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Calicotome Extract as a Friendly Corrosion Inhibitor of Carbon Steel in Polluted NaCl (3.5% NaCl + 16 ppm Na₂S): Chemical and Electrochemical Studies

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THIS study describes the ability of Calicotome extract (CE) to inhibit the corrosion of C-steel in polluted NaCl (3.5%NaCl+ 16 ppm Na₂S) solution which carried out using chemical (weight loss, WL)and electrochemical(potentiodynamic polarization, PP, electrochemical impedance spectroscopy, EIS and electrochemical frequency modulation, EFM) techniques. Langmiur isotherm was tested to describe the adsorption behavior of C-steel surface. The PP measurements revealed that the adsorption of extract affects both anodic and cathodic reactions. The protection efficiency (% IE) increases by rising concentrations, while it lowers with raising the temperature. The C-steel surface morphology in the presence and absence of CE has been tested via Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and (FTIR) spectroscopy measurements. The obtained data from different techniques are in good agreement.

Graphical Abstract
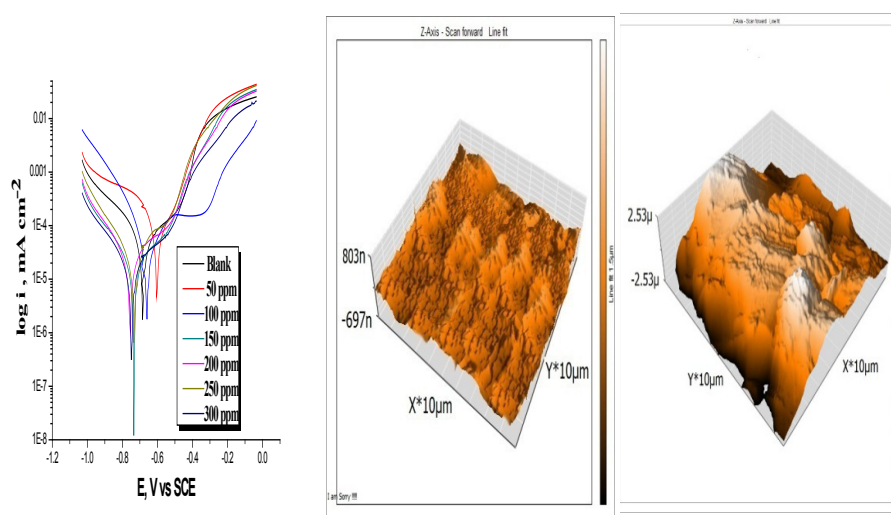
Keywords: Corrosion, Calicotome extract (CE); C-steel, SEM; AFM and FTIR.

Introduction

Corrosion inhibitors are materials additional in few amounts to protect the corrosion of the metal which is in contact with the corrosive medium. The acceptability of plant extract as corrosion inhibitors is because of low cost, safe, availability and renewable source [1-4]. The use of C-steel in manufacturing and installation utilized in petroleum and other industries make it is important to lower the corrosion of C-steel. The use of inhibitor is the most effective way to control the corrosion of steel [5-9]. There are much research have been distributed on the utilized of natural products as corrosion protection[10-25]. A lot of plant extracts employed as effectively as corrosion protection for C-steel ina medium of acid [26- 40].

The present research will discuss the CE as a green inhibitor for protecting C-steel from corrosion in polluted NaCl solution, also to determine and discuss the inhibition mechanism.

Experimental

Materials and Solutions

Preparation of Plant Extract

The present investigation was carried out using the plant namely CE. The sample was purchased from the local market and ground into a fine powder to give 200 g of powdered materials which extracted separately by soaking at room temperature for six times with dichloromethane and methanol solvents, then the extract of the sample was concentrated to near dryness under reduced pressure by using the rotary evaporator at 45°C to achieve the crude extract which kept for further investigation. The extract contains the following major phyto chemical compounds: phenolic, flavonoids, alkaloids, Tannins, saponins, coumarin and sugar.

Stability of the sulfide

Sulfide is an inorganic anion of sulfur with the chemical formula S^{2-} or a compound containing one or more S^{2-} ions. Solutions of sulfide salts are corrosive. Dissolved free sulfides (H_2S, HS^- and S^{2-}) are very aggressive species for the corrosion of many metals such as steel, stainless steel, and copper. Sulfides present in aqueous solution are responsible for stress corrosion cracking (SCC) of steel, and is also known as sulfide stress cracking. Corrosion is a major concern in many industrial installations processing sulfides: sulfide ore mills, deep oil wells, pipelines transporting soured oil, Kraft paper factories.

Tests Utilized for Corrosion Calculations
Weight loss (WL) tests

Square specimens of size 2 cm x 2cm x0.2cm were used for WL tests which were firstly polished to a mirror finish using altered grades (320–1200 grade) of emery papers and then degreased with acetone, washed with bidistilled water and dried with soft paper the last step was weighed and dipped in to the solution test. The WL tests were accepted in polluted NaCl of (3.5%NaCl &16 ppm Na_2S). The %IE and the degree of surface coated (θ) of the CE on corrosion of C-steel were measured as follows in equation (1) [41]:

$$\%IE = \theta \times 100 = [1-(W/W^o)] \times 100 \qquad (1)$$

Where, % IE is the inhibition efficiency & w_1 and w_2 are the weights of the specimen before and after reaction, respectively.

Electrochemical measurements

PP method was taken in a typical three compartments glass cell. The potential range was (-600 to +400 mV vs. SCE) at OCP with a scan rate 1 mVs⁻¹.

Then i_{corr} was calculated for the measurements and was used to calculate the %IE and the θ from Eq. (2) as below:

$$IE \% = \theta \times 100 = [1- (i_{corr(inh)} / i_{corr(free)})] \times 100 \qquad (2)$$

Where $i_{corr(free)}$ and $i_{corr(inh)}$ are the current in the absence and presence of Calicotome extract, correspondingly.

TABLE 1. Weight % of the C-steel specimens.

Element	Fe	C	Mn	P	Si	Cr	Co
Weight %	Balance	0.150-0.200	0.350-0.600	0.016-0.024	0.003-0.098	0.018-0.026	-0.145 0.245

The aggressive media of polluted NaCl were prepared by dilution of (3.5% NaCl &16 ppm Na_2S) by bi-distilled water. The experimental measurements were obtained in the presence and absence of different concentrations of CE

Impedance measurements were done by AC signs of 10 mV peak-to-peak amplitude and at a range of frequency of 10^7 Hz to 0.1Hz. The capacity of double layer C_{dl}, (% IE) and θ were calculated.

EFM technique used two frequencies of range 2 and 5 Hz depending on three conditions [42- 45]. The (i_{corr}), ($β_c$ and $β_a$) and (CF-2, CF-3) (Causality factors) were measured by the greater two peaks

(EFM) and (EIS) technique was performed utilizing the similar manner as earlier with a Gamry framework system depends on ESA400. Gamry apparatus includes software EFM140 for EFM tests and EIS300 for EIS method; the computer has used for summation value. Echem Analyst 5.5 Software was used for drawing and fitting data.

Surface examination

Coins utilized for surface analysis were immersed in polluted NaCl in without and with 300 ppm of Calicotome solutions for 15 h. After this immersion time, the coins were removed, rinsed with bidistilled water many times to remove any residue and dried. The investigation was done by (SEM and AFM) [46,47]. FTIR analyses were tested for C-steel surface before and after immersion 15 h in 300 ppm Calicotome and then compared to the spectra of Calicotome. Fourier transforms infrared spectroscopy was applied to

examine the film formed on the surface of C-steel by Thermo Fisher Nicolet IS10, the USA in the spectral range of 400 – 4500 cm⁻¹.

Results and Discussion

Weight Loss (WL)Test

WL Curves against time at 30°C for C-steel in polluted NaCl existence and nonexistence Calicotome dose were established in Fig. 1. The plots give in the existence of extract fall significantly below that of a free solution. These results led to the conclusion that CE under investigation is truly productive as an inhibitor for C-steel dissolution in polluted NaCl solution and % IE increases by raising the extract concentrations. (Θ) and IE was calculated from Eq. (1).

Effect of Temperature

The influence of temperature on the rate of corrosion of C-steel in polluted NaCl and in the existence of different extract concentrations was studied in the range of temperature 30–50°utilizing WL test. As the temperature rises, the rate of corrosion (k_{corr}) increases and the %IE of the extract decrease as shown in Table 2 for CE. The adsorption performance of CE on C-steel surface occurs among physical adsorption.

Adsorption isotherms

The adsorption isotherms are amongst the most helpful methods for expressing adsorption
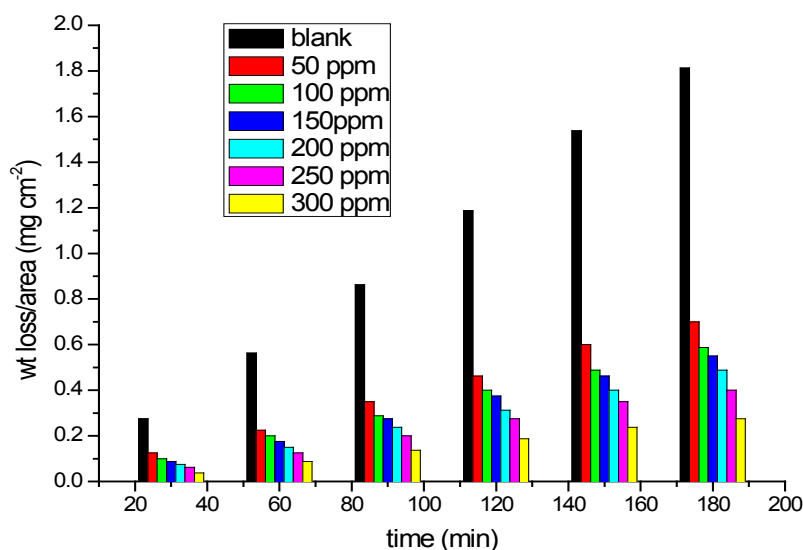

Fig. 1. WL vs. time curves for C-steel corrosion in polluted NaCl with and without various concentrations of CE at 30°C.

quantitatively that characterizes the metal/ inhibitor/ environment system. The common adsorption isotherms fitting were used to analyze the data are Langmuir, Freundlich, Temkin, Flory–Huggins and Frumkin. In the present study, the data of our experiment revealed that the best fit for Langmiur isotherm. Figure 2 shows the plotting of C/θ against C at 30ºC for CE. This plot gave straight lines indicating that the adsorption of CE on C-steel surface obeys Langmuir isotherm:

$$C/ \theta = 1/K_{ads} + C \qquad (3)$$

C is the inhibitor concentration, K_{ads} is the adsorption equilibrium constant.

$$K_{ads} = 1/ 55.5 \exp (-\Delta G°_{ads}/ RT) \qquad (4)$$

T is the Kelvin temperature and 55.5 is the concentration of water in solution (M).

The standard enthalpy $\Delta H°_{ads}$ can be measure dusing the Van't Hoff Eq.(5):

$$\log K_{ads} = (-\Delta H°_{ads}/2.303RT) + constant \qquad (5)$$

Then according to the thermodynamic basic

TABLE 2. Variation of % IE and Ѳ with various concentrations of CE in polluted NaCl solution from WL test after 120 minutes immersion.

[extract], ppm	Ѳ	% IE
50	0.856	85.6
100	0.877	87.7
150	0.897	89.7
200	0.918	91.8
250	0.938	93.8
300	0.959	95.9

TABLE 3. % IE and (k_{corr}) of CE for the corrosion of C-steel in polluted NaCl solution from WL at different (30-50ºC) temperatures.

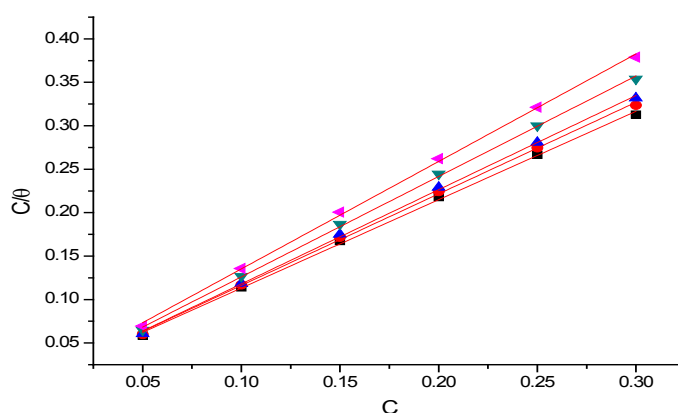| [CE],ppm	30 ºC		35 ºC		40 ºC		45 ºC		50 ºC	
	k_{corr}	%IE	k_{corr}	%IE	k_{corr}	%IE	k_{corr}	%IE	k_{corr}	%IE
50	2.92	85.6	4.60	83.6	5.20	82.4	6.25	77.3	7.91	71.9
100	2.5	87.7	4.2	85.5	4.06	84.5	5.83	78.9	7.08	73.7
150	2.08	89.7	3.00	87.3	3.75	85.7	5.41	80.3	6.70	74.8
200	1.67	91.8	2.50	89.1	3.40	87.3	5.00	81.8	6.30	76.3
250	1.3	93.8	2.08	91	3.00	89.0	4.37	83.3	5.83	77.8
300	0.83	95.9	1.70	92.7	2.53	90.4	3.95	84.8	5.20	79.2

Fig. 2. Langmiur plots of CE on C-steel in polluted NaCl solution at various concentrations,

Eq.(6)ΔS°_{ads} can be calculated.

$$\Delta G^{\circ}_{ads} = \Delta H^{\circ}_{ads} - T\Delta S^{\circ}_{ads} \qquad (6)$$

where ΔS° is the entropy of the system.

These results were recorded in Table 4. The ΔH°_{ads} data were evaluated from the line of log K_{ads} versus 1/T (see Fig. 3). "The positive sign data of ΔH°_{ads} ensures that the process of adsorption is endothermic, and the negative sign data of ΔG°_{ads} means that adsorption occurs spontaneously. From the data of ΔG°_{ads} (around -40 kJ mol^{-1}), CE is adsorbed on C-steel surface by physisorption and chemisorption (mixed adsorption) [48]. A positive sign of ΔS°_{ads} proves that the disorder of corrosion process is increased by utilizing CE (Table 4). Such manner can be described on the basis that temperature increase causes desorption of some adsorbed CE molecules on the C-steel and accordingly leads to the formation of surface organic layer having lower hindrance [49].

Kinetic –Thermodynamic Corrosion Parameters

Activation energies for corrosion procedure (E^*_a) were obtained from Arrhenius relation as follows:

$$\log k_{corr} = \log A - (E^*a / 2.303R)(1/T) \qquad (7)$$

where A is constant, and T is Kelvin temperature [50-51]. Plots of log k_{corr} and 1000/T were illustrated in Fig. 4. Enthalpy of activation for corrosion procedure (ΔH^*) and entropy of activation for corrosion procedure (ΔS^*) were determined by plotting log k_{corr}/T against 1/T (Fig. 5), according to the following Eq.:

$$\log k_{corr}/T = \log (R/ Nh + \Delta S^*/ 2.303R) + (-\Delta H^*/ 2.303R)(1/ T) \qquad (8)$$

where h is constant and N is number of Avogadro. Increasing of E^*_a and ΔH^* with CE was because energy barrier that created in existence of Calicotome extract. ΔH^* values were found to have positive signs, indicating anodic dissolution reaction of C-steel. Negative ΔS^* indicated that from reactants to the activated complex, the
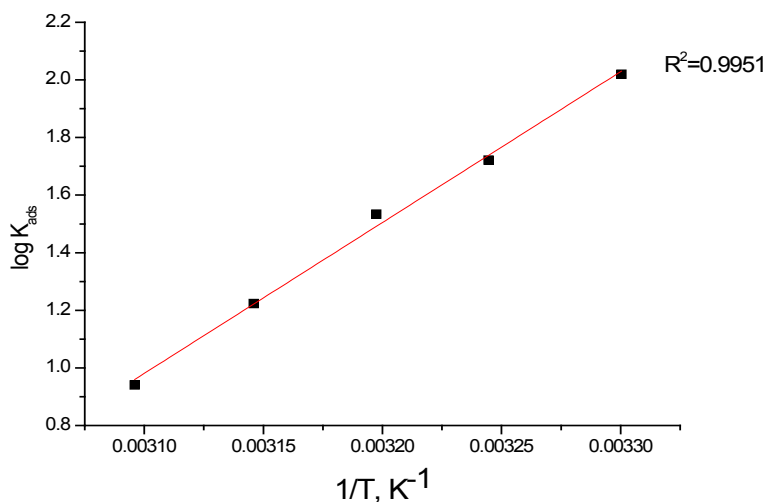

Fig. 3. log K_{ads} was plotted against 1/T (K^{-1}) for CE.

TABLE 4. Langmiur data of CE on C-steel surface in polluted NaCl solution at different temperatures.

Temp °C	Log K_{ads}	- ΔG^{o}_{ads}, kJ mol^{-1}	ΔH^{o}_{ads} kJ mol^{-1}	ΔS^{o}_{ads} kJ mol^{-1} K^{-1}
30	2.02	15.3		44.2
35	1.72	15.5		48.9
40	1.53	21.0	11.8	65.1
45	1.22	21.1		68.6
50	0.940	21.4		68.8

disorder lowered [52-54]. Figure 5 shows a plot of (log k_{corr}) against (1/T) in the case of CE in polluted NaCl solution. Straight lines were obtained with a slope equals to ($\Delta H^* /2.303R$) and the intercept equal to [log ($R/Nh + \Delta S^*/2.303R$)] and their values are recorded in Table 5.

Potentiodynamic Polarization (PP)Tests

Figures 6 shows typical polarization curves for C-steel in polluted NaCl media. "The two distinct regions that appeared were the active dissolution region (apparent Tafel region), and the limiting current region. In absence of inhibitor, a monotonic increase of current with potential was showed by the anodic polarization curve of C-steel until the current reached the maximum value. Current density decreased quickly with a potential increase after this maximum current density value, leads to the formation of an anodic
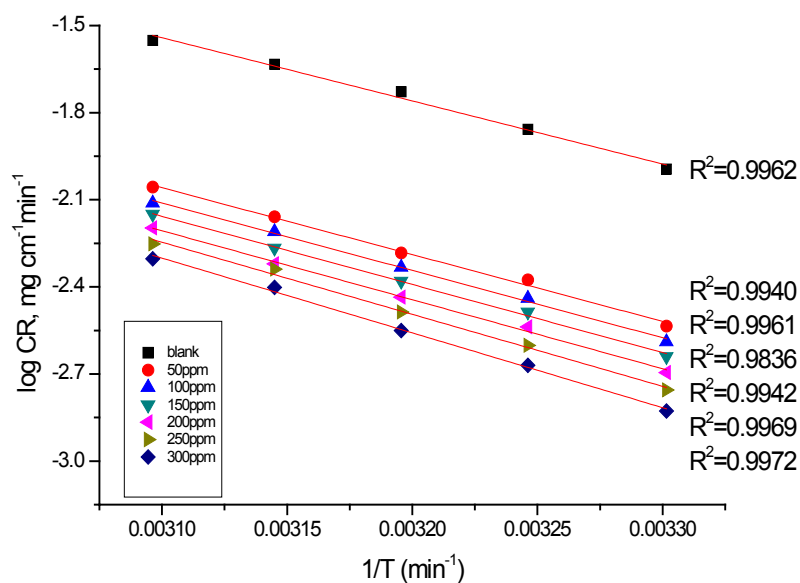

Fig. 4. Arrhenius plots for C-steel in polluted NaCl solution without and with various concentrations of CE.
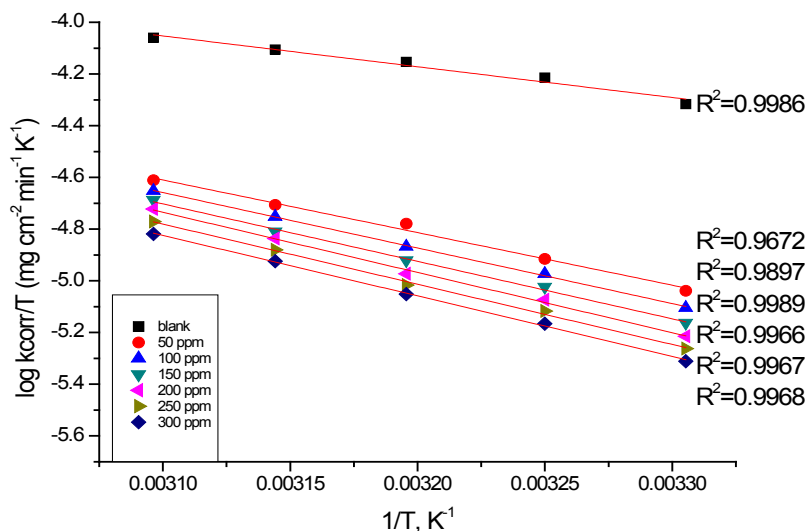

Fig. 5. Log (k_{corr}/T) vs (1000/T) curves for C-steelcorrosion with and without variousconcentrations of CE.

TABLE 5. Activation parameters for C-steel corrosion without and with various concentrations of CE in polluted NaCl solution.

[inh] ppm	E_a^* k Jmol^{-1}	ΔH^* k J mol^{-1}	$-\Delta S^*$ J mol^{-1}K^{-1}
Blank	27.6	22.4	214.2
50	39.1	34.1	207.0
100	41.4	37.9	204.2
150	44.3	39.7	200.0
200	44.9	41.0	197.2
250	45.5	41.7	192.6
300	47.5	41.9	190.2

current peak. In the presence of inhibitor, both the cathodic and anodic current densities were greatly decreased through a wide potential range. From Table 6 various corrosion parameters such as corrosion potential (E_{corr}), (β_a, β_c), the (i_{corr}), the (θ) and (% IE) could be shown. It can see from the experimental results that in all cases, the addition of inhibitor induced a significantly lower in the cathode and anodic currents. The data of E_{corr} were affected and slightly changed by the addition of the inhibitor. This indicates that CE acts as a mixed-type inhibitor. The slopes of anodic and cathodic Tafel lines (β_a and β_c), were slightly changed (Tafel lines are parallel), on increasing the concentration of which indicates that there is no change of the mechanism of inhibition in the presence and absence of inhibitor". The requests of restraint proficiency of inhibitor at various concentrations as given by polarization estimations are recorded in Table 6. The results are in great concurrence with those acquired from WL estimations.

Electrochemical Impedance Spectroscopy (EIS) Tests

Both Nyquist and Bode bends for C-steel corrosion in polluted NaCl only and also in acid in existence of varied dose of CE were obtained by EIS procedure and shown in Fig. 7(a, b). "It is noticed from Nyquist figure that the curves appear semicircular. The frequency dispersion is responsible for the shape of the curve. The special shape of the Nyquist curves confirms that the C-steel corrosion is controlled by charge transfer process [55,56]. It was found that in the Nyquist diagrams the existence of inhibitor leads to rising the diameter of the capacitive loop. Charge transfer resistance (R_{ct}) is responsible for the high-frequency capacitive loop. The double layer capacitance (C_{dl}) is the frequency at which the component of the impedance is maximum and could be measured according to the next balance.

$$C_{dl} = 1 / 2 \quad f_{max} \; R_{ct} \qquad (9)$$

Where R_{ct} is the charge transfer resistance and f_{max} is the frequency at the maximum altitude of the semicircle [57, 58]. The parameters obtained by EIS procedure reported in Table 7. From the results calculated, it was observed that the R_{ct} values increase with increasing CE dose but C_{dl} data lowered. The adsorption of CE on the C-steel surface leads to this result. The results obtain prove that the CE works by forming the protective layer on the C-steel surface which modifies the metal/acid interface". The inhibition efficiency was calculated from the charge transfer resistance data from Eq.10 [59]:

$$\% \; IE_{EIS} = [1 - (R_{ct}^\circ / R_{ct})] \times 100 \qquad (10)$$

Where, R_{ct} and R_{ct}° are resistance values with and without CE, respectively.

Electrochemical Frequency Modulation (EFM) Tests

EFM is a safety dissolution test which is described by speed and precision in computing the present information from Tafel slopes [60]. Figure 9 demonstrates the EFM of C-steel in polluted NaCl solution and 300ppm of CE. The EFM parameters such as (CF-2 and CF-3), (β_c and β_a) and (i_{corr}) can be estimated from the higher current peaks. The CF is nearer to the standard information demonstrated the validity and quality of the calculated data. The %IE increase with the raising of CE concentrations.

SEM Examinations

Figure 10 demonstrates the micrograph given

for C-steel sheets without and with 300 ppm of CE after immersion for just one day.

Atomic Force Microscopy (AFM) Analysis
AFM has been a significant apparatus in order

to evaluate the surface morphology, which is an important method to help in discussing the extract effect on the metal/solution interface[61]. Figure 11a−c, shows the AFM graphs of polished C-steel,
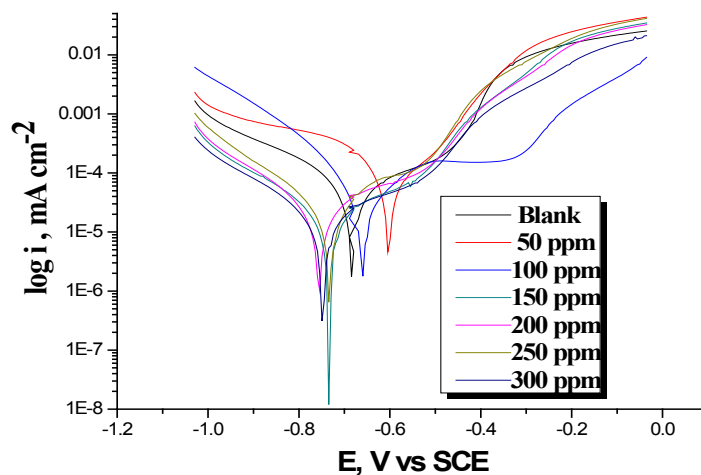

Fig. 6. Tafel plots for C-steel in Polluted NaCl without and with various concentrations of CE at 25ºC.

TABLE 6. i_{corr}, E_{corr}, β_c, β_a, k_{corr}, θ, and % IE for C-steel in polluted NaCl at 30ºC for CE.

Conc, ppm	$-E_{corr.}$, mV vs SCE	i_{corr}· µA cm^{-2}	β_c mV dec^{-1}	β_c, mV dec^{-1}	Θ	% IE
Blank	867.0	301.0	366	390.0	---	---
50	842.0	114.0	281.0	323.0	62.1	62.1
100	783.0	46.2	295.0	287.0	0.847	84.7
150	785.0	43.6	199.0	286.0	0.855	85.5
200	838.0	40.5	216.0	224.0	0.865	86.5
250	813.0	35.5	149.0	185.0	0.882	88.2
300	774.0	24.1	142.0	185.0	0.92	92.0

TABLE 7. EIS parameters for dissolution of C-steel in polluted NaCl solution with and without various concentrations of CE at 30ºC.

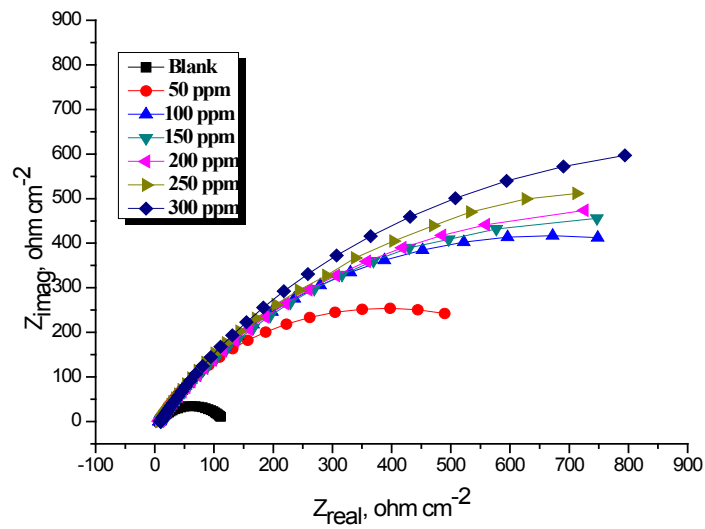| Conc.,ppm,	R_{ct}, Ω cm^2	C_{dl}, µF cm^{-2}	θ	% IE
Blank	110.5	9.77	---	---
50	304.2	4.53	0.637	67.7
100	661.0	3.71	0.833	83.3
150	724.4	1.40	0.847	84.7
200	1219	0.231	0.909	90.9
250	1397	0.129	0.921	92.1
300	1664.0	0.782	0.933	93.3

Fig. 7a. Nyquist plots recorded for dissolution of C-steel in polluted NaCl existence and nonexistence of altered dose of Calicotome extract at 25°C.
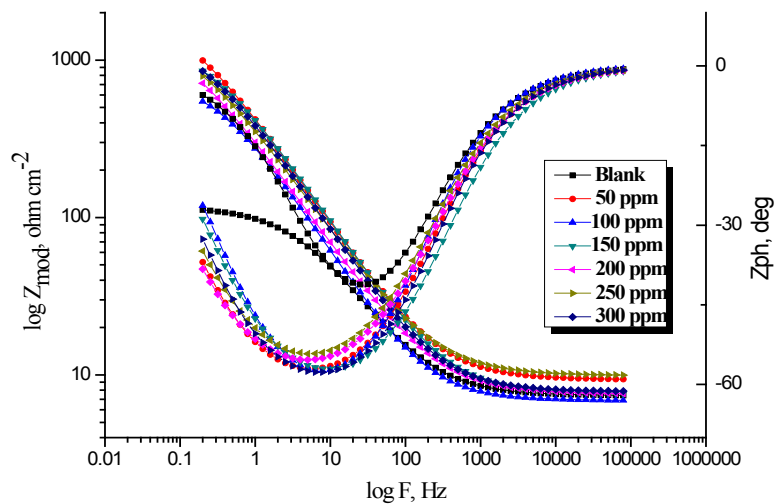

Fig. 7b. Bode plots recorded for dissolution of C-steel in polluted NaCl solution with and without various concentrations of CE at 25°C.
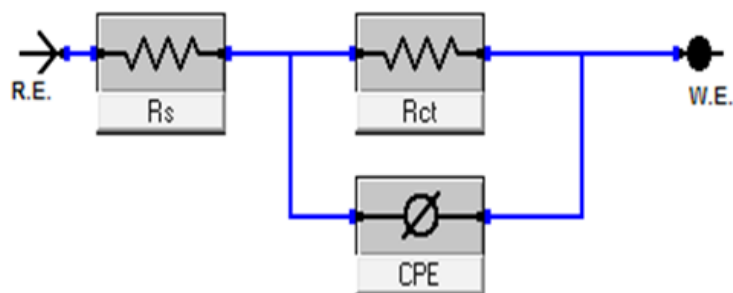

Fig. 8. Circuit applied to fit EIS data.

TABLE 8. Parameters for dissolution of C-steel in polluted NaCl solution with and without various concentrations of CE at 30°C.

% IE	Θ	C.R mpy	CF-3	CF-2	β_c mVdec^{-1}	β_a mVdec^{-1}	i_{corr} μAcm^{-2}	Conc.,ppm
---	---	76.40	2.663	1.978	128.3	61.06	167.2	Blank
67.0	0.670	28	2.80	1.9	69	91	55.1	50
76.5	0.765	19	2.9	2.3	179	131	39.2	100
78.1	0.781	17	3.0	1.9	188	123	36.6	150
78.6	0.786	16	3.4	1.7	100	109	35.7	200
83.2	0.832	12	3.2	1.6	96	103	28.1	250
85.3	0.853	10.8	2.9	1.9	101	127	24.61	300

C-steel in polluted NaCl, which not including CE and C-steel in polluted NaCl containing 300 ppm of CE, respectively. The Sa, Sq and Sp height values are considerably less in the inhibited environment compared to the uninhibited environment (Table 9). These parameters prove that there is a formation of a protective film consisting of Fe^{2+} extract complex and the surface is smoother. The smoothness of the surface is due to the development of Fe^{2+} extract complex on the metal surface, thereby inhibiting the corrosion of C-steel.

TABLE 9. Parameters obtained from AFM for C-steel with corrosive medium containing 300 ppm CE for 24 hours

Parameters	(a) Pure CS	(b) Blank	(c) CE
The roughness average (Sa)	17.46	993.76	163.94
The root mean square (Sq)	22.976	1234. 9	263.94

Fourier transforms infrared spectroscopy (FT-IR) studies

From Fig. 12, it is found that the O-H stretching has changed from 3478 cm^{-1} to 3332 cm^{-1}, "the –C=C stretching frequency appears at 1634 cm^{-1} (multiple bands), the sharp one at 1096 cm^{-1} referring to –CO stretching, the frequency at 2871, 2955 cm^{-1} is due to –CH stretching, the frequency at 1248cm^{-1} referred to –CN stretching frequency. The FTIR spectrum of the film formed on the C-steel immersed in polluted NaCl we

noticed that, the -C=C stretching frequency shifts from 1636 cm^{-1} to 1634 cm^{-1}. The -CO stretching frequency change from 1096 cm^{-1} to 1019 cm^{-1}. These shifts in IR spectra refer to the combination between CE and C-steel happened via existing functional groups in it". Other functional groups have been absent, recommending that via the inhibitor adsorption on the C-steel surface might have occurred through these absent groups [62].

Mechanism of Corrosion Inhibition

The inhibitory mechanism includes the inhibitor adsorption on the C-steel surface dipped in aqueous polluted NaCl. "Four natures of adsorption [63] may occurring contain organic molecules at the interface among C-steel–solution interface: 1) Electrostatic attraction among the charged metal and the charged molecules; 2) Interaction of unshared electron pairs in the molecule through the metal; 3) Interaction of π-electrons in the metal; 4) Summation of all the above. From the observations drawn from the various tests, corrosion protection of C-steel in polluted NaCl solution by CE as designated from WL, PP and EIS tests were found to depend on the concentration and the nature of the extract. Some of the components of the extract may be protonated and these protonated species may be adsorbed on the cathodic sites of the C-steel surface via the π electron of the aromatic ring (Physical adsorption). On the other hand, the lone pair of electron of the heteroatoms (O, N, S) could interact with vacant d-orbital of Fe, thereby inhibit the anodic dissolution of the C-steel (chemical adsorption). Figure 13 represents the
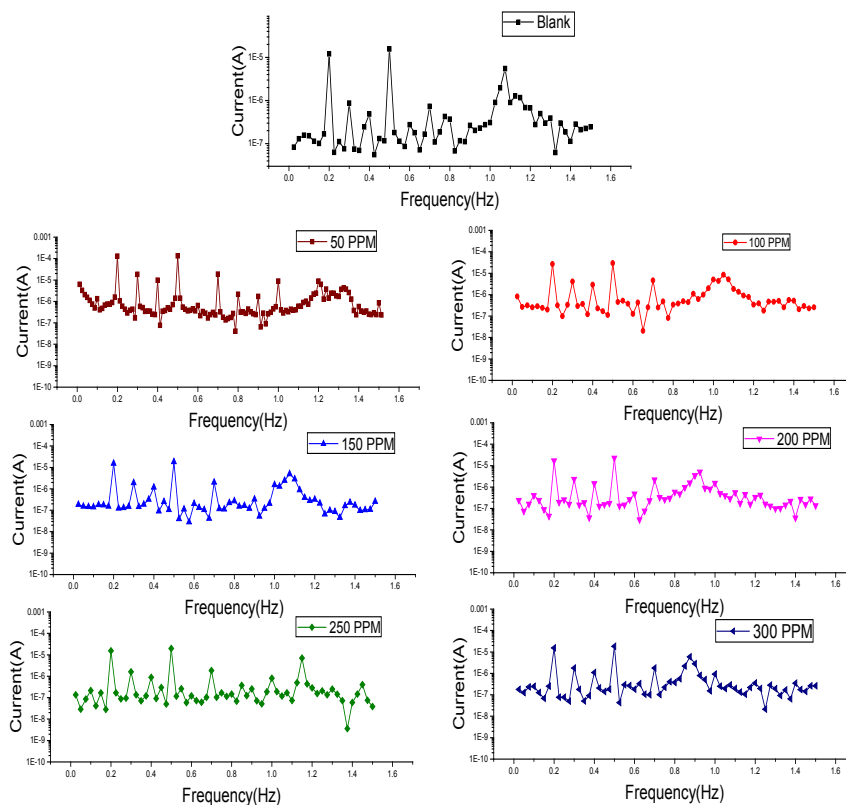
Fig. 9. EFM plots recorded for dissolution of C-steel in polluted NaCl solution with and without various concentrations of CE at 25ºC.
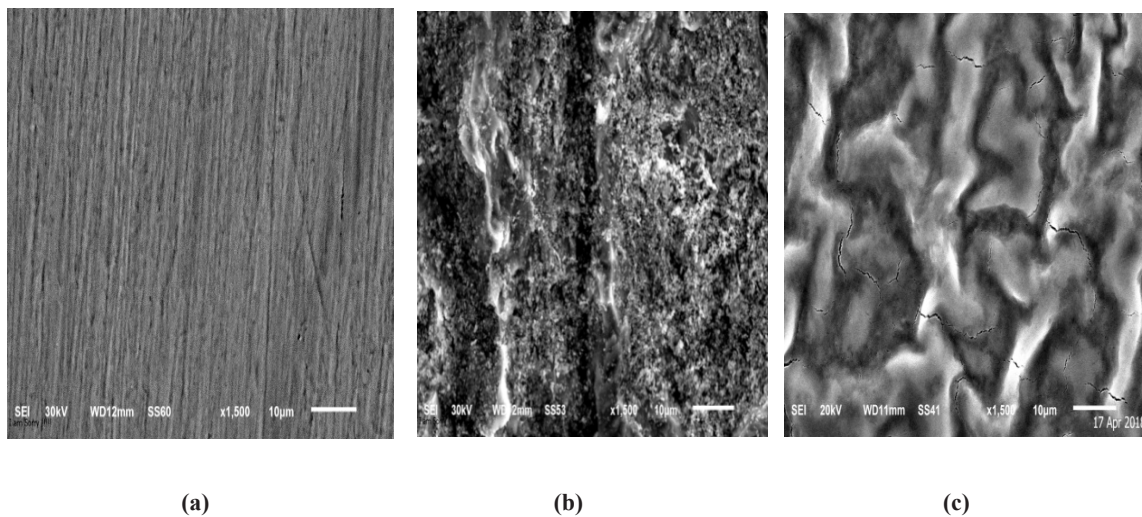

(a)　　　　　　　　　(b)　　　　　　　　　(c)

Fig. 10a. SEM of metal. (b) SEM of metal + polluted NaCl metal. (c) SEM of metal + polluted NaCl + 300 ppm of CE.

(a) Pure CS   **(b) Blank**
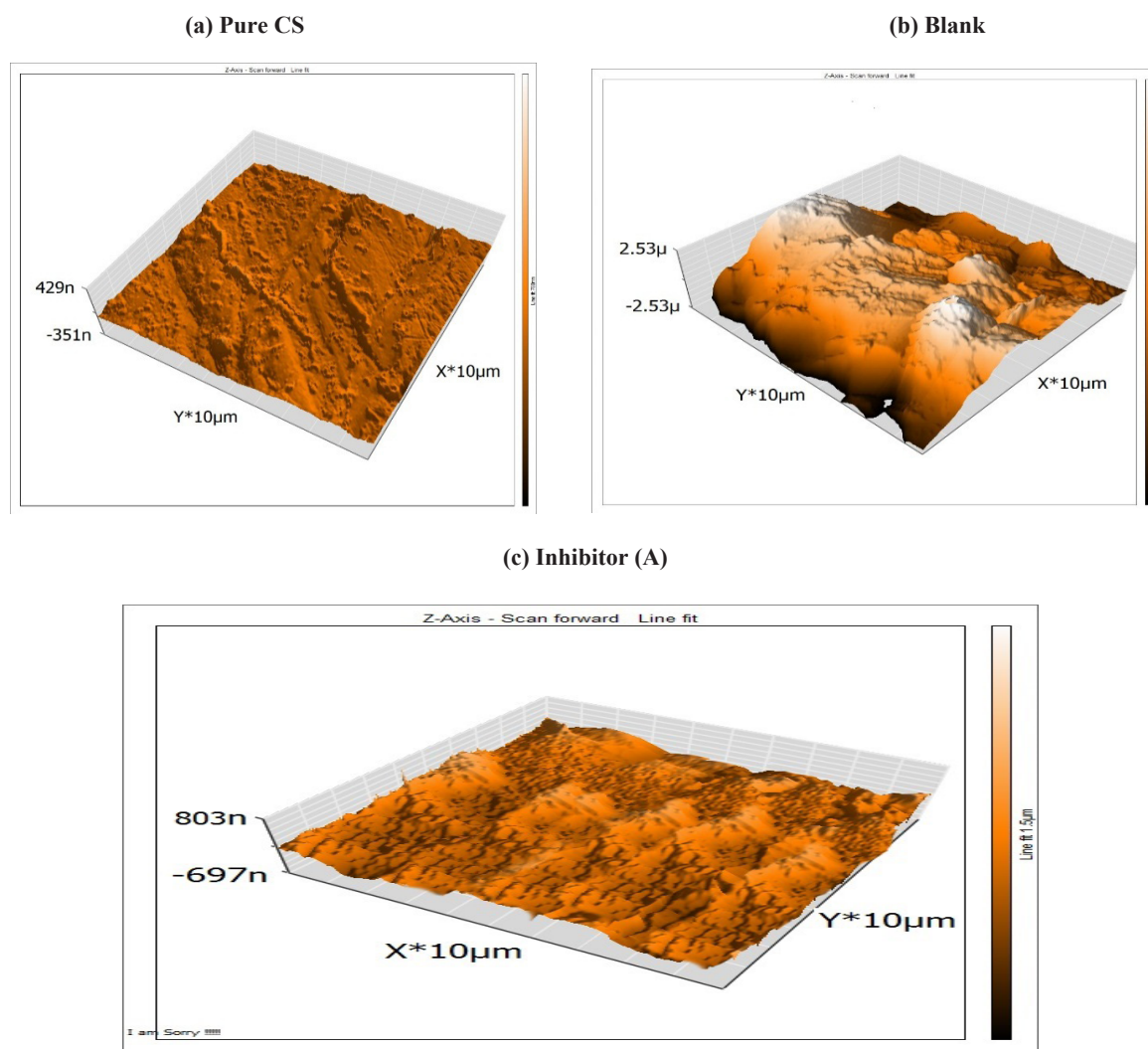

(c) Inhibitor (A)

Fig. 11. AFM images of C-steel surface (a) before of immersion in polluted NaCl (b) after 24 h of immersion in polluted NaCl and (c) after 24 h of immersion in polluted NaCl + 300 ppm of CE at 25ºC.
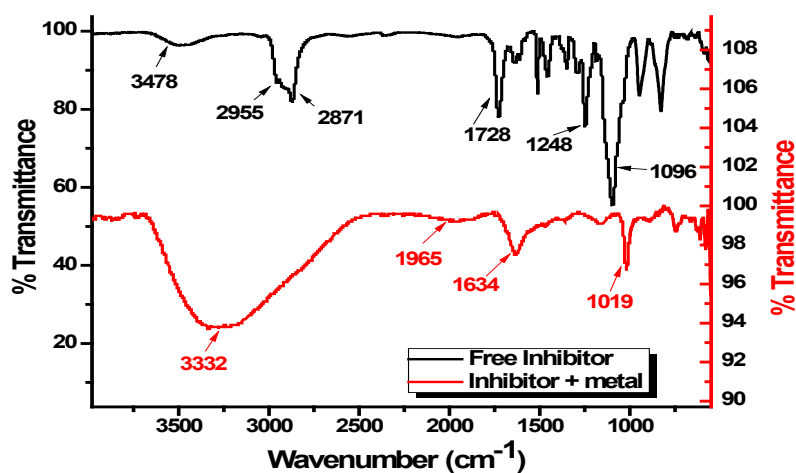

Fig. 12. FTIR spectra of CE sample (black line) and immersed in the 1M HCl +300 ppm CE (red line).
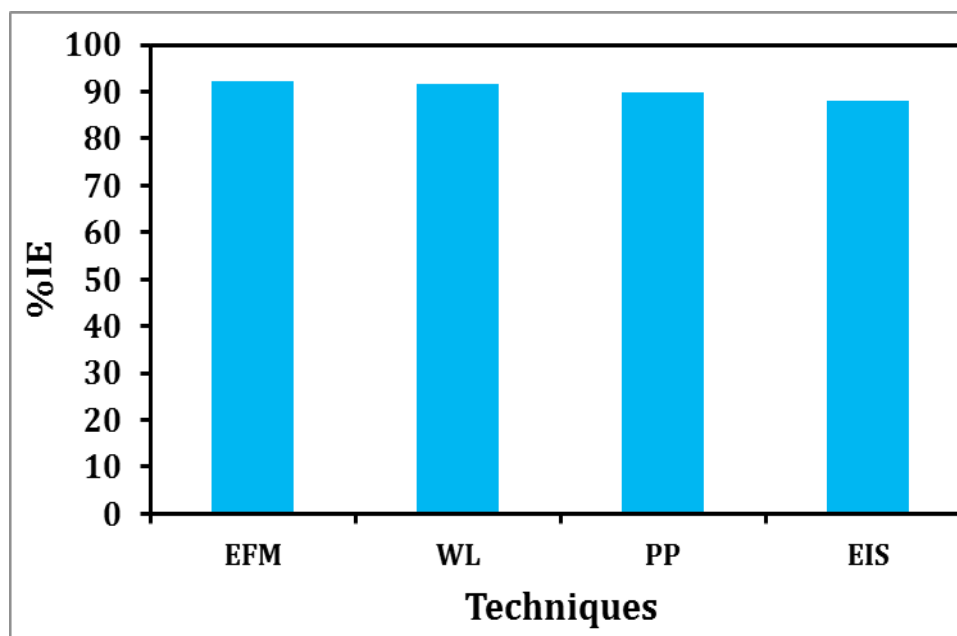
Fig. 13. Comparison between percent IE of 300 ppm CE as obtained from the different techniques.

comparison of %IE of 300 ppm CE obtained by different techniques, as shown from the figure that all techniques gave almost similar results.

Conclusion

The CE shows the corrosion protection for C-steel in polluted NaCl solution, where IE ratio improved by the rise of compound concentration. The IE is decreasing with the rise of temperature resulting from the destruction of the adsorbed CE molecules present on the C-steel surface. The presence of CE on the surface follows the Langmiur equation. Tafel curves showed that CE is mixed-kind inhibitor. C_{dl} reduced while R_{ct} rises by the increasing the CE concentration. The adsorbed film of the CE on the C-steel surface was proved by SEM, AFM and FTIR analysis.

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مستخلص القندول كمثبط صديق لتاكل الصلب الكربوني في كلوريد الصوديوم الملوث: الدراسات الكيميائيه والكهروكيميائيه

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هذه الدراسه تصف قدره مستخلص القندول لتثبيط الصلب الكربوني في محلول كلوريد الصوديوم الملوث (تركيز ٣,٥٪ كلوريد الصوديوم + ١٦جزء في المليون محلول كبريتيد الصوديوم) وذللك باستخدام عدة طرق كيميائيه (طريقه الفقد في الوزن) وطرق كهروكيميائيه (طريقه الاستقطاب الكهربي و طريقه المعاوقه الكهربيه وطريقه التردد الكهروكيميائي المعدل) حيث وجد ان سلوك عمليه الادمصاص تتبع ايزوثيرم لانجمير واظهرت نتائج الاستقطاب ان هذا المستخلص يؤثر علي كل من التفاعل المصعدي والمهبطي (النوع المختلط) حيث ان كفاءه التثبيط تزاد بزياده تركيز المستخلص وتقل بارتفاع درجه الحراره وقد تم اختبار سطح الصلب الكربوني باستخدام ميكروسكوب القوه الذريه و الميكروسكوب الالكتروني الماسح واختبار الاشعه فوق الحمراء وقد دلت النتائج بالطرق المختلفه انها متوافقه تماما.