



Original scientific paper

Substantial enhancement in the anticorrosivity of aluminium alloy 6061 by doxycycline hydrochloride drug

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Abstract

The significant anticorrosive property of the antibiotic drug doxycycline hydrochloride (DCH) was investigated by electrochemical techniques such as potentiodynamic polarization, electrochemical impedance and chronoamperometry. DCH inhibited the pitting corrosion of aluminium alloy 6061 (AA6061) in 3.5 % NaCl media with 90 % efficiency. The adsorption of DCH on AA6061 conform modified Langmuir isotherm by means of comprehensive adsorption. Quantum chemical calculations were evaluated to ascertain the active sites of DCH molecule responsible for adsorption and to support the experimental findings.

Keywords

Corrosion inhibitor; Aluminium alloy; Potentiodynamic polarization; Electrochemical impedance spectroscopy, Adsorption isotherm.

Introduction

Aluminium alloy 6061(AA6061) is an important alloy of aluminium used in a wide range of industrial applications owing to their low cost, light weight, high thermal and good corrosion resistance properties [1]. The corrosion resistance property arises from the ability of AA6061 to form a natural oxide film on its surface [2,3]. In aggressive chloride media, localized corrosion can occur and it leads to the breakdown of the passive layer and pit formation [4,5]. The protection of AA6061 and its oxide films from corrosive chloride attack can be done by using chemical inhibitors.

Organic compounds containing heteroatoms are more efficient corrosion inhibitors for aluminium in 3.5% NaCl media [6-10]. But the development of drugs as inhibitors for metallic corrosion has drawn much attention in the field of corrosion science because the drugs have strong chemical activity, low toxicity and negligible negative impacts on the environment. Hence in the present investigation doxycycline hydrochloride (DCH), which is a tetracycline antibiotic drug useful for the treatment of many infections, has been selected. DCH is used in the treatment of chronic prostatitis, sinusitis, leptospirosis, pelvic inflammatory disease and respiratory tract infections [11-12]. The choice of DCH is based on its structural considerations such as it contains large number of π – electrons along with the hetero atoms like two nitrogen and eight oxygen atoms. In this study, the inhibition performance of DCH molecule on the corrosion of AA6061 in 3.5% NaCl solution has been examined by electrochemical techniques and also quantum chemical calculations were evaluated by ab initio method to confer theoretical support to the experimental findings.

Experimental

Materials

The surface of AA6061 (Bhandari Metal House, K.R. Market, Bangalore, India) having composition 0.25 % Cu, 1.0 % Mg, 0.60 % Si, 0.20 % Cr and remainder being Al was polished with different grades of emery papers (grade No. 400, 600, 800, 1000, and 1200). Afterwards, the polished specimen was immersed in 10 % NaOH aqueous solutions for 30 sec, degreased with acetone and rinsed by millipore water, dried and stored in desiccator. The AA6061 specimens of 1 cm² area (exposed) with a 5 cm long stem isolated with araldite resin were used for electrochemical measurements.

The AR grade NaCl was used to prepare 3.5 % NaCl solution by using millipore water. The millipore water was obtained from Elix 3 Milli-pore system (Resistivity greater than 18 M Ω cm at 25 °C). DCH inhibitor compound was obtained from Ramdev Chemicals India Pvt. Ltd., Mumbai and its structure is given in Figure 1. The different concentrations (0.5, 1.0, 1.5, 2.0 mM) of inhibitor solutions were prepared by dissolving specified amount of inhibitor in 3.5% NaCl solution. The pH of 3.5 % NaCl solution is 6 and all the experiments were carried out at the same pH even in the presence of DCH.

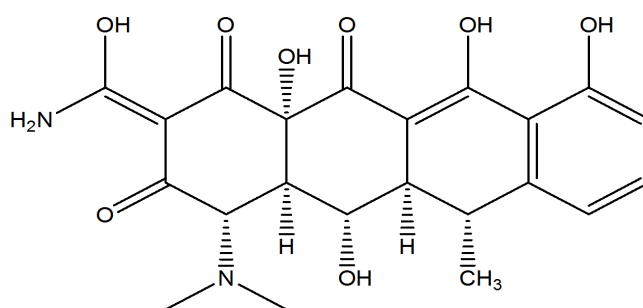


Figure 1. The structure of DCH [13]

Methods

Electrochemical measurements were conducted in a conventional glass cell using the CHI 660C electrochemical analyzer (CH Instruments, Austin, TX, USA) at 302 K. AA6061 specimen (of 1 cm² area), a platinum electrode, and a Ag/AgCl electrode were used as working, auxiliary, and reference electrodes, respectively. Prior to each electrochemical measurement, a stabilization period of 30 min was allowed to establish a steady state open circuit potential (OCP). Each

experiment was carried out in triplicate and the average values of corrosion parameters are reported.

The potentiodynamic polarization measurements were carried out over a potential range of -200 mV to $+200$ mV at OCP with a scan rate of 0.5 mV s^{-1} .

The impedance measurements were carried at OCP in the frequency range 1 MHz to 100 kHz with 5 mV sine wave as the excitation signal. Impedance data were analyzed using ZSimp-Win 3.21 software.

For AA6061, the chronoamperometric curves were obtained by polarizing the working electrode anodically at -0.68 V (Ag/AgCl) for 600 sec in 3.5% NaCl solution.

The surface morphology of the metal samples after immersion in corrosive medium in the absence and presence of 1.5 mM inhibitor was analyzed using scanning electron microscopy (JEOL, JSM 6400, JEOL Datum Shanghai Co. Ltd., Shanghai).

Quantum chemical calculations were performed with complete geometry optimization using standard HyperChem, Release 8.0 software (Hypercube, Inc. GmbH Austria). Geometrical structure of inhibitor molecules was optimized by ab initio method using Hartree–Fock level with 3-21 G basis set. The Polak–Rieberre algorithm which is fast and accurate has been used for computation. The energy parameters in the form of root mean square gradient were kept at 0.1 kcal $mol^{-1} \text{ \AA}^{-1}$.

Results and Discussion

Open-circuit potential (OCP) measurements

The change in the OCP as a function of immersion time for AA6061 in the absence and presence of different concentrations of DCH in 3.5% NaCl is given in Figure 2.

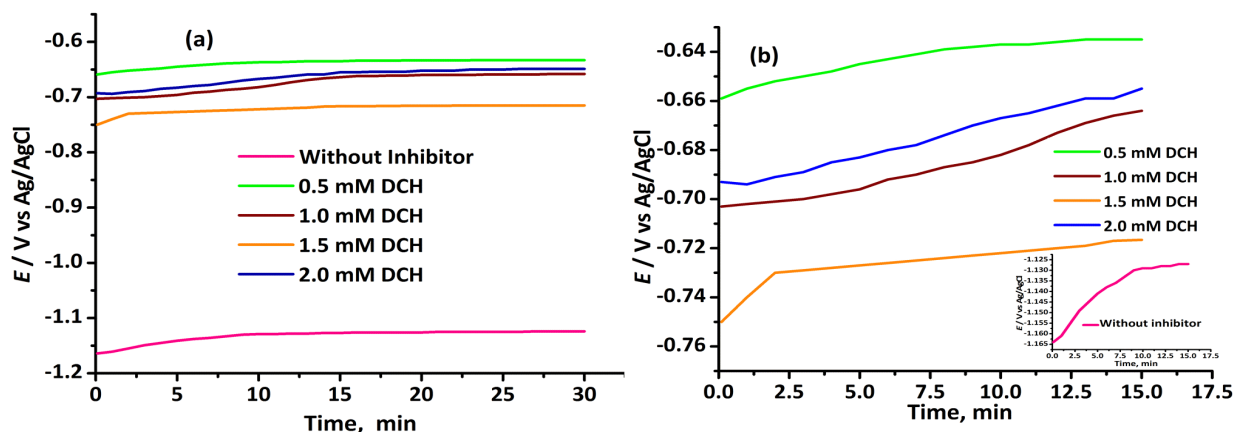


Figure 2. (a) OCP curves obtained for AA6061 in the absence and presence of different concentrations of DCH in 3.5% NaCl and (b) Close up view of Figure (a).

In the beginning, the potential of each solution get slightly varied and became constant after few minutes of immersion. These constant potentials correspond to the free corrosion potential of aluminium in each solution. Compared to uninhibited solution, the OCP shifted towards more positive values in the presence of DCH. The shift in OCP in presence of DCH indicates that the corrosion of aluminium gets decreased to a greater extent in presence of DCH and hence it acts as a better inhibitor.

Potentiodynamic polarization (PDP) measurements

The potentiodynamic polarization curves of AA6061 in 3.5 % NaCl solution in the absence and presence of different concentrations of DCH are presented in Figure 3. The corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), and anodic (β_a), and cathodic (β_c) Tafel slopes were generated from the software installed in the instrument. The percentage inhibition efficiency $\eta_T / \%$ was computed from i_{corr} values using the following expression;

$$\eta_T (\%) = \frac{i_{corr}^o - i_{corr}}{i_{corr}^o} \times 100 \tag{1}$$

where i_{corr}^o and i_{corr} are the corrosion current densities without and with DCH, respectively. The corrosion kinetic data obtained from potentiodynamic polarization curves for AA6061 in 3.5 % NaCl having different concentrations of DCH are depicted in Table 1.

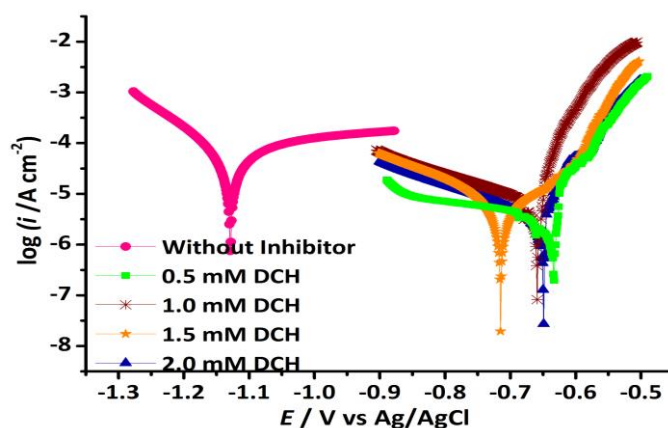


Figure 3. Potentiodynamic polarization curves obtained for AA6061 in 3.5% NaCl in the absence and presence of DCH

It can be seen from the Figure 3 that both the anodic and cathodic branches of the curves shifted towards lower current densities in inhibited solution as compared to uninhibited solution. This indicates that oxygen reduction and aluminium dissolution process are limited by DCH which acts as a mixed type inhibitor by inhibiting the corrosion of metal surface.

Table 1. Potentiodynamic polarization parameters obtained for AA6061 in 3.5% NaCl in the absence and presence of DCH

C / mM	$-E_{corr} / \text{mV}$	$-\beta_c / \text{mV dec}^{-1}$	$\beta_a / \text{mV dec}^{-1}$	$i_{corr} / \mu\text{A cm}^{-2}$	$\eta_T / \%$
Blank	1129±2.4	8.725	3.089	68.71±2.4	
0.5	633±2.6	2.168	17.807	15.16±1.9	78
1.0	659±1.1	3.941	16.901	12.09±1.1	83
1.5	715±1.2	5.401	10.682	6.13±1.9	91
2.0	648±0.9	4.565	21.147	8.39±1.3	88

It can be visualized from Table 1 that enhancing the concentrations of DCH up to 1.5 mM improves the values of both β_a and β_c , and E_{corr} values are shifted to more negative direction in the presence of different concentrations of inhibitor compound. This can be attributed to the formation of strongly adsorbed film on the metal surface where the adsorbed DCH molecules reduce the aggressiveness of Cl^- ions and protect the surface from being pitted. Meanwhile, the

protection efficiency increases up to 1.5 mM concentration of DCH and further increase in the concentration of inhibitor leads to decrease in efficiency. The highest efficiency at 1.5 mM concentration of DCH may be resulted from the maximum surface coverage. However, above this concentration, there may be possibility of interaction between unadsorbed and adsorbed DCH molecules which favors desorption [14]. Consequently, the gradual decrease in efficiency was noticed in chloride media containing DCH greater than 1.5 mM. This suggests that DCH is fairly an effective inhibitor at 1.5 mM concentration for AA6061 in 3.5 % NaCl medium.

Electrochemical Impedance Spectroscopy (EIS)

EIS studies have been carried out to get information on the corrosion and inhibition mechanism. The Nyquist plots obtained for aluminium in 3.5 % NaCl in the absence and presence of DCH are given in Figure 4. The impedance behaviour of AA6061 surface was simulated by an equivalent circuit shown in the inset of Figure 4. In the circuit, R_s represents the solution resistance, R_1 is the charge transfer resistance corresponding to the corrosion reaction at the Al/solution interface, R_2 represents the polarization resistance, which reflects the protective property of the film, CPE_1 and CPE_2 represents the constant phase elements (CPE) as a substitute for the double-layer capacitance (C_{dl}). The impedance of CPE is defined as

$$Z_{CPE} = Q^{-1} (j\omega)^{-n} \quad (2)$$

where Q is the CPE constant, ω is the angular frequency, $j^2 = -1$ is the imaginary number and n is the CPE exponent which gives details about the degree of surface inhomogeneity resulting from surface roughness, inhibitor adsorption, porous layer formation etc.

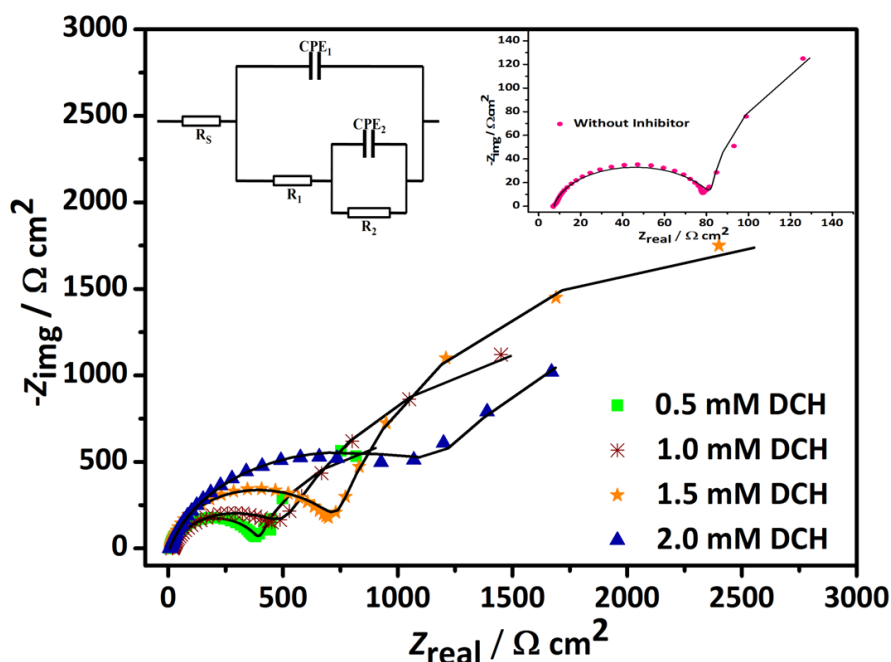


Figure 4. Electrochemical impedance plots obtained for AA6061 in 3.5% NaCl in the absence and presence of different concentrations of DCH

The inhibition efficiency $\eta_z / \%$ was evaluated from total resistance (R_t) values using the following equation

$$\eta_z / \% = \frac{R_t - R_t^0}{R_t} \times 100 \quad (3)$$

where R_t^0 and R_t are the total resistance (where R_t is the sum of R_1 and R_2) in the absence and presence of DCH, respectively. The obtained electrochemical impedance parameters are depicted in Table 2.

As the concentration of DCH increases the diameter of the capacitive loop also increases. But the diameter of the capacitive loop is large at 1.5 mM suggesting that the film formed by the adsorption of DCH molecules on the Al surface become dense and exhibit better protection efficiency. Meanwhile, the diameter of the capacitive loop gets decreased when the concentration is 2 mM. Moreover, each Nyquist plot is composed of two loops and it suggests that there are two major electrochemical kinetic processes on the electrode surface. The high frequency part is due to the adsorption of DCH molecule which leads to the formation of inhibitor film and the second loop at lower frequency is due to the electrochemical corrosion process [15].

Table 2. Impedance parameters obtained for AA6061 in 3.5 % NaCl in the absence and presence of different concentrations of DCH

C /mM	$R_s/\Omega \text{ cm}^2$	$Q_1/\mu\Omega^{-1} \text{ S}^n \text{ cm}^{-2}$	n_1	$R_1/\Omega \text{ cm}^2$	$Q_2/\mu\Omega^{-1} \text{ S}^n \text{ cm}^{-2}$	n_2	$R_2/\Omega \text{ cm}^2$	$\eta_z/\%$
Blank	7.358	130.3	0.91	76.98±2.7	11320	1	381.5±8.6	
0.5	6.975	56.53	0.92	392.9±3.9	6863	0.88	1501±5.8	76
1.0	18.80	131.7	0.83	521.9±5.5	3294	0.85	2991±5.3	87
1.5	11.07	47.75	0.92	757.4±3.8	2130	0.93	3857±8.2	90
2.0	6.933	155.6	0.83	143.5±3.1	2340	1	2337±8.3	88

It is evident from the Table 2 that the presence of DCH in chloride media leads to an increase in the resistance and decrease in CPE values up to 1.5 mM concentration. The decrease in Q values may be due to the decrease in local dielectric constant and/or an increase in the electrical double layer thickness [16]. This infers DCH acts via adsorption at the metal/solution interface. Meanwhile, the increase in R_1 and R_2 values suggest that the amount of DCH molecules adsorbed on the Al surface increases and the adsorbed inhibitor molecules forms a protective film on the electrode surface and consequently hampers the dissolution of aluminium, resulting in an increase in the protection efficiency.

On the other hand, the value of R decreases and Q increases above 1.5 mM concentration which may be due to the desorption of inhibitor molecules at higher concentration above 1.5 mM. Hence, the gradual decrease in protection efficiency was noticed in 3.5 % NaCl media containing DCH greater than 1.5 mM. Also, the factor n_1 values had changed a little; which means that the corrosion reaction on the aluminium surface was inhibited by the absorbed inhibitor film. By reviewing these results it can be considered that DCH is relatively an effective inhibitor at 1.5 mM concentration for AA6061 in 3.5 % NaCl medium.

Chronoamperometric measurements

Potentiostatic current-time experiments were carried out in order to gain information on the corrosion and corrosion inhibition of AA6061 in NaCl solution in the absence and presence of DCH at less negative potentials. The chronoamperometric curves obtained at – 680 mV vs. Ag/AgCl [7] for AA6061 electrode after its immersion for 600 sec in 3.5 % NaCl solution are shown in Figure 5.

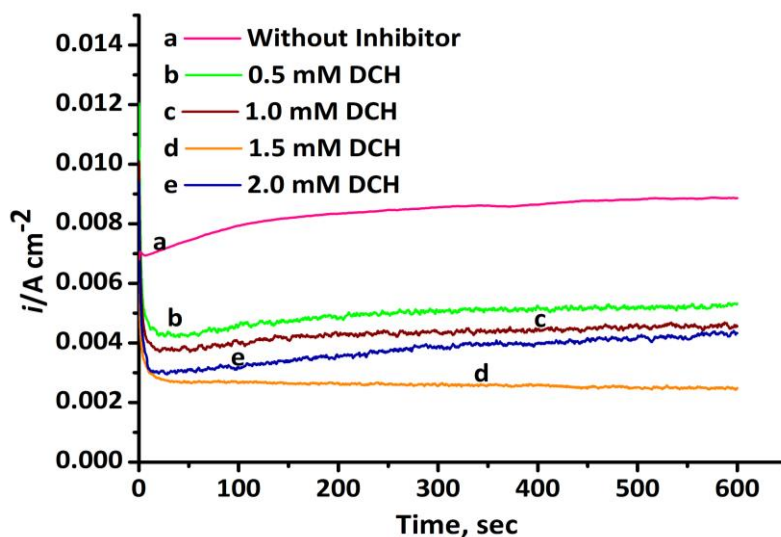


Figure 5. Chronoamperometric curves obtained for AA6061 in 3.5% NaCl in the absence and presence of DCH.

The absolute current of AA6061 gets decreased from the initial moment till the end of the measurement in the presence of DCH. Further, pronounced decreasing of current was obtained with increasing the DCH concentration up to 1.5 mM. This infers that DCH inhibited the dissolution of AA6061 in chloride solution and shows better protection efficiency as an inhibitor at 1.5 mM concentration.

Adsorption isotherm

The fundamental information dealing with the interactions between the inhibitor molecule and the metal surface can be obtained from the adsorption isotherm [17]. The data obtained from the polarization and impedance techniques were tested with several adsorption isotherms and the Langmuir isotherm was found fit well with the experimental data. The Langmuir adsorption isotherm equation is given by:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (4)$$

where C is the inhibitor concentration and K_{ads} is the equilibrium constant of the inhibitor adsorption process and θ is the degree of surface coverage defined as $\eta/100$.

The plot of θ versus C is given in Figure 6(a). Langmuir model assumes monolayer adsorption which occurs only at limited number of sites which are indistinguishable and equivalent. There is no tangential interaction and steric hindrance between the adsorbed molecules even on adjacent sites [18,19]. Langmuir adsorption is graphically represented by a plateau which is an equilibrium saturation point. At this point, no further adsorption takes place once the surface of the adsorbent is completely occupied by a monolayer of inhibitor [20,21]. However, plateau is not observed clearly in Figure 6(a) which may be attributed to the occupancy of more or less typical adsorption site by the adsorbed molecule at the metal solution interface. Meanwhile, the divergence from pure monolayer adsorption may be due to the interactions between adsorbate species on the metal surface as well as changes in the adsorption heat with increasing surface coverage [22] and these aspects were not taken into consideration in derivation of the Langmuir isotherm. Accordingly, Langmuir adsorption isotherm cannot be applied to study the adsorption behaviour

of DCH and hence, it is better to use the modified Langmuir adsorption isotherm [23,24] given by the equation

$$\frac{C}{\theta} = \frac{n}{K_{ads}} + nC \tag{5}$$

where n ($0 < n < 1$) is the heterogeneity character of the surface.

The plot of C/θ versus C is given in Figure 6(b) and it clearly reveals that the linear correlation coefficients (R^2) are almost equal to unity and the slopes are very close to 1. This presumes that the adsorption of DCH on AA6061 alloy follows the modified Langmuir adsorption isotherm.

The equilibrium constant, K_{ads} is related to the standard Gibbs free energy of adsorption ΔG°_{ads} by the relation (6)

$$K_{ads} = \frac{1}{55.5} \exp\left(\frac{\Delta G^{\circ}_{ads}}{RT}\right) \tag{6}$$

where R is the universal gas constant, T is the thermodynamic temperature and 55.5 is the molar concentration of water in the solution expressed in mol L^{-1} .

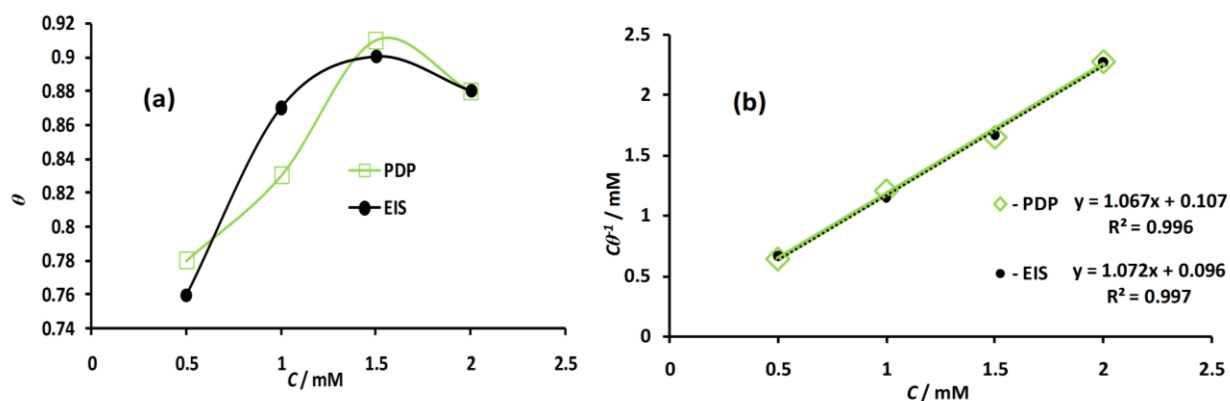


Figure 6. (a) Plot of concentration of DCH versus surface coverage and (b) Langmuir isotherm plot obtained for the adsorption of DCH on the surface of AA6061 in 3.5 % NaCl. [Symbols \square and \bullet represent the data points of PDP and EIS studies respectively, connected with trendlines]

It is generally accepted that for the values of $-\Delta G^{\circ}_{ads}$ up to 20 kJ mol^{-1} are consistent with physisorption, while those around 40 kJ mol^{-1} or higher are associated with chemisorption [25]. Physisorption is due to electrostatic attractive forces between the inhibiting organic ions or dipoles and the electrically charged surface of the metal. Chemisorption is due to interaction between unshared electron pairs or π electrons of the adsorbate with the metal in order to form a coordinate type of bond.

In the present investigation, the $-\Delta G^{\circ}_{ads}$ value obtained from both PDP and EIS techniques are 33.04 and $33.31 \text{ kJ mol}^{-1}$, respectively, and it ensures that the adsorption of DCH on AA6061 involves physisorption as well as chemisorption. In the meantime, the negative value of ΔG°_{ads} signifies the spontaneous adsorption of DCH molecules on AA6061 surface.

Surface morphological studies

The SEM micrographs of AA6061 immersed in 3.5 % NaCl in the absence and presence of 1.5 mM DCH are shown in Figure 7. The surface of AA6061 was severely damaged with large number of pits in 3.5 % NaCl solution. Whereas, a less damaged surface with reduced pits were observed on the surface of AA6061 in presence of DCH in 3.5 % NaCl solution. As a result, it can be

deduced that DCH forms a protective adsorbed layer on metal surface and it hampers the corrosion of AA6061 in 3.5 % NaCl medium.

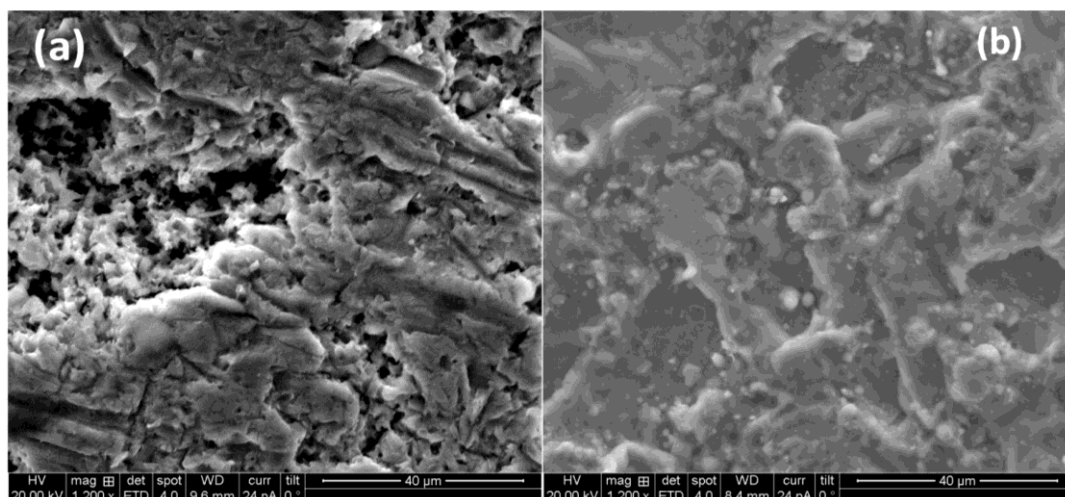


Figure 7. SEM micrographs of AA6061 immersed in (a) 3.5 % NaCl and (b) 3.5% NaCl +1.5 mM DCH

Quantum chemical studies

To study the effect of molecular structure on inhibition efficiency, quantum chemical calculations were performed using the ab initio method [26], and all calculations were carried out with the help of complete geometry optimization using 3-21G basis set. The optimized structure and the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of DCH molecule are shown in Figures 8 and 9.

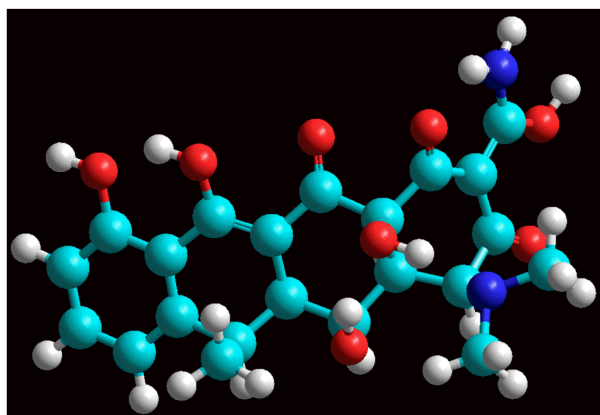


Figure 8. Optimized structure of DCH molecule.

The energies of the frontier molecular orbitals such as E_{HOMO} and E_{LUMO} are significant parameters for the prediction of the reactivity of a chemical species. E_{HOMO} is often associated with the electron-donating ability of a molecule. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to a metal with unoccupied molecular orbitals. A lower value of E_{LUMO} indicates an easier acceptance of electrons from a metal surface [27]. The gap between the LUMO and HOMO energy levels of inhibitor molecules is another important parameter. Low absolute values of the energy band gap ($\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$) means good protection efficiency.

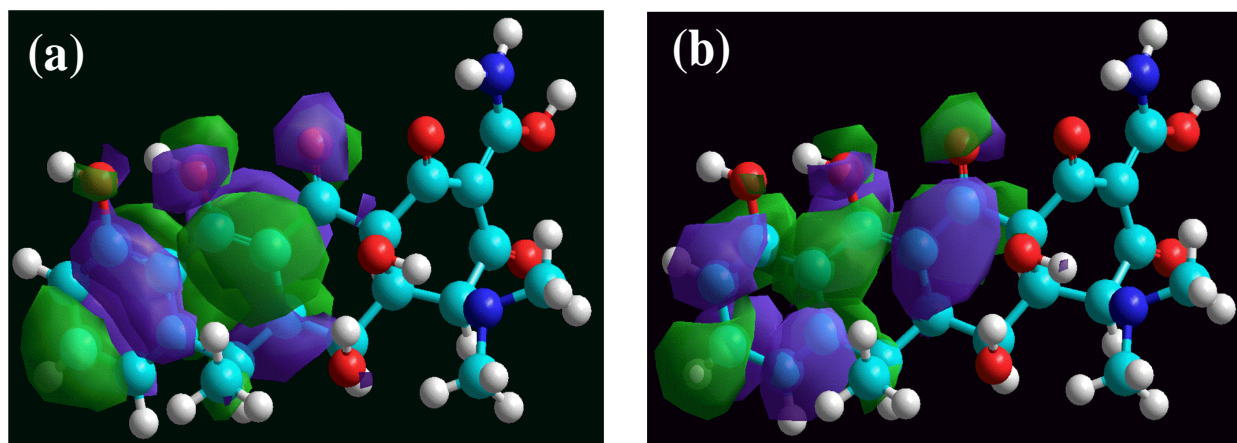


Figure 9. Distribution of (a) HOMO and (b) LUMO in DCH molecule.

From the Figure 9, it can be observed that the HOMO and LUMO orbitals are distributed on the phenyl ring and the oxygen atoms present in its environs. Hence, it can be considered that the oxygen atoms of the hydroxyl groups and carbonyl groups which are in the vicinity of phenyl ring and the π -electrons are the active sites of adsorption of DCH on metal surface. Some quantum chemical parameters such as ionisation potential (I), electron affinity (A), absolute electronegativity (χ), global hardness (η), and global softness (σ) were calculated by the following relations;

$$I = -E_{\text{HOMO}} \quad (7)$$

$$A = -E_{\text{LUMO}} \quad (8)$$

$$\chi = \frac{I + A}{2} \quad (9)$$

$$\eta = \frac{I - A}{2} \quad (10)$$

$$\sigma = \frac{1}{\eta} \quad (11)$$

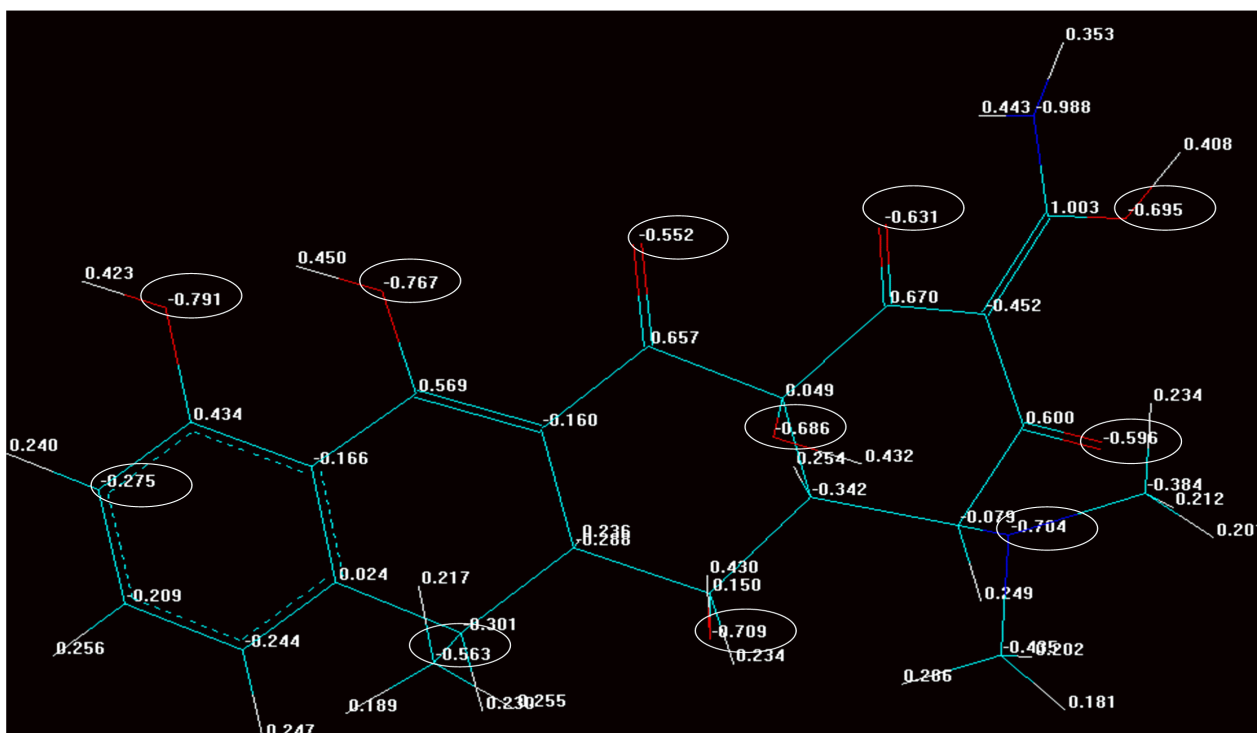
The calculated quantum chemical data are tabulated in Table 3. The high inhibition efficiency of a molecule can be attributed to the high value of dipole moment and low values of ΔE . The results of the high dipole moment and the low energy gap indicate that electron transfer from DCH to the surface takes place during adsorption on the AA6061 surface.

The adsorption centres of organic molecules can also be approximated by net atomic charges in the molecule. The net atomic charges of DCH molecule are given in Figure 10.

It has been reported that as the charge of the adsorbed centre become more negative, the atom more easily donates its electron to the unoccupied orbital of the metal [28]. Hence by visualizing the Figure 10, it can be considered that oxygen atoms and the π -electrons present in the DCH molecule are the active centres of adsorption.

Table 3. Quantum chemical parameters of DCH

Quantum chemical parameters	
$E_{\text{HOMO}}/ \text{eV}$	- 8.041
$E_{\text{LUMO}}/ \text{eV}$	2.291
$\Delta E/ \text{eV}$	10.332
χ/ eV	2.875
η/ eV	5.166
σ/ eV^{-1}	0.194
μ/ D	4.516
Total energy, kcal mol ⁻¹	- 970248.9

**Figure 10.** The net atomic charges of DCH molecule.

Mechanism of inhibition

Based on the experimental results, the following mechanism has been proposed for the corrosion behaviour of AA6061 in 3.5 % NaCl in presence of DCH molecules. In 3.5 % NaCl, the cathodic reduction of oxygen takes place on the surface of aluminium and leads to the formation of oxide film by anodic reaction. Both the cathodic and anodic reactions result in the formation of oxide film are as follows [7,29-31];



The aluminium undergoes pitting corrosion in NaCl solution due to the presence of aggressive chloride ions and it leads to the breakdown of aluminium oxide formed on the metal surface [7]. This phenomenon can be explained by the following reactions;



or



Many of the researchers have explained the mechanism of pitting corrosion in different ways [32-35]. Some of the authors propose that the AlCl_4^{-} formed within the pits get diffuses in to the bulk solution and leads to the pitting corrosion. However, other researchers emphasize that the adsorbed chloride ions reacts with Al^{3+} ions in the oxide lattice and results in the formation of oxychloride complexes, $\text{Al}(\text{OH})_2\text{Cl}_2^{-}$. This complex reduces the stability of oxide film and enhances the dissolution rate of aluminium.

The electrochemical results disclose that the DCH molecules interact with the surface of AA6061 through the process comprehensive adsorption mechanism. Thus, it can be considered that the electrostatic interaction occurs between the inhibitor molecules and charged metal surface. Also, the quantum chemical calculations reveal that the oxygen atoms of hydroxyl groups and carbonyl groups which are in the vicinity of phenyl ring and the π -electrons present in DCH molecule are the active sites responsible for the process of adsorption. Consequently, the inhibitor get adsorbed on the surface of AA6061 through these active sites and it prevents the formation of $\text{Al}(\text{OH})_2\text{Cl}_2^{-}$, on the oxide film. As a result, DCH decreases the aggressiveness of chloride ions and protects the metal surface from pitting corrosion.

Conclusions

The molecule DCH is an efficient corrosion inhibitor for AA6061 in 3.5% NaCl medium. The electrochemical studies reveal that DCH hampers AA6061 corrosion through the process of adsorption. In NaCl medium, the mere adsorption of DCH obeys modified Langmuir adsorption isotherm and follows both physisorption and chemisorption mechanism. Quantum chemical studies disclose that the hetero atoms and the π – electrons present in DCH molecules are the active sites of adsorption which are responsible for the inhibition behaviour.

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