Sample synthesis, characterization, experimental and theoretical study of the inhibitory power of new 8-hydroxyquinoline derivatives for mild steel in 1.0 M HCl

M. Rbaa, F. Benhiba, Ashraf S. Abousalem, M. Galai, Z. Rouifi, H. Oudda, B. Lakhrissi, I. Warad, A. Zarrouk

PII: S0022-2860(20)30480-4

DOI: https://doi.org/10.1016/j.molstruc.2020.128155

Reference: MOLSTR 128155

To appear in: Journal of Molecular Structure

Received Date: 14 October 2019

Revised Date: 27 March 2020

Accepted Date: 28 March 2020

Please cite this article as: M. Rbaa, F. Benhiba, A.S. Abousalem, M. Galai, Z. Rouifi, H. Oudda, B. Lakhrissi, I. Warad, A. Zarrouk, Sample synthesis, characterization, experimental and theoretical study of the inhibitory power of new 8-hydroxyquinoline derivatives for mild steel in 1.0 M HCl/ournal of *Molecular Structure* (2020), doi: https://doi.org/10.1016/j.molstruc.2020.128155.

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier B.V.



CRediT authorship contribution statement

M. Rbaa : Conceived and designed the experiments- Performed the experiments- Wrote the paper.

F. Benhiba: Conceived and designed the experiments- Performed the experiments-Wrote the paper.

A.S. Abousalem: Conceived and designed the experiments- Contributed reagents, materials- Wrote the paper.

M. Galai : Conceived and designed the experiments- Performed the experiments.

Z. Rouifi: Conceived and designed the experiments- Performed the experiments.

H. Oudda : Analyzed and interpreted the data- Contributed reagents, materials, analysis tools or data- Wrote the paper..

B. Lakhrissi : Analyzed and interpreted the data- Contributed reagents, materials, analysis tools or data- Wrote the paper.

I. Warad : Analyzed and interpreted the data- Contributed reagents, materials, analysis tools or data- Wrote the paper.

A. Zarrouk : Analyzed and interpreted the data- Contributed reagents, materials, analysis tools or data- Wrote the paper.

Graphical Abstract



| 1 | Sample Synthesis, characterization, experimental and |
|---|---|
| 2 | theoretical study of the inhibitory power of new |
| 3 | 8-hydroxyquinoline derivatives for mild steel in 1.0 M HCl |
| 4 | |
| 5 | M. Rbaa ^a , F. Benhiba ^{b,c} , Ashraf S. Abousalem ^{d,e} , M. Galai ^f , Z. Rouifi ^b , H. |
| 5 | Oudda ^b , B. Lakhrissi ^a , I. Warad ^g , A. Zarrouk ^c * |
| , | |
| | ^a Laboratory of Organic Chemistry, Catalysis and Environment, Faculty of Sciences, Ibn Tofail |
| | University, PO Box 133, 14000, Kenitra, Morocco. |
| | ^b Laboratory of Separation Procedure, Faculty of Sciences, Ibn Tofail University, PO Box 133, 14000, |
| | Kenitra, Morocco. |
| | University Av Ibn Battuta P O Box 1014 Rabat Morocco |
| | ^d Chemistry Department, Faculty of Sciences, Mansoura University, El-Mansoura 35516, Egypt. |
| | ^e Quality Control Laboratory, Jotun, Egypt. |
| | Laboratory of Materials Engineering and Environment: Modeling and Application, Faculty of |
| | Sciences, Ibn Tofail University BP. 133-14000, Kenitra, Morocco. |
| | "Department of Chemistry and Earth Sciences, PO Box 2713, Qatar University, Doha, Qatar. |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | * Corresponding author. Tel.: +212 665 201 397. Fax.: +212 537 774 261. |

E-mail address: azarrouk@gmail.com (A. Zarrouk).

1 ABSTRACT

2 Some new compounds which are derived from 8-hydroxyquinoline were both prepared and characterized by IR, NMR spectroscopy and elemental analysis. After the successful synthesis, 3 we tested these products as corrosion inhibitors of mild steel (MS) in 1.0 M HCl at 298 K±1. 4 The anticorrosive property was achieved by electrochemical and theoretical methods such as 5 potentiodynamic polarization (PDP), the spectroscopy impedance (EIS), density functional 6 theory (DFT) calculations and the Monte Carlo simulation (MC). The experimental and 7 theoretical results obtained show that these products have an excellent anticorrosive property 8 9 for the MS. The thermodynamic parameters show that all the compounds adsorb to the metal surface by chemical bonds according to the Langmuir adsorption isotherm. The surface 10 morphology was investigated using scanning electron spectroscopy (SEM) coupled with 11 12 energy dispersive spectroscopy (EDS) and the FT-IR analysis. The gravimetric solutions after 6 hours of immersion were analyzed by the UV-Visible spectrometry. 13

14

Keywords: Synthesis; Corrosion inhibition; Mild steel; SEM/EDS; FT-IR analysis; Monte
Carlo simulation.

1 **1. Introduction**

2 Steel is an alloy of iron used in metal construction, tool making, strengthening foundations, and transporting water. A large amount of metals degraded by corrosion, in acidic media. So, 3 the use of corrosion inhibitors has become essential to extend the lifetime of metal part [1]. 4 According to the literature, several authors have reported that the heterocyclic compounds 5 based on 8-hydroxyquinoline showing several applications in various fields such as: 6 Pharmaceutical field, Medicinal, Agrochemical, 7 and analytical chemistry [2-4]. The 8-hydroxyquinoline is a good precursor for the synthesis of novel heterocyclic 8 compounds with multiple advantages such as the preparation of biologically active 9 compounds, metal complexes for use in the physical field and in medicine [5-7]. However, 10 The 8-hydroxyquinoline derivatives are good inhibitors of corrosion of steel in acidic 11 media.For this, today's researchers aim at synthesizing new compounds based on 8-12 13 hydroxyquinoline [8-10].

Our investigation in this work is the combination between two multifunctional heterocyclic 14 15 compounds based on 8-hydroxyquinoline by a simple synthesis. The pure products were 16 tested as corrosion inhibitors of mild steel in 1.0 M HCl at 298 K±1. The anticorrosive property was achieved by electrochemical and theoretical methods such as potentiodynamic 17 polarization (PDP), the spectroscopy impedance (EIS), DFT calculations and the Monte-Carlo 18 simulation (MC). The surface morphology was investigated using scanning electron 19 spectroscopy (SEM) coupled with energy dispersive spectroscopy (EDS) and the FT-IR 20 analysis. The gravimetric solutions after 6 hours of immersion were analyzed by the UV-21 Visible spectrometry (UV-vis). 22

23

24 **2. Experimental**

25 2.1. Materials

1 The materials used in the synthesized part have been published in another study [9]. The 2 corrosion solution (1.0 M HCl) is obtained by the decentralization of HCl (37%) with distilled 3 H_2O . The steel samples are prepared, before immersion in the solutions, by polishing with 4 sand paper until 1200.

5 **2.2. Methods**

6 2.2.1. Chemical synthesis

The two compounds derived from 8-hydroxyquinoline were synthesized by simple and
effective methods in two steps: the first step is the preparation of precursor 5-chloromethyl-8hydroxyquinoline hydrochloride (*5-CMHQ*) from a commercial product 8-hydroxyquinoline
(*8-HQ*). The second step consists in adding the binucleophile compounds to the compound *5- CMHQ* in tetrahydrofuran (*THF*) in the presence of triethylamine (Et₃N) at reflux for 8 hours
to obtain the two compounds, *5-(((2-aminoethyl) amino) methyl) quinolin-8-ol N-HQ* and *5-*((2-aminoethoxy) methyl) quinolin-8-ol O-HQ.



18 **2.2.2. Electrochemical tests**

The inhibition yields of corrosion of mild steel of the compounds synthesized for the
 potentiodynamic polarization study were calculated by equation 1. And the yields of corrosion
 of mild steel for spectroscopy impedance were calculated by equation 2.

$$4 \qquad \eta_{\rm PDP}(\%) = \left[1 - \frac{i_{\rm corr}}{i_{\rm corr}}\right] \times 100 \tag{1}$$

5 i_{corr}° and i_{corr} represent the densities of the corrosion currents in the absence and in the 6 presence of the inhibitor

7
$$\eta_{\rm EIS}(\%) = \frac{R_{\rm p} - R_{\rm p}^0}{R_{\rm p}} \times 100$$
 (2)

8 R_{p}^{0} and R_{p} are the values of the polarization resistance without and with inhibitor, 9 respectively.

10 Regarding the details for the two electrochemical methods used in this study were published11 in another study [9].

12 2.2.3. Computional details

The computional chemical methods used in this work are DFT and MC simulation to corroborate the experimental findings and make it possible to explain and give additional information on the mode of action [10]. The chemical quantum study of *N-HQ and O-HQ* molecules via *DFT/ B3LYP* was based on calculations of quantum chemical descriptors and molecular orbital descriptors using 6-31G (d,p) and 6-311G ++ (d, p) basis sets [11]. The DFT calculations were performed by the aid Gaussian 09 [11]. We used two basis sets for the quantum calculations in order to obtain the appropriate correlation [11].

About Monte Carlo (MC) simulation, we will take into considerations all interactions possible in the system studied (Surface Fe (110)/*N-HQ* and *O-HQ* compounds in an aggressive acid environment with $5H_3O^+$, $5Cl^-$ and $500H_2O$). The MC simulation was performed using

| 1 | Materials Studio 2016 software package [12]. The parameters used to run the MC simulation |
|---|---|
| 2 | are detailed as follows: |

Simulation cell details: Lattice parameter 3D Triclinic, (32.27*32.27*=30.13 Å³) unit cell
size, (13 × 13) unit cell and 40 Å vacuum.

5 Geometry optimization parameter: Algorithm Smart, quality convergence tolerance fine, 6 displacement convergence tolerance 10^{-4} kcal mol⁻¹. All chemical species inserted in the 7 crystal system are optimized using GGA/DPN. The displacement of these species within 8 crystal systems is under the influence of COMPASS force fields [13]. The adsorption (*E* 9 *adsorption*) and binding (E_{binding}) energies of *N-HQ* and *O-HQ* molecules on Fe (110) surfaces in 10 an aggressive acid medium are calculated according to the following two equations [13]:

11 $E_{ads} = E_{T(system)} - E_{T(inhibitor)} - E_{T(iron)} - E_{T(ions)} - E_{T(water)}$ (3)

(4)

- 12 $E_{\text{binding}} = -E_{\text{adsorption}}$
- 13

14 **3. Results and discussion**

15 3.1. Chemical study

16 *3.1.1. General procedure*

We mix (0.01 mol) of 5-(chloromethyl) quinolin-8-ol hydrochloride (5-*CMHQ*) with (0.01 mol) of bi-nucleophilic in The THF, in the presence of Et_3N . The reaction mixture was followed by CCM plate. After evaporation of tetrahydrofuran at 60 °C, the mixture is extracted with chloroform (CHCl₃). After the evaporation of the extraction solvent, a quantity of the ether (C₂H₆O) is added to solidify the product obtained. The crude product was then purified by column chromatography on silica gel and recrystallized from absolute ethanol (scheme 1).

- 24 3.1.2. Spectral data
- 25 5-(((2-aminoethyl) amino) methyl) quinolin-8-ol N-HQ

| 1 | Yield: 50 %. Green solid, Melting Point: 131-133 °C, (Absolute Ethanol). (FT-IR (KBr, |
|----|--|
| 2 | cm ⁻¹) v: 1624 (C=C), 3239 (OH), 1737 (CH ₂), 2362 (C=N). ¹ H NMR (DMSO-d ₆) (δppm): |
| 3 | 2.16 (s, 2 H, CH ₂ -NH ₂), 1.76 (s, 2 H, CH ₂ -NH), 4.86 (s, 1 H, NH ₂), 4.86 (s, 1 H, OH), 7.05- |
| 4 | 7.489.64 (m, 5 H, ArH). ¹³ C NMR (DMSO-d ₆) (δppm):153.28 (C-OH), 62.04 (CH ₂), 30.89 |
| 5 | (C-NH ₂), 110.55-128.20-129.98-139.22-148.10 (ArCH), 130.13-134.07 (ArC). Anal. Calcd |
| 6 | for $C_{12}H_{15}N_3O$ in (%) (M = 231, 29 g/mol) predicted: C, 66.34; H, 6.96; N, 19.34. Found: C, |
| 7 | 66.65; H, 6.38; N, 19.07. |
| 8 | 5-((2-aminoethoxy) methyl) quinolin-8-ol O-HQ |
| 9 | Yield: 65 %. Green solid, Melting Point: 113-115 °C, (Absolute Ethanol). (FT-IR (KBr, |
| 10 | cm ⁻¹) v: 1625 (C=C), 3238 (OH), 2033 (CH ₂), 2361 (C=N). ¹ H NMR (DMSO-d ₆) (δppm): |
| 11 | 7.62 (s, 2 H, CH ₂ -NH ₂), 6.89 (s, 2 H, CH ₂ -O), 6.94 (s, 1 H, OH), 7.89-8.20 (m, 5 H, ArH). ¹³ C |
| 12 | NMR (DMSO-d ₆) (δppm):198.47 (C-OH), 27.98 (C-NH ₂), 124.35-148.41 (ArCH of |
| 13 | quinoline), 131.15-140.72 (ArC of quinoline). Anal. Calcd for $C_{12}H_{14}N_2O_2$ in (%) |
| 14 | (M = 218.25 g/mol) predicted: C, 66.04; H, 6.47; N, 12.84. Found: C, 66.10; H, 6.83; N, |
| 15 | 12.90. |

- 16 **3.2. Corrosion test**
- 17 3.2.1. Potentiodynamic polarization

The potentiodynamic polarization (*PDP*) gives us permission to extract specific parameters on
the corrosion process [14-17]. The data obtained by this technique are summarized in Table 1
and Fig. 1.

The shape of the curves of Fig. 1 shows that of the two organic inhibitors is a mixed type during the reaction with mild steel in 1.0 M HCl [18]. The addition of the two compounds also causes the modification in the values of the anodic and cathodic slopes. This means that the two compounds have been well adsorbed on the surface of the steel [19]. On the other hand, the addition of the two compounds causes a decrease in the values of the current density

(*i*). This can be explained by the formation of an organic film on the surface of the steel that
blocks the passage of electric current [19-21]. The decrease in current density values causes
an increase in the inhibitory efficiency values for the two compounds at different
concentrations (98.2 % for *O-HQ* and 98.5 % for *N-HQ*).

5 3.2.2. Electrochemical impedance spectroscopy

6 The stationary electrochemical technique remains insufficient to characterize the complex 7 mechanisms, involving several reaction stages and having different characteristic kinetics. 8 Moreover, many studies have shown that electrochemical impedance measurements are 9 capable of elementary steps involved in global corrosion and/or protection processes. The use 10 of transient techniques, then becomes essential to elucidate the mechanism of action of the 11 inhibitor. In our case, we carried out the electrochemical impedance measurements for the 12 steel/1.0 M HCl interfaces alone and with inhibitors [22, 23].

We observe that these diagrams (Fig. 2) present a single capacitive loop in the form of a semicircle having a phase shift with respect to the axis of the real (the semicircle center is located below the axis of the real), characteristic of solid electrodes of heterogeneous and irregular surface. The best fit of the parameters of the impedance spectroscopy is obtained by the equivalent circuit shown in Fig. 3. The bode and phase diagrams show that there is a single time constant (τ) which confirms the equivalent circuit pattern found [24, 25].

19 This circuit consists of the electrolyte resistance (R_s) , the polarization resistance (R_p) and a 20 constant phase element (*CPE*).

From Table 2 the addition of the organic compounds caused an increase in the values of the polarization resistance (R_p) , also a decrease in the values of the double layer capacity (C_{dl}) . These results explain the presence of a film on the surface of the steel which confirms the adsorption of the two compounds on the metal surface [26]. The study of the impedance spectroscopy confirms the results of polarization in terms of efficiency (N-HQ > O-HQ). In

acidic media, the nitrogen compounds is more effective than the compounds containing the
oxygen atom, which explains the good resistance of the *N-HQ* compound relative to the *O*-*HQ* compound [24].

4 3.2.3. Influence of temperature and activation parameters

The Fig. S1 shows that the polarization curves vary in a non-symmetrical way in the anode and cathode branches. The increase in temperature causes an increase in current density (*i*) values, which leads to a decrease in the inhibitory efficiency values, but this decrease remains low. In 328 K, the inhibitory efficiency is of the order of 83 % to compose *N-HQ* and 80 % of the compound *O-HQ* (Table 3). However, Both compounds are profitable for the corrosion inhibition of steel in high temperature molar HCl. Therefore, these compounds can be used in the industrial field.

12 Thanks to the effects of the temperature we were able to access the calculation of several 13 activations parameters such as [27]: The activation energy (E_a , Equation 5), The activation 14 enthalpy (ΔH_a , Equation 6) and activation entropy (ΔS_a , Equation 6).

15
$$i_{corr} = A \exp\left(\frac{-E_a}{RT}\right)$$
 (5)

16
$$i_{corr} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a}{R}\right) \exp\left(\frac{\Delta H_a}{RT}\right)$$
 (6)

17 R, A and T are, respectively, constant perfect gas (8.314 J mol⁻¹ K⁻¹),
18 pre-exponential factor and the temperature in Kelvin.

The values of the activation energies have been extracted from the figure S2 and the values of the other two activation parameters (ΔH_a , ΔS_a) were extracted from Figure S3. The results in Table 3 show that after the addition of 10⁻³ M of the inhibitors (*N-HQ* and *O-HQ*) the activation energy (E_a) values become larger relative to the blank solution (1.0 M HCl). This result is explained by the creation of electrostatic interactions in the corrosive

solution in the presence of organic inhibitors [27]. In this study, the corrosion process is endothermic and spontaneous, because the value of the activation enthalpy is positive $(\Delta H_a > 0)$ for the all inhibitors [28]. The very positive values of the activation entropy (ΔS_a) compared to the HCl only solution. This that the two organic compounds are well absorbed on the surface of the steel [29].

6 **3.2.4. Adsorption isotherm**

7 The best description of the adsorption behavior of studied inhibitors was explained by
8 Langmuir adsorption isotherm (Fig. 3) as the average linear regression coefficient values (R²)
9 obtained for N-HQ and O-HQ and slope are very close to unity. All the values are listed in
10 Table 4. The isotherm is given by the following equation (7).

11
$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$
(7)

where C_{inh} is the concentration of inhibitor, θ is the surface coverage degree, and K_{ads} is the adsorptive equilibrium constant. The linear relationships of C_{inh}/θ versus C_{inh} are depicted in **Fig. 3**.

In each study of the corrosion, the only method to study the type of the interactions between metal and inhibitor is the calculation of the thermodynamic adsorption parameters [30]. Among the adsorption parameters that have been calculated in this study is the adsorption energy (ΔG_{ads}° , Equation 8).

$$\Delta G_{ads}^{\circ} = -RT Ln(55.55K_{ads})$$
(8)

According to the literature, if the values of the free energy about -40 kJ/mol mean that there are chemistry-like bonds between the metal and the inhibitor. From Table 4, the values of free energy are about -40 kJ mol. This suggests that the two inhibitors are linked to the steel by chemical bonds, according to Langmuir adsorption isotherm (R² close to unity, Fig. 3)
 [31,32].

3 3.2.5. UV-visible spectrometry

To confirm the complexing property of the two compounds with iron we carried out a study 4 by UV-visible spectroscopy (Fig. 4) [33]. In the case of compounds in HCl alone, the 5 maximum wavelength values (λ_{max}) are of the order of 262.29 nm for the compound **N-HQ** 6 and 256.32 nm for the compound **O-HQ**. On the other hand, in the case of the addition of steel 7 to the solution containing HCl molar and the two inhibitors after 6 h of submersion, the 8 maximum values of wavelengths (λ_{max}) are moving of 262.29 nm at 314.48 nm for the 9 10 compound *N-HQ* and 256.32 nm at 264.36 nm for the compound *O-HQ*. These values (262.29 nm and 256.32nm) of the maximum wavelength (λ_{max}) attributed to the band π - π *, 11 This confirmed that our compound has a complexing property with ferrous ions [33,34]. 12

13 *3.2.6. Surface morphological*

14 3.2.6.1. FTIR-analysis

The surface of the iron after six hours of submersion in acidic solution contains of the 15 quinoline substituted, analyzed by the infrared spectroscopy (Fig. 5.A-D). The observation of 16 the spectra after the addition of the inhibitors (Fig. 5.B,D) shows the presence of the 17 characteristic peaks corresponding to the CH_2 , OH and C = N groups, this shows the presence 18 of the organic chemical substance on the surface of the iron. Moreover, in the spectra of the 19 adsorbed film (Fig. 5.B,D) the intensity of the alcohol (OH) groups of the two compounds is 20 decreased, this decrease signifies that the alcohol (OH) function has become occupied because 21 of complexation between quinoline substituted and of the iron ions [35]. 22

23 3.2.6.2. SEM-EDS analysis

24 The morphology of the surface was characterized by scanning electron spectroscopy coupled

25 with energy dispersion microscopy (SEM-EDS) (Fig. 6.A-C). The surface of the steel in HCl

alone was destroyed by the pitting corrosion (Fig. 6.C). After addition of the compounds *N*-*HQ* and *O*-*HQ* for 6 hours of submersion (Fig. 6.A,B), the surface becomes well protected by
layers of the organic compounds. However, the *EDS* spectra show that there are carbon atoms,
nitrogen and oxygen in the metal surface, this confirmed the our compounds are well
adsorbed on the surface of the steel. The *MEB-EDX* studies confirm the results obtained
during infrared spectroscopy (*FT-IR*).

7 3.3. Theoretical calculations

8 *3.3.1. DFT calculations*

Quantum chemical calculations using the theory of DFT were carried out in order to find 9 relationship between quantum chemical properties and corrosion inhibition of the studied 10 molecules. In this context, the experimental study shows that inhibitors N-HQ and O-HQ are 11 effective against corrosion. While the chemical quantum study of DFT/ B3LYP was based on 12 13 calculations of quantum chemical descriptors and molecular orbital (energy) parameters using the 6-31G (d,p) and 6-311G++ (d, p) basis sets. Frontier molecular orbital's (FMO) namely 14 LUMO (lowest unoccupied molecular orbital) and HOMO (highest occupied molecular 15 orbital) are important for locating the reactive parts in a molecule. Fig. 7 visualizes the 16 different optimized geometry of the quinoline derivatives mentioned for the three studied 17 bases, the electron density distribution of the FMO and the molecular electrostatic potential of 18 surface (MEPS). In Fig. 7, the distribution of HOMO and LUMO is distributed on all the 19 atoms of the aromatic rings of the *N*-HQ and *O*-HQ inhibitors for 6-31G (d, p) and 6-311G++ 20 (d, p) basis sets. This indicates that these atoms may be responsible for the reactivity of the 21 selected molecules. Non attendance of unreal frequency for the different optimized molecules 22 of *N-HQ* and *O-HQ* with the two selected basis sets. 23

The quantum chemical descriptors (*QCD*) were extracted basing on electronic properties of the ground state of the molecular structures. FMO energies such as the E_{HOMO} , the E_{LUMO} and

the energy gap ($\Delta E = E_{LUMO} - E_{HOMO}$) were calculated for all the inhibitors are calculated for the two selected inhibitors at the two used basis sets. In addition, the main parameters describing the chemical reactivity of the tested molecules are global hardness (η), global electronegativity (χ), electrophilicity (ω) and nucleophilicity (ε) index and number displaced electrons from occupied orbitals of the inhibitors to no-occupied orbitals of the metal surface of the iron (110) (ΔN_{110}) were determined using the following different equations [36-40].

7
$$\eta_{inh} = \frac{E_{LUMO} - E_{HOMO}}{2} = \frac{\Delta E_{gap}}{2}$$
(9)

8
$$\chi_{inh} = -\frac{1}{2} (E_{HOMO} + E_{LUMO})$$
 (10)

9
$$\omega_{inh} = \frac{\chi_{inh}^2}{2\eta_{inh}}$$
 (11)

10
$$\varepsilon_{inh} = \frac{1}{\omega_{inh}}$$
 (12)

11
$$\Delta N_{110} = \frac{\phi - \chi_{inh}}{2(\eta_{Fe_{110}} + \eta_{inh})} = \frac{\phi - \chi_{inh}}{2\eta_{inh}}$$
(13)

12 To calculate the ΔN , we introduced the job function (ϕ) which equals the 4.82 eV in the 13 lattice plane (110) of Fe. In addition, the hardness value of Fe (η_{Fe}) is zero for IP = EA which 14 corresponds the metallic bulk [41].

Usually, High value of E_{HOMO} reflects high capacity of an inhibitor to offer its electron to a vacant orbital of the metal. On the other hand, low value of E_{LUMO} translates the great possibility of receiving electrons. In addition, molecules have higher reactivity, they have a lower energy gap (ΔE). The results of these parameters are reported in Table 5. By looking at the values of the calculated parameters at two basis sets for the two molecules studied, we observed that the molecule *N*-*HQ* showed the lowest ΔE_{gap} , the highest E_{HOMO} , the lowest η , the highest χ and the highest ω , all indicating to greater electron donating ability and

molecular reactivity. All these elements justify the high inhibitory efficiency of *N-HQ*, as 1 2 observed from experimental studies. While the theoretical values of ΔN_{110} are not adaptable with the order of the experimental inhibition efficiencies. Concerning the lower values of 3 E_{LUMO} and ε for the compound *N*-HQ in the two basis sets used indicate that the latter have 4 more available centers to accept electrons. This behavior appears in the selected two basis sets 5 6 selected, ie the *N*-HQ remains more reactive than *O*-HQ. The dipole moment (μ) is another 7 very important element used to support the experimental results. This could promote strong electrostatic interactions between the tested structures and the metal surface, this type of 8 9 interaction contribute to better adsorption of *N*-HQ on the carbon steel surface than *O*-HQ. All the calculation results obtained by the two basis sets show that the inhibitory molecule N-10 HQ is more reactive than the inhibitory molecule O-HQ. The results of the calculation allow 11 us to judge that there is a correlation between the calculation of the QCD of the neutral 12 molecules N-HQ and O-HQ and the experimental results. 13

On another side, organic molecules having heteroatoms can be protonated in an acid medium 14 to form ammonium ions. For this, we followed the same procedure what we have previously 15 adopted for the quantum chemical calculation of the protonated forms. The main QCD of the 16 protonated molecules are shown in Table 6. Results presented in this table showed that values 17 of all the parameters are more modified after to the protonation of the studied molecules. 18 Indeed, the values of E_{HOMO} and ΔN_{110} are shifted to more intense and less negative values. 19 This indicates that the protonated molecules can accept electrons in a more important way. 20 This result reflects that the proton forms behave like Lewis acids [42]. 21

While, the decrease in the values of ΔE and the increase in the values of w show that the reactivity of the protonated inhibitors is greater than that of the neutral forms. Meanwhile, the higher values of the dipole moment of the protonated forms indicate that these molecules are the most polarizable when they come into contact with the metal surface. These observationsare generalized for all the results obtained in the three phases mentioned.

3 3.3.2. Fukui functions

Fukui functions (*FF*) population analysis provides information about the number of active centers (atoms) in an inhibitor. Table 7 collates the density values of Fukui functions corresponding to the centers responsible for the electrophilic $(f(r)^{+})$ or nucleophilic $f(r)^{-}$ attack of each atom of the molecules mentioned in both forms: neutral and protonated. The two *FF* of $f_i(r)^{+}$ and $f_i(r)^{-}$ are calculated using the following two equations 14 and 15 [43,44]: $f_i(r)^{+} = q_i(N+1) - q_i(N)$ (14)

11
$$f_i \left(\stackrel{\mathbf{r}}{r} \right)^- = q_i \left(N \right) - q_i \left(N - 1 \right)$$
(15)

Where the charge values of atom i for cation, neutral and anion are qi (N+1), qi (N) and qi (N1), respectively.

14 The values of the $f_i(\stackrel{r}{r})^+$ and $f_i(\stackrel{r}{r})^-$ of *N-HQ* and *O-HQ* are calculated by the of Materials 15 Studio 8 software from Biovia-Accelrys Inc., using a *GGA* exchange-correlation functional in 16 the Dmol³ module with the polarization function *DNP*.

17 Inevitably, sites that are characterized by high values of $f_i(r)^+$, so, these sites are considered as 18 electron acceptors. While, Sites with high values of $f_i(r)^-$ are capable of releasing electrons. 19 Table 7 shows that the atoms that are responsible for the electrophilic attack for two neutral 20 substances *N-HQ* and *O-HQ*, we quote C2, C3, C6, O11 and C13. However, the N7, C8 and 21 C10 atoms of the neutral structures *N-HQ* and *O-HQ* are considered favorable sites for 22 receiving electrons. Concerning the protonated forms and according to Table 7, it is clear that 23 the centers that are responsible for the nucleophilic attack, they are found with lower densities

1 for the two protonated molecules *N*-*HQ* and *O*-*HQ*. This indicates that the protonated form 2 behaves like LEWIS acid (cationic form). So, it's a good electron acceptor. Indeed, we justified 3 this observation by the existence of sites available for electron acceptance (as C2, N7, C8 and 4 C10) and the native values of electron transfer fraction ΔN_{110} (Table 6).

5 *3.3.3. MC simulations*

The objective of a Monte Carlo (MC) simulation is to generate an ensemble of representative 6 configurations under specific conditions for a macromolecular system. The application of 7 disturbance and the random dynamics of a system results in an end stable position. In this 8 study, we were more focused on studying the behavior of the system (Surface Fe (110) / 9 molecules (*N*-HQ and *O*-HQ) in a simulated aggressive acid environment with 5 (H₃O⁺, Cl⁻) 10 and 500 H₂O. The most stable optimized molecules of the investigated 8-hydroxyquinoline 11 derivatives (*N-HQ* and *O-HQ*) was incorporated in the simulation process on Fe (110) 12 13 surface. The orientations of compounds with the least energy in the simulated test solution are displayed in Fig. 8. As evident from this figure, structures were adsorbed onto Fe (110) 14 the aromatic 15 surface in а parallel configuration involving heterocyclic of 8-hydroxyquinoline. This type of interaction is due to the electronic cloud present in aromatic 16 nuclei. In addition, the studied molecules are also adsorbed by the functional groups namely 17 secondary amine function (-N-) for *N-HQ* and the ether function (-o-) for *O-HQ*, which was 18 justified by the presence of free lone pair electron of O and N heteroatom's. 19

To explore the interactions of structures *N*-*HQ* and *O*-*HQ* with the Fe (110) surface of iron, an appropriate analysis for the energy calculations namely the total energy, the adsorption (E_{ads}) energy or interaction (E_{int}) energy (E_{ads} - E_{int}), the reports of energies for the elements of the system being studied (dE_{ads}/dN_i). So, the different values of these energies are illustrated in Table 8. From these data, it obvious that the E_{ads} and E_{tot} energies of *N*-*HQ* and *O*-*HQ* molecules are of large negative values. This indicates that the adsorption could occur readily

and spontaneously on the corroding metal surface [44-46] The E_{ads} of the molecule (*N-HQ*) ($E_{ads} = -5530.897$ kcal/mol) is higher than that of the inhibitor (*O-HQ*) ($E_{ads} = 5521.463$ kcal/mol), which means that the binding ($E_{binding}$) of *N-HQ* molecule with Fe (110) surface in the aggressive environment studies is stronger than *O-HQ*. As shown in Fig. 9, this result is in support of the highest inhibition efficiency of *N-HQ* as obtained from experimental studies.

Further insights on the interaction of the investigated compounds with Fe surface was 7 dervived from analyzing pair correlation functions (*PCF*) g(r). This theoretical function is an 8 established method to measure the bond length between the interacting molecules and the 9 targeted surface substrate [47]. As previously reported in literature, the peaks occur at 1 Å-3.510 Å is related to chemisorption, by contrast the peaks appear further than 3.5 Å is associated 11 with electrostatic interaction [48]. PCF plots of S, N atoms in the investigated compounds are 12 13 displayed in Fig. 10 where it is clear that the highest peaks on both compounds with Fe-atoms appear at distance less than 3.5 A indicating high probability of the formation of chemical 14 15 bonding between investigated molecules with Fe atom surface. Also, the highest peak of **N-HQ** compound is obviously larger than the one of **O-HQ**, this means that the former 16 compound binds more strongly than the latter with the corroding metal surface. 17

18

19

20 **4.** Conclusion

In summary, In this work, we have prepared and characterized two new compounds derived from 8-hydroxyquinoline in one step by a simple synthesis. The two new compounds are tested as corrosion inhibitors for steel in molar HCl by electrochemical (*EIS* and *PDP*) and theoretical (*DFT* and *MC*) methods. The both studies show that both compounds are very good corrosion inhibitors (98 % for the compound *N-HQ* and 96 % for the compound *O-HQ*).

The *PDP* study shows that both inhibitors act as inhibitors of the mixed type and also remain effective at high temperature (328 K). However, the thermodynamic adsorption studies show that the two inhibitors adsorb to the surface of the steel by chemical bonds following isothermal adsorption of Langmuir. Infrared spectroscopy and *SEM-EDX* spectroscopy show that the metal surface has been well protected after the addition of the two inhibitors. Moreover, the analysis of gravimetric solutions by UV-visible spectroscopy (*UV-vis*) shows that both compounds have a complexing property with ferrous ions.

8

9 **References**

10 [1] L.O. Olasunkanmi, M.M. Kabanda, E.E. Ebenso, Quinoxaline derivatives as corrosion

11 inhibitors for mild steel in hydrochloric acid medium: Electrochemical and quantum chemical

- 12 studies, Physica E 76 (2016) 109-126.
- 13 [2] M. Rbaa, A. Oubihi, M. Ouhssine, F. Almalki, T.B. Hadda, A. Zarrouk, B. Lakhrissi,

14 Synthesis of New Heterocyclic Systems Oxazino Derivatives of 8-Hydroxyquinoline: Drug

- 15 Design and POM Analyses of Substituent Effects on their Potential Antibacterial Properties,
- 16 Chem. Data Collect. 24 (2019) 100306.

17 [3] M. Rbaa, S. Jabli, Y. Lakhrissi, M. Ouhssine, F. Almalki, T.B. Hadda, S. M. Moumene,

18 A. Zarrouk, B. Lakhrissi, Synthesis, antibacterial properties and bioinformatics computational

analyses of novel 8-hydroxyquinoline derivatives, Heliyon 5(10) (2019) e02689.

20 [4] M. Rbaa, A.S. Abousalem, M.E. Touhami, I. Warad, F. Bentiss, B. Lakhrissi, A. Zarrouk,

21 Novel Cu (II) and Zn (II) complexes of 8-hydroxyquinoline derivatives as effective corrosion

22 inhibitors for mild steel in 1.0 M HCl solution: Computer modeling supported experimental

- 23 studies, J. Mol. Liq. 290 (2019) 111243.
- 24 [5] O. Fergachi, F. Benhiba, M. Rbaa, M. Ouakki, M. Galai, R. Touir, M.E. Touhami,
- 25 Corrosion Inhibition of Ordinary Steel in 5.0 M HCl Medium by Benzimidazole Derivatives:
- 26 Electrochemical, UV-Visible Spectrometry, and DFT Calculations, J. Bio-and Tribo-
- 27 Corrosion 5(1) (2019) 2-13.
- 28 [6] S. Indira, G. Vinoth, M. Bharathi, K. Shanmuga Bharathi, Synthesis, spectral,
- 29 electrochemical, in-vitro antimicrobial and antioxidant activities of bisphenolic mannich base
- 30 and 8-hydroxyquinoline based mixed ligands and their transition metal complexes, J. Mol.
- 31 Struct. 1198 (2019) 126886.

- 1 [7] M. Rbaa, M. Galai, A.S. Abousalem, B. Lakhrissi, M.E. Touhami, I. Warad, A. Zarrouk,
- 2 Synthetic, spectroscopic characterization, empirical and theoretical investigations on the
- 3 corrosion inhibition characteristics of mild steel in molar hydrochloric acid by three novel 8-
- 4 hydroxyquinoline derivatives, Ionics 13(8) (2019) 1-20.
- [8] S. K. Saha, P. Ghosh, A. Hens, N.C. Murmu, P. Banerjee, Density functional theory and
 molecular dynamics simulation study on corrosion inhibition performance of mild steel by
 mercapto-quinoline Schiff base corrosion inhibitor, Physica E 66 (2015) 332-341.
- 8 [9] M. Rbaa, B. Lakhrissi, Novel oxazole and imidazole based on 8-Hydroxyquinoline as a
 9 Corrosion Inhibition of mild steel in HCl Solution: Insights from Experimental and
- 10 Computational Studies, Surf. Interfaces 15 (2019) 43-59.
- 11 [10] O. Fergachi, F. Benhiba, M. Rbaa, R. Touira, M. Ouakki, M. Galaia, B. Lakhrissi, H.
- 12 Oudda, M. E. Touhami, Experimental and Theoretical Study of Corrosion Inhibition of Mild
- 13 Steel in 1.0 M HCl Medium by 2(-4(hloro phenyl-1H- benzo[d]imidazol)-114 yl)phenyl)methanone, Mat. Res. 6 (21) (2018) 1516-1439.
- 15 [11] A. Zarrouk, B. Hammouti, A. Dafali, M. Bouachrine, H. Zarrok, S. Boukhris, S.S. Al-
- Deyab, A theoretical study on the inhibition efficiencies of some quinoxalines as corrosion
 inhibitors of copperin nitric acid, J. Saudi Chem. Soc. 18 (2014) 450-455.
- [12] M. Rbaa, F. Benhiba, I.B. Obot, H. Oudda, I. Warad, B. Lakhrissi, A. Zarrouk, Two new
 8-hydroxyquinoline derivatives as an efficient corrosion inhibitors for mild steel in
 hydrochloric acid: Synthesis, electrochemical, surface morphological, UV-visible and
- 21 theoretical studies, J. Mol. Liq. 12 (276) (2018) 120-133.
- 22 [13] A. Ramazani, M. Sheikhi, H. Yahyaei, Molecular Structure, NMR, FMO, MEP and NBO
- Analysis of Ethyl-(Z)-3-phenyl-2-(5-phenyl-2H-1,2,3,4-tetraazol-2-yl)-2-propenoate Based on
- HF and DFT Calculations, Chem. Methodol. 1 (2017) 28-48.
- 25 [14] M. Khattabi, F. Benhiba, S. Tabti, A. Djedouani, A. El Assyry, R. Touzani, I. Warad, H.
- 26 Oudda, A. Zarrouk, Performance and computational studies of two soluble pyran derivatives
- as corrosion inhibitors for mild steel in HCl, J. Mol. Struct. 1196 (2019) 231-244.
- 28 [15] J. Cruz, T. Pandiyan, E. Garcia-Ochoa, J. Electroanal. Chem. 583 (2005) 8-16.
- 29 [16] L.M. Rodriguez-Valdez, A. Martínez-Villafañe, D. Glossman-Mitnik, J. Mol. Struct.
- 30 THEOCHEM 713 (2005) 65-70.
- 31 [17] I.B. Obot, N.O. Obi-Egbedi, N.W. Odozi, Acenaphtho [1,2-b] quinoxaline as a novel
- 32 corrosion inhibitor for mild steel in $0.5M H_2SO_4$, Corros. Sci. 52 (2010) 923-926.

- [18] A.Y. El-Etre, A.I. Ali, A novel green inhibitor for C-steel corrosion in 2.0 mol L⁻¹ 1
- hydrochloric acid solution, Chin. J. Chem. Eng. 25(3) (2017) 373-380. 2
- [19] H. Hamani, T. Douadi, M. Al-Noaimi, S. Issaadi, D. Daoud, S. Chafaa, Electrochemical 3
- and quantum chemical studies of some azomethine compounds as corrosion inhibitors for 4
- mild steel in 1 M hydrochloric acid, Corros. Sci. 88 (2014) 234-245. 5
- [20] A. Yousefi, S. A. Aslanzadeh, J. Akbari, Experimental and DFT studies of 1-6 7 methylimidazolium trinitrophenoxide as modifier for corrosion inhibition of SDS for mild steel in hydrochloric acid, Anti-Corros. Methods Mater. 65 (1) (2018) 107-122. 8
- [21] A. Zarrouk, H. Zarrok, Y. Ramli, M. Bouachrine, B. Hammouti, A. Sahibed-dine, F. 9
- Bentiss, Inhibitive properties, adsorption and theoretical study of 3,7-dimethyl-1-(prop-2-yn-10
- 1-yl)quinoxalin-2(1H)-one as efficient corrosion inhibitor for carbon steel in hydrochloric 11
- acid solution, J. Mol. Liq. 222 (2016) 239-252. 12
- [22] K.R. Ansari, M.A. Quraishi, A. Singh, Schiff's base of pyridyl substituted triazoles as 13
- new and effective corrosion inhibitors for mild steel in hydrochloric acid solution, Corros. 14
- 15 Sci. 79 (2014) 5-15.
- [23] T. Douadi, H. Hamani, D. Daoud, M. Al-Noaimi, S. Chafaa, Effect of temperature and 16
- hydrodynamic conditions on corrosion inhibition of an azomethine compounds for mild steel 17 in 1 M HCl solution, J. Taiwan Inst. Chem. Eng. 71 (2017) 388-404.
- 18
- [24] J. Yang, Y. Lu, Z. Guo, J. Gu, C. Gu, Corrosion behaviour of a quenched and partitioned 19 medium carbon steel in 3.5 wt.% NaCl solution, Corros. Sci. 130 (2018) 64-75. 20
- [25] M. El Faydy, M. Galai, M. Ebn Touhami, I. B. Obot, B. Lakhrissi, A. Zarrouk, 21
- Anticorrosion potential of some 5-amino-8-hydroxyguinolines derivatives on carbon steel in 22
- hydrochloric acid solution: gravimetric, electrochemical, surface morphological, UV-visible, 23
- DFT and Monte Carlo simulations, J. Mol. Liq. 248 (2017) 1014-1027. 24
- [26] J. Yang, Y. Lu, Z. Guo, J. Gu, C. Gu, Corrosion behaviour of a quenched and partitioned 25 medium carbon steel in 3.5 wt.% NaCl solution, Corros. Sci. 130 (2018) 64-75.
- 26
- [27] H. Tayebi, H. Bourazmi, B. Himmi, A. El Assyry, Y. Ramli, A. Zarrouk, A. Geunbour, 27
- 28 B. Hammouti, Eno E. Ebenso, An electrochemical and theoretical evaluation of new quinoline
- derivative as a corrosion inhibitor for carbon steel in HCl solutions, Der Pharm. Lett. 6(6) 29 (2014) 20-34. 30
- [28] B. Hirschorn, M.E. Orazem, B. Tribollet, V. Vivier, I. Frateur, M. Musiani, 31
- Determination of effective capacitance and film thickness from constant-phase-element 32 parameters, Electrochim. Acta 55 (21) (2010) 6218-6227. 33

- 1 [29] M. Rbaa, M. Galai, Y. El Kacimi, M. Ouakki, R. Touir, B. Lakhrissi, M.E. Touhami,
- 2 Adsorption Properties and Inhibition of Carbon Steel Corrosion in a Hydrochloric Solution by
- 3 2-(4, 5-diphenyl-4, 5-dihydro-1h-imidazol-2-yl)-5-methoxyphenol, Port. Electrochim. Acta 35
- 4 (6) (2017) 323-338.
- 5 [30] H. Zarrok, S.S. Al-Deyab, A. Zarrouk, R. Salghi, B. Hammouti, H. Oudda, M.
- 6 Bouachrine, F. Bentiss, Thermodynamic Characterisation and Density Functional Theory
- 7 Investigation of 1,1',5,5'-Tetramethyl-1H, 1'H-3,3'- Bipyrazole as Corrosion Inhibitor of C38
- 8 Steel Corrosion in HCl, Int. J. Electrochem. Sci. 7 (2012) 4047-4063.
- 9 [31] O. Dagdag, A. El Harfi, O. Cherkaoui, Z. Safi, N. Wazzan, L. Guo, R.T. Jalgham,
- 10 Rheological, electrochemical, surface, DFT and molecular dynamics simulation studies on the
- 11 anticorrosive properties of new epoxy monomer compound for steel in 1 M HCl solution,
- 12 RSC adv. 9 (8) (2019) 4454-4462.
- 13 [32] I. Ahamad, R. Prasad, M.A. Quraishi, Thermodynamic, electrochemical and quantum
- chemical investigation of some Schiff bases as corrosion inhibitors for mild steel in
 hydrochloric acid solutions, Corros, Sci. 52 (2010) 933-942.
- 16 [33] E.A. Noor, A.H. Al-Moubaraki, Thermodynamic study of metal corrosion and inhibitor
- adsorption processes in mild steel/1-methyl-4 [4'(-X)-styry] pyridinium iodides/hydrochloric
- 18 acid systems, Mater. Chem. Phys. 110 (2008) 145-154.
- 19 [34] Y. Abboud, A. Abourriche, T. Saffaj, M. Berrada, M. Charrouf, A. Bennamara, H.
- 20 Hannache, A novel azo dye, 8-quinolinol-5-azoantipyrine as corrosion inhibitor for mild steel
- 21 in acidic media, Desalination 237 (1-3) (2009) 175-189.
- 22 [35] M. Gopiraman, N. Selvakumaran, D. Kesavan, Adsorption and corrosion inhibition
- 23 behaviour of N-(phenylcarbamothioyl) benzamide on mild steel in acidic medium, Prog. Org.
- 24 Coat. 73(1) (2012) 104-111.
- 25 [36] C. Wang, C. Lai, B. Xie, X. Guo, D. Fu, B. Li, S. Zhu, Corrosion inhibition of mild steel
- 26 in HCl medium by S-benzyl-O, O'-bis (2-naphthyl) dithiophosphate with ultra-long lifespan,
- 27 Results Phys. 10 (2018) 558-567.
- [37] L. Jiang, Y. Qiang, Z. Lei, J. Wang, Z. Qin, B. Xiang, Excellent corrosion inhibition
 performance of novel quinoline derivatives on mild steel in HCl media: experimental and
- 30 computational investigations, J. Mol. Liq. 255 (2018) 53-63.
- 31 [38] F. Benhiba, H. Zarrok, A. Elmidaoui, M. El Hezzat, R. Touir, A. Guenbour, A. Zarrouk,
- 32 S.Boukhris, H.Oudda, Theoretical prediction and experimental study of 2-phenyl-1, 4-

- Journal Pre-proof
- 1 dihydroquinoxaline as a novel corrosion inhibitor for carbon steel in 1.0 HCl, J. Mater.
- 2 Environ. Sci. 6 (8)(2015) 2301-2314.
- 3 [39] R. Nabah, F. Benhiba, Y. Ramli, M. Ouakki, M. Cherkaoui, H. Oudda, R. Touir, I.
- 4 Warad, A. Zarrouk, Corrosion inhibition Study of 5, 5-diphenylimidazolidine-2, 4-dione for
- 5 Mild Steel corrosion in 1 M HCl solution: Experimental, theoretical computational and Monte
- 6 Carlo simulations studies, Anal. Bioanal. Electrochem. 10(10) (2018)1375-1398.
- 7 [40] D.V. Andreeva, E.V. Skorb, D.G. Shchukin, Layer-by-layer polyelectrolyte/inhibitor
- nanostructures for metal corrosion protection, ACS Appl. Mater. Interfaces 2(7) (2010) 19541962.
- 10 [41] A. Zarrouk, I. El Ouali, M. Bouachrine, B. Hammouti, Y. Ramli, E. M. Essassi, I. Warad,
- 11 A. Aouniti, R. Salghi, Theoretical approach to the corrosion inhibition efficiency of some
- 12 quinoxaline derivatives of steel in acid media using the DFT method, Res. Chem. Intermed.
- 13 39 (2013) 1125-1133.
- 14 [42] Ş. Erdoğan, Z.S. Safi, S. Kaya, D. Ö. Işın, L. Guo, C. Kaya, A computational study on
- 15 corrosion inhibition performances of novel quinoline derivatives against the corrosion of iron.
- 16 J. Mol. Struct. 1134 (2017) 751-761.
- 17 [43] M. El Faydy, R. Touir, M. Ebn Touhami, A. Zarrouk, C. Jama, B. Lakhrissi, L. O.
- 18 Olasunkanmi, E. E. Ebenso, F. Bentiss, Corrosion inhibition performance of newly
- 19 synthesized 5-alkoxymethyl-8-hydroxyquinoline derivatives for carbon steel in 1 M HCl
- 20 solution: experimental, DFT and Monte Carlo simulation studies, Phys. Chem. Chem. Phys. 20
- 21 (2018) 20167-20187.
- 22 [44] H. Mi, G. Xiao, X. Chen, Theoretical evaluation of corrosion inhibition performance of
- three antipyrine compounds, Comput. Theor. Chem. 1072 (2015) 7-14.
- [45] A. Fouda, G. Elewady, K. Shalabi, H.A. El-Aziz, Alcamines as corrosion inhibitors for
 reinforced steel and their effect on cement based materials and mortar performance, RSC
- 26 Adv. 5 (2015) 36957-36968.
- 27 [46] L. Guo, S. Zhang, W. Li, G. Hu, X. Li, Experimental and computational studies of two
- antibacterial drugs as corrosion inhibitors for mild steel in acid media, Mater. Corros. 65
 (2014) 935-942.
- 30 [47] A.S. Fouda, M.A. Ismail, A.S. Abousalem, G.Y. Elewady, Experimental and theoretical
- 31 studies on corrosion inhibition of 4-amidinophenyl-2, 2'-bifuran and its analogues in acidic
- 32 media, RSC Adv. **7** (2017) 46414-46430.

[48] A.S. Fouda, M.A. Ismail, G.Y. Elewady, A.S. Abousalem, Evaluation of 4 amidinophenyl-2, 2'-bithiophene and its aza-analogue as novel corrosion inhibitors for CS in
 acidic media: experimental and theoretical study, J. Mol. Liq. 240 (2017) 372-388.





- 2 Fig.1. Curves obtenaid of M-steel in 1.0 M HCl without and with the addition of *N-HQ* and
- *O-HQ* at 298 K.







Fig. 2. Nyquist diagram of steel in 1.0 M HCl, the equivalent circuit used for the sizing of
impedance spectra and Bode-phase diagrams of steel after immersion in HCl solution at
different concentrations of inhibitor *N-HQ* and *O-HQ* at 298 K.



2 Fig. 3. The isotherm Langmuir adsorption quinoline derivatives studied on the surface of mild









2 Fig. 4. UV-visible spectra of the two compounds in HCl alone (black) and in presence of the







Fig. 5. Film analysis formed after the corrosion test by infrared spectroscopy (FT-IR) with the

3 presence of the *N*-*HQ* and *O*-*HQ*.

O-HQ(A)









- Fig. 6. Surface analysis of M-steel before (C) and after (A,B) submersion for six hours in 1.0
- M HCl with 10^{-3} M of *N-HQ* and *O-HQ*.



Fig.7. Optimized geometry of the quinoline derivatives mentioned for the three studied bases,
the electron density distribution of the *FMO* and the *MEPS* parameters using the 6-31G (d, p)
and 6-311G ++(d, p) basis sets with B3LYP Hybrid functional.





Fig. 8. Top and side views of the best adsorption of the *N-HQ* and *O-HQ* on the Fe (110)
surface in acidic solution.

| | | 96 | 19% |
|---|-----|-----|------|
| | | 20. | 1270 |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| - | | | |
| 0 | | | |
| | | | |
| _ | | | |
| | | | |
| | | | |
| -5 | | | |
| - E | | | |
| (Kca | | | |
| | 50% | | |
| S Y I ■ 91.6: | 5% | | |
| S Y ■ 91.6: | 5% | | |
| Eint (K.C.) | 5% | | |
| E = = = = = = = = = = = = = = = = = = = | 5% | | |
| S N 91.6: | 5% | | |
| E | 5% | | |
| Eint(Eint(Eint(Eint(| 5% | | |
| E 91.6: | 5% | | |
| E M E E E E E E E E E E E E E | 5% | | |

- 2 Fig. 9. Correlation of interaction energies (in kcal/mol) with inhibition efficiencies (%) I_{Eexp}
- 3 of two inhibitors *N-HQ* and *O-HQ*.





- 13 <u>Tables</u>

1 Table 1

- 2 Data obtenaid of M-steel in 1.0 M HCl at 298 K at different concentrations of *N-HQ* and
- з О**-***HQ*.

| Medium | Conc. | $-E_{corr}$ | i | Tafel slopes | Tafel slopes ($mV dec^{-1}$) | |
|--------|------------------|--------------|---------------------|--------------|--------------------------------|------|
| | (M) | (mV vs. SCE) | $(\mu A \ cm^{-2})$ | $-\beta_c$ | β_a | (%) |
| 1M HCl | 00 | 424.6 | 719.3 | 43.4 | 39.0 | |
| O-HQ | 10-6 | 509.8 | 78.5 | 48.4 | 37.6 | 89.1 |
| | 10 ⁻⁵ | 492.1 | 54.8 | 45.6 | 37.0 | 92.4 |
| | 10 ⁻⁴ | 487.0 | 16.9 | 48.8 | 36.8 | 97.6 |
| | 10 ⁻³ | 479.8 | 13.1 | 44.1 | 108.6 | 98.2 |
| N-HQ | 10-6 | 492.4 | 28.5 | 50.0 | 33.8 | 96.0 |
| | 10 ⁻⁵ | 486.9 | 24.6 | 45.3 | 36.9 | 96.6 |
| | 10-4 | 477.5 | 18.7 | 50.1 | 34.2 | 97.4 |
| | 10 ⁻³ | 477.3 | 10.7 | 43.7 | 39.1 | 98.5 |

4

5 Table 2

6 Electrochemical parameters of steel in 1.0 M HCl, before and after addition different

| 7 concentrat | ions of | compounds | at | 298 | K. |
|--------------|---------|-----------|----|-----|----|
|--------------|---------|-----------|----|-----|----|

| Medium | С | R _s | R _p | C _{dl} | n _{dl} | $\eta_{ m EIS}$ |
|-----------|------------------|-------------------------|-------------------------|---------------------------|-----------------|-----------------|
| | (M) | $(\Omega \text{ cm}^2)$ | $(\Omega \text{ cm}^2)$ | $(\mu F \text{ cm}^{-2})$ | | % |
| 1.0 M HCl | 0 | 0.91 | 5.34 | 471 | 0.760 | _ |
| N-HQ | 10-6 | 1.97 | 100.5 | 89.1 | 0.859 | 94.7 |
| | 10 ⁻⁵ | 1.54 | 242.9 | 58.9 | 0.837 | 97.8 |
| | 10^{-4} | 1.94 | 303.0 | 45.9 | 0.871 | 98.2 |
| | 10-3 | 1.74 | 497.2 | 35.6 | 0.858 | 98.9 |
| О-НQ | 10-6 | 1.68 | 170.6 | 64.6 | 0.851 | 96.9 |
| | 10 ⁻⁵ | 1.71 | 207.7 | 41.4 | 0.876 | 97.4 |
| | 10 ⁻⁴ | 1.43 | 477.1 | 37.0 | 0.865 | 98.9 |
| | 10-3 | 1.56 | 474.3 | 12.3 | 0.866 | 98.9 |
| | | | | | | |

8

9 Table 3

1 Electrochemical and Activation parameters, E_a , ΔH_a and ΔS_a of the dissolution of metal in 1.0

| Temp | E _{corr} | i | β _c | β_a | η_{PDP} | Ea | ΔH_a | ΔS_a |
|-------|-------------------|--------------|----------------------|----------------------|--------------|----------------------|----------------------|-------------------------------------|
| (K) | mV/SCE | $\mu A/cm^2$ | mV dec ⁻¹ | mV dec ⁻¹ | % | kJ mol ⁻¹ | kJ mol ⁻¹ | J mol ⁻¹ K ⁻¹ |
| Blank | | | | | | | | |
| 298±2 | 424.6 | 719.3 | 43.4 | 39.0 | | 27.9 | 25.1 | -107.3 |
| 308±2 | 454.5 | 735.9 | 126.6 | 95.7 | | | — | |
| 318±2 | 456.2 | 1152.3 | 140.1 | 93.2 | | _ | | |
| 328±2 | 456.0 | 1950.6 | 139.8 | 98.0 | | — | — | |
| N-HQ | | | | | | C. | | |
| 298±2 | 479.8 | 13.1 | 48.8 | 36.8 | 98.16 | 59.4 | 56.9 | -34.3 |
| 308±2 | 475.8 | 19.0 | 47.6 | 40.7 | 97.35 | Θ | | |
| 318±2 | 481.9 | 39.1 | 50.4 | 37.5 | 94.56 |)_ | | |
| 328±2 | 479.5 | 120.0 | 39.4 | 45.8 | 83.31 | _ | — | |
| О-НQ | | | | | X | | | |
| 298±2 | 477.3 | 18.7 | 43.7 | 39.1 | 97.40 | 60.8 | 58.3 | -23.9 |
| 308±2 | 480.7 | 38.8 | 51.3 | 40.2 | 94.90 | | | |
| 318±2 | 467.3 | 120.1 | 51.7 | 37.0 | 83.33 | | — | |
| 328±2 | 490.5 | 140.2 | 50.4 | 38.2 | 80.50 | — | — | |

2 M HCl with and without protection.

4 Table 4

- 5 Constant value K_{ads} and the calculated free energy for the inhibitors from the Langmuir
- 6 isotherm.

| Inhibitor | K _{ads} | \mathbb{R}^2 | - ΔG_{ads}° |
|-----------|------------------------|----------------|----------------------------|
| | $(L \text{ mol}^{-1})$ | | (kJ mol ⁻¹) |
| N-HQ | 406257 | 0.99 | 41.95 |
| O-HQ | 207039 | 0.99 | 40.28 |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

| | Journal Pre-proof |
|---|-------------------|
| 1 | |
| 2 | |
| 3 | |

4 Table 5

5 Calculated the *QCD* for non-protonated molecules *N*-*HQ* and *O*-*HQ* for the three studied

```
6 bases in the gas phase using the 6-31G (d,p) and 6-311G ++(d,p) basis sets with B3LYP
```

7 Hybrid functional.

| Inhibitors | $E_{\rm HOMO}$ | $E_{\rm LUMO}$ | ΔE_{gap} | η | χ | ω | E | μ | ΔN_{110} |
|-------------------|---------------------|---------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|--------------------|
| | (eV) | (eV) | (eV) | (eV) | (eV) | (eV) | $(eV)^{T}$ | (D) | |
| B3LYP/6-31G(d, p) | | | | | | | | | |
| N-HO | -5.572 | -1.496 | 4.076 | 2.038 | 3.534 | 3.064 | 0.326 | 2.951 | 0.316 |
| ~ | | | | | | | | | |
| 0-НО | -5.578 | -1.464 | 4.114 | 2.057 | 3.521 | 3.013 | 0.332 | 2.779 | 0.316 |
| 0 Hg | 0.070 | 11101 | | 2.007 | 0.021 | 0.010 | 0.002 | 2.,,,, | 0.010 |
| B3LYP/6-311G++ (| d, p) | | | | | | | | |
| N-HQ | <mark>-5.945</mark> | <mark>-1.893</mark> | <mark>4.052</mark> | 2.026 | <mark>3.919</mark> | <mark>3.700</mark> | <mark>0.264</mark> | <mark>3.284</mark> | <mark>0.222</mark> |
| | | | | | | | | | |
| O-HQ | <mark>-5.949</mark> | <mark>-1.904</mark> | <mark>4.045</mark> | <mark>2.022</mark> | <mark>3.926</mark> | <mark>3.811</mark> | <mark>0.262</mark> | <mark>3.304</mark> | <mark>0.221</mark> |
| | | | | | | | | | |
| 8 | | | | | | | | | |
| 9 | | | | | | | | | |
| 10 | | | | | | | | | |
| 10 | | | | | | | | | |
| 11 | | | | | | | | | |
| 12 | | | | | | | | | |
| 10 | | | | | | | | | |
| 15 | | | | | | | | | |
| 14 | | | | | | | | | |
| 15 | | | | | | | | | |
| 10 | | | | | | | | | |
| 16 | | | | | | | | | |
| 17 Table 6 | | | | | | | | | |

1 Calculated the QCD for protonated molecules *N*-HQ and *O*-HQ for the three studied bases in

2 the gas phase using the 6-31G (d,p) and 6-311G ++ (d, p) basis sets with B3LYP Hybrid

3 functional.

| Inhibitors | E _{HOMO} (eV) | E _{LUMO} (eV) | ΔE_{gap} (eV) | η (eV) | χ (eV) | ω (eV) | ε (eV) | μ (D) | ΔN_{110} |
|-------------------|---------------------------|---------------------------|-----------------------|--------------------|--------------------|---------------------|--------------------|--------------------|---------------------|
| B3LYP/6-3 | 1G(d, p) | | | | | | | | |
| N-HQ | -8.300 | -6.802 | 1.498 | 0.749 | 7.551 | 38.062 | 0.026 | 9.147 | -1.823 |
| O-HQ | -8.469 | -6.512 | 1.957 | 0.978 | 7.490 | 28.670 | 0.035 | 8.821 | -1.365 |
| B3LYP/6-3 | 11G++ (d, p) | | | | | | | | |
| N-HQ | -8.683 | <mark>-7.353</mark> | <mark>1.330</mark> | <mark>0.665</mark> | <mark>8.018</mark> | <mark>48.337</mark> | <mark>0.021</mark> | <mark>9.156</mark> | <mark>-2.405</mark> |
| | | | | | | | | | |
| <mark>О-НQ</mark> | -8.690 | <mark>-6.976</mark> | <mark>1.714</mark> | <mark>0.857</mark> | <mark>7.833</mark> | <mark>35.797</mark> | <mark>0.028</mark> | <mark>9.021</mark> | <mark>-1.758</mark> |
| | | | | \bigcirc | | | | | |
| 4 | | | | | | | | | |

- 5 **Table 7**
- 6 Fukui functions for the neutral and Protonated of *N-HQ* and *O-HQ* compounds.

| Forms | Neutral | | | | Protonated | | | |
|------------|---|------------|---|--|---|------------|---|--|
| Inhibitors | O-HQ | N. | N-HQ | | O-HQ | | N-HQ | |
| FF | $f_i \left(\stackrel{\mathbf{r}}{r} \right)^+$ | $f(r)^{-}$ | $f_i \left(\stackrel{\mathbf{r}}{r} \right)^+$ | $f\left(\stackrel{\mathbf{r}}{r}\right)^{-}$ | $f_i \left(\stackrel{\mathbf{r}}{r} \right)^+$ | $f(r)^{-}$ | $f_i \left(\stackrel{\mathbf{r}}{r} \right)^+$ | $f\left(\stackrel{\mathbf{r}}{r}\right)^{-}$ |
| C1 | 0.033 | 0.026 | 0.029 | 0.019 | 0.027 | 0.000 | 0.027 | 0.002 |
| C2 | 0.038 | 0.062 | 0.036 | 0.050 | 0.051 | 0.000 | 0.050 | 0.001 |
| C3 | 0.042 | 0.053 | 0.042 | 0.046 | 0.030 | 0.014 | 0.030 | 0.015 |
| C4 | 0.020 | 0.028 | 0.015 | 0.025 | 0.032 | 0.006 | 0.033 | 0.005 |
| C5 | -0.002 | 0.005 | -0.006 | 0.007 | -0.001 | 0.003 | -0.000 | 0.003 |
| C6 | 0.041 | 0.085 | 0.044 | 0.060 | 0.035 | -0.009 | 0.038 | -0.011 |
| N7 | 0.097 | 0.028 | 0.103 | 0.019 | 0.063 | 0.006 | 0.065 | 0.004 |
| C8 | 0.051 | 0.031 | 0.048 | 0.029 | 0.096 | 0.012 | 0.097 | 0.012 |
| С9 | 0.028 | 0.030 | 0.025 | 0.027 | 0.009 | 0.008 | 0.008 | 0.009 |
| C10 | 0.106 | 0.023 | 0.110 | 0.012 | 0.122 | -0.005 | 0.121 | -0.005 |
| 011 | 0.051 | 0.121 | 0.057 | 0.091 | 0.029 | 0.012 | 0.029 | 0.013 |

| Journal Pre-proof | | | | | | | | | |
|-------------------|--------|--------|--------|--------|--------|--------|--------|--------|--|
| C12 | -0.010 | -0.014 | -0.012 | -0.024 | -0.007 | -0.023 | -0.011 | -0.016 | |
| 013 | -0.001 | 0.002 | -0.019 | -0.023 | 0.007 | -0.016 | -0.016 | -0.027 | |
| C14 | -0.021 | -0.023 | -0.007 | -0.021 | -0.022 | -0.017 | -0.008 | -0.070 | |
| C15 | -0.008 | -0.008 | | | -0.007 | -0.071 | | | |
| N16 | 0.007 | 0.008 | | | 0.004 | 0.374 | | | |
| N15 | | | 0.007 | 0.049 | | | 0.005 | 0.337 | |
| N30 | | | -0.004 | 0.020 | | | -0.005 | 0.000 | |

Table 8

Outputs and descriptors (in Kcal mol^{-1}) for the lowest adsorption configurations for (*O-HQ* or

N-HQ) / 500 H₂O/5H₃O⁺ /5Cl⁻/Fe (110)) systems calculated by Adsorption Locator codes.

| Molecules | Etot | E _{ads} | $E_{\ binding}$ | N-HQ: | H_3O^+ : | H_2O : | Cl ⁻ : |
|-----------|-----------|------------------|-----------------|------------------------|------------------------|------------------------|-------------------|
| | | | | dE _{ads} /dNi | dE _{ads} /dNi | dE _{ads} /dNi | dE_{ads}/dNi |
| О-НQ | -5448.223 | -5521.463 | 5521.463 | -205.676 | -146.715 | -9.3169 | -3.297 |
| N-HQ | -5454.563 | -5530.897 | 5530.897 | -206.126 | -148.264 | -10.245 | -1.179 |
| 5 | | | | | | | |
| 6 | | | | | | | |
| | | | | | | | |

Highlights

- Novel quinoline derivatives have been synthesized and characterized.
- The surface morphology was examined by SEM/EDS, FTIR and UV-visible spectroscopy.
- The experimental results were correlated with DFT and MC stimulation results.

Journal Pre-proof

Dear Editor-in-Chief,

This statement is to certify that all Authors of the article "Sample Synthesis, characterization, experimental and theoretical study of the inhibitory power of new 8-hydroxyquinoline derivatives for mild steel in 1.0 M HCl" have been seen and approved the manuscript being submitted. We warrant that the article is the Auhor's original work. We warrant that the article has not received prior publication and is not under consideration for publication elsewhere. No conflict of interest exists, or if such conflict exists, the exact nature must be declared. On behalf of all Co-Authors, the corresponding Author shall bear full responsibility for the submission.

All Authors agree that author list is correct in its content and order and that no modification to the author list can be made without the formal approval of the Editor-in-Chief, and all Authors accept that the Editor-in-Chief's decisions over acceptance or rejection.