

GREEN INHIBITION OF CORROSION OF MILD STEEL IN ACID MEDIUM

P.A.Jeeva* and S.Karthikeyan

*School of Mechanical Engineering, VIT University, Vellore, Tamilnadu,
India.*

(*Corresponding author: p.a.jeeva@gmail.com)

Abstract

Corrosion behavior of mild steel in 1M Sulphuric acid with an anti-bacterial agent, viz., Clonazepam [CPZ] as corrosion inhibitor has been studied by using mass loss, potentiodynamic polarization, electrochemical impedance spectroscopy and hydrogen permeation studies. All these techniques reveal that inhibition efficiency increases with the increase in the concentration of antibacterial agent. Polarization studies indicated that inhibitor acted as cathodic inhibitor. It was found that the adsorption of green inhibitor on the mild steel surface obeying Langmuir adsorption isotherm.

Keywords: Mild Steel; Corrosion Inhibition; Clonazepam; Adsorption Isotherm; Green inhibitor

Introduction

Mild steel is an important class of metals due to its outstanding mechanical properties. It is widely used under different conditions in chemical and allied industries in handling acidic, alkaline and salt solutions. Mild steel is used in industries as pipelines for petroleum industries, storage tanks, reaction vessel and chemical batteries [1]. Acid solutions are widely used in many industrial processes like acid cleaning, pickling and descaling due to their chemical properties [2-5]. Acids cause damage to the

steel substrate, because of their corrosive nature. Several methods were used to reduce the corrosion of metals in acidic medium, but the use of inhibitors is most widely employed [6-10].

Organic compounds are widely used as corrosion inhibitors for mild steel in acidic media [11-16]. The rate of corrosion retards by adsorption of organic inhibitors on the mild steel surface. The inhibitors block the reactive parts by replacing water molecules and form a dense barrier layer on the metal surface. The majority of the organic inhibitors are toxic, highly expensive and non environment friendly. Research activities in recent times are booming on developing the cheap, non-toxic drugs as environment friendly corrosion inhibitors [17-21].

The aim of this study is to examine the corrosion protection efficacy of Clonazepam [CZP] for mild steel corrosion in 1M H_2SO_4 . We came to know no concrete report is available for the use this compound as corrosion inhibitor in 1M H_2SO_4 . From the literature the higher concentration of H_2SO_4 acts as pickling solution for mild steel for electroplating, battery electrodes using sulfur containing organic compounds. Use of these inhibitors in 1M H_2SO_4 will reduce the metal loss in acid medium. The antibacterial drug, Clonazepam [CZP] is in a group of drugs called benzodiazepines (ben-zoe-dye-AZE-eh-peens). It affects chemicals in the brain that may become unbalanced and cause anxiety. It is used to treat seizure disorders or panic disorder.

The inhibition efficiency of this green inhibitor was monitored using mass loss measurement, potentiodynamic polarization studies, impedance techniques, hydrogen permeation studies and diffuse reflectance methods.

2. Experimental Section

2.1. Materials

Mild steel specimens of size 1x4 cm² were used for weight loss and electrochemical studies. The aggressive solution of 1M H₂SO₄ (AR Grade) was used for all the studies. The antibiotic namely Clonazepam was purchased from the medicine shop and used as such. The structures of the antibiotics are given in the figure 1.

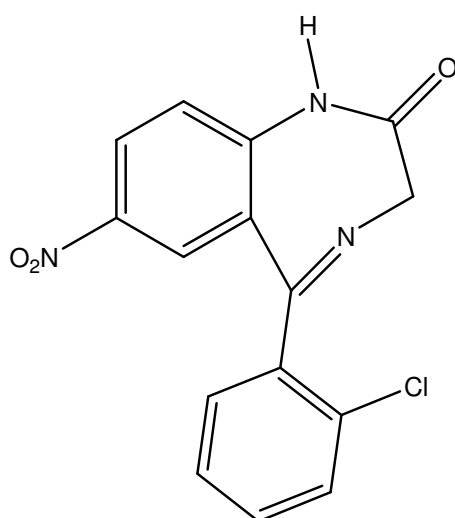


Figure 1. Structure of Clonazepam [CZP]

Chemically, clonazepam is 5-(2-chlorophenyl)-1,3-dihydro-7-nitro-2H-1,4-benzodiazepin-2-one. It is a light yellow crystalline powder. It has a molecular weight of 315.72

Electrochemical experiments were carried out using a three electrode cell assembly with mild steel samples as working electrode, 4cm² area of platinum as counter electrode and Hg/Hg₂SO₄/1M H₂SO₄ as the reference electrode. The surfaces of corroded and corrosion inhibited mild steel specimens were examined by diffuse reflectance studies in the region 200–700 nm using U-3400 spectrometer (UV-VIS-NIR Spectrometer, Hitachi, Japan).

2.2. Mass loss studies

The concentrations of inhibitor used for weight loss and electrochemical study were from $25 \times 10^{-4} \text{M}$ to $75 \times 10^{-4} \text{M}$. Mild steel specimens of size $1 \times 4 \text{ cm}^2$ were abraded with different emery papers and degreased with trichloroethylene. The cleaned samples were then washed with double distilled water and finally dried and kept in the desicator. The mass loss study was carried out at room temperature for 3 hours in $1 \text{M H}_2\text{SO}_4$. The experiments were performed in triplicate. The inhibition efficiency (IE %) was determined by the following equation

$$\text{Inhibition Efficiency (IE \%)} = (W_0 - W_i / W_0) \times 100$$

where W_0 & W_i are the mass loss values in the absence and presence of Clonazepam.

2.3. Electrochemical studies

Potentiodynamic polarization measurements were done out in a conventional three electrode cylindrical glass cell, using CH electrochemical analyzer. The solution was deaerated for 20 minute before carryout the polarization studies. The working electrode was kept at its corrosion potential for 10 min. until a steady state was achieved. The mild steel surface was exposed to various concentrations of inhibitor in 100mL of $1 \text{M H}_2\text{SO}_4$ at room temperature. The inhibition efficiency (IE %) was calculated using the equation.

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

where I_0 and I are the corrosion current density without and with the inhibitor respectively.

The potentiodynamic current-potential curves were noted by changing the electrode potential automatically from -750mV to $+150 \text{mV}$ versus the open circuit potential. The corresponding corrosion current (I_{corr}) was recorded. Tafel plots were built by plotting E versus $\log I$. Corrosion Potential

(E_{corr}), corrosion current density (I_{corr}) and cathodic and anodic slopes (β_c and β_a) were calculated according to known procedures.

Impedance measurements were performed 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 diagrams were plotted in the nyquist representation. Charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) values were acquired from nyquist plot [25, 26]. The percentage inhibition efficiency was calculated from the equation

$$\text{Inhibition Efficiency (IE\%)} = \left(\frac{C_{\text{dl}} - C_{\text{dl}}'}{C_{\text{dl}}} \right) \times 100$$

where C_{dl} and C_{dl}' are the corrosion current of mild steel with and without inhibitor respectively.

2.4. Hydrogen permeation studies

The hydrogen permeation study was monitored using an adaptation of modified Devanathan and Stachurski's, two compartment cell as described elsewhere [27]. Hydrogen permeation currents were noted in the absence and presence of inhibitors.

2.5. Diffuse reflectance spectroscopy

The surfaces of corroded and corrosion inhibited mild steel specimens were scrutinized by diffuse reflectance studies in the region 200– 700 nm using U-3400 spectrometer [UV-VIS-NIR Spectrometer, Hitachi, Japan].

3. Results and Discussion

3.1. Mass loss studies

The values of inhibition efficiency (IE%), corrosion rate (CR) and surface coverage(θ) calculated for Clonazepam in 1M H_2SO_4 at different concentrations from the mass loss data are summarized in the table-1. It is noticeable that inhibition efficiency boosts with increase in the

inhibitor concentration. In addition the rate of corrosion has reduced with increase in inhibitor concentration. Maximum inhibition efficiency is obtained at 75×10^{-4} M concentrations of the inhibitor.

Table 1. values of Inhibition Efficiency, Corrosion rate and Surface coverage for the corrosion of mild steel in 1M H_2SO_4 in presence of different concentrations of Clonazepam from mass loss measurements.

Inhibitor Conc. (M)	Inhibition Efficiency	Surface Coverage [θ]
Blank	-	-
Clonazepam		
5×10^{-3}	78.0	0.78
20×10^{-3}	89.92	0.89
35×10^{-3}	98.62	0.99

3.2. Potentiodynamic polarization studies

Polarization plots for mild steel in 1M H_2SO_4 containing different concentrations of green inhibitor for two antibiotics are summarized in table -2. The values of corrosion potential (E_{corr}), corrosion current densities (I_{corr}), anodic Tafel slope (β_a), cathodic Tafel slope (β_c) surface coverage (θ) and inhibition efficiency (IE%) were calculated using polarization curves. According to the results, corrosion current (I_{corr}) value diminishes with increase in the concentration of the Clonazepam drug. The inhibition efficiency (IE %) and surface coverage (θ) increases with increase in inhibitor concentration for all the three antibiotics. The maximum inhibition efficiency was achieved at 75×10^{-4} M concentration of the

inhibitor. It has been observed that both β_a and β_c are reduced, but the values of β_c are decreased to a greater extent. This indicates that the compound behaved as cathodic inhibitor.

Table 2: Electrochemical parameters and Inhibition Efficiency for corrosion of mild steel in 1M H₂SO₄ obtained by Polarization method in presence of different concentrations of Clonazepam drug.

Inhibitor Con. [M]	E _{corr} [mV vs SCE]	I _{corr} [μA cm ⁻²]	β _a [mV dec ⁻¹]	β _c [mV dec ⁻¹]	Inhibitor efficiency [%]	Surface coverage [θ]
Blank	-390.12	545.00	81.8	131.6	-	-
Clonazepam						
m						
5×10 ⁻³	-339.22	123.17	66.4	122.5	77.40	0.77
20×10 ⁻³	-323.43	59.95	52.3	114.3	89.00	0.89
35×10 ⁻³	-315.17	9.81	50.8	80.2	98.20	0.98

3.3. Electrochemical impedance studies

values of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) derived from Nyquist plots are shown in table 3. The values of R_{ct} are appeared to increase with increase in concentration of inhibitors in 1M H₂SO₄. It is cleared that values of C_{dl} are fetched down by increasing concentrations of inhibitors in the acid. This can be attributed to the dominant adsorption of the green inhibitor on the mild steel surface.

Table 3: Electrochemical parameters and Inhibition efficiency for corrosion of mild steel in 1M H₂SO₄ obtained by Impedance method in presence of different concentrations of Clonazepam drug.

Inhibitor Con. [M]	R _{ct} [Ω cm ²]	C _{d1} [F cm ⁻²]	Inhibition efficiency [%]	Surface coverage[θ]
Blank	31	0.470	-	-
Clonazepam				
5×10 ⁻³	115.6	0.105	77.60	0.77
20×10 ⁻³	167.3	0.050	89.20	0.89
35×10 ⁻³	265.62	0.008	98.20	0.98

3.4. UV spectral reflectance studies

The reflectance plots for polished specimen, specimen dipped in 1M H₂SO₄ and various concentrations of Clonazepam are given in the figure.2. The percentage of reflectance is maximum for polished mild steel and it progressively diminishes for the specimen dipped in 1M H₂SO₄ solution. This observation unveils that the change in surface property is due to the corrosion of mild steel in acid. Also the reflectance percentage of steel in the presence of green inhibitor is higher than steel as immersed in blank. This endorses that the surface property of steel has not transformed further due to the formation of protective layer on the mild steel surface. The reflectance percentage declines with increase in

thickness of the inhibitor film formed on metal surface. Similar findings has been made by Madhavan et al [29].

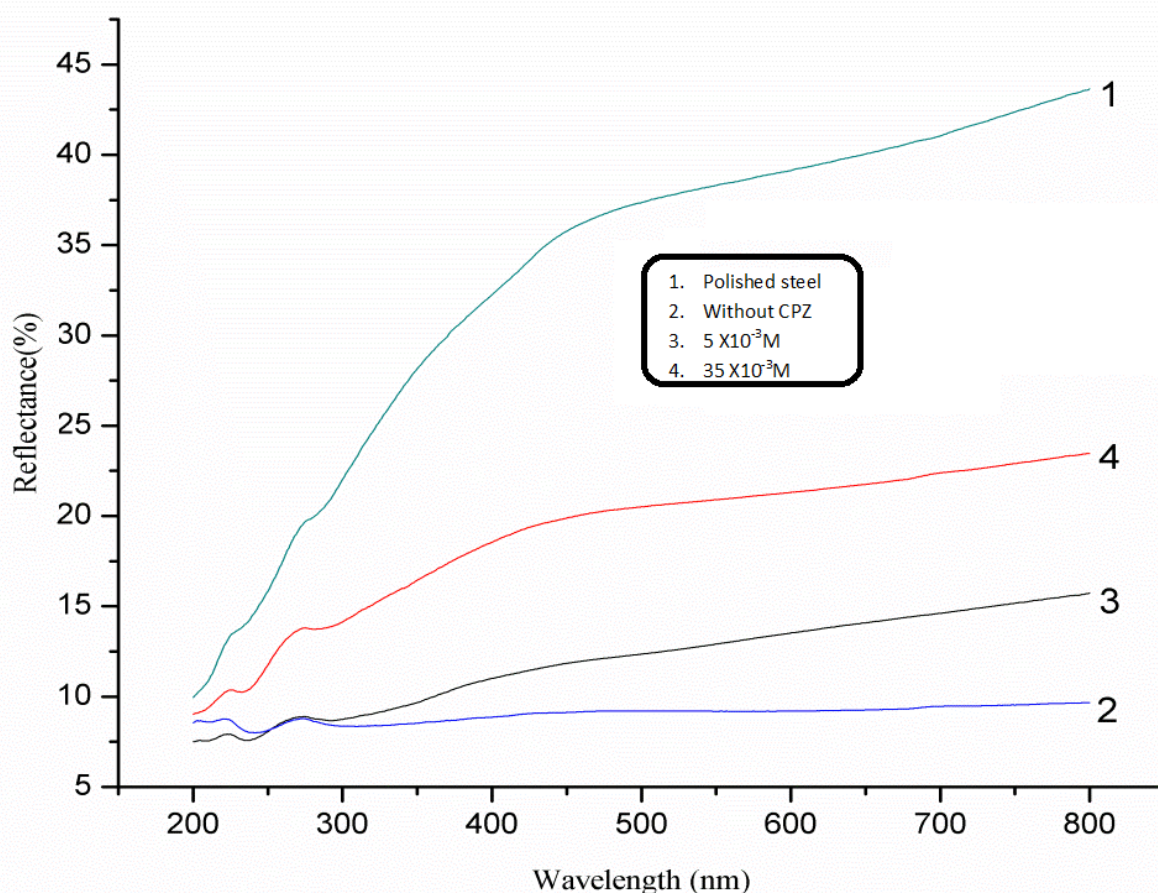


Figure 2: UV Reflectance curves of mild steel in 1M H₂SO₄ solution with various concentrations of the inhibitor.

3.5. Adsorption isotherm and thermodynamic parameters

The inhibitive action of inhibitor in extremely belligerent media is due to its adsorption on the metal surface. The degree of surface Coverage (θ) for different concentrations of Clonazepam in 1M H₂SO₄ has been calculated from mass loss, polarization and electrochemical impedance studies. The attained

data was tested graphically for fitting suitable isotherm [30-32]. Almost a straight line was obtained by plotting $\log (C/\theta)$ vs $\log C$ shown in Figure-3, which demonstrates that the adsorption of these compounds on steel surface observes Langmuir adsorption isotherm.

The Langmuir isotherm for the adsorbed layers is given by the equation [33],

$$C_{inh}/\theta = 1/K_{ads} + C_{inh}$$

where K_{ads} is the equilibrium constant of the adsorption/desorption process. Adsorption equilibrium constant [K_{ads}] and free energy of adsorption [ΔG^0_{ads}] were calculated using the equation ³⁴

$$K_{ads} = 1/C_{inh} \times \theta/(1-\theta)$$

$$\Delta G^0_{ads} = -2.303RT \log [55.5K_{ads}]$$

where 55.5 is the molar concentration of water in solution [35]. R is the gas constant, T is the temperature. The values of adsorption equilibrium constant [K_{ads}] and free energy of adsorption [ΔG^0_{ads}] are given in table-4. The negative values of [ΔG^0_{ads}] pointed out that adsorption of inhibitor is spontaneous process. It is reported that values of [ΔG^0_{ads}] is of order 20 kJmol^{-1} or lower indicates a physisorption, those of order of -40kJmol^{-1} or higher involve charge sharing or transfer from the inhibitors to the metal surface specifies a chemisorptions [36-38]. The values of free energy of adsorption [ΔG^0_{ads}] in our experiment lies in the range -28 to -32 kJmol^{-1} , signifying that the adsorption is not a simple physisorption, but it may contain some other interactions [39].

Table 4: Gibbs free energy parameters and adsorption equilibrium constant [K] of green inhibitor at various temperatures evaluated by weight loss method.

Clonazepam		
Temperature (K)	k_{ads}	$-\Delta G_{ads}^0$ (kJmol ⁻¹)
313	955	28.27
323	1188	29.82
333	1364	31.16

3.6. Hydrogen permeation measurements

Hydrogen permeation currents are recorded in H₂SO₄ in the absence and presence of Clonazepam drug. This study has been taken up with a plan of selecting the inhibitors with a view to their effectiveness on the lessening of hydrogen uptake ⁴⁰. The values of permeation current with respect to time are given in table-5.

The inhibitor brings down the permeation current to the extent of 50%. Thus a definite correlation exists between the corrosion inhibition efficiency and the extent of reduction in the permeation current of this compound. It is a known fact that lower β_c value for an inhibiting compound, the smaller is the corrosion and hydrogen ingress on the metal. An increase in the β_c value, leads to rise in the energy barrier for proton discharge and increase in the evolution of hydrogen. This in turn leads to higher entry of hydrogen through the steel surface .

Table 5: Values of permeation current for mild steel in 1M H₂SO₄ and in presence of green inhibitor with respect to change in time

Time (min.)	Permeation Current (μ A)	
	1M H ₂ SO ₄	Clonazepam
0	10.2	2,9
5	11.5	4.6
10	12.1	4.8
15	12.0	5.0
20	12.6	5.2
25	13.0	13.0
30	13.0	13,0
35	13.0	13.0
40	13.0	13.0

3.7. Mechanism of corrosion inhibition

The adsorption of Clonazepam onto the mild steel surface is found to be majorly physical in nature. Physical adsorption is a process of electrostatic attraction between charged species in the solution and the metal surface. If the metal surface is positively charged, the adsorption of negatively charged species is facilitated. Positively charged species can also adsorb on the positively charged metal surface with the help of negatively charged intermediate, which adsorb first on the positively charged metal surface and allows positively charged species to adsorb on it. Thus the adsorption of Clonazepam may take place in two different ways as

- (i) The protonated Clonazepam in acid solution may adsorb electrostatically to the anion covered mild steel surface through their protonated form.

- (ii) The inhibitors may compete with acid anions for the sites at the water covered surface and adsorb by donating electrons to the mild steel surface [40– 42].

Conclusions

1. The use of Clonazepam antibiotic as green corrosion inhibitor in 1M H_2SO_4 was thoroughly studied using mass loss, potentiodynamic polarization, impedance measurements and hydrogen permeation studies.
2. The adsorption of green inhibitor on mild steel surface follows Langmuir adsorption isotherm. The adsorption of compounds on steel surface is further confirmed by diffuse reflectance spectra .

References

1. Zhang J; Liu J; Yu W; Yan Y; You L ; Liu L , *Corros. Sci.*, **2010**, 52 2059.
2. Obot I B, Obi-Egbedi N O and Umoren S A 2009 *Int. J. Electrochem. Sci.* **4** 863.
3. Vishwanatham S and Anil Kumar 2005 *Corros. Rev.* **23** 181.
4. Eddy N O, Ebenso E E and Ibok U J 2010 *J. Appl. Electrochem.* **40** 445.
5. Ebenso E E, Alemu H, Umoren S A and Obot I B 2008 *Int. J. Electrochem. Sci.* **3** 1325.
6. Shukla S K, Quraishi M A and Prakash R 2008 *Corros. Sci.* **50** 2867.
7. Ranney M W 1976 *Inhibitors—Manufacture and Technology*; Noyes Data Corp: NJ.
8. Singh A K, Shukla S K, Singh M and Quraishi M A 2011 *Mater. Chem. Phys.* **129** 68.
9. Shukla S K and Quraishi M A 2010 *Mater. Chem. Phys.* **120** 142.
10. Eddy N O and Ebenso E E 2008 *Afri J of Pure & Appl Chem* **2(6)** 1.
11. Lagrenee M, Mernari B, Bouanis M, Traisnel M and Bentiss F 2002 *Corros Sci* **44** 573.

12. Quraishi M A and Khan S 2006 J Appl Electrochem **36** 539.
13. Quraishi M A, Athar M and Ali H 2002 Br Corros J **37** 155.
14. Hasanov R, Sadikoglu M and S. Bilgic 2007 Appl. Surf. Sci. **253** 3913.
15. Chetouani A, Hammouti B, Benhadda T and Daoudi M 2005 Appl. Surf. Sci. **249** 375.
16. Bouklah M, Hammouti B, Lagrenee M and Bentiss F 2006 Corros. Sci. **48** 2831.
17. Abdallah M 2002 Corros Sci **44** 717.
18. Abdallah M 2004 Corros Sci **46** 1981.
19. El-Naggar M M 2004 Corros Sci **49(5)** 2226.
20. Solmaz R , Kardas G , Yazici B and Erbil M 2005 Protection of Metals **41(6)** 581.
21. Sing W T, Lee C L ,Yeo S L, Lim S P, Sim M M 2001 Bioorg Med Chem Lett. **11** 91.
22. Nnabuk O. Eddy, Eno E. Ebenso and Udo J. Ibok 2010 J Appl Electrochem **40** 445.
23. Nnabuk O. Eddy, Udo J. Ibok , Eno E. Ebenso, Ahmed El Nemr and El Sayed H.ElAshry 2009 J Mol Model **15** 1085.
24. Nnabuk O E, Siaka A A, Atiku A F and Muhammad A 2011 Innovations in Science and Engineering **1** 79.
25. Bentiss F, Lagrenee M, Traisnel M and Hornez JC 1999 Corros Sci. **41** 789.
26. Ashassi-Sorkhabi H, Shaabani B and Seifzadeh D 2005 Electrochim Acta **50** 3446.
27. Devanathan M A V and Stachurski Z 1962 Proc.Roy.Soc. **270 A** 90.
28. Shukla S K and Quraishi M A 2009 Corros. Sci. doi:10.1016/j.corros.2009.05.020.
29. Madhavan K, Quraishi M A, Karthikeyan S and Venkatakrishna Iyer S 2000 J.Electrochem Soc. India **49** 183.
30. Ayse Ongun Yuce and Gulfeza Kardas 2012 Corrosion Science **58** 86.

31. Eddy N O and Ebenso E E 2010 E-Journal of Chemistry, **7** S442.
32. Eddy N O, Odoemelam S A and Mbaba A J 2008 African Journal of Pure and Applied Chemistry **2** 132.
33. Lebrini M, Traisnel M, Lagrenée M, Mernari B and Bentiss F 2008 Corros. Sci. **50** 473.
34. Morad M S and Kamal El-Dean A M 2006 Corros. Sci. **48** 3398.
35. Tang L , Mu G and Liu G 2003 Corros. Sci. **45** 2251.
36. Khamis E, Bellucci F, Latanision R M and El-Ashry E S H 1991 Corrosion **47** 677.
37. Geler E and Azambuja D S 2000 Corros. Sci. **42** 631.
38. Abiola O K 2006 Corros. Sci. **48** 3078.
39. Singh A K and Quaraishi M A 2010 Corros. Sci. **52** 1529.
40. Madhavan K, Karthikeyan S and Venkatakrishna Iyer S 2001 J. Electrochem Soc. India **50** 37.
41. Dehr I and Ozcan M 2006 Mater. Chem. Phys. **98** 316.
42. Keles H, Keles M, Dehri I and Serindag O 2008 Mater. Chem. Phys. **112** 173.