

CORROSION INHIBITION EFFICIENCY, EXPERIMENTAL AND QUANTUM CHEMICAL STUDIES OF NEUTRAL RED DYE FOR CARBON STEEL IN PERCHLORIC ACIDIC MEDIA

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Abstract. The Neutral Red (NR) has been investigated as a corrosion inhibitor for carbon steel (C-steel) in 1M perchloric acid using a weight loss method and theoretical calculations based on density functional theory (DFT). The obtained results revealed that NR is an effective inhibitor and its inhibition efficiency increases with the increasing concentration to attain 89.50 % at $5 \cdot 10^{-3}$ M at 293 K. The thermodynamic parameters as enthalpy, entropy and Gibbs free energy for both dissolution and adsorption processes are calculated and discussed. Moreover, the free energy of adsorption showed that the corrosion inhibition takes place by a spontaneous physicochemical adsorption of inhibitor molecules on the C-steel surface. The results show that the calculated values of the quantum chemical parameters indicate a possible existing link between the effectiveness of the inhibitor and its electronic properties.

Keywords: Neutral Red dye, carbon steel, perchloric acid, thermodynamic parameters, DFT.

1. Introduction

Many industries, such as energy, automotive, chemical, household appliances and food suffer great economic losses because of the corrosion damages. Corrosion studies are a subject of interest to interdisciplinary research communities, combining areas of materials science, chemical engineering, physics, environmental, metallurgy and civil engineering. Carbon steels are composed of a mixture of metallic iron and

carbon and being used extensively in every sector due to high mechanical properties and low cost. The wastes and residues of the metallic component damage in relation to corrosion are countless and include cracks, loss of time and arrest of the production, structural and mechanical damage, pollution, economic problems, and also large-scale ecological damage. Hence, these negative effects can be minimized or eliminated using diverse techniques to protect the surface of the metal from the aggressive environments.

The inhibition efficiency is often related to different variables such as: chemical structure of inhibitor and its amount in the medium, composition and metal nature, aggressive electrolyte, pH, temperature and immersion time.^{1,2} Moreover, it is also related to the number of active adsorption centers in the molecule, its adsorption abilities, and its electronic structure.

Studies on corrosion inhibition performance of dyes have shown that organic dyes are effective in retarding the corrosion in acid or base environments.^{3,4} Different types of dyes are commercially available. They are produced annually to be applied in various domains including paper industries, printing, plastics, cosmetics, leather, textile industry, pharmaceuticals, agrofood industries and medical industry.⁵⁻⁷ Organic compounds that are mainly efficient often contain heteroatoms which are; oxygen, sulfur and nitrogen in a conjugated system.^{8,9}

Some studies given by several researchers reported that some organic dyes are quite effective in retarding the corrosion of iron and steel in aggressive acid environments.¹⁰⁻²⁰ Neutral Red dye has proved its ability to act as an efficient corrosion inhibitor on cold rolled steel in 1.0M hydrochloric acid solution using the weight loss technique. This result indicated that NR dye acts as a promising inhibitor by adsorption on the cold rolled steel surface.¹⁰ The present work represents a comparative study of the inhibition efficiency of Neutral Red dye on the corrosion behavior of carbon steel in 1M perchloric acid using the weight loss and theoretical calculations. The effects of concentration, temperature and immersion

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time on the performance of inhibitor have been studied. The thermodynamic and kinetic parameters have also been determined and interpreted.

2. Experimental

2.1. Specimen Preparation

The composition of C-steel used in this work was (wt %): C 0.37, Mn 0.68, Cu 0.16, Cr 0.077, Ni 0.059, Si 0.023, S 0.016, Ti 0.011, Co 0.009 and the balance being Fe. Before proceeding to any test, the specimens of C-steel were mechanically abraded with different grades emery paper. This was followed by washing with distilled water, degreasing with acetone and then dried using a hot air blower before dipping in the corrosive or/and anti-corrosive medium.

2.3. Solutions

Analytical grade 70–72 % perchloric acid solution from Sigma-Aldrich was used to prepare the corrosive aqueous solution. The solution was prepared by dilution of the commercial HClO₄ solution using distilled water. Neutral Red of analytical grade was acquired from Sigma Aldrich chemicals and solutions of concentrations range from 5·10⁻⁵ to 5·10⁻³ M were prepared.

2.4. Weight Loss Method

The weight loss techniques furnish more realistic results than the electrochemical techniques because the experimental conditions are approached in a manner which resembles the real-life conditions. Loss in weight of samples was resolved by finding the weight difference between the C-steel substrates before and after insertion in perchloric acid. Each sample was weighed by an electronic balance (±0.0001 g) and then placed in the acid solution (50 mL). The time of the immersion was 2 h at the temperature range of 293–333 K. All measurements were done in triplicate, and the average value of the weight loss was noted.

The following equations were used to calculate the corrosion rate (*CR*), the inhibition efficiencies (*IE*) and the surface coverage (*θ*):^{21,22}

$$CR = \frac{\Delta W}{S \cdot t} \quad (1)$$

$$IE = \frac{CR' - CR}{CR'} \cdot 100 \quad (2)$$

$$\theta = \frac{IE}{100} \quad (3)$$

where ΔW is the weight loss, g; S is the total area of the specimen, cm²; t is the exposure time, h; CR' and CR are

the corrosion rates of C-steel samples in the absence and presence of inhibitor, respectively, g·cm⁻²·h⁻¹.

2.5. Theoretical Calculations

Quantum chemical studies for the molecules of NR as a corrosion inhibitor were performed using DFT calculation with Gaussian-09 program/ B3LYP/6-31G* level of theory. The high value of the highest occupied molecular orbital (HOMO) of the molecules shows its tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbitals. The energy of the lowest unoccupied molecular orbital (LUMO) indicates the ability of the molecule to accept electrons. The significant factors have been calculated using the electronic values of the most stable structure of the studied NR molecules.

The energy gap (ΔE_{gap}) and the global electronic chemical potential (μ) are determined as follow [20, 23]:

$$\Delta E_{gap} = E_{LUMO} - E_{HOMO} \quad (4)$$

$$\mu = 0.5(E_{LUMO} + E_{HOMO}) \quad (5)$$

The hardness (η) and softness (σ) are global chemical descriptors that measure the molecular stability and reactivity and are given by Eq. (6) and (7).²⁴

$$\eta = 0.5(E_{LUMO} - E_{HOMO}) \quad (6)$$

$$\sigma = 1/\eta \quad (7)$$

The chemical hardness fundamentally signifies the resistance towards deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction.

Electrophilicity index (ω) measures the stabilization in energy after a system accepts further amount of electron charge from the environment, this index is helpful for the prediction of the direction of corrosion. The electrophilicity index is calculated as:^{25,26}

$$\omega = \frac{\mu^2}{2\eta} \quad (8)$$

According to the simple charge transfer model for donation and back-donation of charges, an electronic backdonation process might be occurring governing the interaction between the inhibitor molecule and the metal surface. Thus back-donation of charges from the inhibitor to a metallic surface is given as:²⁷

$$\Delta E_{back-donation} = -\frac{\eta}{4} \quad (9)$$

where $\Delta E_{back-donation}$ value of inhibitor is less than zero and the value of hardness of the same inhibitor is greater than zero which basically means that the molecule is favoured energetically.

The number of transferred electrons (ΔN) can be calculated as:²⁸

$$\Delta N = \frac{\chi_{Fe} - \chi_{Inh}}{2(\eta_{Fe} + \eta_{Inh})} \quad (10)$$

where χ_{Fe} and χ_{Inh} are the absolute electronegativities of iron and inhibitor, η_{Fe} and η_{Inh} are the absolute hardness of iron and the inhibitor, respectively.

The theoretical values ($\chi = 7.0 \text{ eV}\cdot\text{mol}^{-1}$ and $\eta = 0 \text{ eV}\cdot\text{mol}^{-1}$) for iron were obtained from the literature.²⁹

3. Results and Discussion

3.1. Effect of Concentration and Temperature on Corrosion Rates and Inhibition Efficiency

The corrosion inhibition performance of Neutral Red dye against corrosion was investigated by monitoring

the weight loss as the process took place. The weight loss measurements were determined in 1M HClO₄ without and with different concentration of NR (from $5\cdot 10^{-5}$ to $5\cdot 10^{-3}$ M) for two hours immersion time. Table 1 shows the variation of concentration and temperature of NR with *IE* and *CR*. The *IE* increases with the increase in concentration of the inhibitor because of the availability of a large number of adsorption sites that are brought by many molecule concentrations of NR. The maximum *IE* of 84.97 % was obtained at the optimum concentration of $1\cdot 10^{-3}$ M at 303 K. Beyond this concentration, the inhibition efficiency was observed stable (85.27 % for $5\cdot 10^{-3}$ M); this behavior was attributed to the saturation of inhibitor molecule on C-steel surface.

Table 1. The values of corrosion rate and inhibition efficiency from the weight loss for different concentrations of Neutral Red dye in 1M HClO₄ at different temperatures

$C_{Inh}, \text{mol}\cdot\text{L}^{-1}$	T, K	$CR, \text{mg}\cdot\text{cm}^{-2}\cdot\text{h}^{-1}$	$IE, \%$
0	293	2.00	–
	303	3.60	–
	313	7.90	–
	323	18.1	–
	333	33.6	–
$5\cdot 10^{-5}$	293	0.85	57.50
	303	1.71	52.51
	313	4.26	46.07
	323	11.23	37.95
	333	23.99	28.60
$7.5\cdot 10^{-5}$	293	0.62	69.01
	303	1.43	60.28
	313	3.54	55.19
	323	9.42	47.95
	333	20.20	39.87
10^{-4}	293	0.41	78.97
	303	0.97	72.99
	313	2.56	67.59
	323	7.49	58.61
	333	16.74	50.17
10^{-3}	293	0.22	89.01
	303	0.54	84.97
	313	1.9	75.93
	323	5.78	68.05
	333	13.01	61.27
$5\cdot 10^{-3}$	293	0.21	89.50
	303	0.53	85.27
	313	1.88	76.20
	323	5.62	68.94
	333	12.81	61.87

The *IE* obtained at optimum concentration were 89.01 % at 293 K and 61.27 % at 333 K, the minimum and maximum temperatures, respectively. The decrease in *IE* of Neutral Red at these temperatures showed the instability of NR when it was subjected to higher temperatures. At higher temperatures, NR was desorbed from C-steel surface. It can also be observed from Table 1 that when the temperature increases, the *CR* increases too. Neutral Red dye has been found to work properly at lower temperatures with poor inhibition capabilities at higher temperatures.

3.2. Effect of Immersion Time

Time duration of the surface exposed to the corrosive environment directly affects the rate of corrosion to occur. To determine the stability of the inhibitor film and the rate of inhibitor adsorption, immersion time studies were conducted. The immersion periods were varied from 1 to 24 h at a temperature of 303 K. The results, shown in Fig. 1, indicate the effect of immersion time on the inhibition efficiency and corrosion rate of Neutral Red. The increase in inhibition efficiency with increasing immersion time is due to the increase in the surface coverage with time until to 2 h of immersion (84.92 %), then it decreases to 63.91 % within 24 h. The decrease in the inhibition efficiency was attributed to the corrosion inhibitors desorption from C-steel surface.²⁰

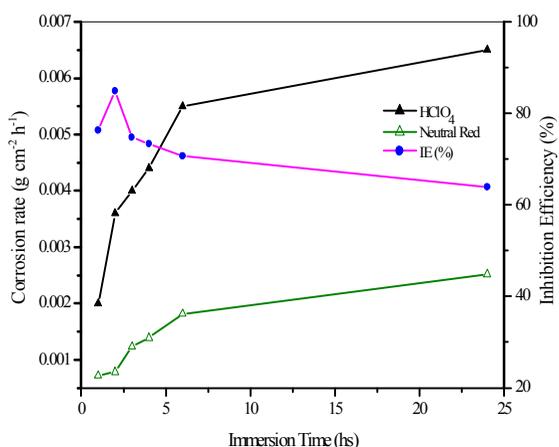


Fig. 1. Variation of inhibition efficiency and corrosion rate vs immersion time for C-steel at 10^{-3} M of Neutral Red dye

The corrosion rate increased rapidly in the absence of inhibitor but in the presence of NR the *CR* increased slightly with a longer period of immersion. Furthermore, the increase in *CR* after a long period of exposure time can be attributed to a less concentration or limited number of available NR molecules in the HClO₄ solution to stop or reduce metal dissolution. It is evident that after that the inhibitor molecules had been desorbed from the metal surface, so they became inactive and therefore did not take part in the inhibition process.

3.3. Thermodynamic and Kinetic Parameters

Important information on the mechanism of the inhibitor action could be obtained by comparing the apparent activation energy (E_a), derived in the presence of inhibitor and its absence. The E_a values were calculated using the Arrhenius equation:³⁰

$$CR = A \times \exp\left(-\frac{E_a}{RT}\right) \quad (11)$$

where *CR* is the corrosion rate, *A* is a constant, *R* is the gas constant ($R = 8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$) and *T* is the temperature, K.

The values of E_a (Table 2) for C-steel in 1M HClO₄ without and with different concentrations of inhibitors were obtained from the slope of the plot of $\ln(CR)$ versus $1/T$ (Fig. 2).

The values of activation enthalpy ΔH_a and activation entropy ΔS_a can be calculated by the slope and intercept of the above plot (Fig. 3), using the following transition state equation (12).³¹

$$\ln\left(\frac{CR}{T}\right) = \left[\ln\left(\frac{R}{Nh}\right) + \frac{\Delta S_a}{R} \right] - \frac{\Delta H_a}{RT} \quad (12)$$

where *N* is Avogadro number, *h* is Plank's constant. A plot of $\ln(CR/T)$ vs. $1/T$ gave a straight line with a slope of $(-\Delta H_a/R)$ and an intercept of $[(\ln(R/Nh) + (\Delta S_a/R))]$ from which the values of ΔH_a and ΔS_a can be calculated (Table 2).

The desorption of adsorbed inhibitor due to the enhanced solution agitation by higher rates of hydrogen gas evolution at raised temperature is possible and can cause the ability of the inhibitor to be adsorbed on the C-steel surface to reduce.³² For physical adsorption, the inhibition efficiency is expected to decrease with the increasing temperature, but for chemical adsorption, the inhibition efficiency is expected to increase with the increasing temperature.³³ The $\Delta H_a > 0$ in the absence and presence of different concentrations inhibitors reflects the endothermic nature of C-steel dissolution. This simply means that the dissolution process of steel is difficult. The values of entropy were negative both in the absence and presence of inhibitors implying that a decrease in disorder occurred when proceeding from the reactant to the product.

The change in Gibbs energy can be deduced at 298 K by Eq. (13):

$$\Delta G_a = \Delta H_a - T\Delta S_a \quad (13)$$

The free Gibbs energy (for corrosion) increases with the addition of NR in the perchloric acid from 86.95 to 93.78 kJ·mol⁻¹. The $\Delta G_a > 0$ means a non-spontaneous corrosion reaction and it increases with increasing the concentration of inhibitor. Moreover, the higher values of ΔG_a of the process in an inhibitor presence when compared to that in its absence is attributed to its physisorption, while the opposite one is the case with chemisorptions.

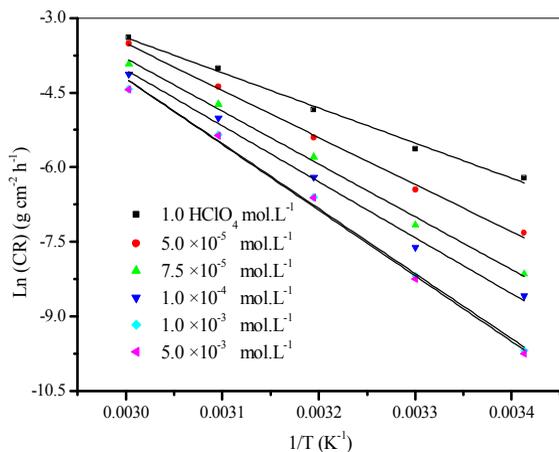


Fig. 2. Arrhenius plots for the corrosion of C-steel in 1M HClO₄ medium in the absence and presence of different concentrations of Neutral Red dye

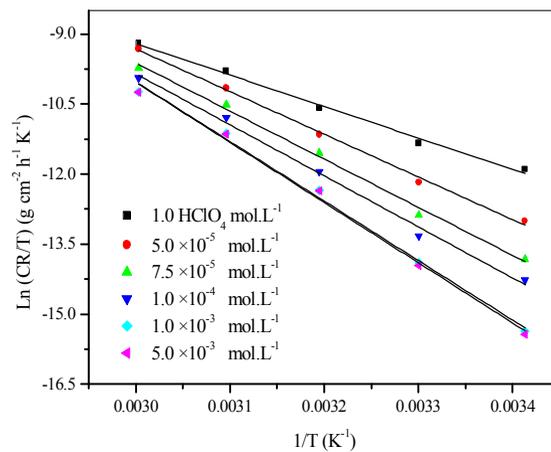


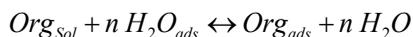
Fig. 3. Alternative Arrhenius plots for C-steel dissolution in 1M HClO₄ medium in the absence and presence of different concentrations of Neutral Red dye

Table 2. Activation parameters for the C-steel dissolution in 1M HClO₄ in the absence and presence of different concentrations of Neutral Red dye

C, mol·L ⁻¹	R ²	E _{as} , kJ·mol ⁻¹	R ²	ΔH _{as} , kJ·mol ⁻¹	ΔS _{as} , J·mol ⁻¹ ·K ⁻¹	ΔG _{as} , kJ·mol ⁻¹
HClO ₄	0.994	58.79	0.996	56.20	-105.43	86.95
5 10 ⁻⁵	0.994	69.32	0.994	66.72	-76.78	89.21
7.5 10 ⁻⁵	0.996	71.81	0.997	69.22	-70.49	90.58
10 ⁻⁴	0.997	76.20	0.995	73.60	-58.97	92.05
10 ⁻³	0.996	85.95	0.996	83.35	-31.21	93.43
5 10 ⁻³	0.996	86.23	0.997	83.63	-30.49	93.78

3.4. Adsorption Isotherm

The adsorption isotherm explains the interaction between inhibitor molecules and the C-steel surface.³⁴ The adsorption of dye molecules at the metal solution interface reduces the corrosion rate and it is considered as a substitution adsorption process where an organic compound from the aqueous media displaces the water molecules associated with the surface (H₂O_{ads}).



where *n* is the number of water molecules replaced by the adsorption of one inhibitor molecule.

The mechanism of adsorption of organic molecule on the metal surface in the corrosive media can be established using the surface coverage and inhibitor efficiency. The data were used graphically using different isotherms. Among all, the Langmuir adsorption isotherm was found to be the best description of the adsorption. Langmuir model is based on the hypothesis that each site of metal surface has adsorbed species (Eq. (14)).³¹

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{14}$$

where *θ* is the surface coverage by the inhibitor molecule, *C* is the concentration and *K_{ads}* is the equilibrium constant for the adsorption-desorption process.

The plots of *C_{Inh}/θ* against *C_{Inh}* (Fig. 4) yield a straight line with approximately unit slope, indicating that the inhibitor under study obeys the Langmuir adsorption isotherm.

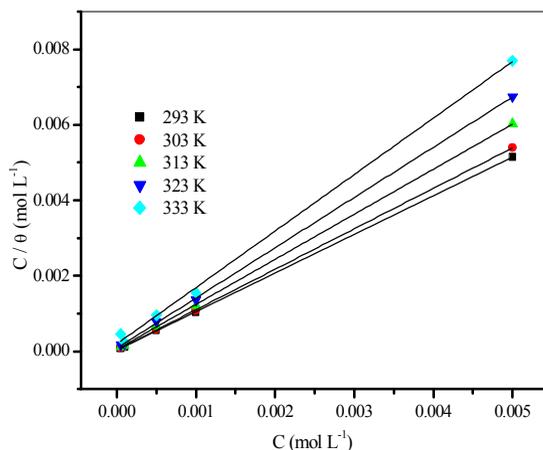


Fig. 4. Langmuir adsorption isotherms at different temperatures

The free energy of the adsorption of inhibitor on the C-steel surface can be evaluated with the following equation:^{35,36}

$$\Delta G_{ads} = -RT \ln(55.5 K_{ads}) \quad (15)$$

where R is the gas constant, $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ and T is the absolute temperature, K. The constant value of 55.5 is the concentration of water in the solution, $\text{mol}\cdot\text{L}^{-1}$.

In this study, the negative value of the enthalpy of adsorption is $-18.59 \text{ kJ}\cdot\text{mol}^{-1}$ indicating that the adsorption of the inhibitor on the C-steel is an exothermic process. The higher value of the equilibrium constant at lower temperature reflects the higher adsorption ability of the NR on the carbon steel surface.³¹ The negative value of adsorption enthalpy reflects the exothermic nature of the adsorption of NR dye on the C-steel surface in the perchloric acid solution. The positive values of ΔS_{ads} indicate an increase in the entropy due to the adsorption of Neutral Red dye on the C-steel surface. The values of ΔG_{ads} are usually interpreted in relation to the nature of the adsorption process: whether it is physisorption or chemisorption. Generally, if the values of ΔG_{ads} are more than $-20 \text{ kJ}\cdot\text{mol}^{-1}$, then the physisorption mechanism is favored, whereas if the values of ΔG_{ads} are $-40 \text{ kJ}\cdot\text{mol}^{-1}$ or lower, then the adsorption process is chemisorption. As seen from Table 3, the obtained ΔG_{ads} ranges from -34.42 to $-36.42 \text{ kJ}\cdot\text{mol}^{-1}$, which is between -20 and $-40 \text{ kJ}\cdot\text{mol}^{-1}$. Thus, the process cannot be classified as a chemisorption or physisorption but it is rather a mix of both of them.

3.5. Quantum Calculations

The experimental study was completed by a theoretical study at the B3LYP/6-31G* level in order to

correlate the experimental results with the molecular structure and electronic properties of NR dye (Fig. 5). The energy of HOMO and LUMO, the total energy (ΔE_{gap}), back-donation of charges ($\Delta E_{back-donation}$), the number of transferred electrons (ΔN), the electronic chemical potential (μ), the softness (σ), the electrophilicity index (ω) and the global hardness (η) were calculated and listed in Table 4.

The electrophilicity index (ω) is helpful for the prediction of the direction of corrosion. A small electrophilicity value describes a good nucleophile while a high electrophilicity value characterizes a good electrophile.²⁰ The energy gap is another important descriptor that must be considered. Literature reveals that a larger value of the energy gap indicates the low reactivity to a chemical species because the energy gap is related to the softness or hardness of a given molecule.³⁷ From Table 4, it is shown that NR inhibitor has a higher E_{HOMO} (-4.98 eV) energy and lower E_{LUMO} (-1.63 eV), as well as low energy difference value ΔE_{gap} (3.35 eV) between E_{HOMO} and E_{LUMO} . The number of electrons transferred (ΔN) was also calculated and tabulated in Table 4. The charge transfer is of the order of 1.10 eV and hence shows that the Neutral Red inhibitor is a strong electron donor power because it is lower than 3.60 eV . If the fractions of electrons transferred are lower than 3.6 eV , the inhibition efficiency increases with increasing electron-donating capacity on the metal surface.³⁸ The NR inhibitor has a good chemical reactivity with the metal surface due to the decrease in a hardness value ($\eta = 1.67 \text{ eV}$) and the increase in softness ($\sigma = 0.59 \text{ eV}^{-1}$). The $\Delta E_{back-donation} < 0$ and $\eta > 0$ indicates that the back-donation of the molecule is energetically favored.³⁹

Table 3. Thermodynamic parameters for the adsorption of Neutral Red in 1M HClO_4 solution on C-steel at different temperatures

T, K	R^2	$K_{ads} \cdot 10^3, \text{L mol}^{-1}$	$\Delta H_{ads}, \text{kJ}\cdot\text{mol}^{-1}$	$\Delta S_{ads}, \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$\Delta G_{ads}, \text{kJ}\cdot\text{mol}^{-1}$
293	0.999	24.69	-18.59	54.02	-34.42
303	0.999	19.45		54.13	-34.99
313	0.999	19.90		56.28	-36.21
323	0.999	13.47		54.88	-36.32
333	0.999	9.32		53.54	-36.42

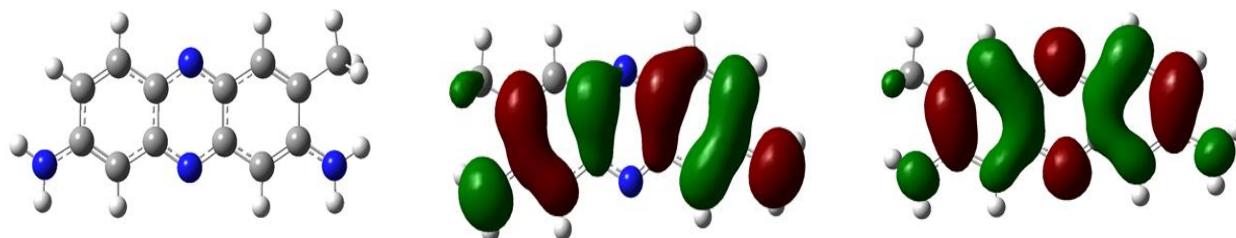


Fig. 5. Optimized structure (a), HOMO (b) and LUMO (c) orbitals for Neutral Red molecule using DFT approach

Table 4. HOMO and LUMO energies, global reaces μ , η , ω , σ , ΔN , ΔE_{gap} and $\Delta E_{back-donation}$ for the Neutral Red studied compound at B3LYP/6-31G* level of theory

Substrate	E_{HOMO}	E_{LUMO}	μ	η	ω	σ	ΔN	ΔE_{gap}	$\Delta E_{back-donation}$
NR	-4.98	-1.63	-3.30	1.67	3.27	0.59	1.10	3.35	-0.41

4. Conclusions

The inhibition efficiency of C-steel corrosion in 1.0M HClO₄ by Neutral Red has been investigated using both weight loss and quantum chemical calculations. The weight loss measurements showed that the Neutral Red acts as an excellent effective inhibitor and its inhibition efficiency increases with its concentration. The weight loss measurement proved that the inhibition efficiency increases with immersion time until 2 h and decreases after this value. It is also found that the adsorption of NR dye obeys the Langmuir isotherm adsorption. The values of thermodynamic parameters show that the adsorption process is both physical and chemical. Quantum chemical approach was adequately used to explain the correlation between the C-steel corrosion inhibition and molecular structure of the compound.

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ЕФЕКТИВНІСТЬ ІНГІБУВАННЯ КОРОЗІЇ, ЕКСПЕРИМЕНТАЛЬНІ ТА КВАНТОВІ ХІМІЧНІ ДОСЛІДЖЕННЯ НЕЙТРАЛЬНОГО ЧЕРВОНОГО ДЛІЯ ВУГЛЕЦЕВОЇ СТАЛІ У ПЕРХЛОРНИХ КИСЛИХ СЕРЕДОВИЩАХ

Анотація. Як інгібітор корозії вуглецевої сталі (С-сталь) досліджено барвник нейтральний червоний (НЧ) в 1М хлорній кислоті за допомогою методу втрати маси та теоретичних розрахунків, заснованих на теорії функціоналу густини (DFT). Визначено, що нейтральний червоний є ефективним інгібітором, і його ефективність інгібування за температури 293 К зростає до 89,50 % із збільшенням концентрації до $5 \cdot 10^{-3}$ М. Для процесів розчинення і адсорбції розраховано такі термодинамічні параметри, як ентальпія, ентропія та вільна енергія Гіббса. Встановлено, що пригнічення корозії відбувається внаслідок спонтанної фізико-хімічної адсорбції молекул інгібіторів на поверхні С-сталі. За допомогою розрахованих квантових хімічних параметрів показана можливість існування зв'язку між ефективністю інгібітора та його електронними властивостями.

Ключові слова: барвник нейтральний червоний, вуглецева сталь, хлорна кислота, термодинамічні параметри, DFT.