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تثبيط تآكل الفولاذ الكربوني في محلول حمض الكبريت باستعمال خلاصة نبات حشيش الازوز

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المخلص:

تمت دراسة تأثير الخلاصة الطبيعية لنبات حشيش الازوز على تثبيط تآكل الفولاذ الكربوني في وسط محلول حمض الكبريت وذلك بطريقة فقدان الوزن وديناميكا جهد الاستقطاب وقياسات مطيافية الممانعة (EIS). أظهرت النتائج التجريبية التي تم الحصول عليها بأن خلاصة النبات المشار إليه هي مثبط جيد لتآكل المعدن الذي تم فحصه في وسط حمض الكبريت ذي ال 0.5 مولارية و أن فعالية الحماية تزداد عند زيادة التركيز لتصل الى نسبة 94% عند التركيز 4 غ/ل. دراسات ديناميكا جهد الاستقطاب كشفت بأن المثبط المدروس يتصرف كمثبط كاثودي. وبينت نتائج مطيافية الممانعة (EIS) بان التغير في معاملات الممانعة (مقاومة انتقال الشحنات و سعة الطبقة المزدوجة) مع التركيز لمستخلص نبات حشيش الازوز هو مؤشر على امتزاز جزيئي يؤدي إلى تشكيل طبقة واقية على سطح الفولاذ الكربوني. تمت دراسة تأثير درجة الحرارة و بيّنت أن قيم كفاءة التثبيط تتناقص مع الزيادة في درجة الحرارة. وأفادت النتائج أن امتزاز المركب تحت الدراسة على سطح الصلب يخضع لمنحنيات لانجمير للامتزاز. كما تم تعيين بعض الوظائف الحرارية مثل طاقة التثبيط والمحتوى الحراري لعملية تآكل الفولاذ الكربوني في وسط حمضي.

2004; Lecante et al., 2011; Lebrini et al., 2011; Benali et al., 2012; Bammou et al., 2011; Larif et al., 2012).

Plant extract is low-cost and environmentally safe, and so the main advantage of using plant extract as the corrosion inhibitor is due to both economic and environmental benefits. Up to now, many plant extracts have been used as effective corrosion inhibitors of iron or steel in acidic media (Satapathy et al., 2009; Chellammal et al., 2010; Behpoura et al., 2012; Hamdy and El-Gendy, 2013; Sethuraman et al., 2013).

In our laboratory, many studies have been published on the use of natural products as corrosion inhibitors in acidic media. Among these compounds we cite some extracts and essential oils such as: Verbena extract (Ben Hmamou et al., 2012a), Chamomile extract (Ben Hmamou et al., 2012b), *Marrubium Vulgare* L. extract (Ben Hmamou et al., 2012), Argan extracts (Ben Hmamou et al., 2012a,b; A a et al., 2011, 2012) Chamomile essential oil (Ben Hmamou et al., 2012c), Carob seed oil (Ben Hmamou et al., 2012d), Verbena essential oil (Ben Hmamou et al., 2012e), Prickly pear seed oil (Ben Hmamou et al., 2012f), Fennel oil (Lahhit et al., 2011) and Thymus oil (Bammou et al., 2010). These compounds tested have been reported to be excellent inhibitors for metals and alloys in acidic solutions.

The aim of the present work is to study the effect of the addition of *Chenopodium Ambrosioides* Extract (CAE) on the behavior of carbon steel corrosion in 0.5 M sulfuric acid solution.

2. Materials and methods

2.1. Material preparation and solutions

Carbon steel was used throughout the experiments. The chemical composition of carbon steel is given in Table 1.

The aggressive solution 0.5 M sulfuric acid was prepared by dilution of an Analytical Grade 98% H₂SO₄ with double distilled water. All experiments were carried out in 0.5 M H₂SO₄ solution in the absence and presence of different concentrations (0.1, 0.5, 1, 2 and 4 g/l) of CAE.

Stock solution of the plant extract was prepared by stirring cold weighed amounts of the *Chenopodium Ambrosioides* Extracts plant for 24 h in 1 M HCl solution. The resulting solution was filtered. This extract of this plant was used to study the corrosion inhibition properties and to prepare the required concentrations. The solution tests are freshly prepared before each experiment.

2.2. Gravimetric analysis

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat cooling condenser. The carbon steel specimens used have a rectangular form (2 · 1 · 0.3 cm). The duration of tests was 6 h at 298 K in

0.5 M H₂SO₄ solution containing different concentrations of CAE.

The specimens were abraded with a series of emery paper (grade 800 1200) and then washed thoroughly with acetone and double distilled water. After weighing precisely, the specimens were immersed in beakers which contained 100 ml acid solutions with different concentrations of CAE at a certain temperature maintained by a water thermostat. All the aggressive acid solutions were open to air. After 6 h the specimens were taken out, washed, dried, and weighed exactly.

2.3. Potentiodynamic polarization

Polarization measurements were carried out in a conventional three-electrode electrolytic cell. Saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes respectively. The working electrode is in the form of a rectangular disk from carbon steel of the surface 0.32 cm². These electrodes are connected to Voltalab PGZ 100 piloted by ordinate associated to Volta Master 4 software. The scan rate was 1 mV/s started from an initial potential of –1000 to 0 mV/SCE. Before recording each curve, a stabilization time of 30 min was allowed, which was proved to be satisfactory to attain a stable value for E_{cor} . All experiments were repeated three times at the desired temperature of –1 °C. Corrosion current densities were obtained from the polarization curves by linear extrapolation of the Tafel curves.

2.4. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was carried out with the same equipment used for the polarization measurements, leaving the frequency response analyzer out of consideration. Quasi-potentiostatic polarization curves were obtained using a sweep rate of 1 mV s⁻¹. After the determination of steady-state current at a given potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz was superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potential after 30 min of exposure. All potentials were reported versus saturated calomel electrode (SCE). The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

2.5. Scanning electron microscopy (SEM)

The morphology of state surface was performed using a JEOL JSM-5800 Scanning Electron Microscopy. The analysis by SEM was carried out on the surface of carbon steel samples before immersion and this after immersion in the acidic solutions with and without the optimal concentration of CAE inhibitor.

3. Results and discussion

3.1. Weight loss tests

The corrosion rate (W_{cor}) of tested metal in 0.5 M H₂SO₄ solution at different concentrations of CAE was determined after 6 h of immersion time at 298 K. The obtained values of the

Table 1 Chemical composition of C-steel.

Element	C	Si	Mn	Cu	S	Fe
Weight%	0.179	0.165	0.439	0.203	0.034	Balance

Table 2 Steel weight loss data and inhibition efficiency of CAE in 0.5 M H₂SO₄.

Conc. (g/l)	W_{cor} (mg cm ⁻² h ⁻¹)	E_w (%)
Blank	1.5482	
0.1	0.8732	44
0.5	0.5914	62
1.0	0.4490	71
2.0	0.2322	85
4.0	0.1223	92

gravimetric corrosion rates (W_{cor}) and the inhibition efficiency (E_w) are represented in Table 2. The inhibition efficiency (E_w) (%) corrosion in the case of this method was calculated from the following equation:

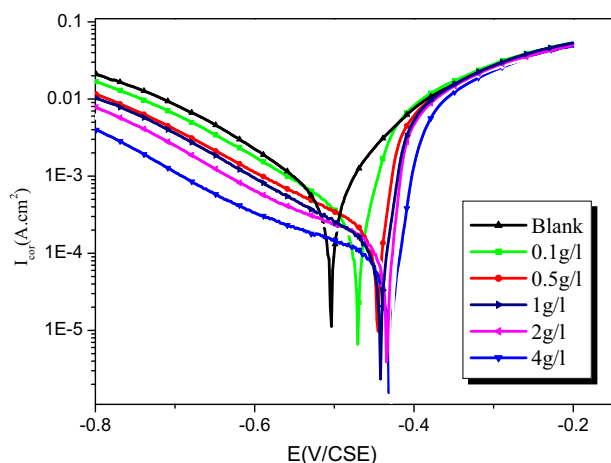
$$E_w(\%) = \left(\frac{W_{\text{cor}}^{\circ} - W_{\text{cor}}}{W_{\text{cor}}^{\circ}} \right) \times 100 \quad (1)$$

where W_{cor}° and W_{cor} are the corrosion rates of carbon steel due to the dissolution in 0.5 M H₂SO₄ in the absence and the presence of definite concentrations of the CAE, respectively.

Results obtained from gravimetric measurements show for inhibitor tested that the corrosion rate values decrease when the concentration of CAE increases. From the analysis of Table 2 it is very clear that protection efficiency increased with the increase in concentration from 0.1 to 4 g/l for the inhibitor studied. We noted that CAE used in this study showed very excellent corrosion inhibitor for carbon steel in 0.5 M H₂SO₄. The best action is attained in the presence of 4 g/l CAE.

3.2. Polarization results

The effect of CAE concentration on the corrosion behavior of carbon steel electrode in 0.5 M sulfuric acid solutions has been studied by polarization measurements and the recorded Tafel plots are shown in Fig. 1. From polarization curves, the electrochemical parameters as obtained are shown in Table 3. These include corrosion potential (E_{cor}), corrosion current

**Figure 1** Potentiodynamic polarization curves for steel in 0.5 M H₂SO₄ at various concentrations of CAE at 298 K.**Table 3** Potentiodynamic polarization parameters for steel in 0.5 M H₂SO₄ at various concentrations of CAE at 298 K.

Conc. (g/l)	I_{cor} (μA/cm ²)	E_{cor} (mV/SCE)	b_c (mV/dec)	E_p (%)
Blank	830	-505	-192	
0.1	448	-468	-195	46
0.5	290	-446	-198	65
1.0	209	-443	-191	75
2.0	149	-434	-190	82
4.0	52	-432	-189	94

density (I_{cor}) determined by extrapolation of the cathodic Tafel line to the corrosion potential, and cathodic Tafel slope (b_c). The inhibition efficiency E_p (%) is calculated from the values of I_{cor} with the relation:

$$E_p(\%) = \left(\frac{I_{\text{cor}}^{\circ} - I_{\text{cor}}}{I_{\text{cor}}^{\circ}} \right) \times 100 \quad (2)$$

where I_{cor} and I_{cor}° were the corrosion current densities with and without inhibitor.

Inspection of polarization curves and electrochemical parameter reveals that cathodic current densities decrease considerably in the presence of CAE inhibitor in acidic media. On the other hand, a compound is usually classified as an anodic or a cathodic type inhibitor when the change in E_{corr} value is larger than 85 mV (Musa et al., 2010; Zhang et al., 2011). Since the small displacement of the corrosion potential was about 73 mV (Table 2) after the addition of the CAE, suggesting that the inhibitor acted as a mixed-type inhibitor with tendency to anodic inhibitor.

Tafel behavior characterized by linear regions in the vicinity of the corrosion potential indicates that the hydrogen evolution reaction is activation controlled. In the presence of CAE, the slight change of the cathodic Tafel slope (b_c) indicates that the corrosion mechanism of carbon steel does not change. The free corrosion potential determined after 30 min of immersion does not change in the existence of the inhibitor. The dependence of the inhibition efficiency versus the inhibitor concentration of CAE is also showed in Table 3. The inhibition efficiency obtained indicates that CAE acts as effective inhibitor. Indeed, the values 4 g/l.

3.3. Electrochemical impedance spectroscopy measurements

The Nyquist representations of impedance behavior of carbon steel in 0.5 M H₂SO₄ in the absence and the presence at different concentrations of CAE plotted at open circuit potential (E_{cor}) at 298 K after 30 min are given in Fig. 2.

It is observed from Fig. 2a and Fig. 2b, the impedance diagrams show depressed semicircles indicating a charge transfer process mainly controls the corrosion of carbon steel. In fact, the presence of CAE enhances the value of charge transfer resistance (R_{ct}) in acidic solution (Hukovic-Metikos et al., 2002). The diameter of the capacitive loop in the presence of CAE is larger than that in the blank solution, and increases with the inhibitor concentration. This indicates that the impedance of inhibited substrate increases with the inhibitor concentration.

The EIS results of these capacitive loops are simulated by the equivalent circuit exposed in Fig. 3 to purify electric

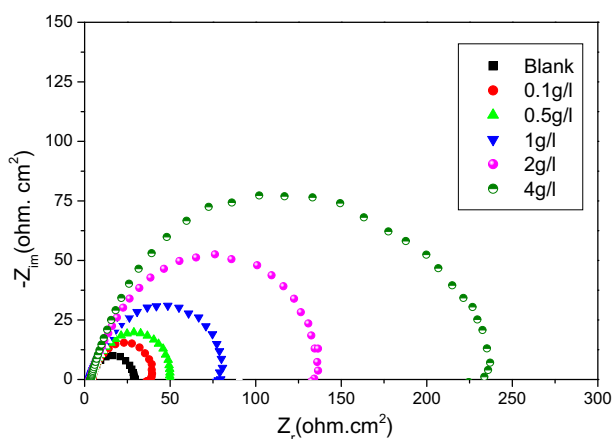


Figure 2a Nyquist plots of steel in 0.5 M H₂SO₄ without and with different concentrations of CAE at 298 K.

models that could verify or rule out mechanistic models and permit the calculation of numerical values corresponding to the physical and/or chemical properties of the electrochemical system under investigation (Priya et al., 2008). The impedance parameters derived from these studies using Z-view software are summarized in Table 4. The values of charge transfer resistance (R_{ct}) that increased with inhibitor concentrations may suggest the formation of a protective film on the electrode/solution interface (Anejjar et al., 2014; Bentiss et al., 2000; Murlidharan et al., 1995). The values of surface inhomogeneity coefficient (n) decrease with increasing of the inhibitor concentration. The value of capacitance (C_{dl}) can be calculated from CPE (Q) and a resistor (R_{ct}), using the following relation (Martinez and Metikos-Hukovic, 2003; Ma et al., 2000):

$$C_{dl} = (Q \cdot R_{ct}^{1-n})^{1/n} \quad (3)$$

The decrease in C_{dl} may be due to the adsorption of this compound on the metal surface leading to the formation of layer from acidic solution (Lebrini et al., 2007). The inhibition efficiency got from the charge transfer resistance is calculated by:

$$E_{EIS}(\%) = \left(\frac{R_t^0 - R_t}{R_t^0} \right) \times 100 \quad (4)$$

where R_t and R_t^0 are the transfer resistance in the absence and presence of *Chenopodium Ambrosioides* inhibitor, respectively.

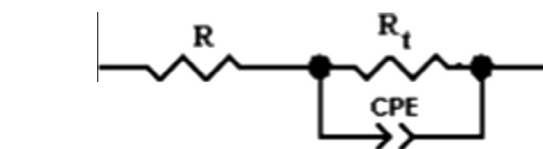
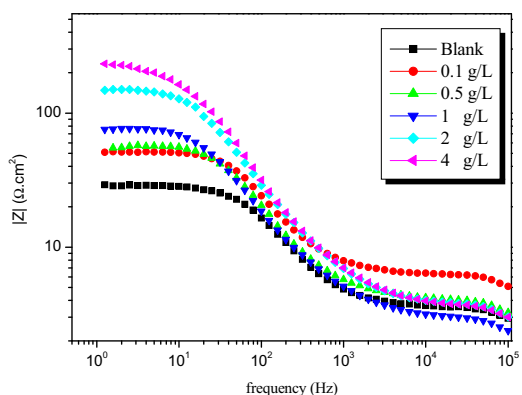


Figure 3 The equivalent circuit of the impedance spectra obtained for CAE at 298 K.

The elevation values of inhibition efficiency by increasing inhibitor concentration can be attributed to the increase in the number of adsorbed organic molecules against carbon steel surface.

The smaller inductive loop obtained at lower frequency in the graphs can be attributed to the relaxation of adsorbed compounds (Aoki et al., 2002). The inhibition efficiency value calculated from EIS data is in good agreement with those obtained from electrochemical polarization and weight loss methods.

3.4. Effect of temperature

Figs. 4 and 5 show the effect of temperature on the corrosion behavior of carbon steel using polarization methods at the temperature range of 298–328 K in the absence and the presence of CAE at 4 g/l in 0.5 M H₂SO₄. Table 5 summarizes the electrochemical parameters deduced from the impedance spectra using Zview software and inhibition efficiency determined by relation (4). From these results, we note the important diminution of R_{ct} values when the temperatures of blank solution increase. In the presence of the tested inhibitor, the dissolution of carbon steel is extensively retarded. The inhibition efficiencies are found to decrease with increasing the solution temperature from 303 to 333 K. This behavior can be interpreted on the basis that the increase in temperature results in desorption of the inhibitor from the surface of carbon steel. Similar behavior was observed in the case of *Ervatamia coronaria* extract in the same medium (Sethuraman et al., 2013).

Since it is known that the corrosion rate is inversely proportional to R_{ct} , the values of $\log(1/R_{ct})$ and $\log(R_{ct}T)^{-1}$ were plotted as a function of $10^3/T$ in Figs. 6 and 7 for the corrosion carbon steel in 0.5 M sulfuric acid solutions in the absence and presence of CAE at 4 g/l. The values of activation energy E_a and activation enthalpy ΔH_a^\ddagger were estimated using Arrhenius equation and transition state equation:

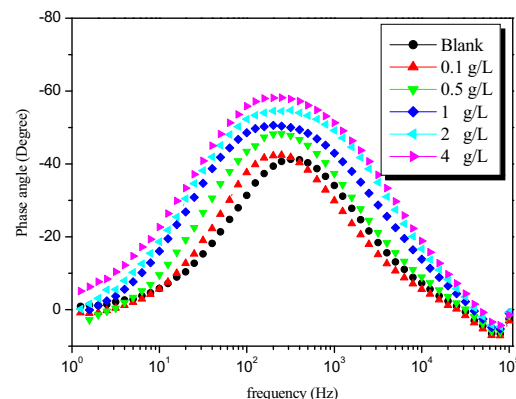


Figure 2b Bode plots of steel in 0.5 M H₂SO₄ without and with different concentrations of CAE at 298 K.

Table 4 Impedance parameters for corrosion of steel in 0.5 M H₂SO₄ without and with different concentrations of CAE at 298 K.

Concentration (g/l)	R_f (Ω cm ²)	n	Q (S ⁿ / Ω cm ²)	C_{dl} (μ F cm ⁻²)	E_{EIS} (%)
Blank	26	0.86	$1.5 \cdot 10^{-4}$	61	
0.1	45	0.89	$1.1 \cdot 10^{-4}$	57	42
0.5	61	0.84	$1.36 \cdot 10^{-4}$	55	57
1.0	77	0.82	$1.38 \cdot 10^{-4}$	51	66
2.0	150	0.81	$1.16 \cdot 10^{-4}$	42	83
4.0	238	0.80	$0.97 \cdot 10^{-4}$	38	89

$$\frac{1}{R_{tc}} = A \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

$$\frac{1}{TR_{tc}} = \frac{R}{Nh} \exp\left(\frac{\Delta S_a^*}{R}\right) \exp\left(-\frac{\Delta H_a^*}{RT}\right) \quad (6)$$

where A is the Arrhenius pre-exponential factor, R is the perfect gas constant, N is Avogadro's number and h is Plank's constant. The values of E_a , ΔH_a^* were estimated from the precedent equations given in Table 6.

It is clear that the activation energy increases in the presence of CAE extract and consequently the rate of corrosion decreases.

The positive sign of ΔH_a^* shows that the corrosion process of carbon steel is an endothermic phenomenon signifying that its dissolution is slow in the presence of CAE (Guan et al., 2004).

The analysis of results of Table 6 shows that the values of E_a and ΔH_a^* enhanced with the inhibitor concentration suggest that the energy barrier of corrosion reaction increases with presence of CAE extract. This means that the corrosion reaction will further be pushed to surface sites that are characterized by progressively higher values of E_a in the presence of the inhibitor (Larabi et al., 2007).

3.5. Adsorption isotherm

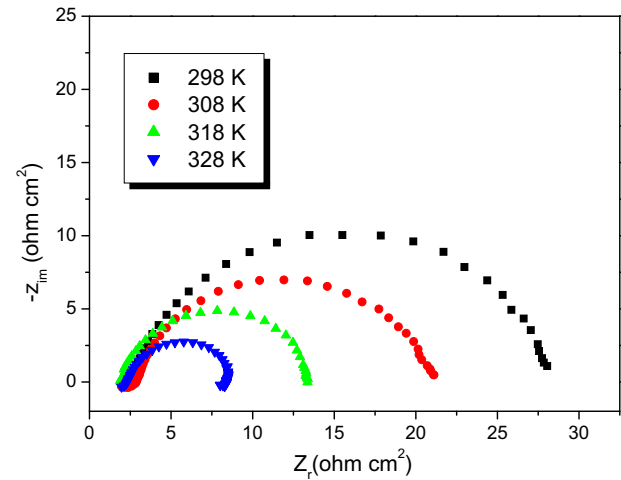
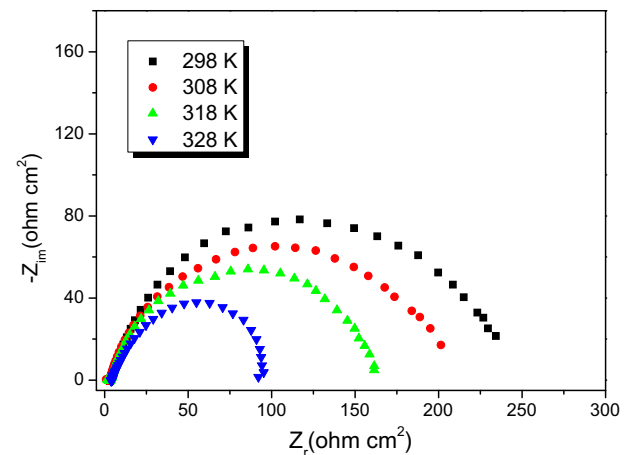
The mechanism of the interaction between inhibitor and the electrode surface can be explained using adsorption isotherms. The surface coverage values (θ) for different concentrations of CAE in 0.5 M H₂SO₄ solution using the following formula are:

$$\theta = \frac{E_{EIS}(\%)}{100} \quad (7)$$

The linear regression obtained by plotting the graph of C_{inh}/θ vs. C_{inh} is present in Fig. 8. The adsorption of CAE on the carbon steel surface in 0.5 M H₂SO₄ solution obeyed the Langmuir adsorption isotherm following relation:

$$\frac{C_{inh}}{\theta} = \frac{1}{k_{ads}} + C_{inh} \quad (8)$$

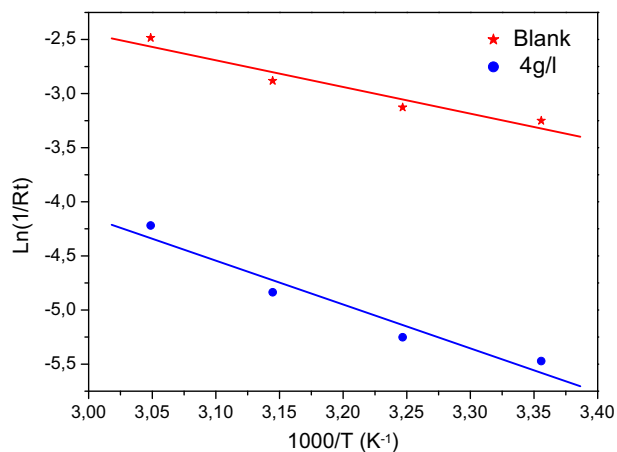
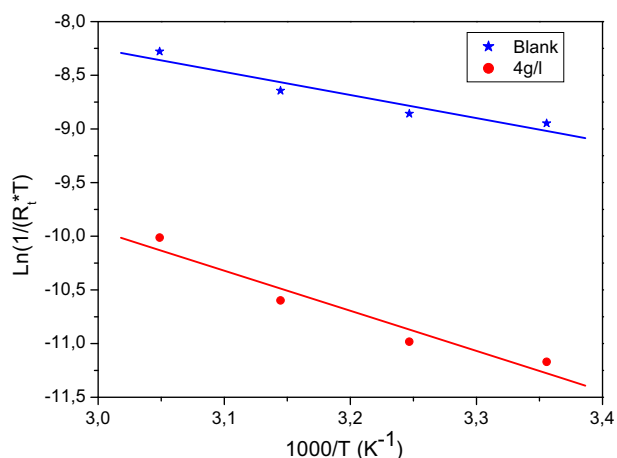
It should be noted that, CAE is composed of numerous naturally occurring organic compounds and revealed the presence of phenolic compounds, tannins, flavonoids, steroids and others (Sousa et al., 2012; Matos, 1997). Accordingly, the inhibitive action of CAE could be attributed to the adsorption of its components on the steel surface. The main constituents of CAE contain O, N atoms in functional groups (O-H, C=O, C-O, N-H) and O-heterocyclic rings, which meet the general characteristics of typical corrosion inhibitors. Thus, it is

**Figure 4** Nyquist plots for corrosion of steel in 0.5 M H₂SO₄ at different temperature.**Figure 5** Nyquist plots for corrosion of steel in 0.5 M H₂SO₄ + 4 g/l CAE at different temperatures.

reasonable to deduce that the flavonoids, ginkgolides and aminoacids in CAE exhibit the inhibition performance. These main chemical compounds of CAE might be protonated in acid media. The charge of the metal surface is determined by the minus value of $E_{cor} - E_q = 0$ (zero charge potential) (Schweinsberg and Ashworth, 1988; Deng and Li, 2012). The $E_q = 0$ of iron is -550 mV vs. SCE in H₂SO₄ (Roy et al., 1988). In the present system, the values of E_{cor} in 0.5 M

Table 5 Impedance parameters for corrosion of steel in 0.5 M H₂SO₄ without and with different concentrations of CAE at 298 K.

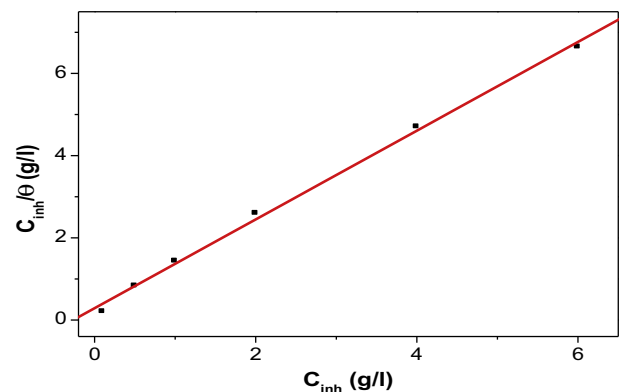
	Temp. (K)	R_t (Ω cm ²)	n	Q (S ⁿ / Ω cm ²)	C_{dl} (μ F cm ⁻²)	E_{EIS} (%)
Blank	298	26	0.86	$1.5 \cdot 10^{-4}$	61	
	308	23	0.84	$1.8 \cdot 10^{-4}$	63	
	318	18	0.86	$1.65 \cdot 10^{-4}$	64	
	328	14	0.88	$1.64 \cdot 10^{-4}$	70	
4 g/l	298	238	0.82	$0.97 \cdot 10^{-4}$	38	89
	308	191	0.81	$1.34 \cdot 10^{-4}$	54	88
	318	148	0.81	$1.55 \cdot 10^{-4}$	60	88
	328	75	0.79	$1.89 \cdot 10^{-4}$	62	82

**Figure 6** Arrhenius plots of steel in 0.5 M H₂SO₄ with and without 4 g/l CAE.**Figure 7** Variation of $\ln(1/(R_t \cdot T))$ versus $10^3/T$ for blank and 0.5 M H₂SO₄ + 4 g/l of CAE.

H₂SO₄ are -505 mV vs. SCE. The steel surface charges are positive in 0.5 M H₂SO₄ solutions because of $E_{corr} - E_q = 0 > 0$. The acid anions of SO₄²⁻ could be specifically adsorbed; they create excess negative charge toward the solution, and favor more adsorption of the cations (Bentiss et al., 2000). Then the protonated inhibitor may adsorb on the negatively charged metal surface through electrostatic interactions. In other

Table 6 The value of activation parameters for steel in 0.5 M H₂SO₄ in the absence and presence of 4 g/l of CAE.

	E_a (kJ mol ⁻¹)	ΔH_a^s (kJ mol ⁻¹)
Blank	20.50	17.91
4 g/l	33.70	31.1

**Figure 8** Langmuir isotherm adsorption of CAE on the steel electrode in 0.5 M H₂SO₄ obtained by Zview (EIS).

words, there is a synergism between SO₄²⁻ and protonated inhibitor. When protonated chemical molecules in CAE are adsorbed on steel surface, a coordinate bond may be formed by partial transference of electrons from O, N atoms to vacant d orbitals of Fe. In addition, owing to lone-pair electrons of O, N atoms in CAE, CAE may combine with freshly generated Fe²⁺ ions on steel surface to form the metal inhibitor complexes. These complexes might get adsorbed onto steel surface by van der Waals force to form a protective film which keeps C38 steel from corrosion. Survey of the literature showed the suitability of CAE (alone and in combination with lecithin and citric acid) for stabilization of unsaturated compounds in the food and pharmaceutical industry has been suggested (Gawlik-Dziki et al., 2013). The effect is essentially due to the presence of monoterpenes as caridole and 1,2,3,4-tetrahydro-p-menthane (Gawlik-Dziki et al., 2013).

3.6. SEM analysis

Surface state of carbon steel electrode was studied by scanning electron microscopy, Fig. 9 presents a SEM image obtained on

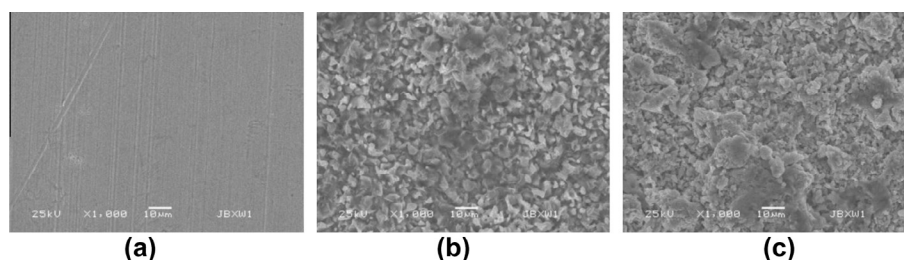


Figure 9 SEM (x1000) of carbon steel (a) before immersion (b) after 6 h of immersion in 0.5 M H₂SO₄ (C) after 6 h of immersion in 0.5 M H₂SO₄ + 4 g/l of CAE.

the carbon steel surface before immersion and after its immersion in 0.5 M H₂SO₄ with and without the addition of the CAE at 4 g/l during 06 h at 298 K.

From Fig. 9a, it can be seen that the fresh carbon steel surface state was uniform. Nevertheless, after immersion a radical change of the surface state is observed. In the case the absence of inhibitor the surface state was strongly damaged due to some cracks and pits as a result of the attack of corrosive solution (Fig. 9b). In the presence of CAE inhibitor, SEM micrograph showed in Fig. 9c provides the formation of thick films on carbon steel surface. It is revealed that there is a good protective layer adsorbed on the specimen's surface which is responsible for the inhibition of corrosion.

4. Conclusion

From the principal result of the present work we can conclude that:

- CAE mainly acts as excellent inhibitor for the corrosion of carbon steel in 0.5 M H₂SO₄.
- Inhibition efficiency increases with an increase in the concentration of CAE.
- The inhibition efficiency is not affected generally with temperature.
- A good agreement is obtained for the inhibition efficiency determined by gravimetric, EIS and polarization methods.
- The adsorption of CAE on the carbon steel surface obeys the Langmuir isotherm model.

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