

Green inhibition of carbon steel corrosion by fish oil in hydrochloric acid medium

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Abstract

Corrosion is a major problem of the destruction of various materials, especially metals. The highest effect of corrosion processes increased during pollution. The environmental toxicity of organic corrosion inhibitors has prompted the search for green corrosion inhibitors as they are biodegradable, do not contain heavy metals or other toxic compounds and readily available and renewable. The effect of fish oil as a green inhibitor of carbon steel corrosion has been investigated in a 1 M hydrochloric acid solution using polarization curves, electrochemical impedance spectroscopy (EIS) and gravimetric techniques. The obtained results reveal that fish oil effectively inhibits the corrosion of carbon steel. The highest inhibition efficacy value is 91.82% obtained by potentiodynamic polarization and 92.96% by electrochemical impedance spectroscopy at the maximum concentration tested. The inhibition efficiency increased with increasing concentration of tested oil, although he's remainder stable with increasing temperature. The polarization curves show that the tested oil can be considered as a mixed type inhibitor and that the absorption of the inhibitor on the carbon steel electrode obeys the Langmuir isotherm. The EIS results indicate that changes in impedance parameters are related to the adsorption of fish oil on the surface of the alloy.

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1. Introduction

Nowadays, metals and their alloys are widely used in various technological and industrial applications because of their excellent structural and mechanical strength [1-14]. Hydrochloric acid and sulfuric acid are most often used in various industrial processes, such as acid etching of steel, removal of scale in metallurgy, acid cleaning of boilers and acidification of oil wells [15-18]. The dissolution of the metal in the corrosive medium is not only a problem. It is a source of waste of raw materials and energy and also contributes to environmental pollution. In terms of protection against corrosion, it is possible to act on the material itself, on its surface and on the environment with which it is in contact. Therefore, the corrosion inhibitors are of particular importance and many scientists are researching this topic. Chemical compounds used as corrosion inhibitors are the most used substances to reduce the dissolution of various metals and, consequently, increase their life. The choice of a good corrosion inhibitor depends on its economic availability, its effectiveness in inhibiting the substrate and its side effects on the environment. Most organic substances used as corrosion inhibitors can be adsorbed onto the metal surface by heteroatoms such as nitrogen, oxygen, sulfur, and phosphorus, as well as by multiple bonds or aromatic rings. [19-20]. These organic inhibitors are generally adsorbed on the metal surface by the formation of a coordinate covalent bond (chemical adsorption) or the electrostatic interaction between the metal and the inhibitor (physical adsorption), and sometimes following the two paths, thus preventing metal dissolution in the acid medium [21]. The constituents of the metal and its alloys, the concentration, and structure of the inhibitor and the temperature of the metal environment are important factors in determining the extent of adsorption, which in turn determines the effectiveness of inhibition [22]. The purpose of this work was to investigate fish oil (FO) inhibition efficiencies on carbon steel corrosion in a 1.0 M HCl solution, using electrochemical techniques such as polarization potentiodynamic (PDP), electrochemical impedance spectroscopy (EIS) and weight loss measurements (WL). The effect of temperature on the effectiveness of this inhibitor for the corrosion of carbon steel in a 1.0 M HCl solution in the range of 298-328 K has been studied

2. Experimental

2.1. Plant material

Fish oil was obtained from Belhassan Industrial and Commercial Complex (CIBEL), Morocco.

2.2. Analytical determination of oil

The Fatty acid composition was determined using the International Standard Organisation (Organization) method [23]. Fatty acids (FA) were converted to methyl esters before analysis by shaking a solution of 60 mg oil and 3 mL of hexane with 0.3 mL of 2 N methanolic potassium hydroxide. They were analyzed by gas chromatograph (Varian CP-3800, Varian Inc.) equipped with an FID. The column used was a CP- Wax 52CB column (30 m×0.25 mm i.d.; Varian Inc., Middelburg, The Netherlands). The carrier gas was helium, and the total gas flow rate was 1 mL/min. The initial column temperature was 170 °C, the final temperature 230 °C, and the temperature was increased by steps of 4 °C/min. The injector and detector temperature was 230 °C. Data were processed using Varian Star Workstation v 6.30 (Varian Inc., Walnut Creek, CA, USA). The results were expressed as the relative percentage of each fatty acid present in the sample.

2.3. Solutions and Preparation of Specimens

Aggressive solutions of 1.0 M HCl were prepared by dilution of 37% HCl of analytical grade. The inhibitor concentration range used was between 0.5g / L and 0.05g / L in 1M HCl. All solutions were prepared from bidistilled water. Table 1 shows the chemical composition of the working electrode. The steel electrode was mounted in

polyester. It was mechanically polished with 400, 600, 800 and 1200 emery papers, washed with acetone and bidistilled water and introduced into the cell. The gravimetric measurements were performed by immersing the carbon steel samples in a 1.0 M HCl solution, without and with different concentrations of the studied inhibitor, for 6.0 hours, at 298 K. All the electrochemical studies were carried in a corrosion cell kit with a three-electrode configuration. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as an auxiliary electrode. The working electrode was carbon steel. All potentials given in this study were referred to that reference electrode (SCE). The working electrode was immersed in the test solution for 30 min, to establish steady-state open circuit potential (E_{ocp}) ou (OCP). After obtaining OCP the electrochemical measurements were performed. All electrochemical tests have been performed in aerated solutions at 298 K. The system impedance was measured as a function of the frequency of the applied signal, and its value is given in the complex plane for each frequency. The electrochemical impedance spectroscopy (EIS) tests were carried out at OCP, in the frequency range from 10 kHz to 100 MHz, with a signal amplitude of 10 mV, using a Voltalab (PGZ 100) Potentiostat/Galvanostat coupled to a computer equipped with Voltamaster 4 software.

Table 1: Chemical composition of steel specimens.

Elements	Fe	C	Si	Mn	Cu	S	Cr	Co	Ti	Ni
Mass %	98.307	0.38	0.23	0.68	0.16	0.016	0.077	0.09	0.011	0.059

3. Results and discussion

3.1. Fatty acid composition

Table 2: Fatty acid Composition of fish oil.

	Fish oil	Codex
Fatty Acid	g/100g	
Lauric Acid C12 : 0	0.1±0.1	-----
Myristic C14 : 0	8.2±0.1	4,0-21,5
Pentadecanoic Acid C15 : 0	0.1±0.1	ND-1,5
Palmitic Acid C16: 0	19.0±0.1	9,0-25,5
Heptdecanoic Acid C17 : 0	1.8±0.1	ND-1,5
Stearic Acid C18 : 0	4.0±0.1	1,5-9,0
Arachidic Acid C20:0	0.4±0.1	0,2-1,5
Saturated Fatty Acids (SFA)	33.6±0.1	
Pentadecenoic Acid C15 : 1	0.4±0.1	-----
Palmitoleic Acid C16 : 1	8.6±0.1	5,5-17,5
Heptadecenoic Acid C17 : 1	2.4±0.1	-----
Oleic Acid C18:1	10.4±0.1	ND
Gondoic Acid C20:1	0.3±0.1	ND-2,5
Erucic Acid C22:1	3.8±0.1	ND-4,1
Monounsaturated Fatty Acid (MUFA)	25.9±0.1	
Linoleic Acid C18:2	1.3±0.1	0,2-4,5
Linolenic Acid C18:3	3.0±0.1	ND-3,0
Ecosodienoic Acid C20:2	1.8±0.1	-----
Arachidonic Acid C20:4	1.1±0.1	ND-1,0
Ecosapentaenoic Acid C20:5 EPA	21.2±0.1	8,0-25,0
Docosadienoic Acid C22:2	1.6±0.1	-----
Docosahexanoic Acid C22:6 DHA	10.5±0.1	2,5-15,5
Polyunsaturated Fatty Acid (PUFA)	40.5±0.1	

Fish oils often have a higher degree of unsaturation than oils from plants and other animals. Indeed, the fatty acid composition is an essential indicator of the nutritional value of the oil [24-25]. Fish oil is considered as the main source of Eicosapentaenoic acid (EPA) and Docosahexaenoic acid (DHA). These fatty acids (DHA and EPA) are well documented with regard to the positive impact on health [26-27]. The content of EPA and DHA in fish oil is dependent on the type of fish, the fish diet, seawater temperatures and geographic location of the catch [28].

The fatty acid composition of fish oil is given in **Table 2**. It shows that this oil is richer in unsaturated fatty acids (66.48 g/100g), or twice the saturated fatty acids (33.6 g/100g). Most of the polyunsaturated fatty acids (PUPA) present in our oil are EPA (21.2 g/100g) and DHA (10.5 g/100g).

3.2. Electrochemical impedance spectroscopy (EIS)

EIS technique was applied to investigate the electrode /electrolyte interface and corrosion processes that occur on the carbon steel surface in the absence and presence of fish oil (FO). EIS measurements were made at open circuit potential in a wide frequency range at 298K, to confirm the the complete characterization of the interface and surface processes. Figure 1 shows Nyquist plots for carbon steel in 1.0 M HCl solution in the absence and presence of different concentrations of fish oil at the open circuit potential. The values of the charge-transfer resistance (R_{ct}) were obtained from the difference in real component of impedance at lower and higher frequencies as suggested by Tsuru and Haruyama [29]. The double-layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) are found as represented in equation [30-35]:

$$c_{dl} = (2\pi f_{max} . R_{ct})^{-1} \quad (1)$$

Where f_{max} is the frequency value at which the imaginary component (Z_{im}) of impedance is maximum. The inhibition efficiency can be calculated by the following formula:

$$E_{Rct} \% = \frac{R'_{ct} - R_{ct}}{R'_{ct}} \times 100 \quad (2)$$

Where R_{ct} and R'_{ct} is the charge transfer resistances in uninhibited and inhibited solutions respectively.

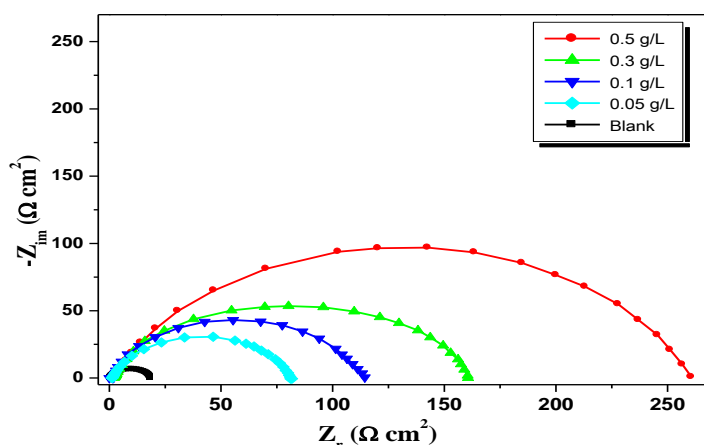


Fig.1: Nyquist plots for carbon steel immersed in 1.0M HCl solution in the absence and presence at various concentrations of fish oil.

The diameter of the semicircle increases after the addition of fish oil to the aggressive solution. This increase gets more and more pronounced with increasing fish oil concentration. The electrochemical parameters derived from EIS measurements (including, R_{ct} , transfer charge, double layer capacitance C_{dl} and the inhibitor efficiency values E_{Rct} (%))

are given in Table 3. Double layer capacitance values were obtained at the maximum frequency (f_{\max}) at which the imaginary component of the Nyquist plot is maximum and calculated using the equation (1) .

Table 3 . Impedance parameters and inhibition efficiency for the corrosion of carbon steel in 1 M HCl without and with the addition of various concentrations of fish oil at 298 K.

Inhibitor	C(g/L)	$R_{ct}(\Omega.cm^2)$	$C_{dl}(\mu F/cm^2)$	$E_{Rct}(\%)$
Blank	1M	18	221.16	-
FO	0.5	256	41	92.96
	0.3	162	65	88.80
	0.1	115	92	84.34
	0.05	82	129	78.04

The results summarized in Table 3 clearly show that fish oil is an inhibitor of steel corrosion in 1M HCl at all concentrations used and that the inhibition efficiency ($E_{Rct}\%$) increases continuously with increasing concentrations at 298K. EIS results show also that the R_{ct} values increase and the C_{dl} values decrease with increasing the inhibitor concentration. The increase in R_{ct} value can be attributed to the formation of a protective film on the metal/solution interface [36]. On the other hand, the decrease in C_{dl} values can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer. It can be assumed that the decrease of C_{dl} values is caused by the gradual replacement of water molecules by adsorption of inhibitor molecules on the carbon steel surface [37-39]. EIS spectra of the fish oil were analyzed using the equivalent circuit which is shown in Figure 2. It indicates that a single charge transfer reaction and fits well with our experimental results. The constant phase element, CPE, is introduced in the circuit instead of a pure double-layer capacitor to give a more accurate fit [40].

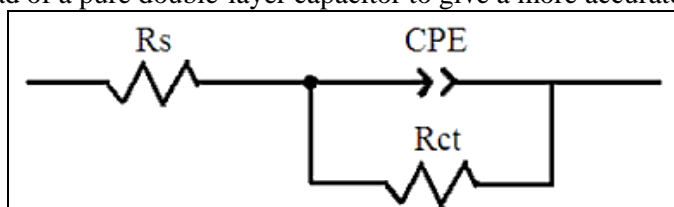


Fig.2 Equivalent circuit model used to fit the impedance spectra.

3.3. Potentiodynamic polarization measurements

Figure 3 shows the potentiodynamic polarization curves for carbon steel corrosion in 1.0 M HCl solution, without and with different fish oil concentrations, at 298 K. Electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic Tafel slope (β_c) and percentage inhibition efficiency were determined and summarized in Table 3. The I_{corr} values were used to calculate the inhibition efficiency ($E_I\%$), using equation 3:

$$E_I (\%) = \left(1 - \frac{I'_{corr}}{I_{corr}}\right) \times 100 \quad (3)$$

Where I'_{corr} and I_{corr} are the corrosion current densities in inhibited and uninhibited media, respectively. It is clearlyAlso noticed from Fig. 3 that the anodic and cathodic current densities effectively decreased as the fish oil concentration in the acidic solution increased and, generally, with a slight shift in the E_{corr} values, suggesting that the inhibitor molecules retarded the corrosion process. In the acidic media, carbon steel oxidative dissolution in the anodic region, and hydrogen reduction in the cathodic region are observed in the Tafel plots. Also, the parallel cathodic Tafel

curves in Fig. 3 show that the hydrogen evolution was activation controlled and that the reduction mechanism was not affected by the inhibitor presence [41]

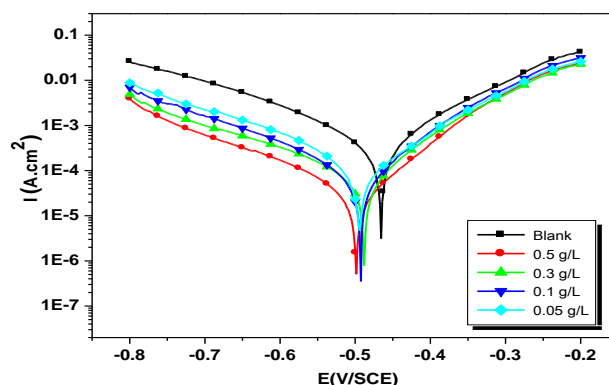


Fig.3 Potentiodynamic polarization curves of carbon steel in a 1.0 M HCl solution, in the presence and absence of different fish oil concentrations, at 298 K.

Table 4. Carbon steel PDP parameters at various fish oil concentrations in a 1.0 M HCl solution, and the corresponding inhibition efficiency, at 298 K.

Inhibitor	Conc	$-E_{\text{corr}}$ (mV/SCE)	$-\beta_c$ (mV dec ⁻¹)	I_{corr} ($\mu\text{A cm}^{-2}$)	E_i (%)
Blank	1M	463	168	636	-
	0.5 g/L	498	182	52	91.82
	0.3 g/L	487	187	78	87.73
FO	0.1 g/L	494	189	99	84.43
	0.05 g/L	494	214	142	77.67

Corrosion current density I_{corr} decreased noticeably with the rise in fish oil concentration. Additionally, as shown in Table 1, the E_{corr} values in the presence of the inhibitor were slightly less negative than that in the absence of the inhibitor. Therefore, it can be arranged as a mixed-type inhibitor in acidic medium, and the inhibition of fish oil on carbon steel electrode is caused by geometric blocking effects.

3.4. Weight loss measurements

The effect of the fish oil inhibitor concentration on carbon steel samples corrosion in a 1.0 M HCl solution was studied using weight loss measurements at 298 K, for 6 hours immersion time. The obtained data are listed in Table 4.

In the case of the weight-loss method, the inhibition efficiency (E_w %) was determined by the following equation:

$$E_w(\%) = \frac{W_{\text{corr}} - W'_{\text{corr}}}{W_{\text{corr}}} \times 100 \quad (4)$$

Where W_{corr} and W'_{corr} are the corrosion rate of carbon steel in 1.0 M HCl in the absence and presence of inhibitor, respectively. Results clearly show that the inhibition efficiency (E_w %) increased with an increasing inhibitor concentration and at 0.5g/L concentration, fish oil exhibited a maximum inhibition efficiency (91,50%), which represents an excellent corrosion inhibitor. On the other hand, it is also clearly noticed from Fig. 4 that carbon steel

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corrosion rate (W) decreased with an increasing inhibitor concentration. This behavior can be attributed to the increase in fish oil adsorption at the carbon steel/solution interface, as its concentration increased [42].

Table 5. Effect of oil fish concentrations on the corrosion data of carbon steel in acidic solution.

Inhibitor	Concentrations g/L	W_{corr} (mg. h ⁻¹ .cm ⁻²)	E _w (%)
Blank	-	1.203	-
FO	0.5	0.102	91.50
	0.3	0.148	87.67
	0.1	0.193	83.93
	0.05	0.271	77.43

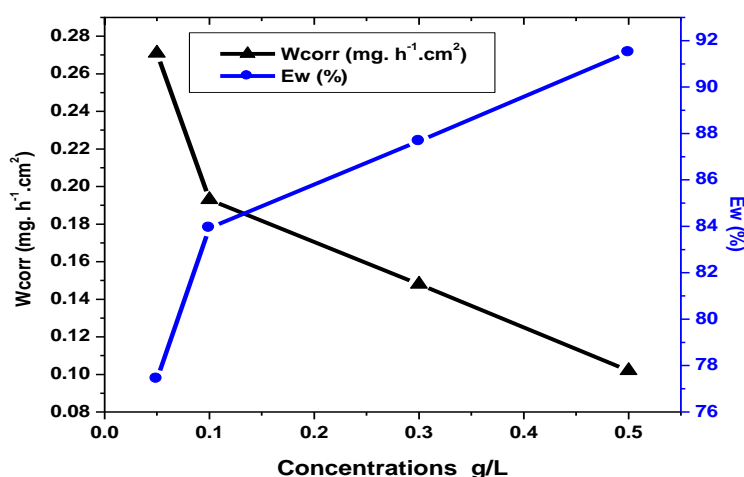


Fig. 4 Relationship between the inhibition efficiency, corrosion rate and inhibitor concentration for carbon steel, after 6 hours of immersion time in a 1.0 M HCl solution, at 298 K.

3.5. Effect of temperature

The effect of temperature is very important because of its impact on interface electrode alloy/solution behavior. The impedance spectroscopy curves of carbon steel in 1 M HCl without and with the addition of fish oil as inhibitor were recorded at various temperatures between 298K and 328 K (Figs. 5 and 6). Electrochemical parameters obtained from these plots and the inhibition efficiencies evaluated from I_{corr} values are listed in Table 6. On the other hand, the values of R_{ct} were employed to calculate values of the corrosion current density (I_{corr}) at various temperatures in the absence and presence of fish oil using the following equation [43]:

$$I_{\text{corr}} = RT \cdot (z \cdot F \cdot R_{\text{ct}})^{-1} \quad (5)$$

Where R is the universal gas constant ($R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature, z is the valence of iron ($z = 2$), F is the Faraday constant ($F = 96485 \text{ coulomb}$) and R_{ct} is the charge transfer resistance.

The logarithm of the corrosion rate of carbon steel I_{corr} can be represented as a straight-line function of $1000/T$ (Arrhenius equation, Figures.6-7)

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$$I_{corr} = A \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

Where A is the Arrhenius factor, E_a is the apparent activation corrosion energy, R is the perfect gas constant and T the absolute temperature.

The activation parameters for the studied system (E_a , ΔH_a and ΔS_a) were estimated from the Arrhenius equation and transition state equation (Eq :6-7):

$$I_{corr} = \frac{RT}{Nh} \cdot \exp\left(\frac{\Delta S_a}{R}\right) \cdot \exp\left(-\frac{\Delta H_a}{RT}\right) \quad (7)$$

Where N is the Avogadro's number, h is the Plank's constant, and ΔH_a and ΔS_a are the enthalpy and the entropy changes of activation corrosion energies for the transition state complex. The apparent activation energy was determined from the slopes of $\ln I_{corr}$ vs $1/T$ graph depicted in Fig. 6.

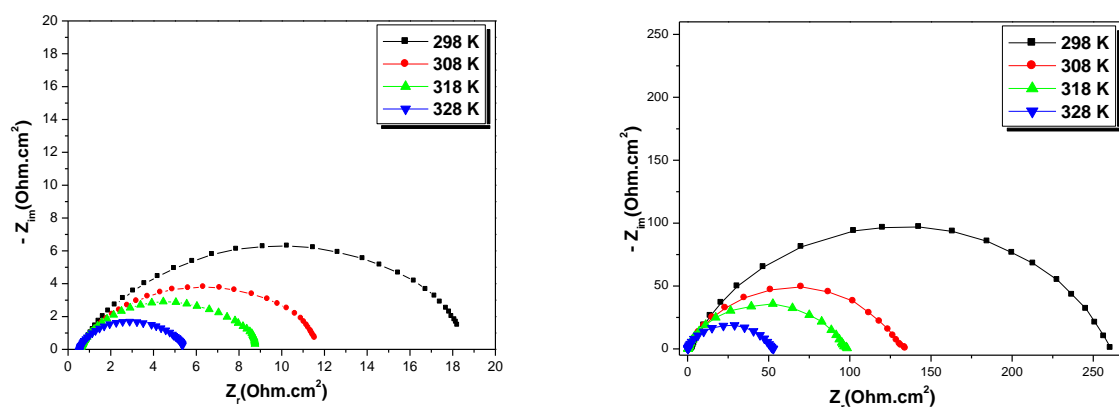


Fig. 5. Nyquist diagrams for carbon steel in 1 M HCl + 0.5 g/L of fish oil at different Temperatures.

Table 6: Temperature effect on the carbon steel corrosion in free acid with 0.5g/L of fish oil.

Inhibitor	Temp (K)	R_{ct} ($\Omega.cm^2$)	C_{dl} ($\mu F/cm^2$)	E_{Rct} (%)
Blank	298	18	221.16	-
	308	11	229.78	-
	318	8	199.04	-
	328	5	201.56	-
FO	298	256	41.46	84.35
	308	131	48,62	79.24
	318	89	59,63	79.49
	328	58	68,60	84.37

The curves of variation of $\ln I_{corr}$ versus $1/T$ and $\ln (I_{corr}/T)$ versus $1/T$ are recorded in Fig. 6 and Fig.7, respectively. The curves obtained in the form of lines obey the Arrhenius law, thus satisfying the relations 6 and 7, and all the regression coefficients are close to 1. The activation parameters in fish oil absence and presence are summarized in Table 7. E_a values determined in solutions with fish oil are higher than those in the inhibitor absence, suggesting that the energy barrier of the corrosion reaction increased, which means that carbon steel dissolution is difficult [44]. High

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E_a values are generally associated with low corrosion rates, while low E_a values are associated with high corrosion rates. However, ΔH_a positive sign reflects the endothermic nature of the carbon steel dissolution process, suggesting that this is slow in the presence of a fish oil inhibitor [45]. On the other hand, Table 7 shows that ΔS_a values increased in the inhibitor presence, compared to the blank solution, which means that an increase in disorder took place during a course of the transition from the reactant to the activated complex, during the corrosion process [46-47].

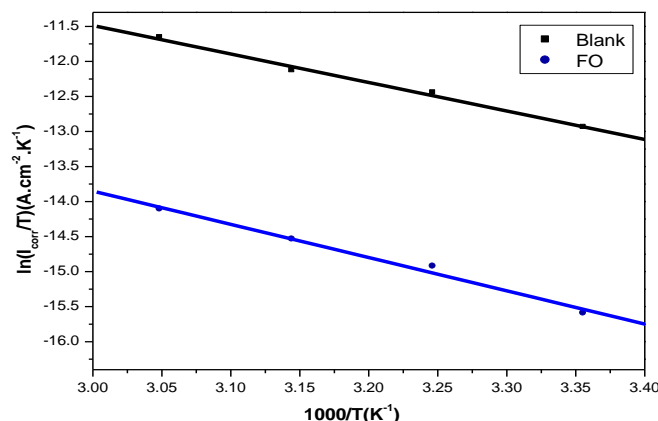


Fig. 6 Plots for carbon steel in a 1.0 M HCl solution and 1.0 M HCl + 0,5g/L of fish oil.

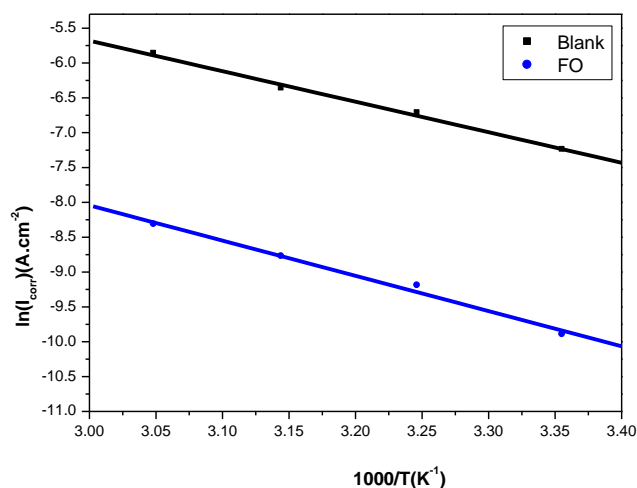


Fig. 7 Transition state plots for carbon steel in a 1.0 M HCl solution, and 1.0 M HCl + 0,5g/L of fish oil.

Table 7. Corrosion kinetic parameters for carbon steel in a 1.0 M HCl solution, in the presence and absence of 0,5g/L of fish oil.

Inhibitor	E_a (kJ/mol)	ΔH_a (kJ/mol)	ΔS_a (J/mol K)
Blank	36.38	33.79	-191.53
FO	42.01	39.42	-194.28

3.6. Adsorption isotherm

Adsorption isotherm gives essential information about the interaction between the inhibitor and the alloy surface. Langmuir adsorption isotherm was found to provide the best description of the adsorption behavior of the investigated inhibitor. The Langmuir isotherm is given by an equation [48]:

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

Where C_{inh} is the inhibitor concentration, θ the fraction of the surface covered determined by $E_w(\%)/100$, K_{ads} the equilibrium constant. Plots of C_{inh}/θ against C_{inh} yield straight lines as shown in Figure 8.

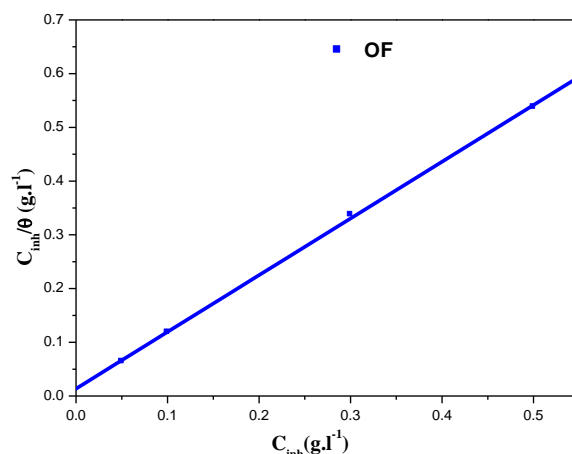


Fig.8 Langmuir adsorption plots for carbon steel in 1.0 M HCl at 298 K in the presence of different concentrations of fish oil.

The linear relationship of C_{inh}/θ versus C_{inh} in different concentrations of inhibitor presented in Fig. 8, possesses a slope near to unit with the correlation coefficient R^2 that is close to 1, thus, the adsorption of fish oil on steel surface obeys the Langmuir adsorption isotherm.

4. Conclusion

Fish oil was valorized as an effective inhibitor to the corrosion of carbon steel in 1 M HCl solution by weight loss measurement, EIS and current–potential measurements. The results obtained lead to the following conclusions:

- The polarization studies showed that fish oil inhibits both cathodic hydrogen reduction reactions and anodic metal dissolution, and it acts as a mixed-type inhibitor of corrosion.
- The inhibition efficiency of fish oil increases with the increase of inhibition concentration.
- The adsorption of the fish oil compound on the carbon steel surface in 1 M HCl solution obeys to the Langmuir adsorption model.
- The values of inhibition efficiencies obtained from the different independent quantitative techniques used show the validity of the results. We found that Fish oil is effective in inhibiting the corrosion of carbon steel in an acid medium.

References

- [1] B. El Makrini, H. Lgaz, K. Toumiat, R. Salghi, S. Jodeh, G. Hanbali, M. Belkhaouda, M. Zougagh, Res J Pharm Biol Chem Sci.7(5) (2016)2277-2285.
- [2] M. Larouj, M. Belkhaouda, H. Lgaz, R. Salghi, S. Jodeh, S. Samhan, H. Serrar, S. Boukhris, M. Zougagh, H. Oudda, Der Pharma Chemica, 8(2) (2016)114-133.
- [3] R. Salghi, S. Jodeh, Eno E. Ebenso, H. Lgaz, D. Ben Hmamou, M. Belkhaouda, I. H. Ali, M. Messali, B. Hammouti, S. Fattouch, Int. J. Electrochem. Sci., (12) (2017) 3283– 3295.

- [4] A. Batah, M. Belkhaouda, L. Bammou, A. Anejjar, R. Salghi, A. chetouani, L. Bazzi, B. Hammouti, Moroccan Journal of Chemitry;5 (4) (2017)580-589
- [5] S. Kharacha, A. Batah, M. Belkhaouda, L. Bazzi, L. Bammou, R. Salghi, O. Jbara, A. Tara Moroccan Journal of Chemistry, 6(2) (2018)294-306.
- [6] A. Batah, A. Anejjar, M. Belkhaouda, L. Bammou, R. Salghi, L. Bazzi, B. Hammouti Appl. J. Envir. Eng. Sci.;2 (2) (2016)56-71
- [7] B. El Makrini, H. Lgaz, M. Larouj, R. Salghi, A. Rasem Hasan, M. Belkhaouda, S. Jodeh, M. Zougagh, H. Oudda, Der Pharma Chemica, 2016, 8(2):256-268
- [8] E. Azzouyayar, L. Bazzi, M. Belkhaouda, A. Lamiri, M. Essahli, Inter. Journal of Advanced Scientific and Technical Research, 4(4) (2014)
- [9] E. Azzouyayar, L. Bazzi, M. Essahli, M. Belkhaouda, A. Lamiri ; Chemical Science Review and Letters, , 3(11S) (2014)80-87
- [10] A. Batah, A. Anejjar, M. Belkhaouda, L. Bammou, R. Salghi, L. Bazzi, B. Hammouti, A. Chetouani, Moroccan Journal of Chemitry,;5(3) (2017)404-416
- [11] A. Batah, A. Anejjar, L. Bammou, M. Belkhaouda, R. Salghi, L. Bazzi, J. Mater. Environ. Sci.,; 8(9)(2017)3070-3080
- [12] M. Belkhaouda, L. Bammou, R. Salghi, A. Zarrouk, D. Ben Hmamou, H. Zarrok, M. Assouag, B. Hammouti and S. S. Al-Deyab, Der Pharmacia Lettre, , 5 (2) (2013)143-152
- [13] L. Afia, H. Lgaz, M. Zougagh, M. Belkhaouda, S. Jodeh, M. Algarra, Appl. J. Envir. Eng. Sci. 2 N°2(2016) 42-55
- [14] B. El Makrini, K. Toumiat, H. Lgaz, R. Salghi, S. Jodeh, G. Hanbali, M. Belkhaouda, M. Zougagh, Research Journal of Pharmaceutical, Biological and Chemical Sciences, RJPBCS 7(5) (2016) 2286-2294
- [15] M. Belkhaouda, L. Bammou, A. Zarrouk, R. Salghi, E. E. Ebenso, H. Zarrok, B. Hammouti, L. Bazzi, I. Warad. Int. J. Electrochem. Sci.,; (8) (2013)7425 – 7436
- [16] Bousskri A, Anejjar A, Lgaz H, et al. Appl J Environ Eng Sci.;1(1) (2015)96-113
- [17] N. Lotfi, H. Lgaz, M. Belkhaouda, M. Larouj, R. Salghi, S. Jodeh, H. Oudda, B. Hammouti, Arabian J. of Chem. and Environ. Res.,1 (1) (2014)13–23
- [18] A. Bousskri, H. Lgaz, S. Jodeh, et al. Appl J Environ Eng Sci.;2(1) (2016)1.....
- [19] Bammou L, Belkhaouda M, Salghi R, Benali O, Zarrouk A, Al-Deyab S. S, Warad I, Zarrok H, Hammouti B, Int. J. Electrochem. Sci., (9) (2014)1506 – 1521.
- [20] L. Bammou, M. Belkhaouda, R. Salghi, A. Zarrouk, H. Zarrok, B. Hammouti, Journal of the Association of Arab Universities for Basic and Applied Sciences 16 (2014) 83–90
- [21] C.M. Goulart, A. Esteves-Souza, C.A. Martinez-Huitle, et al. Corros Sci.;67(2013)281.....
- [22] I. Obot, N. Obi-Egbedi, S. Umoren Corros Sci., 51(8) (2009)1868.
- [23] Gharby S, Harhar H, Bouzoubaa Z, Elmadani Z, and Charrouf .J. Mater. Environ. Sci. 2015; 6 (1):254-263.
- [24] Gharby S., Harhar H., Matthäus B., Bouzoubaa Z., Charrouf Z .Journal of Taibah University for Science. 2016; (10): 100–106.
- [25] Gharby S, Harhar H., Z. Bouzoubaa, A. Asdadi, A. El Yadini, Z. Charrouf. Journal of the Saudi Society of Agricultural Sciences. 2017; (16): 105–111.
- [26] M. E.Cuvelier, M. N. Maillard. O.C.L. 19(2) (2012)125-132.
- [27] R. A. M Strijbosch, S. Lee, D.A. Arsenault, C.Andersson, K.M.Gura, B. R.Bistrian and M.Puder. *Metabolism*.; (57)(2008)5698–5707.

- [28] M. Farssi, S. Gharby, R. Mamouni, H. Harhar, BE. Kartah, et A. Laknifli, Moroccan Journal of Chemistry; 6 (2) (2018)615 – 622.
- [29] H. B. Ouici, M. Belkhouda, O. Benali, R. Salghi, L. Bammou, A. Zarrouk & B. Hammouti Research Chemical Intermediates 41(2015)4617–4634
- [30] D. Gopi, K. M. Govindaraju, L. Kavitha, J. Appl. Electrochem. 40 (2010) 1349.
- [31] M. Faustin, A. Maciuk, P. Salvin, C. Roos, M. Lebrini, Corros. Sci.,92 (2015)287.
- [32] A. Essaghouni, H. Elmsellem, M. Boulhaoua, M. Ellouz, M. El Hafi, N. K. Sebbar, E. M. Essassi, M. Bouabdellaoui, A. Aouniti and B. Hammouti,DerPharmaChemica., 8(2) (2016) 347-355.
- [33] Elmsellem H., Nacer H., Halaimia F., Aouniti A., Lakehal I., Chetouani A., Al-Deyab S. S., Warad I., Touzani R., Hammouti B, Int. J. Electrochem, Sci.,; (9)(2014)5328.
- [34] LebriniM., RobertF., RoosC., Int. J. Corros. (2013). doi:10.1155/2013/139798
- [35] MallaiyaK., SubramaniamR., SrikandanS.S., GowriS., RajasekaranN., SelvarajA., Corrosion,; (64) (2008)541.
- [36] N. K. Sebbar, H. Elmsellem, K. Abdu, I. Ben Maïmoun, A. Dahdouh, H. Steli, C. Ad,M. Ellouz1,N. Abad1, B. El Mahi, M. Ali Shariati and E. M. Essassi. j.mar.chim.heterocycl .;16 (1) (2017)166
- [37] Elmsellem H., Basbas N., Chetouani A., Aouniti A., Radi S., Messali M., Hammouti B., Portugaliae. Electrochimica Acta,; (2) (2014)77.
- [38] Elmsellem H., Karrouchi K., Aouniti A., Hammouti B., Radi S., Taoufik J., Ansar M., Dahmani M., Steli H. and El Mahi B., Der PharmaChemica,;7(10) (2015)237.
- [39] KosariA., MoayedMH., DavoodiA., ParviziR., MomeniM., EshghiH., MoradiH., Corros. Sci.; (78) (2014)138.
- [40] Ansari K.R., Quraishi M.A., Singh A., Corros. Sci.,; 5(2014)79.
- [41] Bentiss F, Jama C, Mernari B, et al. Corros Sci.,;51(8) (2009)1628.
- [42] Obot I, Obi-Egbedi N. Curr Appl Phys.,;11(3) (2011)382.
- [43] Batah A , Chebli H, Belkhaouda M, Bammou , Salghi R, Anejjar A, Chebli B, Zaafrani M. Appl. J. Envir. Eng. Sci.,;3 (4) (2017)443.
- [44] Gomma GK, Wahdan MH. Mater Chem Phys.,;39(3) (1995)209.
- [45] Gerengi H, Darowicki K, Bereket G, et al. Corros Sci.,;51(11) (2009)2573.
- [46] Singh AK, Quraishi M. Corros Sci.,;53(4) (2011)1288.
- [47] Khamis E, Hosny A, Elhadary S. Afinidad;52(456) (1995)95.
- [48] Bouoidina A, El-Hajjaji F., Chaouch M., Abdellaoui A., Elmsellem H., Rais Z., Filali Baba M., Lahkimi A., Hammouti B. and Taleb M., Der Pharma Chemica,;8(13) (2016)149.