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Effect of anise oil as a green inhibitor on steel corrosion behaviour

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Abstract

The effect of oil of anise (OA) as an eco-friendly inhibitor for carbon steel corrosion have been investigated in 1.0 M hydrochloric acid solution by polarization curves, electrochemical impedance spectroscopy (EIS) and gravimetric techniques. Anise oil efficiently inhibited the carbon steel corrosion. The highest value of inhibition efficiency is 95.3% obtained by potentiodynamic polarization and 92.93% by electrochemical impedance spectroscopy measurement at maximum concentration tested. The inhibition efficiency augmented with increase in anise oil concentration but reduced with growth in temperature. Polarization curves show that the tested oil may be considered as mixed type inhibitor and the inhibitor absorption on the carbon steel electrode obeys the Langmuir isotherm. The EIS results indicate that the changes in impedance parameters are related to the adsorption of OA on the alloy surface.

Keywords: Anise oil, green inhibitor, corrosion

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1. Introduction

The investigation of corrosion of iron and its alloys is a subject of enormous experimental preoccupation seen the economic losses and environmental pollution caused by this phenomenon during manufacture of metal alloys [1-2]. The use of chemical inhibitors is the important method of protecting metallic materials against dissolution owing to corrosion phenomenon [3-6]. Toxicity and the high cost of chemical compounds are led researchers to look for other alternatives using green inhibitor extracted from various plants. The green or ecofriendly inhibitors exhibited excellent efficiency as corrosion inhibitors for different metals and alloys in acidic media [7-9]; some tested the effect of oil compounds [10-13], while others studied the use of extract compounds [14-18]. The objective of the present work is to investigate the effect of anise oil on the inhibition behaviour for carbon steel corrosion in 1.0 M hydrochloric acid using potentiodynamic polarization, electrochemical impedance spectroscopy and gravimetric measurements.

2. Experimental conditions

2.1. Electrode, solution and electrochemical cell

The experiment test were executed on carbon steel electrode of the following composition (wt.%): 0.370 % C, 0.230 % Si, 0.680 % Mn, 0.016 % S, 0.077 % Cr, 0.011 % Ti, 0.059 % Ni, 0.009 % Co, 0.160 % Cu, and Fe balance. The samples were polished mechanically with different grades (600, 800, and 1200) silicon carbide paper, degreased in acetone, washed with distilled water and dried in warm prior to each use. The test solution was prepared from analytical-grade 37 % HCl with bi-distilled water. The corrosion behaviour was tested in 1.0 M HCl solution in the absence and presence of different concentrations of anise oil. The electrochemical cell used in this study is equipped with three electrodes. The sample of carbon steel constitute the working electrode, the reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode.

2.2. Gravimetric measurements

The gravimetric tests were realized on the carbon steel specimens having as form sheets of 2.5 cm 2.0 cm 0.6 cm that were polished with different grades of emery papers (600, 800 and 1200) and then washed with acetone and bi-distilled water. Before and after 6h of immersion in the acidic medium with and without addition of different concentrations of anise oil (0.5, 1.0, 2.0 and 4.0 g/L) at 303 K, the samples are weighed using analytical balance of accurately.

The corrosion rate (**C_R**) was calculated by the following equation:

$$C_R = \frac{w}{St} \qquad (1)$$

Where w is the weight loss of carbon steel specimen, S was the total area of one carbon steel sheet, and t was time of immersion. The inhibition efficiency (IE_{wt} %) obtained from corrosion rate can be evaluated using the following Equation:

$$IE_{wt}\% = \frac{C_R^o - C_R}{C_R^o} \qquad (2)$$

2.3. Electrochemical techniques

Electrochemical measurements were conducted using a PGZ100 potentiostat operated by VoltaMaster 4 software. The study of interface electrode/solution by electrochemical impedance spectroscopy (EIS) were realized after 30 min immersion at corrosion potential (Ecor) at the considered temperature. The recording of curves was drawed over a frequency range of 100 kHz -10 mHz, with a signal amplitude perturbation of 5 mV. The EIS data were treated with Zview 2 software, also the equivalent circuit were deducted. The inhibition efficiency (IE_{Rt}%) from charge transfer resistance was evaluated using the equation :

$$IE_{Rt}(\%) = \frac{R_t - R_t^0}{R_t} \times 100 \qquad (3)$$

Where R_t^0 and R_t are the charge transfer resistance values without and with anise oil, respectively.

The Potentiodynamic polarization curves were performed by increasing the potential with a scan rate of 1 mV/s from -800 mV to 200 mV against SCE with the same equipments used in electrochemical impedance spectroscopy. The electrochemical parameters related to the polarization curves: corrosion potential (Ecor), corrosion current density (Icor), anodic (ba) and cathodic (bc) Tafel slopes were deduced from Origin software. The inhibition efficiency (IE_{Icor} %) from Icor was calculated using the equation:

$$IE_{Icor}(\%) = \frac{I^0_{cor} - I_{cor}}{I^0_{cor}} \times 100 \quad (4)$$

Where Icor and I°cor are the corrosion current densities the inhibited and the uninhibited solutions by anise oil, respectively.

3. Results and discussion

3.1. Concentration effect

3.1.1. Gravimetric tests

Different corrosion rates (C_R) and inhibition efficiencies (IE_{wt} %) values obtained by gravimetric measurements for natural compound tested as inhibitor on the corrosion behaviour of carbon steel at different concentrations in 1.0 HCl are summarized in Table 1.

Table 1. Corrosion parameters obtained from gravimetric measurements for carbon steel in 1.0 M HCl containing various concentration of anise oil at 303 K.

Inhibitor	Concentration (g/L)	C_R (mg cm^{-2} h^{-1})	IE_w (%)	Θ
Blank	-	1.135	-	-
OA	4.0	0.059	**94.80**	0.948
	2.0	0.185	**83.70**	0.837
	1.0	0.338	**70.22**	0.702
	0.5	0.444	**60.88**	0.608

From Table 1 and the fig. 1, it is clear that the decreasing of corrosion rate is accompanied to the rising of inhibition efficiency values when increasing the concentration of the tested compound. we can be concluded that the portion of electrode area protected by molecules of tested inhibitor and that leads to an increase in the inhibition efficiencies.

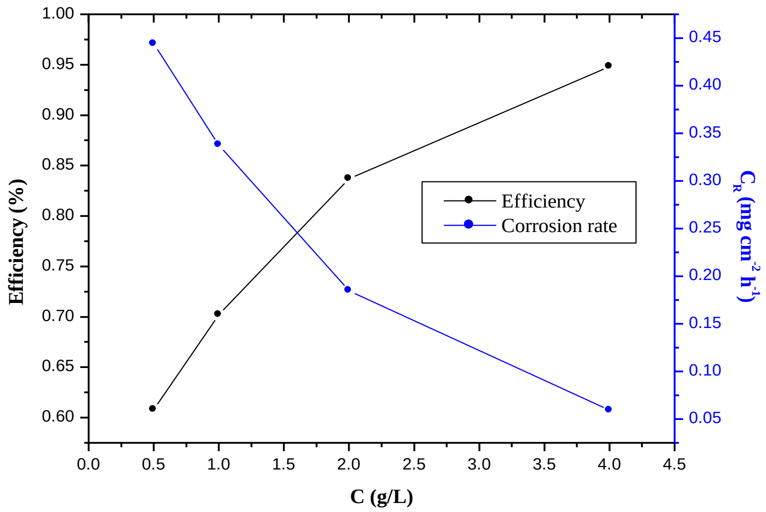

Figure 1. Relationship between the corrosion rate, the inhibition efficiency and OA concentrations for carbon steel after 6 h immersion in 1.0 M HCl at 303 K.

3.1.2. Polarization results

The influence of the anise oil on the corrosion and inhibition of carbon steel in 1.0 HCl solutions was studied. Fig. 2 exhibited the potentiodynamic polarization curves of carbon steel in uninhibited and inhibited solutions by different concentrations of anise oil. The various electrochemical corrosion parameters determined from this curves and the inhibition efficiency (IE) estimated using equation (4) are compiled in Table 2.

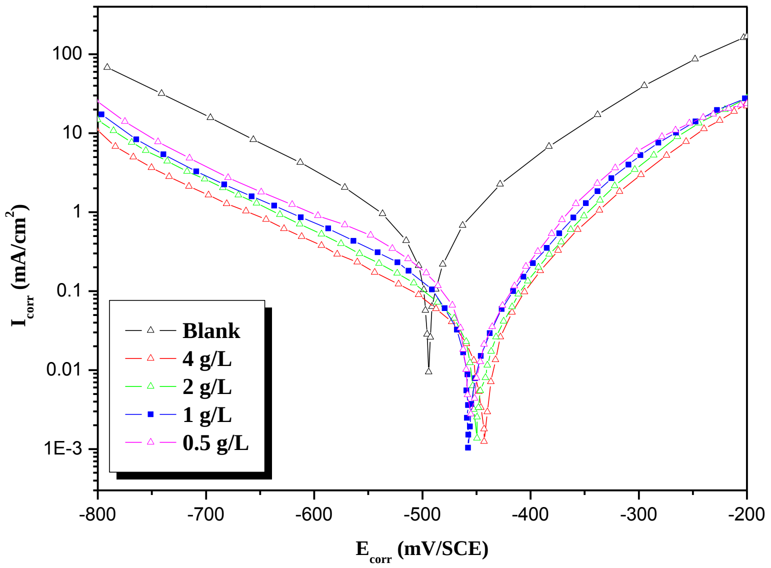

Figure 2. Polarisation curves of carbon steel in 1.0 M HCl for carbon steel at various concentrations of OA at 303K

Table 2. Polarization data of carbon steel in 1.0 M HCl without and with various concentrations of OA at 303 K.

Inhibitor	C (g/L)	$-E_{cor}$ (mV/SCE)	-βc (mV dec^{-1})	I_{cor} (µA cm^{-2})	IE_{Icor} (%)	Θ
Blank	-	496.0	162.00	564.0	-	-
Anise oil	4.0	448.3	157.72	26.3	**95.3**	0.953
	2.0	450.0	143.42	95.6	**83.0**	0.830
	1.0	451.3	167.88	161.5	**71.4**	0.714
	0.5	451.8	160.72	213.0	**62.2**	0.622

We can be seen from the figure, the cathodic and anodic current densities decrease clearly with the introduction of anise oil in the corrosive solution and the corrosion potential (E_{cor}) in inhibited solution slightly displaced toward the positive direction compared to the uninhibited solution.

Tafel behaviour characterised by linear regions in the vicinity of the potential of corrosion, indicates that the process of reduction of the hydrogen is an activation control. The cathodic polarization curves offer to parallel Tafel lines showing that there is no change of the hydrogen evolution reaction process then of addition of anise oil in the corrosive medium. Addition of anise oil in the corrosive medium reduces the anodic current density related to metal dissolution, thus that the cathodic hydrogen evolution reaction. Inspection of Table 2, It is clear that the value of corrosion current density (I_{cor}) clearly diminish with addition of inhibitor for various concentrations. The highest value of inhibition efficiency is recorded at the optimum concentration 4.0 g/L. we can concluded that the tested oil is excellent inhibitor for carbon steel in acidic medium.

3.1.3. Electrochemical impedance spectroscopy measurements

Electrochemical impedance spectroscopy is a very destined and effective instrument to study of corrosion process. Also we permit to establish the electrical circuit for studied system (metal/solution).

Nyquist plot for carbon steel recorded in the both cases of uninhibited and inhibited acid solution by anise oil concentrations are shown in Fig. 3.

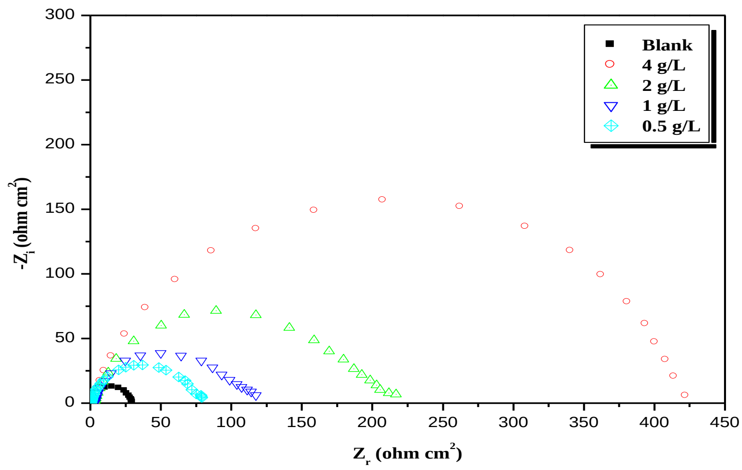

Figure 3. Nyquist diagrams for carbon steel in 1.0 M HCl containing different concentrations of OA at 303 K

The impedance diagram obtained for different inhibited solution (0.5 - 4.0 g/L) by anise oil is very similar for that recorded in the absence of inhibitor, this indicate that the interface mechanism is no modified [19]. They present a single depressed capacitive semi-circle. The impedance parameters obtained by fitting the EIS data Fig.4 by equivalent circuit using Zview software, and the values of inhibition efficiencies are summarized in Table 2. The equivalent circuit includes of a resistor R_t, in parallel with constant phase element (CPE) in serie with a electrolyte resistor R_s (Fig. 5).

Table 2. Impedance parameters for corrosion of carbon steel in 1.0 M HCl in the absence and presence of different concentrations of OA at 303 K.

Inhibitor	C (g/L)	R_{ct} (Ω cm^2)	n	Q×10^{-4} (s^n Ω^{-1}cm^{-2})	C_{dl} (μF cm^{-2})	IE_{Rt} (%)	Θ
Blank	-	29 .35	0.91	1.7610	91.63	-	-
Anise oil	4.0	415.3	0.91	0.2166	13.59	**92.93**	0.929
	2.0	197.6	0.88	0.3612	18.41	**85.14**	0.851
	1.0	105.2	0.90	0.4203	23.01	**72.10**	0.721
	0.5	72.36	0.94	0.6119	43.29	**59.43**	0.594

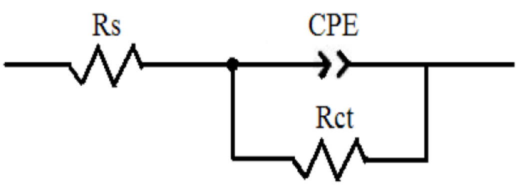

Figure 4. EIS Nyquist plots for carbon steel in 1.0 M HCl with 0.5 g/L ANIS interface: dotted lines experimental data; dashed line calculated.

The CPE representing the metal–solution interface considered as a capacitor with irregular surface. The CPE impedance is given as follows [20]:

$$Z_{CPE} = \frac{1}{Y_0(j\omega)^n} \quad (5)$$

where Y_0 is the constant of CPE, j is the imaginary unit, ω is the angular frequency and n is the CPE exponent which can be explained as a degree of surface inhomogeneity.

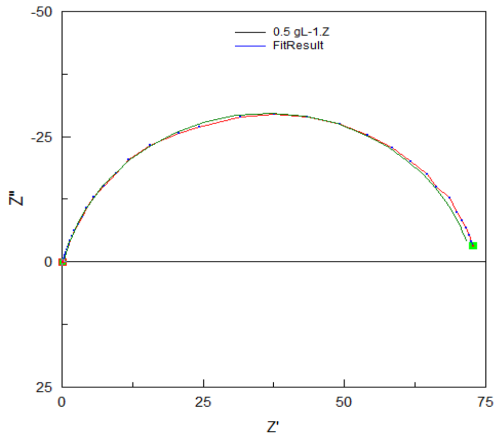

Figure 5. Equivalent electrical circuit corresponding to the corrosion process on the carbon steel in hydrochloric acid.

Inspection of EIS data, the charge-transfer resistance value R_t increased with increasing inhibitor concentration, indicating that the recovery of the metal surface is performed by the adsorption of inhibitor molecules. The decrease in C_{dl} with increases of inhibitor concentration, this behaviour can be du to a rise in the thickness of the double layer and/or a diminution in local dielectric constant, this variation explained the inhibitor molecule function by adsorption at electrode/solution interface [21]. We can conclude thus, the EIS result confirms that obtained by the potentiodynamic polarisation and gravimetric measurements.

3.2. Effect of temperature

The study effect of temperature is very important seen your their impact on interface metal-solution behaviour. The polarization curves of carbon steel in 1 M HCl without and with addition of anise oil as inhibitor recorded at various temperatures between 303 K and 333 K (Figs. 6 and 7). Electrochemical parameters obtained from these plots and the inhibition efficiencies evaluated from I_{cor} values are listed in Table 3.

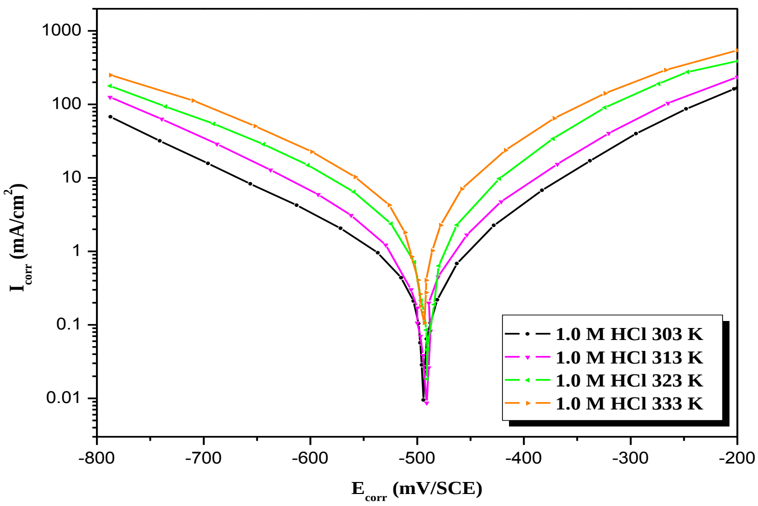

Figure 6. Potentiodynamic polarisation curves of carbon steel in 1.0 M HCl at different temperatures.

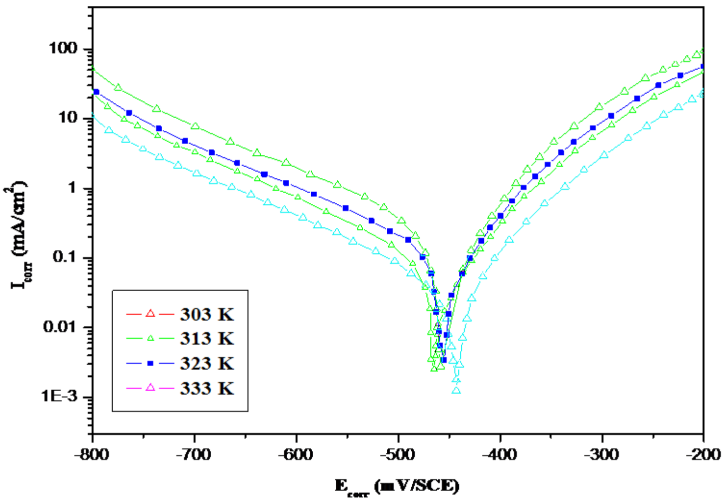

Figure 7. Potentiodynamic polarisation curves of carbon steel in 1.0 M HCl in the presence of 4 g/L ANIS at different temperatures.

Table 3. The influence of temperature on the electrochemical parameters for carbon steel electrode immersed in 1.0 M HCl and 1.0 M HCl + 4 g/L ANIS.

Inhibitor	Temp (K)	$-E_{corr}$ (mV/SCE)	$-\beta c$ (mV dec^{-1})	I_{corr} (µA cm^{-2})	η_{Tafel} (%)
Blank	303	496	162.5	564	-
	313	498	154.5	773	-
	323	492	176.0	1244	-
	333	497	192.0	1650	-
Anise oil	303	448.3	157.72	26.3	**95.3**
	313	450.1	152.08	103.8	**86.6**
	323	450.6	160.71	294.1	**76.3**
	333	453.1	152.07	577.9	**64.9**

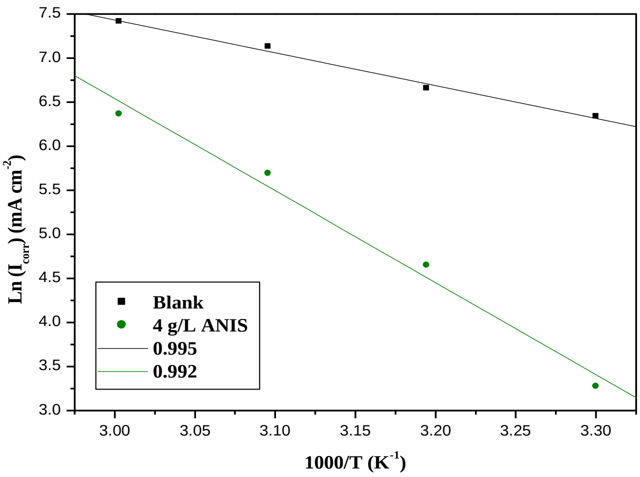

Figure 8. Arrhenius plots for mild steel in 1.0 M HCl and 1.0 M HCl + 4 g/L ANIS.

The increase in corrosion rate is more marked with the temperature increase for the uninhibited corrosive medium but the dissolution of the carbon steel alloy slowed with addition of inhibitor at various temperatures compared to uninhibited solution, whereas the values of inhibition efficiency are decreased with growth in temperature.

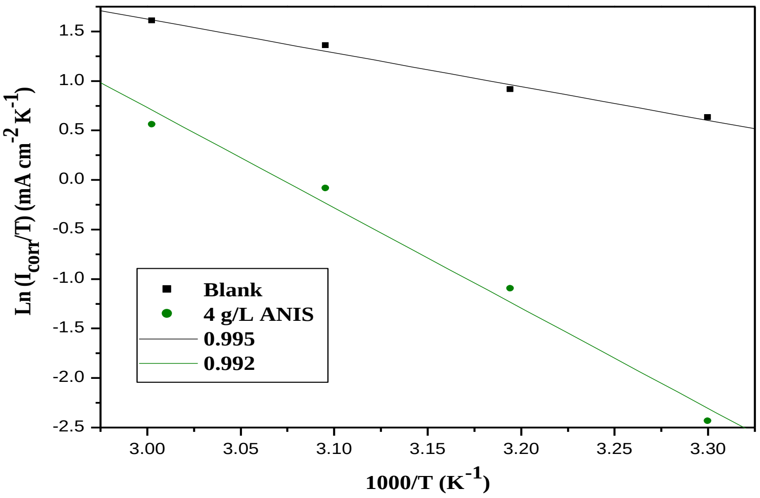

Figure 9. Transition state plots for mild steel in 1.0 M HCl and 1.0 M HCl + 4 g/L ANIS.

The activation parameters of the dissolution process such as the activation energy (E_a), the activation enthalpy (ΔH_a) and the activation entropy (ΔS_a) may be determined using the Arrhenius formula and transition state equation cited in previous works [22]. Arrhenius plot for carbon steel in hydrochloric acid with and without anise oil is exposed in Figs.8 and 9. The activation energy (Ea) values can be deduced from straight lines with a slope of (Ea/2.303R) and are given in Table 5. The increase in activation energy value with addition of inhibitor can be due to the reduction in the adsorption of the molecules on the carbon steel surface with increase in temperature [23]. Other researchers interpret this variation by formation of an adsorption film of physical/electrostatic nature [24].

Table 5. Corrosion kinetic parameters for mild steel in 1.0 M HCl in the presence and absence of 4 g/L ANIS.

Inhibitor	E_a (kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (J mol^{-1} K^{-1})	$E_a - \Delta H_a$
Blank	31.00	28.35	-98.8	2.65
4 g/L (AO)	86.77	84.13	61.11	2.64

The value of ΔH_a and ΔS_a deduced using the slope and an intercept of Fig.8 are listed in Table 5. The positive sign of ΔH_a for inhibited and uninhibited solution reflect the endothermic nature of the carbon steel dissolution process and suggesting that the dissolution of this alloy is slowed by addition of anise oil [25]. The obtained result verified the celebrated thermodynamic relation between E_a and ΔH_a (Table 5).

$$E_a - \Delta H_a = RT \quad (6)$$

The positive sign of ΔS_a in presence of the inhibitor shows that the system passed from an orderly to a more random arrangement. some authors interprets this increase in values of entropy via the adsorption of inhibitor molecules on metal surface from the acid solution that can be considered as substitution between the inhibitor molecules and the water molecules on electrode surface [26]

3.3. Adsorption considerations

The adsorption isotherm test was realized to give more information about the interaction between inhibitor molecules and the steel electrode. The surface coverage (θ) for different concentrations of anise oil in acidic medium has been calculated from polarization curves values, and listed in Table 2, according to the following equation:

$$\theta = 1 - \frac{I_{cor}}{I^0_{cor}} \qquad (7)$$

A plot of C_{inh}/ θ vs C_{inh} inhibitor concentration presents a right line (Fig. 3) testifying that the inhibitor molecules are adsorbed following the Langmuir isotherm, which is given according to equation:

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

Where k_{ads} are the equilibrium constant of the adsorption process.

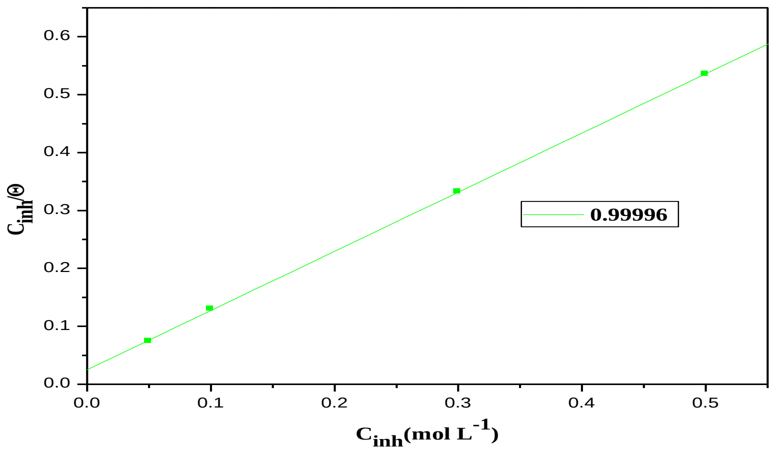

Figure 10. Langmuir adsorption of anise oil on the carbon steel surface in 1.0 M HCl solution at 303K.

Conclusion

Anise oil is considered as a green inhibitor for carbon steel in 1.0 M HCl, the inhibition efficiency of this compound obtained by various techniques exceeds 92% for concentration 4.0 g/L. The variation of values of double layer capacitance (C_{dl}) linked to the capacitance parameters caused by adsorption of inhibitor molecules on the electrode surface. The adsorption isotherm of anise oil on carbon steel electrode obeys to Langmuir isotherm.

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