2) list the( $\theta$ ) and the (%IE) taken from mass reduction calculation by equation (1).

**Table 1. The effect of different concentration of CA extract on the corrosion rate (CR) ( $\text{mg cm}^{-2}\text{min}^{-1}$ ) and inhibition efficiency (%IE) of carbon steelin 0.5 M  $\text{H}_2\text{SO}_4$  solutionat 25°C.**

Conc., ppm	Weight loss, $\text{mg/cm}^2$	C.R., $\text{mg cm}^{-2} \text{min}^{-1}$	$\theta$	%IE
0.5 MH <sub>2</sub> SO <sub>4</sub>	54.65	0.4554	--	
25	23.29	0.194	0.574	57.4
50	18.792	0.1566	0.656	65.6
75	16.75	0.1395	0.693	69.3
75	11.88	0.099	0.783	78.3
125	10.44	0.087	0.808	80.8
150	7.44	0.062	0.863	86.3

The inhibition action observed of the CA extract could be ascribed to the adsorption of its CA on metal. The layer formed from the adsorbed molecules isolates the surface of metal from the acidic solution which limits the dissolution of the latter by blocking of the sites of corrosion and hence lowering the rate of corrosion with higher efficiency as their rise of CA concentrations [27].

#### Polarization curves

Figure 2 shows potentiodynamic polarization diagrams recorded for C steel in 0.5 M  $\text{H}_2\text{SO}_4$  solutions with and without various CA concentrations at 25°C.

Nobe and Lee [28] gave the occurrence of a current peak between limiting-current regions and the apparent-Tafel during potential sweep experiments.

The kinetics of anodic and cathodic reactions was studied by polarization measurements. Figure (2) indicates the effect of addition of CA on anodic and cathodic polarization curves of carbon steel in 0.5 M  $\text{H}_2\text{SO}_4$ . Both cathodic and anodic reactions were noted to subsidize when the plant extract is added to the test solution, in turn of confirms that this additive reduced the metal dissolution, also suppressed the evolution of hydrogen reaction. The parallel cathodic Tafel diagrams in Figure (2) given that the evolution of hydrogen is activation-controlled and the reduction mechanism is not affected by the presence of the plant extract inhibitor [23,30]. The data of  $\beta_a$  and  $\beta_c$  changed slightly with rise inhibitor concentration indicated the effect of this extract on the kinetics of metal dissolution and of hydrogen evolution. In addition, the results recorded in Table(3) show that the addition of the investigated extract lowers both cathodic and anodic currents without any significant change in corrosion potential. The Tafel polarization results were consistent with those of weight loss method.

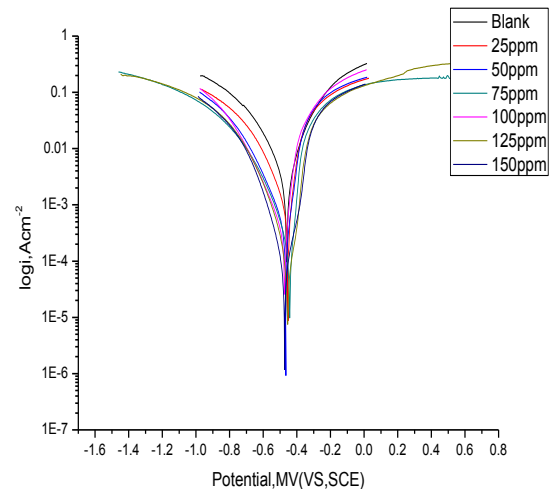
#### Electrochemical impedance spectroscopy (EIS)

Figure (3) shows impedance curves for metal in 0.5 M  $\text{H}_2\text{SO}_4$  solution without and with various concentrations of CA.

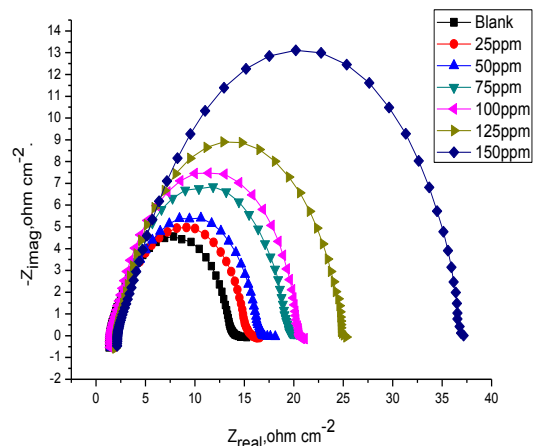
It is found that the obtained Nyquist plots are not perfect semicircle due to frequency dispersion and this behavior can be attributed to roughness and in homogeneities of the electrode surface [31, 32].

When there is non-ideal frequency response, it is common practice to use distributed circuit elements in an equivalent circuit. The most widely employed is the constant phase element (CPE). In general a CPE is used in a model in place of a capacitor to compensate for in homogeneities in the system [33]. It was obtain that the semicircle diameters rise with

higher the extract concentration. This given that the polarization resistance of the oxide layer rise with rise the CA concentration and the lower capacitive semicircle are often given to the surface roughness and inhomogeneities[34]. The value yield that, each impedance curve contain of a higher capacitive loop with lower dispersion frequencies (inductive arc) [35-37].



**Figure 2. Potentiodynamic polarization diagrams for the dissolution of carbon steelin 0.5 M  $\text{H}_2\text{SO}_4$  without and with concentrations of CA extract at 25°C.**



**Figure 3. Nyquist diagram for metal in 0.5 M  $\text{H}_2\text{SO}_4$  solutions without and with of various concentrations of CA at 25°C.**

The equivalent electrical circuit model given in Figure (4) was utilized to analyze the result impedance data. The model contains of (CPE) the constant phase angle element, ( $R_s$ ) the resistance of solution and ( $R_{ct}$ ) the resistance charge-transfer of the interfacial corrosion reaction. The validity of CPE is illustrated as:

$$Y_{CPE} = Y_o (j\omega)^n \quad (4)$$

Where

$n$  = the exponential,

$\omega$  = the angular frequency,

$j$  = is the imaginary root and

$Y_o$  = the magnitude term [38].

Table 2. Value of mass reduction calculation for metal in 0.5M H<sub>2</sub>SO<sub>4</sub> solution with and without concentrations of CA at 25–45°C.

Conc., ppm	Temp., °C	C.R., mgcm <sup>-2</sup> min <sup>-1</sup>	θ	IE%
25	25	0.194	0.5738	57.38
	30	0.278	0.446	44.6
	35	0.3659	0.33	33
	40	0.471	0.237	23.7
	45	0.5166	0.199	19.9
50	25	0.1566	0.656	65.6
	30	0.195	0.61	61.0
	35	0.271	0.503	50.3
	40	0.372	0.398	39.8
	45	0.407	0.3689	36.89
75	25	0.1395	0.693	69.3
	30	0.1611	0.679	67.9
	35	0.244	0.5517	55.17
	40	0.296	0.521	52.1
	45	0.3324	0.4846	48.46
100	25	0.099	0.783	78.3
	30	0.131	0.739	73.9
	35	0.1955	0.642	64.2
	40	0.2385	0.614	61.4
	45	0.267	0.586	58.6
125	25	0.087	0.808	80.8
	30	0.1046	0.79	79.0
	35	0.1348	0.753	75.3
	40	0.1866	0.698	69.8
	45	0.211	0.672	67.2
150	25	0.062	0.8638	86.38
	30	0.077	0.845	84.5
	35	0.1009	0.815	81.5
	40	0.1287	0.791	79.1
	45	0.1659	0.742	74.2

Table 3. Potentiodynamic data of carbon steel in in 0.5 MH<sub>2</sub>SO<sub>4</sub>with and without various concentrations of CA extract

Concentration, ppm	i <sub>corr</sub> , μA cm <sup>-2</sup>	-E <sub>corr</sub> , mV vs. SCE	β <sub>a</sub> , mVdec <sup>-1</sup>	β <sub>c</sub> , mVdec <sup>-1</sup>	CR, mm y <sup>-1</sup>	θ	η %
0.5 MH <sub>2</sub> SO <sub>4</sub>	264	559	266.0	167.4	150	--	--
25	143	549	220.0	150.7	80	0.458	45.8
50	110	538	210.1	130.4	60	0.583	58.3
75	85	523	190.5	110.3	48	0.678	67.8
75	75	518	160.0	105.4	33	0.716	71.6
125	61	498	141.1	96.0	28	0.769	76.9
150	55	488	118.7	88.1	18	0.79	79.0

Data reported in the literature [39]“showed that the diffusion process is controlled by diffusion of dissolved oxygen from the bulk solution to the electrode surface and the Warburg impedance, which is observed in the low frequency regions, is ascribed to diffusion of oxygen to the alloy surface this diffusion tail still appears, even in presence of high concentrations of the investigated extract, means that the corrosion behavior of alloy without as well as present of CA is influenced by mass transport”.

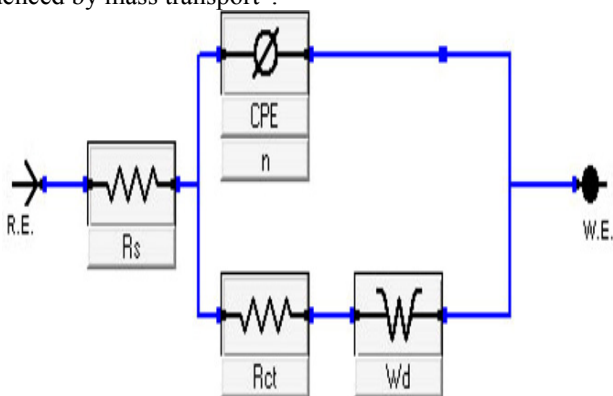


Figure 4. Equivalent circuit for fitting impedance data for C steel in 0.5 MH<sub>2</sub>SO<sub>4</sub>solutions

Also, Bode curves for the C steel in 0.5 MH<sub>2</sub>SO<sub>4</sub> are illustrated in Figure (5). In which the increase frequency corresponding to R<sub>Ω</sub> the resistance electrolyte (ohmic resistance), while the decrease frequency as the sum of (R<sub>ct</sub> + R<sub>Ω</sub>), where R<sub>ct</sub>= first approximation measured by both the polarization resistance of the dissolution and electrolytic conductance of the oxide film and re-passivation mechanism.

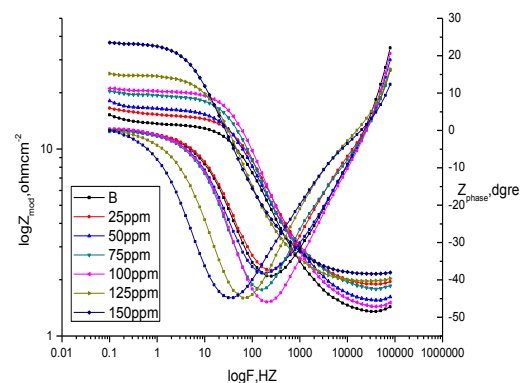


Figure 5. Bode curves for C steel in 1M H<sub>2</sub>SO<sub>4</sub> solutions with and without of CA concentrations at 25°C



**Table 4. Parameters by fitting the Nyquist curves shown in Fig. 3 with the circuit equivalent in Fig. 5 for C steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions with and without CA extract at 25°C**

Concentration, ppm.	R <sub>ct</sub> , Ωcm <sup>2</sup>	Y <sub>o</sub>	C <sub>dl</sub> , ×10 <sup>4</sup> μF cm <sup>-2</sup>	Θ	% IE
0.5 MH <sub>2</sub> SO <sub>4</sub>	12.96	1.00	144	---	---
25	13.75	2.00	55	0.057	5.7
50	15.50	3.00	54	0.164	16.4
75	18.07	4.00	53	0.283	28.3
100	19.48	5.00	50	0.335	33.5
125	23.40	6.00	47	0.446	44.6
150	47.33	6.00	45	0.726	72.6

At both decrease and rise frequency limits, the phase angle between potential (θ) and the current, suggested a data of about 0°, corresponded to the resistance behavior of (R<sub>Ω</sub> + R<sub>ct</sub>) and R<sub>Ω</sub>.

The main parameters deduced from the analysis of Nyquist diagram are:

- The resistance of charge transfer R<sub>ct</sub>(diameter of high frequency loop)
- The capacity of double layer C<sub>dl</sub> which is defined as :

$$C_{dl} = \frac{1}{2\pi R_{ct} f_{max}} \quad (5)$$

Where

Z<sub>imag</sub>=the impedance is a maximum

f<sub>max</sub>= maximum frequency.

R<sub>ct</sub>= data given from impedance resulted for various inhibitor concentration, (%IE) inhibition efficiency can calculated from following equation:

$$\% IE = \left(1 - \frac{R_{ct}^0}{R_{ct}}\right) \times 50 \quad (6)$$

Where

R<sub>ct</sub><sup>0</sup>=the charge transfer resistance without CA extract and

R<sub>ct</sub>= the charge transfer resistance with CA extract.

From the impedance resulted in Table (4), we can discuss that the data of R<sub>ct</sub> rise with the higher in the CA extract concentration and this indicates the formation of a cover protective film on the metal by the adsorption lead to higher in the inhibition efficiency in sulfuric acid. While the data of C<sub>dl</sub> lower with rise the extract concentrations comparison with uninhibited, due to replacement water molecules by inhibitor molecules which lead to lower in local dielectric constant [40, 41].

#### Electrochemical frequency modulation (EFM)

EFM is a nondestructive corrosion method that can directly given the corrosion current data without prior knowledge of Tafel slopes, and with only a little signal of polarizing [42].

Fig. 6 shows the frequency spectrum of the response current of pure metal in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions not only the frequencies input, but also contains frequency CA extract which are the sum and multiples of the two frequencies input. "The harmonic and intermodulation peaks are clearly visible and are much larger than the background noise, the two large peaks, with amplitude of about 75 μA, are the response to the 40 and 50 mHz (2 and 5 Hz) excitation frequencies, it is important to note that between the peaks there is nearly no current response (<50 mA), the experimental EFM data were treated using two different models, complete diffusion control of the cathodic reaction and the activation model, for the latter, a set of three non-linear equations had been solved, assuming that the corrosion potential does not change due to

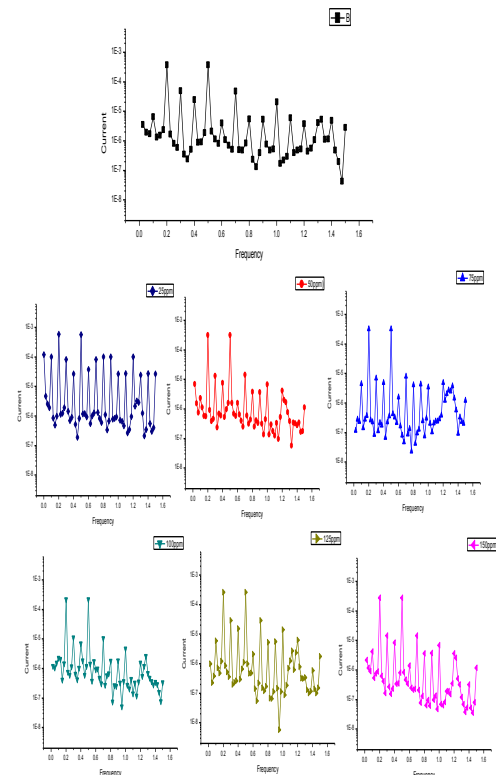
the polarization of the working electrode"[43]. The higher peaks were utilized to measured causality factors (CF-2 and CF-3), the corrosion current density (i<sub>corr</sub>), and the Tafel slopes (β<sub>c</sub> and β<sub>a</sub>). These parameters of electrochemical were simultaneously calculated by Gamry software, and written in Table 5 lead to the CA extract act as inhibitor for C steel corrosion of in 0.5 M H<sub>2</sub>SO<sub>4</sub> through adsorption. The causality factors given from experimental technique are equal to the theoretical data (2 and 3) indicating calculated value are verified and data is a good [44]. IE<sub>EFM</sub> % raises by higher concentrations of CA extract and measured as follows:

$$IE \%_{EFM} = \left(1 - \frac{i_{corr}^0}{i_{corr}}\right) \times 50 \quad (7)$$

Where

i<sub>corr</sub><sup>0</sup>= corrosion current densities without CA extract,

i<sub>corr</sub>= corrosion current densities with CA extract.



**Figure 6 (a-g). Intermodulation spectrums for the corrosion of C steel in 0.5 M H<sub>2</sub>SO<sub>4</sub> without and with various concentrations of CA at 25°C**

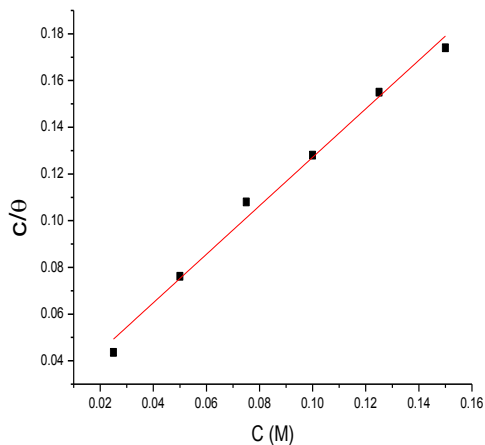
**Table 5. Electrochemical kinetic parameters obtained by EFM technique for metal in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions with CA at 25 °C.**

Concentration, ppm	$i_{\text{corr}}$ , $\mu\text{A}$	$\beta_a$ , $\text{mV dec}^{-1}$	$\beta_c$ , $\text{mV dec}^{-1}$	C.R. mpy	CF-2	CF-3	$\theta$	%IE
0.5 M H <sub>2</sub> SO <sub>4</sub>	748.2	85.700	276.9	341.90	2.17	1.53	---	---
25	551.6	98.930	134.5	252.10	1.92	2.53	0.263	26.3
50	491.5	92.410	106.2	224.60	1.76	3.18	0.343	34.3
75	455.8	110.200	165.5	208.30	1.86	2.99	0.391	39.1
100	435.8	87.430	122.1	199.10	1.91	2.94	0.418	41.8
125	360.2	67.650	124.5	164.60	1.96	3.00	0.519	51.9
150	253.5	25.130	32.15	115.80	3.08	3.15	0.661	66.1

### Adsorption Isotherm

The mode and interaction degree between an inhibitor and Carbon steel surface have been widely observed with the application of adsorption isotherms, "the adsorption of extract occurs because the interaction energy between a metal surface and inhibitor is increase than that between water molecules and metal[45, 46], To obtain the adsorption isotherms, the surface coverage ( $\theta$ ) given from mass loss technique was calculated as a function of inhibitor concentration. The data of  $\theta$  were then draw to fit the best suitable model of adsorption"[47]. Experiment were made to fit the result value to different isotherms contain Langmuir, Frumkin, Freundlich, Temkin isotherms. By far the data were best fitted by adsorption Langmuir isotherm as seen in Figure 7[48]:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad (8)$$



**Figure 7. Langmuir adsorption diagram for metal in 0.5 M H<sub>2</sub>SO<sub>4</sub> with CA concentrations at 25 °C.**

### Kinetic-thermodynamic corrosion parameters

Mass reduction experimental was taken at various temperatures (25 °C–45 °C) with various CA extract concentration. The corrosion rate rise with the rise in temperature for CA extracts (Table 2). The inhibition efficiency decrease with temperature. The parameter of corrosion without and with of CA extract against temperature 25–45 °C has been written in Table 2. ( $E_a^*$ ) The apparent energy of activation for metal in 0.5 M H<sub>2</sub>SO<sub>4</sub> was measured from the slope of curves by utilized Arrhenius equation:

$$\log k = \frac{-E_a^*}{2.303 RT} + \log A \quad (9)$$

Where

A = factor of Arrhenius pre-exponential,

$E_a^*$  = the apparent activation energy,

k = rate of corrosion,

T = temperature absolute, and

R = universal gas constant.

By draw  $\log k$  Vs.  $1/T$  the data of ( $E_a^*$ ) has been measured ( $E_a^* = (\text{slope}) 2.303 \times R$ ) (Fig. 8). From the reaction measured Activation energy in 0.5 M H<sub>2</sub>SO<sub>4</sub> rise in the presence of CA extract (Table 6). This rise in activation energy  $E_a^*$  lead to the found of physical bonds were strengthen by lowering the temperature. This data supports the idea that the adsorption of CA extract on the Carbon steel surface may be physical. The obtained data suggest that CA inhibits the corrosion reaction by rise in activation energy. This could be study by adsorption on the surface of metal lead to a barrier for mass and charge transfer [49]. Moreover, the relatively increase data of activation energy with CA extract given a process of physical adsorption.

The data ( $\Delta H^*$ ) change of enthalpy and ( $\Delta S^*$ ) change of entropy can be measured by utilized by formula:

$$k = \left( \frac{RT}{Nh} \right) \exp \left( \frac{\Delta S^*}{R} \right) \exp \left( \frac{\Delta H^*}{RT} \right) \quad (10)$$

where

$\Delta H^*$  = the enthalpy of activation,

N = Avogadro number,

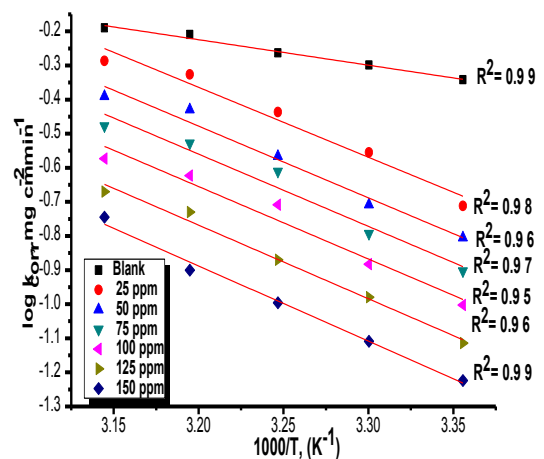
$\Delta S^*$  = the entropy of activation,

h = Planck's constant, and

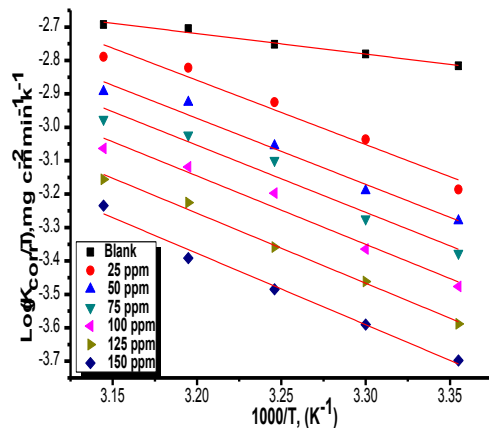
k = rate of corrosion.

A draw of  $\log(k/T)$  vs.  $1/T$  (Fig. 9) given a straight line, with an intercept of  $[\log(R/Nh) + \Delta S^*/2.303R]$  and a slope of  $(\Delta H^*/2.303R)$ , from which the data of  $\Delta H^*$  and  $\Delta S^*$  can be measured (Table 6). The -ve  $\Delta H^*$  lead to that the adsorption is exothermic process.

The -ve  $\Delta S^*$  for the inhibitor lead to that activated complex in the rate determining step performance an association rather than a dissociation step [50]



**Figure 8. 1/T vs. log k diagrams for metal in 0.5 M H<sub>2</sub>SO<sub>4</sub> with and without various concentrations of CA.**



**Figure 9.**  $1/T$  vs.  $\log k/T$  curves for metal in 0.5  $\text{MH}_2\text{SO}_4$  with and without CA concentrations.

#### Corrosion inhibition mechanism

The adsorption of plant extract compounds can be illustrated by two main types of interactions: chemisorptions and physical adsorption. In general, physical adsorption need to the presence of both the charged species and electrically charged surface of the metal in solution. The surface charge of the metal is given the electric field existing at the metal/solution interface. This is possible in case of a positive as well as a negative charge of the surface.

**Table 6.** Activation parameters for C steel with and without CA concentrations in 0.5  $\text{MH}_2\text{SO}_4$ .

Conc. ppm	$E_a^*$ , $\text{kJ mol}^{-1}$	$\Delta H^*$ , $\text{kJ mol}^{-1}$	$-\Delta S^*$ , $\text{J mol}^{-1}\text{K}^{-1}$
0.5 M $\text{H}_2\text{SO}_4$	14	5.1	211.9
25	39	15.9	134.4
50	40	16.4	133.4
75	40.5	16.7	133.0
100	40.7	17	132.4
125	41	17.	131.6
150	41.5	17.8	131.0

The presence of a transition metal, having vacant, low-energy electron orbital and an inhibitor with molecules having relatively loosely bound electrons or heteroatom's with a lone pair of electrons is necessary for the inhibiting action [52]. Generally, two types of mechanisms of inhibition were proposed. One was the formation of polymeric complexes with C steel ions ( $\text{Cu}^+$  and  $\text{Cu}^{+2}$ ) depending on the applied conditions [53, 54]. The other was the chemical adsorption of CA on C steel surfaces [55, 56]. "The inhibition action of CA does not occur by the simple blocking at the surface of C steel, especially at high temperature, this might be attributed to the different adsorption capacities of the CA extract on the C steel surface at different temperatures, it has been studied that with the increase in temperature, the desorption effect of CA on C steel surface decreased some of the hydrophilic groups with positively charged atoms ( $\text{O}^+$ ) desorbed from the surface of C steel and did more work to prevent the  $\text{H}^+$  from getting nearer to the metal surface".

#### Conclusions

From the overall experimental results the following conclusions can be deduced:

1. The CA shows good performance as corrosion inhibitor in 0.5  $\text{MH}_2\text{SO}_4$ .

2. The data obtained from mass loss given that the inhibiting action rise with rise extract concentration and lower with the higher temperature.

3. The CA inhibits the corrosion by getting adsorbed on the carbon steel surface following adsorption Langmuir isotherm.

4. The inhibition efficiencies calculated by mass reduction, EIS and Tafel polarization techniques are in reasonably good agreement.

#### References

- Trabanelli G., *Corrosion*, 47 (1991) 410.
- Singh D. N., Dey A. K., *Corrosion*, 49 (1993) 594.
- Banerjee G., Malhotra S. N., *Corrosion*, 48 (1992) 10.
- Arab S. T., Noor E. A., *Corrosion*, 49 (1993) 122.
- Raspini I. A., *Corrosion*, 49 (1993) 821.
- Khadraoui A., Khelifa A., Touafri L., Hamitouche H., Mehdaoui R., *J. Mater. Environ. Sci.* 4 (2013) 663.
- Elachouri M., Hajji M. S., Salem M., Kertit S., Coudert R., Essassi. E. M., *Corros. Sci.*, 37 (1995) 381.
- Luo H., Guan Y. C., Han K. N., *Corrosion*, 54 (1998) 619.
- Migahed M. A., Azzam E. M. S., Al-Sabagh A. M., *Mater. Chem. Phys.* 85 (754) 273.
- Villamil R. F. V., Corio P., Rubim J. C., SilivaAgostinho M. L., *J. Electroanal. Chem.*, 472 (1999) 112.
- Hari Kumar and S. Karthikeyan., *J. Mater. Environ. Sci.* 3 (5) (2012) 925–934.
- Hadi Z.M. Al-Sawaad, Alaa S.K. Al-Mubarak, Athir M. HaddadI., *J. Mater. Environ. Sci.* 1 (4) (2010) 227-238.
- Abd El Rehim S. S., Hassan H., Amin M. A., *Mater. Chem. Phys.*, 78 (753) 337.
- Guo R., Liu T., Wei X., *Colloids Surf, A*, 209 (752) 37.
- Branzoi V., Golgovici F., Branzoi F., *Mater. Chem. Phys.* 78 (752) 122.
- Parikh K. S., Joshi K. J., *Trans. SAEST*, 39 (754) 29.
- Chauhan J. S., *Asian Journal of Chemistry*, 21 (759) 1975.
- Sangeetha T. V., Fredimoses M., *E-Journal of Chemistry*, 8 (2011) (S1), S1-S6.
- Fernando Sílvio de Souza, Cristiano Giacomelli, Reinaldo Simões Gonçalves, Almir Spinelli, *Materials Science and Engineering*, 32 (2012) 2436.
- Abd-El-Nabey B. A., Abdel-Gaber A. M., El. Said Ali M., Khamis E., El-Housseiny S., *J. Electrochem. Sci.*, 8(2013) 5851.
- Kew World Checklist of Selected Plant Families.
- Atala, A. (2012). "A new ingredient: The introduction of priprioca in gastronomy". *International Journal of Gastronomy and Food Science* 1: 61–81.
- Eeva M., Salo J. P., Oksman-Caldentey K. M., *J Pharm Biomed Anal.* 1998; 16(5):717. "Determination of the main tropane alkaloids from transformed Cyperus Articulates plants by capillary zone electrophoresis".
- Mu G. N., Zhao T. P., Liu M., Gu T., *Corrosion*, 52 (1996) 853.
- Parr R. G., Donnelly R. A., Levy M. Palke W. E., *J. Chem. Phys.*, 68(1978) 3801.
- Bosch R. W., Hubrecht J., Bogaerts W. F., Syrett B. C., *Corrosion*, 57(751) 60.
- Zhang D. Q., Cai Q. R., He X. M., Gao L. X., Kim G. S., *Mater. Chem. Phys.* 114 (759) 612.
- Lee H. P., Nobe K., *J. Electrochem. Soc.* 133 (1986) 2035.
- Tao Z. H., Zhang S. T., Li W. H., Hou B. R., *Corros. Sci.* 51 (759) 2588.

30. Ferreira E. S.,Giacomelli C., Giacomelli, F. C., Spinelli A., *Mater. Chem.Phys.*83 (754) 129.
31. Paskossy T., *J. Electroanal. Chem.*, 364 (1994) 111.
32. Growcock F. B.,Jasinski J. H., *J. Electrochem. Soc.*, 136 (1989) 2310.
33. Abd El-Rehim S. S., Khaled K. F.,Abd El-Shafi N. S., *Electrochim. Acta*, 51 (756) 3269.
34. Metikos M.,Hukovic R., Bobic Z. Gwabac S., *J. Appl. Elactrochem.*, 24 (1994) 772.
35. Caprani A., Epelboin I., Morel Ph., Takenouti H., *proceedings of the 4<sup>th</sup> European sym. on Corros. Inhibitors*, (1975)571.
36. Bessone J., Mayer C., TuttnerK.,Lorenz W. J.,*Electrochim. Acta*, 28 (1983) 171.
37. Epelboin I., Keddami M., Takenouti H.,*J. Appl. Electrochem.*, 2 (1972) 71.
38. Benedetti A. V.,Sumodjo P. T. A., Nobe K., Cabot P. L., Proud W. G., *ElectrochimicaActa*, 40 (1995) 2657.
39. Ma H., Chen S., Niu L., Zhao S., Li S., Li D., *J. Appl. Electrochem.* 32 (752) 65.
40. Li X. H.,Deng S. D., Fu H., *J. Appl. Electrochem.*, 40 (2010) 1641.
41. Lagrenee M., Mernari B., Bouanis M., Traisnel M., Bentiss F., *Corros. Sci.*, 44 (752) 573.
42. Kus E., Mansfeld F., *Corros. Sci.*, 48 (756) 965.
43. Caignan G. A., Metcalf S. K., Holt E. M., *J.Chem. Cryst*, 30 (750) 415.
44. Abdel-Rehim S. S., Khaled K. F., Abd-Elshafi N. S., *Electrochim. Acta*, 51 (756) 3269.
45. Bockris J. O., Swinkels D. A. J., *J. Electrochem. Soc.*, 111 (1964)736.
46. Saleh M. M., Atia A. A., *J. Appl. Electrochem.*, 36 (756) 899.
47. Narvez L., Cano E., Bastidas D. M., *J. Appl. Electrochem.*, 35 (755) 499.
48. Li X. H., Deng S. D., Fu H., *Corros. Sci.*, 51 (759) 1344.
49. Putilova I. K., Balezin S. A., Barasanik Y. P., *Metallic Corrosion Inhibitors, Oxford: Pergamon Press*, (1960) 30.
50. Saliyan V. R., Adhikari A. V., *Bull. Mater. Sci.*, 31 (757) 699.
51. Li Y., Zhao P., Liang Q., Hou B., *Appl. Surf. Sci.*, 252 (755) 1245.
52. Mehaute A. H., Greppe G., *Solid State Ionics*, 9–10 (1989) 17.
53. Brusic V., Frisch M. A., Eldridge B. N., Novak F. P., Kauman F. B., Rush B. M., Frankel G. S., *J. Electrochem. Soc.* 138 (1991) 2253.
54. Antonijevic M. M., Petrovic M. B., *Int. J. Electrochem. Sci.*3 (758) 1.
55. Musiani M. M., Mengoli G., *J. Electroanal. Chem.* 217 (1987) 187.
56. Lewis G., *Corrosion*34 (1978) 424.