JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 7 submitted 4 February 2014

Azithromycin : A Potential Corrosion inhibitor for Aluminum 2024 in acidic medium

N.V.Lakshmi[1], S.Karthikeyan[1], N.Arivazhagan[2]*

[1] Surface Engineering Research lab, CNBT, VIT University, Vellore -632014, India

[2]Manufacturing Division, School of Mechanical and building Sciences, VIT University, Vellore -632014, India

Abstract

The significance of Azithromycin (AZ) on corrosion of aluminium alloy 2024 in 0.1N Hydrochloric acid was examined using weight loss measurements, Tafel polarization studies and scanning electron microscopy. The results indicated that AZ is a good inhibitor for aluminium alloy in 0.1N HCl and maximum efficiency obtained was 91% at 450ppm concentration of azithromycin. Potentiostatic Polarization analyses displayed that AZ works as a mixed type of inhibitor. Electrochemical impedance plots were used to examine the mechanism of corrosion. Quantum chemical studies were done for azithromycin and its various quantum chemical parameters were calculated and tabulated.

Keywords: Corrosion, Azithromycin, Aluminium 2024, Quantum chemical

1. Introduction

The Aluminium alloy 2024 is largely used in aerospace industries because of its ideal weight to strength ratio. The high strength of the alloy 2024 is due the presence of alloying element predominantly copper and this makes alloy more prone to localized corrosion due to discrimination of the intermetallic particles in grain boundaries [1-2].Generally hydrochloric acid is used for pickling, chemical and electrochemical etching of Al. Numerous methods are used to shrink the corrosion rate of metals in

1* corresponding author (skarthikeyanphd@yahoo.co.in)

ISSN 1466-8858 Volume 17, Preprint 7 submitted 4 February 2014

acids, and in the midst of different methods practice of inhibitor is utmost common. Many organic compounds were used as corrosion inhibitor [3-7]. But currently use of antibiotics as corrosion inhibitors is increased tremendously because of less toxicity and eco-friendly nature. Heterocyclic compounds holding hetro atoms such as sulphur, nitrogen and oxygen atoms comprising multiple bonds adsorb on the metal surface and thus act as active corrosion inhibitor for aluminium 2024 in acid medium [8-13]. A meticulous examination was used to explore the inhibition properties of azithromycin. The corrosion inhibiting capability of azithromycin might be due to its arrangement of atoms. Various studies demonstrate that azithromycin is prospective corrosion inhibitor. Azithromycin is an active antibiotic used for treat bacterial and respiratory tract infections which falls under the class of azalide, which is a subclass of macrolide antibiotics.

2. Experimental Details

2.1Materials and methods

Materials employed for the analyses were Aluminium 2024 sheet of compositions (wt. %), Cu (4.3), Mn (0.5), Mg (1.3) and appreciable amount of Si, Zn, Ni, Cr in addition to Al balance. The sheet was then cut into number of sample of each 4 x 1 x 3 cm dimensions were used for weight loss and electrochemical studies. Each sample was mechanically polished followed by degreasing with acetone then washed with double distilled water and finally dried. Electrochemical experiments were conducted in three electrode cell assembly with Al as working electrode. Platinum wire as counter and Ag/Agcl/kcl (sat) as reference electrode.AR grade Hydrochloric acid and double distilled water are used to make 0.1N HCl for all experimentations.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 7 submitted 4 February 2014

2.2 Inhibitor

The antibiotic namely azithromycin was purchased from corresponding manufacturer and used without further purification. The structure of azithromycin is shown in fig 1.AZ contains methyl substituted nitrogen atom incorporated into the lactone ring, thus making the lactone ring 15 membered. With this structure it is likely to act as good inhibitor.

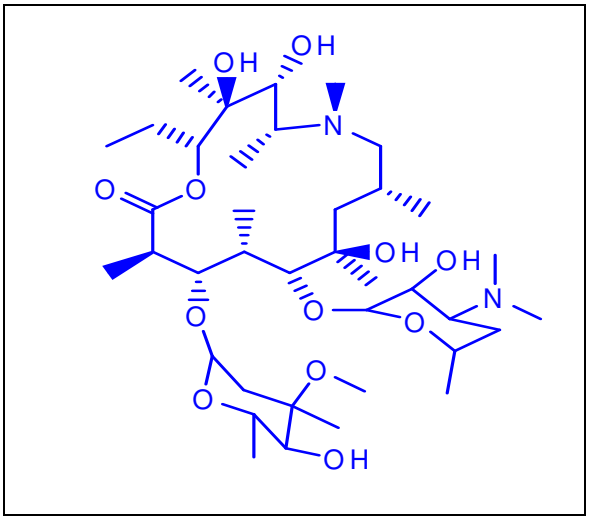


FIG 1 Structure of Azithromycin

2.3 Weight loss studies

The inhibitor was initially screened by a weight loss method [12].various samples Al were submerged in 0.1 N HCl solution comprising diverse concentrations of inhibitors (AZ).Samples were weighed before and after immersion and weight loss was estimated. The surface coverage (□) and inhibition efficiency were determined by means of following equations. Surface coverage (□) $= W_o-W/W_o$

Inhibition efficiency (%) $= W_o-W/W_o$ X 100

Where, W_o – Weight loss without inhibitor

ISSN 1466-8858 Volume 17, Preprint 7 submitted 4 February 2014

W – Weight loss using varied concentrations of inhibitors

2.4 Tafel polarization studies

Tafel Polarization studies were carried out in a conventional three – electrode cylindrical glass cell, using CH electrochemical analyzer (Model660E). Before to computing the polarization graphs the solution was deaerated for 20 min. and the working electrode was sustained at its corrosion potential for 10 min for attaining a steady state. The Al 2024 surface was bare to different concentrations of azithromycin in 100mL of 0.1N HCl at room temperature. The inhibition efficiency (IE %) was estimated using the equation

Inhibition Efficiency (IE %) = $(I_0 - I / I_0) \times 100$

Where I_0 and I are the corrosion current density in absence and presence of inhibitor respectively.

The current-potential curves were documented by altering the electrode potential from -750mV to +150mV versus the open circuit potential. The resultant corrosion current (I corr) was recorded. Tafel plots were made by plotting E versus log I. Corrosion Potential (E corr), corrosion current density (I corr) and cathodic (βc) and anodic slopes (βa) were intended from known procedures.

2.5. Impedance studies

Impedance studies were carried out in the frequency range from 0.1 to 10000 Hz using amplitude of 20 mV and 10 mV peak to peak with an AC signal at the open-circuit potential .The impedance graphs were schemed in the nyquist representation. Charge transfer resistance (R_{ct}) values were acquired by subtracting the high-frequency impedance. The inhibition efficiency was obtained from the equation:

Inhibition Efficiency (IE %) = $(R_{ct} - R_{ct} / R_{ct}) \times 100$

ISSN 1466-8858 Volume 17, Preprint 7 submitted 4 February 2014

Where R'_{ct} and R_{ct} are the corrosion current of Aluminum 2024 with and without treatment of inhibitor respectively.

2.6 Surface Morphology studies

The Scanning electron microscopies (SEM) Model: S-3000H, Hitachi, Japan, was used to observe the specimen's surface which is dipped in 0.1 N hydrochloric acid and with inhibitor solutions [15].

2.7 Theoretical Analysis

Quantum studies were done using MOPAC 2000 program of CS Chemoffice packet program. The highest occupied molecular orbital (HOMO)energy, lowest unoccupied molecular orbital (LUMO) energy, Dipole moment (μ), hardness(η), absolute softness(σ) and total energy of the molecule were intended with the above given software package.

3. RESULTS AND DISCUSSION

3.1 weight loss Studies

The values of inhibition efficiency (IE %) and the rate of corrosion from weight loss studies at diverse concentrations of azithromycin are précised in table-1. It displays that the compound successfully inhibits the corrosion of aluminium alloy 2024 in 0.1 N HCl medium. Extreme inhibition efficiency and decreased corrosion rate is due to the influence of amplified adsorption and enlarged coverage of inhibitor on aluminium surface with growth in the inhibitor concentration.

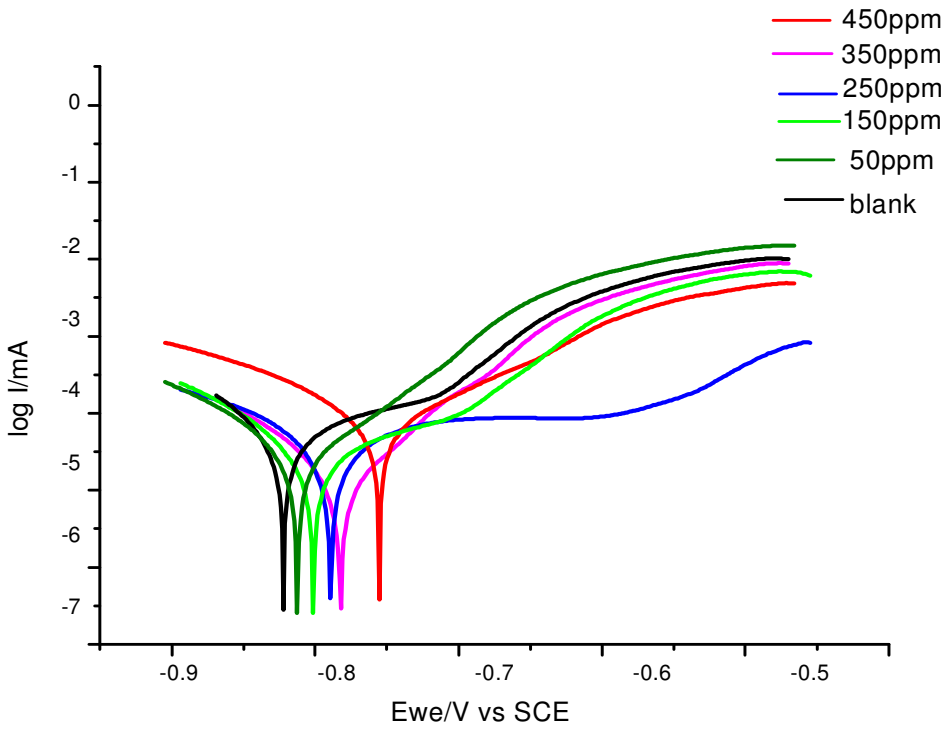
The corrosion inhibition by azithromycin may possibly be due to the following interactions:

1. The interaction between the lone pairs of electrons on exo oxygen and nitrogen atoms.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 7 submitted 4 February 2014

2. The interactions between unshared electron pairs in azacyclopenta-decane15-one ring along with eight electron releasing methyl groups with positively charged aluminium surface.

3.2 Potentiodynamic polarization studies



JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 7 submitted 4 February 2014

FIG 2 Tafel curves of Aluminium alloy 2024 in 0.1N HCl at various concentrations of Azithromycin

Tafel curves for aluminum alloy 2024 in HCl medium at various concentrations of azithromycin are presented in figure-2. The parameters such as corrosion potential (E_{corr}), current densities (I_{corr}), anodic tafel slopes (β_a) and cathodic tafel slopes (β_c) and inhibition efficiency were studied from Tafel polarization curves as a function azithromycin concentration are displayed in table- 2. It can be realized from the table that values of Tafel slopes and I_{corr} are very much diminished in contrast to the metal surface without inhibitor. It is also revealed that growing the concentrations of azithromycin amplifies the β_a and β_c in imbalanced fashion approving that the inhibition of corrosion of Al alloy in HCl medium is in mixed control [14-16]. Values of E_{corr} are progressed to less negative values in the existence of different concentrations of AZ. This might be the cause for developing resolutely adherent adsorbed film of AZ on the Aluminum alloy. It marked that most of the values of inhibition efficiency found by weight loss procedures and Tafel polarization method are with virtuous agreement.

3.4 Impedance studies

The Nyquist illustrations of impedance performance of aluminium alloy 2024 in acidic medium with and without azithromycin is used to compute charge transfer resistance (R_t)and double layer capacitance (C_{dl}) values which are tabularized in table-3. From the table, it is found that values of R_{ct} increases at the expenditure of double layer capacitance with growth in AZ concentration [17]. This contributes to the improved adsorption of the AZ antibiotic on the Al alloy surface with intensification of drug concentration.

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 7 submitted 4 February 2014

A plot of surface coverage (ø) against log C exhibited a straight line plot endorsing that the adsorption of AZ on Al alloy surface from HCl medium followed Temkins adsorption isotherm. This is main confirmation to corrosion inhibition of azithromycin, as a consequence of its adsorption on the aluminum surface.

3.5 Quantum chemical studies:

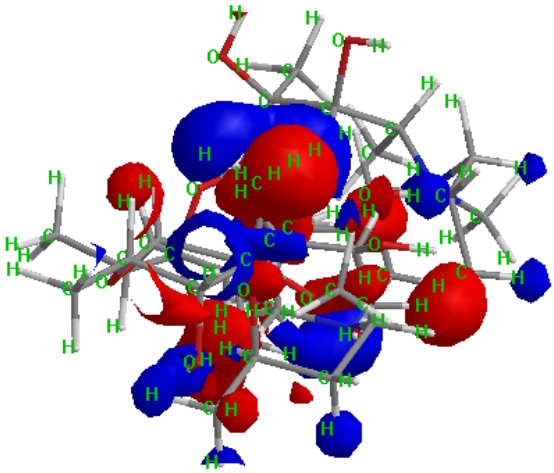


FIG 4.a. HOMO OF AZ

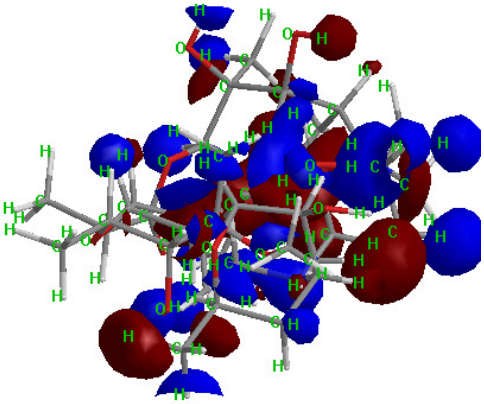


FIG 4.b. LUMO OF AZ

The quantum chemical aspects such as highest occupied molecular orbital (E_{HOMO}) energy, lowest unoccupied molecular orbital (E_{LUMO}) energy, LUMO- HOMO, energy gap (ΔE), dipole moment (μ), [18-21] are summarized in table -4 and in figure 4 a and 4.b. Azithromycin revealed greater inhibition efficiency due to its improved dipole moment values by the existence of electron receiving lactones and N-Oxime groups with unshared electron pairs on nitrogen . A peculaity in HOMO and LUMO values were noted.Both energy orbitals are showing almost similar distribution of electrons on the

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 7 submitted 4 February 2014

atoms being responsible for adsorbtion. It is evident that , If the values of ΔE is above 2, the adsorption of inhibitors will be effective on steel surface.

3.6 Scanning electron microscopy:

SEM micrographs are communicative of the modifications that complement both corrosion and defense of the Aluminium alloy in acidic environment [22]. Figure-5 shows the SEM of Al alloy in 0.1N HCl, which illustrates cracks, random grooves signifying the injury produced to the alloy surface by HCl. Figure-6 spectacles SEM images of aluminium alloy treated with 0.1 N HCl comprising 450pm of AZ, screening the look of layered surface along with nonappearance of unsystematic grooves marked the adsorption of azithromycin on Al alloy 2024.

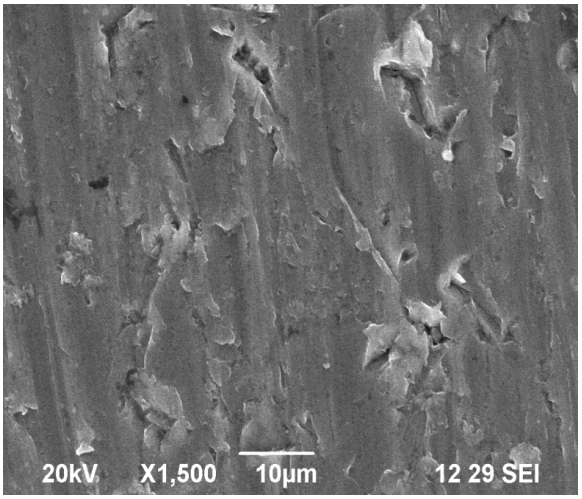


FIG 5 Scanning electron microscopy of Al alloy 2024 dipped in 0.1N HCl

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 7 submitted 4 February 2014

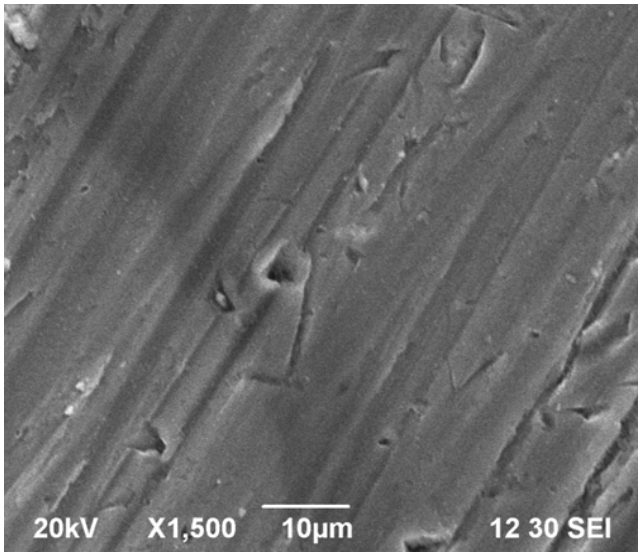


FIG 6 Scanning electron microscopy of Al alloy 2024 dipped in 0.1N HCl using 450ppm of azithromycin

4. Conclusions

1. Azithromycin performs as worthy inhibitor for corrosion inhibition of aluminium alloy 2024 in acidic environment.

2. Tafel polarization investigation confirms that azithromycin is a mixed kind of inhibitor.

3. The azithromycin act as good inhibitor which is demonstrated from improved R_{ct} and diminished C_{dl} values.

5. SEM images established the development of defensive layer of AZ on Al alloy 2024.

6. The values of HOMO, LUMO, ΔE and μ resultant from quantum chemical studies validated the outcomes of chemical and electrochemical studies.

References:

1. Highly effective organic corrosion inhibitors for 2024 aluminium alloy, S.Lamaka, M.Zheludkevich, K.Yasakau, Electrochimica acta, volume 52, pp. 7231–7247,2007

2. Antifungal drugs as corrosion inhibitors for aluminium in 0.1 M HCl

I.B. Obot , N.O. Obi-Egbedi , S.A. Umoren, Corrosion science, volume 51, pp. 1868-1875, 2009

3. Schiff bases as corrosion inhibitor for aluminium in HCl solution
Serpil Safak , Berrin Duran , Aysel Yurt, Gulsen Turkoglu, Corrosion science, volume 54, pp. 251-259, 2012

4. The inhibitive effect of some tetrazole derivatives towards Al corrosion in acid solution: Chemical, electrochemical and theoretical studies, K.F. Khaleda,b, M.M. Al-Qahtanib, Materials chemistry and physics, volume 113, pp. 150-158, 2009

5. Effect of some organic inhibitors on the corrosion behavior of Cu-Fe and Cu-Al-Fe alloys in sulphuric acid solution, N.H. Hela, H.E. El-fifky, M.R. Negem, Journal of Corrosion Science &Engineering, Vol.10, 2006

6. Ethane-2- thioamido-4-amino-N-(5-methylisoxazol-3-yl)-benzene sulfonamide: A novel inhibitor for the corrosion of mild steel in 1N HCl , S. Karthikeyan, N. Arivazhagan, S. Narayanan, Journal of Corrosion Science &Engineering, Vol.16, 2013

7. Inhibition of acidic corrosion of pure aluminum by some organic compounds, A.K. Maayta , N.A.F. Al-Rawashdeh, Corrosion science, volume 46, pp. 1129-1140, 2004

8. Experimental and theoretical studies of cloxacillin on the corrosion of mild steel in 1M H_2SO_4 S. Harikumar and S. Karthikeyan, Journal of corrosion science and engineering, Vol.16, 2013

9. Corrosion Inhibition performance of cetirizine on mild steel in 1m H_2SO_4, R.S.Dubey, K.U.Singh, Journal of Corrosion Science &Engineering, Vol.14, 2011

10. Antibacterial drugs as corrosion inhibitors for corrosion of aluminium in hydrochloric solution, M. Abdallah, Corrosion science, volume 46, pp 1981-1996, 2004

11.Torsemide and Furosemide as Green Inhibitors for the Corrosion of Mild Steel in Hydrochloric Acid Medium, S. Harikumar and S. Karthikeyan, Industrial and Engineering Chemistry Research, 52(22), pp. 7457-7469, 2013

ISSN 1466-8858 Volume 17, Preprint 7 submitted 4 February 2014

12. Corrosion inhibition of aluminum 6063 using some pharmaceutical compounds, A.S. Fouda , A.A. Al-Sarawy , F.Sh. Ahmed c, H.M. El-Abbasy, Corrosion science, volume 51, pp. 485-492, 2009

13. Inhibition of mild steel corrosion in hydrochloric acid solution by cloxacillin drug, S. Harikumar and S. Karthikeyan, Journal of Materials and Environmental Studies, Vol.5, pp. 925-934, 2012

14. Mechanism of corrosion and its inhibition, K. Madhavan, PhD Thesis, Alagappa University, India, June 1996

15.Adsorption Characteristics and Corrosion Inhibitive Properties of Clotrimazole for Aluminium Corrosion in Hydrochloric Acid, I.B. Obot, N.O. Obi-Egbedi, S.A. Umoren, Int. J. Electrochem. Sci, Vol. 4, pp. 863-877, 2009

16.The effect of inhibitor on the corrosion of aluminum alloys in acidic solutions, R.Rosliza,W.Wan Nik, H.Senin, Materials chemistry and physics, volume 107, pp. 281-288, 2008

17. The Structure of the Electrical Double Layer at the Metal Solution Interface, M.A. Devanathan, B. Tilak, Chem.Revs, 65, pp635, 1965

18. Gu Hough, Zhou Zhongbai, Tao Yingachu , Yao Luaw, Wahan Dauxe Xuebao, Ziran Kexuebaw, 2, pp57, 1982

19. G. Trabanelli and Zucchui F.Revon, Corrosion and coatings, 1, pp47, 1973

20. A.K. Lahiri, N.G. Banerjee, NML. Tech. Journal, 5, pp33, 1963

21. The use of quantum chemical methods in corrosion inhibitor studies, Gokhan Gece, corrosion science, volume 50, pp 2981-2992, 2008

22. Corrosion Inhibition of Mild Steel in 1M H2SO4 by Ampicillin as an Inhibitor, S. Harikumar and S. Karthikeyan, Journal of Corrosion Science &Engineering, Vol.16, 2013

JCSE The Journal of Corrosion Science and Engineering
ISSN 1466-8858 Volume 17, Preprint 7 submitted 4 February 2014

Table 1. Inhibition efficiency, corrosion rate and surface coverage for the corrosion of aluminium alloy 2024 in 0.1N HCl with different measures of azithromycin gained from weight loss studies

Concentration (ppm)	Corrosion rate ($mgcm^{-2}h^{-1}$)	Inhibition efficiency (IE %)	Surface coverage (□)
Blank	0.01728	–	–
50	0.00864	50	0.5000
150	0.00677	61	0.6082
250	0.00485	72	0.7193
350	0.00294	83	0.8298
450	0.00161	91	0.9068

Table 2. Electrochemical parameters of aluminium alloy 2024 in 0.1N HCl with different measures of azithromycin from Tafel polarization studies.

Concentration of Inhibitor (ppm)	E_{corr} (mV)	Tafel slopes in mV in dec^{-1}		I_{corr} $mA\ cm^{-1}$	Inhibition efficiency (%)
		β_a	β_c		
Blank	-0.821	70	123	0.841	–
50	-0.810	79	111	0.415	51
150	-0.801	72	126	0.305	64
250	-0.790	76	120	0.239	72
350	-0.780	78	131	0.141	83
450	-0.753	73	119	0.094	89

ISSN 1466-8858 Volume 17, Preprint 7 submitted 4 February 2014

Table 3.Electrochemical impedance parameters and its inhibition efficiency for the corrosion of aluminium alloy 2024 in 0.1N HCl with different measures of azithromycin.

Concentration of Inhibitor (ppm)	Charge Transfer resistance (R_{ct}) Ohm.cm^2	Double layer capacitance (C_{dl}) μF.cm^{-2}	Inhibition efficiency (%)
Blank	1.25	2.764×10^{-4}	-
50	2.58	1.064×10^{-4}	52
150	3.15	6.017×10^{-5}	60
250	4.33	2.884×10^{-5}	71
350	6.81	1.670×10^{-5}	82
450	11.6	7.460×10^{-6}	89

Table 4: Quantum chemical data of Azithromycin

Compound	LUMO (eV)	HOMO (eV)	ΔE (Cal.Mol^{-1})	Dipole moment (Debye)
Azithromycin	25.968	23.989	1.979	3.2