Chitosan biopolymer effect on copper corrosion in 3.5 wt.% NaCl solution: Electrochemical and quantum chemical studies

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Abstract

The inhibition of copper corrosion by chitosan biopolymer in 3.5 wt.% NaCl solution was assessed using electrochemical impedance spectroscopy, potentiodynamic polarization and quantum chemical methods. Results obtained show that Chitosan inhibited copper dissolution in the corrosive medium. The adsorption of the studied inhibitor on the metallic surface was found to follow Langmuir adsorption model. The inhibition efficiency increased with the inhibitor concentration. From polarization measurements, Chitosan can be classified as mixed-type corrosion inhibitor. The Gibbs free energy of adsorption value revealed that the adsorption process of chitosan is endothermic and mainly by a physisorption mechanism following Langmuir adsorption isotherm model. Surface analysis performed using optic microscopy has confirmed the existence of a protective film of chitosan molecules onto copper surface. Moreover, quantum chemical calculations at B3LYP level with 6-31G (d, p) basis set lead to molecular descriptors such as E_{HOMO} (energy of the highest occupied molecular orbital), E_{LUMO} (energy of the lowest unoccupied molecular orbital), ΔE (energy gap) and μ (dipole moment). The global reactivity descriptors such as χ (electronegativity), η (global hardness), S (global softness) and ω (electrophilicity index) were derived using Koopman's theorem and analyzed. The local reactivity parameters, including Fukui functions and dual descriptor were determined and discussed. Experimental and theoretical data were in good agreement.

Keywords: *chitosan, corrosion inhibition, electrochemical, quantum chemical.*

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1. Introduction

Corrosion induced by seawater causes the rapid degradation of the metal structures exposed to it and therefore jeopardizes their proper functioning. This problem of corrosion is of great concern since the repair of the resulted structures has been proved to be an expensive process. The use of inhibitors seems to be the best way to overcome this corrosion problem. These compounds can adsorb on metal surface and block the active surface sites to reduce the corrosion rate. Benzotriazole (BTA) has long been known to

protect metal surface from corrosion with excellent corrosion inhibition performance but the disadvantage of BTA is its toxicity [1]. Their poisonous properties limit the field of their applications [2–4]. Due to high toxicity and environmental regulation restrictions, the researchers are diverted to focus on developing environmentally safe and biodegradable corrosion inhibitors. Several studies have been carried out using heteroatom (nitrogen, oxygen, sulfur...) compounds and have shown good inhibitory efficiency on different materials in different corrosive media [5–9]. Due to its molecular structure and non-toxicity, the chitosan biopolymer (Scheme 1) is one of potential candidate to safe protected metal against corrosion [10, 11]. This paper aims to evaluate the ability of chitosan biopolymer to act as corrosion inhibitor for copper in 3.5 wt.% aqueous NaCl solution. Its effectiveness against corrosion was validated using potentiodynamic polarization tests and electrochemical impedance spectroscopy tests. In contrast to the chitosan studies found in the literature [11], we have, in addition to global reactivity parameters, determined the parameters of local reactivity such as Fukui functions and dual descriptor.

Scheme 1. Chemical structure of chitosan.

2. Materials and methods

2.1 Samples

The cylindrical samples of copper with a purity of 99.9% are mounted in glass tubes of suitable diameter to provide an exposed active geometrical surface area of 3.14 cm² to the corrosive medium. Prior to each test, copper substrates were grinded with abrasive papers of decreasing particle size (400, 800, 1000, 1200 and 2000), rinsed with Milli-Q water (18.2 MΩ·cm), degreased with ethanol and then rinsed again with Milli-Q water and dried in air.

2.2 Solutions

The corrosive medium consists of a 3.5 wt.% sodium chloride solution which is obtained by dissolving Sigma-Aldrich sodium chloride (99.5%) in deionized water. The analytical Chitosan was purchased from Sigma-Aldrich. The solutions of concentrations ranging from 100 to 1000 ppm were prepared by dilution. All tests are carried out in solutions with

magnetic and aerated stirring. A Thermo-cryostat Lauda model E100 permitted to keep the electrolyte at the fixed temperature.

2.3 Electrochemical measurements

The electrochemical measurements were performed in a three-electrode cell with a volume of 0.5 L. The working electrode (WE) was copper samples, the counter electrode (CE) was a platinum wire, and the reference (Ref) electrode was a saturated calomel electrode (SCE: 0.241 V/SHE). The electrochemical study (Electrochemical impedance spectroscopy (EIS), potentiodynamic, and linear polarization) of the behavior of copper in contact with the corrosive medium in the absence or in the presence of inhibitor is carried out using an experimental device composed of a Potentiostat-Galvanostat MODULAB, a DELL computer equipped with MODULAB XM ECS software allowing data processing.

2.3.1 Potentiodynamic polarization measurements

The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -300 to 150 mV with a scan rate of 0.2 mV s^{-1} .

2.3.2 Electrochemical impedance spectroscopy (EIS)

The impedance measurements are carried out at 25°C after 1 h of immersion time in 3.5 wt.% NaCl solution with or without inhibitor. The amplitude of the applied sinusoidal voltage to the drop potential is 10 mV peak-to-peak at frequencies between 10^{-2} and 6.104 Hz with 10 points per decade. Impedance data has been analyzed and fitted by using ZView2.3 impedance software. All the impedance diagrams were performed in potentiostatic mode at the open circuit potential and presented in the Nyquist diagram ($\text{Re}-j\text{Im}$) where Re is the real and $-j\text{Im}$ is the imaginary part in Bode plane.

2.4 Surface Analysis

The morphology of the sample surface after immersion of 72 h in the 3.5 wt.% NaCl solution with or without inhibitor was analyzed with a LEICA DM6000 M optical microscope equipped with LAS V4.9 software.

2.5 Quantum chemical calculations

The present quantum calculations have been performed with Gaussian 09 series of program package [12]. In our calculations, we have used Becke's three parameter exchange functional along with the Lee-Yang-Parr non local correlation functional (B3LYP) [13] using 6-31G (d, p) basis set. Figure 1 presents the optimized structure of chitosan.

The theoretical-experimental consistency can be analyzed through two levels: global reactivity and local reactivity.

Figure 1. Optimized structure of chitosan by B3LYP/6-31G (d, p).

2.5.1 Global reactivity

For N -electrons system with total energy E , the electronegativity is given by equation 1:

$$\chi = -\mu_P = -\left(\frac{\partial E}{\partial N}\right)_{\nu(\vec{r})} \quad (1)$$

Where μ_P and $\nu(\vec{r})$ are the chemical and external potentials respectively. The chemical hardness η which is defined as the second derivative of E with respect to N is then given by equation 2:

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu(\vec{r})} \quad (2)$$

The global softness S is the inverse of the global hardness as seen in equation 3:

$$S = \frac{1}{\eta} \quad (3)$$

According to Koopman's theorem [14], the ionization potential I can be approximated as the negative of the highest occupied molecular orbital (HOMO) energy:

$$I = -E_{\text{HOMO}} \quad (4)$$

The negative of the lowest unoccupied molecular orbital (LUMO) energy is related to the electron affinity A :

$$A = -E_{\text{LUMO}} \quad (5)$$

The electronegativity was obtained using the ionization energy I and the electron affinity A as given in Equation 6:

$$\chi = \frac{I + A}{2} \quad (6)$$

The hardness which is the reciprocal of the electronegativity was obtained by equation 7:

$$\eta = \frac{I - A}{2} \quad (7)$$

When the organic molecule is in contact with the metal, electrons flow from the system with lower electronegativity to that of higher electronegativity until the chemical potential becomes equal. The fraction of electrons transferred, ΔN , was estimated according to Pearson [15]:

$$\Delta N = \frac{\chi_{\text{Cu}} - \chi_{\text{inh}}}{2(\eta_{\text{Cu}} + \eta_{\text{inh}})} \quad (8)$$

In this study, we used theoretical values of χ_{Cu} and η_{Cu} ($\chi_{\text{Cu}} = 4.98$ eV [16] and $\eta_{\text{Cu}} = 0$ [17]).

The global electrophilicity index, introduced by Parr [16] is given by equation (9):

$$\omega = \frac{\chi^2}{2\eta} \quad (9)$$

2.5.2 Local reactivity

The Fukui functions were used to analyze the local reactivity of chitosan as an inhibitor for the corrosion of copper. The condensed Fukui functions and dual descriptor are parameters which enable us to distinguish each part of the studied compound on the basis of its chemical behavior due to different substituent functional groups. The Fukui function is defined as the derivative of the electronic density $\rho(r)$ with respect to the number N of electrons:

$$f(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{\nu(r)} \quad (10)$$

The condensed Fukui functions provide information about atoms in a molecule that have a tendency to either donate (nucleophilic character) or accept (electrophilic character) an electron or a pair of electrons [18]. The nucleophilic and electrophilic Fukui function for an atom k [19] can be computed using a finite difference approximation as seen in equations 11, 12 respectively:

$$f_k^+ = [q_k(N+1) - q_k(N)] \quad \text{for nucleophilic attack (11)}$$

$$f_k^- = [q_k(N) - q_k(N-1)] \quad \text{for electrophilic attack (12)}$$

where $q_k(N+1)$, $q_k(N)$ and $q_k(N-1)$ are the charges of the atoms on the systems with $(N+1)$, N and $(N-1)$ electrons respectively.

Recently, it has been reported [20] that a new descriptor has been introduced [21, 22] which allows the determination of individual sites within the molecule with particular behaviors. A mathematical analysis reveals that dual descriptor is a more accurate tool than nucleophilic and electrophilic Fukui functions [23]. This descriptor is defined through equation 13:

$$\Delta f(r) = \left(\frac{\partial f(r)}{\partial N} \right)_{v(r)} \quad (13)$$

The condensed form [21] of the dual descriptor is given by equation 14:

$$\Delta f_k(r) = f_k^+ - f_k^- \quad (14)$$

When $\Delta f_k(r) > 0$, the process is driven by a nucleophilic attack and atom k acts as an electrophile; conversely, when $\Delta f_k(r) < 0$ the process is driven by an electrophilic attack on atom k acts as a nucleophile. The dual descriptor $\Delta f_k(r)$ is defined within the range, $\{-1; 1\}$ what really facilitates interpretation [23].

3. Results and discussion

3.1 Open circuit potential

The most immediately measurable electrochemical parameter, open circuit potential technique provides preliminary information on the nature of current processes at the metal/electrolyte interface: corrosion, passivation. The evolution of open circuit potential of the copper electrode in a 3.5 wt.% NaCl solution without and with different concentrations of chitosan is illustrated in Figure 2.

In blank solution, the open circuit potential of the copper electrode slightly evolves from -220 to -255 mV/SCE during the first hours of immersion due to the dissolution of copper and the formation of the corrosion product film. We can observe some small potential fluctuations during the immersion. A slight shift of the open circuit potential towards more negative values was also observed.

Under the presence of chitosan in NaCl solution E_{OC} shifts to more negative values and the magnitude of such shifts increases with increasing chitosan concentration. These results suggest that chitosan would exert a predominant cathodic effect in inhibiting copper corrosion in corrosive media [24]. The rise in corrosion potential after the initial decrease is indicative of the interruption of corrosion process by the formation and thickening corrosion products and chitosan film at the copper surface [25].

Figure 2. Effect of chitosan on the evolution of open circuit potential for Cu in 3.5 wt.% NaCl solution at 25°C.

3.2 Potentiodynamic measurements

Potentiodynamic polarization curves were recorded to obtain information about the influence of chitosan on anodic and cathodic processes on copper corrosion in the test solution. Figure 3 shows the polarization curves of the copper in an aerated 3.5% NaCl solution without and with addition of chitosan at different concentrations. The polarization curves were plotted after one hour of immersion in saline solution.

Figure 3. Potentiodynamic polarization curves for copper in 3.5 % NaCl solution without and with different concentrations of chitosan at 25°C.

It can be seen on potentiodynamic curves that increasing chitosan concentrations move cathodic branch of polarization curves toward lower current densities. The corrosion potential shifted toward more negative values. A compound is generally recognized as

anodic or cathodic if the variation of E_{corr} equal ± 85 mV/ECS. In this paper, E_{corr} shifted around -66 mV/ECS, less than ± 85 mV/SCE (see Table 1). Thus, chitosan is classified as mixed-type inhibitor with a great cathodic trend [26]. Corrosion parameters derived from the potentiodynamic polarization curves by Tafel extrapolation method are presented in the Table 1, along with the values of the inhibition efficiency calculated from equation (15)

$$\eta = \frac{j_{\text{corr}} - j_{\text{corr}}^{\text{inh}}}{j_{\text{corr}}} \times 100 \quad (15)$$

j_{corr} and $j_{\text{corr}}^{\text{inh}}$ (mA/cm²) are the corrosion current densities of the copper after immersion in 3.5 wt.% NaCl medium without or with addition of inhibitor respectively.

Table 1. Electrochemical parameters and inhibition efficiency of Chitosan for copper in 3.5 wt.% NaCl solution.

Concentration (ppm)	E_{corr} (mV/ECS)	j_{corr} ($\mu\text{A} \cdot \text{cm}^{-2}$)	b_a (mV/dec)	$-b_c$ (mV/dec)	R_p ($\Omega \cdot \text{cm}^2$)	η (%)
0	−224	46.5	48	94	336.60	–
100	−280	7.5	63	176	3047.1	83
300	−287	5.9	61	165	3718.4	87.31
500	−290	5.0	61	134	4129.8	89.24
1000	−287	4.5	65	148	4944.0	90.32

It can be observed from Table 1 that, the inhibition efficiency increases with the chitosan concentration in the corrosive medium whereas the corrosion current densities (j_{corr}) decrease for the same concentration range.

3.3 Adsorption isotherms

Chitosan protects the copper by adsorbing on its surface, so it would be important to determine the adsorption isotherm according to which these molecules adsorb on the metal surface. Adsorption isotherms tested in this paper were the models of Langmuir, Temkin, Freundlich (see Table 2).

Table 2. Isotherms parameters.

Langmuir		Temkin		Freundlich	
R^2	Slope	R^2	Slope	R^2	Slope
0.9999	1.0991	0.9978	1.1234	0.9968	1.1456

The best fit is obtained for Langmuir adsorption isotherm ($R^2 \approx 1$ and a slope very close to 1). Langmuir adsorption isotherm is defined by equation 16.

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (16)$$

Where $\theta(\text{theta}) = \frac{j_{corr} - j_{corr(inh)}}{j_{corr}}$ is the coverage rate and K_{ads} is the equilibrium constant of the adsorption process.

The curve of C_{inh}/θ as a function of the C_{inh} (inhibitor concentration) is shown in Figure 4. The obtained graph is linear at the study temperature, indicating that the adsorption of chitosan on the copper surface obeys the Langmuir adsorption isotherm [27].

Figure 4. Langmuir adsorption isotherms for chitosan on the copper surface in 3.5 wt.% NaCl solution at 25°C.

The equilibrium constant of the adsorption process K_{ads} is related to the free enthalpy of adsorption by the equation 17 [28].

$$\Delta G_{ads}^0 = -RT \ln 10^6 K_{ads} \quad (17)$$

In the equation (17), 10^6 is the concentration of water molecules expressed in $\text{mg} \cdot \text{L}^{-1}$, T is absolute temperature while R is universal gas constant.

The determined values of K_{ads} and ΔG_{ads}^0 have been recorded in Table 3.

Table 3. The adsorption parameters of NAC on copper in 3.5% NaCl.

R^2	n	Intercept	$K_{ads} (\text{L} / \text{mg})$	$\Delta G_{ads}^0 (\text{kJ} \cdot \text{mol}^{-1})$
0.9999	1.0991	12.47	0.08	-27.977

The negative values of ΔG_{ads}^0 indicate that the adsorption process proceeds spontaneously and stability of the adsorbed layer [29], and its value $-27.977 \text{ kJ} \cdot \text{mol}^{-1}$

indicates that chitosan adsorb on copper by both physisorption and chemisorption mechanism [30].

3.4 Electrochemical impedance spectroscopy measurements

Electrochemical Impedance Spectroscopy (EIS) was also performed in order to validate the inhibition efficiency. The electrochemical impedance Z is a complex number depending of the ac-frequency. To facilitate the analysis of impedance spectra, an equivalent electrical circuit (Figure 5) with two-time constant elements often used for copper in neutral media [31] was used to fit the impedance data.

Figure 5. Electrochemical equivalent circuit used to fit impedance data.

R_s is the resistance of the solution between the working electrode and the reference electrode, R_f is the resistance of the adsorbed film formed on the copper surface, and R_{ct} represents the charge transfer resistance linked to the dissolution of copper. CPE_f and CPE_{dl} are the constant phase elements. Figure 6 shows the Nyquist diagrams in the complex plane (opposite of the imaginary part of the impedance $-Z_{Im}$ vs. real part of the impedance Z_{Re}) plotted at E_{corr} after 1 h of immersion in corrosive media, without and with chitosan biopolymer.

Figure 6. Nyquist diagrams for copper in blank solution and with different concentrations of chitosan.

Nyquist diagrams present two badly separated capacitive loops; the first loop in high frequency (HF) range, and the second one in the low frequency (LF) range. The first capacitive loop can be related to charge transfer in the corrosion process. The presence of the second capacitive loop may be attributed to the adsorption of inhibitor molecules on the metal surface and/or all other accumulated species at the metal/solution interface (inhibitor molecules, corrosion products, *etc.*) [32]. The diameters of semicircles increase with increasing chitosan concentrations comparatively with blank solution. This increase of capacitive loop size with the addition of chitosan shows that a barrier gradually forms on the copper surface, protecting it from corrosion.

Figure 7 shows the Bode representation of copper samples plotted at E_{corr} after 1 h of immersion time in 3.5 wt.% NaCl solution without or with different concentrations of the studied biopolymer (chitosan).

Figure 7. Bode representation of copper samples plotted at E_{corr} after 1 h of immersion in 3.5 wt.% NaCl solution without and with different concentrations of chitosan.

In the presence of chitosan, the impedance values of the Cu electrode increased, especially at low frequencies; this effect was increased as the concentration increased to 1000 ppm. According to Sherif *et al.* [33], the higher the impedance values at low frequencies, the higher the passivation of the metal surface against corrosion.

3.5 Optic microscopy

Figure 8 shows the picture of the copper samples after immersion in a 3.5 wt.% NaCl solution for 72 h at 25°C without or with inhibitor (500 ppm).

The surface of the sample in the blank solution (Figure 8b) is strongly corroded if compared with the fresh grinded surface (Figure 8a). The corrosion products cover virtually the entire surface of the metal. In the presence of chitosan (Figure 8c), the copper surface is less corroded, confirming that the metal surface was fully covered with the inhibitor molecules and a protective inhibitor film was formed during the immersion. These results suggest the inhibitor effect of chitosan biopolymer.

Figure 8. Optical micrographs of copper samples: (8a) bare sample, (8b) immersed in the blank solution and (8c) immersed in 3.5 wt.% NaCl with 500 ppm of chitosan for 72 h at 25°C.

3.6 Quantum chemistry calculations

3.6.1 Global parameters

In Table 4, we list the values of selected quantum chemical parameters calculated for the studied compound by using DFT methods.

Table 4. Molecular and reactivity descriptors of chitosan.

Descriptor	Value	Descriptor	Value
E_{HOMO} (eV)	−5.0545	I (eV)	5.0545
E_{LUMO} (eV)	0.8510	A (eV)	−0.8510
ΔE (eV)	5.9055	μ (Debye)	1.1509
ΔN	0.1315	η (eV)	2.9528
S (eV) ^{−1}	0.3387	ω	2.9920
χ (eV)	4.2035	TE (a.u)	−1182.9559

The energies [17] of the frontier orbitals E_{HOMO} (energy of the highest occupied molecular orbital) and E_{LUMO} (energy of the lowest unoccupied molecular orbital) are important in defining the reactivity of a chemical compound. E_{HOMO} is often associated with the electron donating ability of a molecule whereas E_{LUMO} indicates the ability of a molecule to accept electrons. Therefore, a high value of E_{HOMO} and a low value of E_{LUMO}

suggest efficient adsorption process. The values obtained in the present study ($E_{\text{HOMO}} = -5.0545$ eV and $E_{\text{LUMO}} = 0.8510$ eV) are comparable to that obtained for adsorption inhibitors in the literature [34]. The energy gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) is another parameter that correlates with the reactivity of the organic molecules. Generally, the lower the energy gap, the better the electron transfer process. In this work, the low value of energy gap ($\Delta E = 5.9055$ eV) could explain the high inhibition efficiency value ($IE (\%) = 90.32$ % for $C_{\text{inh}} = 1000$ ppm at $T = 25^\circ\text{C}$). HOMO and LUMO diagrams of the inhibitor are presented in Figure 9.

Figure 9. HOMO (A) and LUMO (B) diagrams of chitosan by B3LYP/6-31G (d, p).

As seen in Figure 9, the density HOMO is distributed around the right side of the inhibiting molecule whereas the LUMO density is distributed around the left side. So, these regions are probably the active areas where transfers of electrons could be done (from chitosan to copper or vice-versa).

The dipole moment (μ) is another important parameter which measures the asymmetry in molecular charge distribution [20]. It provides information about the polarity of a molecule. However, there is no consensus concerning the correlation between the dipole moment and inhibitive effectiveness [35]. According to some authors, low values of dipole moment favor inhibitor molecules accumulation on the surface thus increasing inhibition efficiency [36, 37]. On the other hands some researchers state that a high value of dipole moment lead to a good inhibition efficiency of an organic molecule [38]. The ionization potential (I) and the electronic affinity (A) are respectively (5.0545 eV) and (-0.8510 eV). This low value of (I) and the high value of electron affinity indicate the capacity of the molecule both to donate and accept electron. The electronegativity (χ) indicates the capacity of a system to attract electrons; whereas the hardness (η) expresses the degree of reactivity of the system (low values of hardness indicate a tendency to donate electrons). In our work, the low value of the electronegativity of the studied molecule when compared to that of copper and the low value of hardness (2.9528 eV) confirm the positive value of the fraction of electrons transferred ($\Delta N = 0.1315$), indicating a possible motion of electrons from the inhibitor to the metal. The electrophilicity index measures the propensity of chemical species to accept electrons; a high value of electrophilicity index

describes a good electrophile while a small value of electrophilicity index describes a good nucleophile. In this work the obtained value ($\omega = 2.9920$ eV) shows the good capacity of chitosan to accept electrons.

3.6.2 Local parameters

Fukui functions compute local reactivity indices that makes possible to rationalize the reactivity of individual molecular orbital contributions. The condensed Fukui function and dual descriptor allow one distinguish each part of the molecule on the basis of its distinct chemical behavior due to the different substituted functional group. The preferred site for nucleophilic attack is the atom in the molecule where the value of f_k^+ is maximum and it is associated with the LUMO energy while the site for electrophilic attack is controlled by the values of f_k^- which is associated with the HOMO energy. The nucleophilic attack will occur where f_k^+ value is maximum and $\Delta f_k(r)$ is positive whereas the electrophilic attack will occur where f_k^- is maximum and $\Delta f_k(r)$ is negative. The calculated Mulliken atomic charges, Fukui functions and dual descriptor by DFT at the B3YLP/6-31G (d, p) level are displayed in Table 5.

Table 5. Calculated Mulliken atomic charges, Fukui functions and dual descriptor by DFT B3YLP/6-31G (d, p).

Atom	$q(N+1)$	$q(N)$	$q(N-1)$	f_k^+	f_k^-	$\Delta f_k(r) = f_k^+ - f_k^-$
1C	0.299998	0.279736	0.2466	0.020262	0.033136	-0.012874
2C	0.242098	0.22381	0.20475	0.018288	0.01906	-0.000772
3C	0.141247	0.126202	0.096777	0.015045	0.029425	-0.01438
4C	0.536323	0.51974	0.489991	0.016583	0.029749	-0.013166
5C	0.243363	0.232901	0.196637	0.010462	0.036264	-0.025802
11O	-0.522289	-0.523967	-0.523756	0.001678	-0.000211	0.001889
12C	0.305041	0.252893	0.206559	0.052148	0.046334	0.005814
15O	-0.126529	-0.230801	-0.272835	0.104272	0.042034	0.062238
17O	-0.221549	-0.255485	-0.353434	0.033936	0.097949	-0.064013
19O	-0.210265	-0.250707	-0.448702	0.040442	0.197995	-0.157553
21N	-0.000448	-0.127537	-0.232646	0.127089	0.105109	0.02198
24C	0.287775	0.259893	0.250672	0.027882	0.009221	0.018661
25C	0.302009	0.285401	0.27121	0.016608	0.014191	0.002417
26C	0.293994	0.254727	0.244333	0.039267	0.010394	0.028873
29C	0.114409	0.087211	0.069009	0.027198	0.018202	0.008996

Atom	$q(N+1)$	$q(N)$	$q(N-1)$	f_k^+	f_k^-	$\Delta f_k(r) = f_k^+ - f_k^-$
31C	0.347354	0.277261	0.223619	0.070093	0.053642	0.016451
35O	-0.493079	-0.528088	-0.530739	0.035009	0.002651	0.032358
36O	-0.135256	-0.23488	-0.266366	0.099624	0.031486	0.068138
38N	-0.058903	-0.128953	-0.288174	0.07005	0.159221	-0.089171
41O	-0.409237	-0.507293	-0.514208	0.098056	0.006915	0.091141
42C	0.266293	0.224734	0.205495	0.041559	0.019239	0.02232
45O	-0.202351	-0.236797	-0.274792	0.034446	0.037995	-0.003549

It can be easily observed from shaded rows in Table 5 that (21 N) with the maximum value of f_k^+ and positive value of $\Delta f_k(r)$ is the most probable nucleophilic attack site, while (19 O) with the maximum value of f_k^- and negative value of $\Delta f_k(r)$ is the most probable electrophilic attack site.

4. Conclusion

The results of the present study can be concluded as follows:

- The inhibition efficiency of chitosan biopolymer is concentration dependent;
- The studied molecule adsorbs on copper according to the Langmuir isotherm;
- The values of free energy of adsorption suggest both physisorption and chemisorptions with a predominant physisorption;
- Potentiodynamic polarization data reveal that the studied inhibitor is mixed-type with cathodic trend;
- Impedance studies revealed that the inhibitor reduced the corrosion rate by increasing the resistance of the system, and that of charge transfer;
- The optic micrographs confirm the formation of a protective layer on the metal surface;
- The quantum descriptors confirm the good inhibition efficiency of chitosan;
- Theoretical results are consistent with the experimental data.

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