

Effectiveness of organic compounds for preventing mild steel corrosion in an acidic environment: A review article

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Abstract- One of the most significant, effective, and organic molecules that serves as a useful corrosion inhibitor. According to all investigations, organic chemicals, particularly those containing sulphur (S), nitrogen (N), and oxygen (O), have a strong inhibitory efficacy. Metal structures can sustain severe damage from corrosion, which is a major problem in many sectors. Organic corrosion inhibitors are substances that act as protective films on metal surfaces to slow or stop corrosion. This review focused on the efficiency of organic compounds at resisting corrosion, and it looked at how some of these compounds halted the corrosion of mild steel in acidic solutions. It did this by using electrochemical techniques like polarization and electrochemical impedance. These investigations show that temperature decreases corrosion inhibition efficiency while concentration boosts it. Adsorption behaviour and thermodynamic variables were also looked at in these studies. SEM micrographs were used to analyse the surface morphology of the mild steel sample in both the presence and absence of an inhibitor.

Key Words: Scanning Electron Spectroscopy, Adsorption, Corrosion Inhibitor, Drugs, Quantum Mechanics.

1. Introduction:

Mild steel is the most prominent iron alloy. Mild steel has stronger mechanical durability. Due to its simple processing and inexpensive production, it has been employed extensively in industries. When steel is subjected to procedures involving acid pickling, industrial washing, acid descaling, and oil wet cleaning, corrosion develops and results in considerable financial losses [1-3]. One of the best and most affordable methods to prevent corrosion is through the administration of inhibitors. Steel inhibitors for corrosion with aromatic and heterocyclic rings and functional groups of oxygen, nitrogen, phosphorus, and sulphate are widely known. [4-6]. As corrosion inhibitor molecules are absorbed by the metal surface, they create barriers that screen mild steel from the majority of the solution and inhibit corrosion [7-9]. This paper highlights research on the effects of various corrosion inhibitors on the corrosion of mild steel in an acidic medium. In order to investigate how different drugs limit corrosion, we used electrochemical frequency modulation, electrochemical impedance spectroscopy, linear polarization resistance, and potentiodynamic polarization measurements. For a number of drugs, activation energy and the pre-exponential factor were also calculated, along with the thermodynamic properties (enthalpy, entropy, and free energy of adsorption). By using the semi-empirical AM1 technique, a number of quantum chemical parameters and the Mulliken charge densities for omeprazole were calculated in order to shed additional light on the mechanism of stopping the corrosion process. Several electronic properties of the fluconazole molecule in neutral and protonated versions were also computed using a quantum chemistry method to see if there is any correlation between the inhibitory action and the fluconazole molecule's molecular structure. The benzene ring, nitrogen, and oxygen atoms are among the centers of activity in the adsorption of fluconazole molecules, according to research in quantum chemistry. In order to determine the number of reactions, the effectiveness of the inhibition, and the level of surface covering, thermometric and gasometric measurements were made. The PM3 method, implemented in the HyperChem software, is used in theoretical experiments to assess the relationship between chemical structure and inhibitory effectiveness. For mild steel, aluminum, copper, iron, and zinc in various concentrations of acidic and alkaline solutions, drugs are strong corrosion inhibitors.

2. Corrosion Inhibitors

Chemicals those are included as corrosion inhibitors to prevent corrosive conditions in relatively small concentrations or delay corrosion without significantly interacting with the surrounding elements [8]. From 1 to 15000 ppm, the concentration can change [9]. In industries like oil extraction, processing, and the chemical ones, corrosion inhibitors are crucial. In the presence of corrosion inhibitors, the corrosion process is either delayed or the rate of metal oxidation is slowed [10]. By coating a whole metallic substrate with inhibitors, the technique of inhibition stops corrosive species from attacking it [11]. There are many definitions for inhibitors; however the According to International Standard Organization

“A chemical substance which retards the corrosion when added to an environment in small concentration without significantly changing the concentration of any other corrosive agent.” The metallic surface is shielded by inhibitors that have been adsorbed there. Inhibitors prevent corrosion by reducing the mobility of metal ions through the polarization effect. Inhibitors make metallic surfaces more electrically resistive. Corrosion inhibitors effectively cause ions and molecules to adsorb on metal surfaces and decrease reactant diffusion to the metal surface. Both chemical and inorganic inhibitors can be categorized as inhibitors. The activities of inorganic inhibitors might be either cathodic or anodic. The organic inhibitors can operate either as an adsorbent or as a cathodic-anodic combination. Inorganic corrosion inhibitors function better over a wider range of temperatures for longer periods of time than organic corrosion inhibitors do. Organic corrosion inhibitors are less damaging than inorganic corrosion inhibitors, although being more expensive. Organic inhibitors have the ability to adsorb on metal surfaces by utilizing heteroatoms such as O, N, S, and P. [12-14]

3. Organic Inhibitors

Utilizing organic substances as inhibitors is one of the most effective methods for preventing metals from corroding, particularly in conditions of acidity. Various types of organic inhibitors have been developed to prevent corrosion. organic compounds that contain sulfur, nitrogen, and oxygen atoms Corrosion is slowed down as a result of molecules that inhibit corrosion being adsorbed on the surface of the metal. When corrosion inhibitors are absorbed, they are primarily controlled by a molecule's physical properties, such as its functional group, steric factor, molecular weight, structure, aromaticity, electron density of the donor atoms, and p-orbital nature of the donating electrons. Additionally, the molecules' electrical structure plays an important role [13–26]. The substances that are utilized as organic inhibitors can function either as cathodic, anodic, or cathodic-anodic, either separately or in combination. Using the surface adsorption method, they can also create a film. Some examples are benzotriazole, benzthiazole, mercaptobenzothiazole (MBT), amines, urea, heterocyclic nitrogen, and sulfur-containing substances, as well as caffeine, succinic acid, ascorbic acid, and extracts of numerous natural resources. Ethanolamine carbonate, dicycloexilamonio benzoate, and diisopropylammonium nitrite are examples of corrosion inhibitors for the volatile vapor phase [22–24].

The following are crucial considerations when deciding whether to utilize an inhibitor in a study.

- Technically and economically feasible should be requirements for using inhibitor.
- The inhibitors shouldn't impair the liquid's ability to be processed further.
- A rise in temperature or an increase in electrolyte content shouldn't have a negative impact on the inhibitors' efficacy.
- The effectiveness of the inhibitors should not be harmed by the buildup of corrosion products.
- The substance in contact with the electrolyte should have a negligibly low hydrogen diffusion rate.
- The inhibitor must to be environmentally benign and biodegradable.[25-26]

Table -1: The Properties of a Few Organic Corrosion Inhibitors

Organic Corrosion Inhibitors	Metal surface	surface analysis techniques	Effect of Treatment Time	Features	Influence of inhibitor concentration on the effectiveness of inhibition	Ref
Benzaldehyde thiosemicarbazone (BTSC)	HCl 10% on zinc surface	SEM-EDS Scanning Electron Microscope and FTIR	With an increase in immersion time up to 3 hours in a 4% BTSC solution, the inhibition efficiency gradually increased.	At relatively low temperatures, the production of protective coating is more prevalent..	In 4% BTSC solution at 298 K, the highest possible inhibition efficiency of 87% was attained.	27
Condensation product between amino benzoic acid and furfural	In 0.5N HCl, mild steel	The adsorbate coating was confirmed by investigations of the metal	FFAB was used at a concentration of (2% w/v). From two to six hours were spent treating the samples in various	With an increase in the temperature of the corrosive medium, it was discovered that the protective	With a 0.5M solution of hydrochloric acid, FFAB demonstrated good corrosion resistance. At 2% FFAB at 303–333K,	28

(FFAB)		surface using Scanning Electron Microscope	ways.	effectiveness provided by FFAB decreased.	the protection efficiency was 78%.	
2,2'-(1,4-phenylenebis(methanylydene)) The compound PMBMH is bis(N-(3-methoxyphenyl)hydrazinecarbothioamide).	In 1N HCl, mild steel	Scanning Electron Microscope	The inhibitor's highest protective efficacy was obtained at a concentration of 0.0005 M, at 303 K, and a 5-hour immersion period.	As the temperature rises, the effectiveness of inhibition decreases.	At 303 K, the highest efficiency of 95% was achieved in 0.0005 M of PMBMH.	29
thiazole derivatives, bromo acetyl coumarine (BAC), and acetyl coumarine (AC)	Zinc in 0.1 M HCl	EIS	The inhibition efficiency was gradually increased with increase in immersion period	In the following order: BAC > thiazole derivatives > AC, the %IE was maximum for BAC. With higher inhibitor concentration, inhibition efficiency increased.	Acetyl coumarine (AC), bromo acetyl coumarine (BAC), and thiazole derivatives of AC and BAC each had a maximum efficiency of 89% and 82-86%, respectively.	30
ATSC is also known as N-[(1E)-(4-methoxyphenyl)methylene]hydrazine carbothioamide.	zinc in 0.2M HCl	FTIR with Scanning Electron Microscope	When treating samples in a 3% ATSC solution, the protection efficiency increased significantly as immersion time increased up to 5 hours before remaining nearly constant.	With the rise in temperature, the protection's effectiveness somewhat declined.	Good corrosion resistance and a maximum protection efficacy of roughly 84% were demonstrated by ATSC at 5% at 300 K.	31
2-chloro 3-formyl quinoline	Mild steel (1M HCl)	SEM-Scanning electron microscopy	The inhibitor's highest protective efficacy was at a concentration of 200 ppm, at 303 K, and for 4 hours of immersion.	The effectiveness of inhibition rises with increasing inhibitor concentration but falls with rising temperature.	Maximum inhibitory efficiency of 2-chloro 3-formyl quinoline is around 85% up to 323 K temperature.	32
N-cyclohexylidene-2-(6-methoxynaphthalen-2-yl)propanehydrazide (HYD-2) (E)-N-(2,4-dimethoxybenzylidene)-2-(6-methoxynaphthalen-2-yl)propanehydrazide (HYD-1)	Mild steel (1M HCl)	Scanning Electron Microscope coupled with the EDX	The inhibitor had a maximal protective efficacy after 24 hours of immersion at a concentration of 5×10^{-3} M and temperatures ranging from 303 K to 333 K.	As the temperature rises, the surface's corrosion rate increases and its protectiveness decreases.	At an ideal concentration of 5×10^{-3} at 303-333K, HYD-1 and HYD-2 showed maximal inhibitory efficiencies of 96% and 84%, respectively.	33

Hydralazine hydrochloride	Mild steel (1M HCl)	Scanning Electron Microscope	The inhibitor's highest protective efficiency was achieved at a concentration of 500 ppm, at temperatures ranging from 303 K to 333 K, and a 4 h immersion time.	At higher temperatures, hydralazine hydrochloride proved an effective inhibitor.	With increasing inhibitor concentration, the efficiency of inhibition improved; 500 ppm of hydralazine hydrochloride demonstrated the highest inhibition efficiency of about 82%. at 303 - 333K	34
Flectofenine	Mild Steel in 1M HCl	Scanning Electron Microscope	Concentration of 500 ppm, 323 K. a 2 h immersion time, the inhibitor had a maximum protection efficacy	As the temperature rose up to 323 K, the effectiveness of inhibition increased.	With increasing inhibitor concentration, inhibition efficiency improved; 500 ppm of flectofenine demonstrated the highest inhibition efficiency of 75%. At 323K	35
Praziquantel	Mild Steel in 1M HCl	Scanning Electron Microscope	The inhibitor's highest protective efficacy was at a concentration of 250 ppm, at temperatures ranging from 323 K, and a 4h immersion time.	As the temperature rose up to 323 K, the effectiveness of inhibition increased.	The highest efficiency of 85.71% was achieved at 250 ppm of the inhibitor at 323 K.	36
Mono Azo Dyes Derived from 4,5,6,7-Tetrahydro-1,3-benzothiazole	Mild Steel in 1M HCl	Scanning Electron Microscope and EDX	As a result, for temperatures starting at 303 K, the inhibition efficiency rises with an increase in inhibitor concentrations. immersion time,	As the temperature rose up to 303K, the effectiveness of the inhibition increased..	exhibited a highest inhibitory effectiveness of 83% at 2.5 ppm at 303 k	37
4-Chloro,8-(Trifluoromethyl)Quinoline (CTQ)	Mild steel -1M HCl	Scanning Electron Microscope	As the concentration of the inhibitor rises, the effectiveness of the inhibition increases.	Up to 303K, temperature increases resulted in greater inhibition effectiveness.	The highest efficiency was 95.32% at 303K and 40 ppm of inhibitor.	38

Table 2: A list of drugs that prevent corrosion in various mediums

SI.No	Metal/alloy	Acidic Medium	Inhibitor	Type of drug	Ref
1.	Mild Steel	H ₂ SO ₄ acidic solution(1M, 1.5M, 2M, and 2.5M)	PenicillinV potassium	Antibiotic drug	39
2.	Mild Steel	Acidic solution 1M HCl	Streptomycin	Antibiotic	40
3.	Aluminium	Acidic solution 1 M HCl	Fluconazole &Clotrimazole	Antifungal	41
4.	Mild Steel	Acidic solution 1M HCl	Cefixime	Antibiotic	42
5.	Carbon steel	acid solution(1 mol L ⁻¹ HCl)	Sulfathiazole	Antibacterial	43
6.	Aluminum 6063	sodium hydroxide 2M	Omeprazole	Anti-inflammatory	44

7.	Mild Steel	Acidic solution 1M HCl	Cefacetrile	Antibiotic	45
8.	Mild Steel	Acidic solution 1M HCl	Rantidine	Histamine-2 blocker agent	46
9.	Mild Steel	Acidic solution 1M HCl	Tinidazole	Antiprotozoal & Antibacterial agent	47
10.	Mild Steel	Acidic solution 1M HCl	Chloroquine diphosphate	Anti-malarial	48
11.	Carbon steel	H ₂ SO ₄ acid solution 0.5M	Cefotaxime & Cefazolin	Antibacterial	49
12.	Carbon steel	Acid solution (0.1mol L ⁻¹ H ₂ SO ₄) & acetic acid 0.25 mol L ⁻¹ + sodium acetate buffer solution 0.25 mol L ⁻¹	Paracetamol & Carbamazepine	Analgesic-Antipyretic	50
13.	Copper	Acid solutions 0.1M HCl	Septazole	Antibacterial	51
14.	Mild Steel	Acidic solution 1M HCl	Diclofenac sodium	Anti-inflammatory & Analgesic	52
15.	Carbon steel	Acid solution (1M H ₂ SO ₄)	Lornoxicam & Tenoxicam	NSAID	53
16.	Mild Steel	Acidic solution 1M HCl	Trazodone	Anti-depressant	54
17.	Mild Steel	Acid solution (1M HCl)	Meclizine	Antihistamine	55
18.	Copper	Acidic solution 0.1M HCl	Streptoquin & Septazole	Antibiotic	56
19.	Mild Steel	Acidic solution 0.1M HCl	Amlodipine	Anti-hypertensive	57
20.	Mild Steel	2% KOH & 2% NaCl Alkaline solution	Amoxicillin	Anti-bacterial	58
21.	Mild Steel	HCl, HNO ₃ , H ₂ SO ₄ 1M	Dicloxacillin Cefuroxime Cefadroxil Cefixime Amoxicillin	Antibiotic	59
22.	Mild Steel	1M HCl, HNO ₃ , H ₂ SO ₄	Isoconazole Itraconazole Clotrimazole Fluconazole Ketoconazole	Anti-fungal	60
23.	Mild Steel	H ₂ SO ₄ acid solution 0.5M	Aspirin	Analgesic	61
24.	Carbon steel	H ₂ SO ₄ acid solution 1N	Cefixime	Antibiotic	62
25.	Mild Steel	Acid solution (0.1M HCl)	Cephalexin	Antibiotic	63
26.	Mild Steel	Acid solution (0.1M HCl)	Sulphadoxine & pyrimethamine	Anti-malarial	64
27.	Carbon Steel	Acid solution (1M HCl)	Phenytoin Sodium	Anti-convulsant	65
28.	Mild Steel	1M H ₂ SO ₄ acid solution	Vancomycin	Antibacterial	66
29.	Stainless steel	Acid solution (2M HCl)	Tenormin	Cardio-vascular	67
30.	Mild Steel	Acid solution (1M HCl)	Fluconazole	Anti-fungal	68
31.	Zinc	Acid solution (2M HCl)	Guaifenesin	Expectorant	69
32.	Mild Steel	Acid solution (0.1M HCl)	Amodiaquine	Anti-malarial & Anti-Inflammatory	70

33.	Mild Steel	Acid solution of 1M HCl & 1M H ₂ SO ₄	Ambroxol	Expectorant	71
34.	Carbon steel	Acid solution (1M HCl)	Acetazolamide	Diuretic	72

4. Investigation techniques for corrosion

In addition to quantum chemical calculations, the inhibition effectiveness of organic inhibitors was investigated using weight loss, potentiodynamic polarization, and electrochemical measurements. We looked at the molecular structure, concentration, and temperature variables which impact the inhibition of corrosion. The surface morphology of the steel sample in the presence and absence of the inhibitor was examined using scanning electron microscopy (SEM) micrographs and EDX analysis. To determine which adsorption isotherm fits the inhibitor's adsorption on the metal surface in acid solution the best, various isotherms including Temkin, Freundlich, and Langmuir were examined.

5. Weight Loss Measurements

The difference in weight between the metal wire areas that had been dipped in the corrosion solution, percentage of weight loss were calculated by using the standard method. The % inhibition efficiency was calculated with the formula below. [73]

$$IE = \frac{W_u - W_i}{W_u} \times 100$$

Where I.E is the effectiveness of inhibition

W_i = Weight loss in an inhibitory solution,

W_u = Weight loss in a control solution.

6. Electrochemical studies

Conventional three electrode cells with a counter electrode, reference electrode, and working electrode were applied to the polarization studies. Potential polarization curves were performed by adjusting the electrode potential around the open circuit potential. Corrosion-related variables like E_{corr}, I_{corr}, a, and Aarecord of c was made from the tafel graph.

6.1 Electrochemical frequency modulation

Impedance measurements in the frequency range from 100 kHz to 0.1Hz with peak to peak amplitudes of 5 mV were made using ac signals at an open-circuit potential. Examining and evaluating the experimental impedance was done using the analogous circuit. The charge transfer resistance R_{ct} (diameter of the high-frequency loop) and the double layer capacity C_{dl} are the key variables that may be inferred from the examination of the Nyquist diagram. The charge transfer resistance can be determined by correlating the Nyquist plots at high and low frequencies.(R_{ct}) values were determined. As a result, using Eq. (1), the charge-transfer resistance may be used to determine the inhibition efficiency (IE%) and the degree of surface covering (θ).

$$IE\% = \theta \times 100 = \frac{[R_{ct}^i - R_{ct}^s]}{R_{ct}^i} \times 100 \text{-----(1)}$$

Where,

R_{ct}ⁱ= The solutions' charge-transfer resistances in an unhindered state.

For an inhibited solution,

R_{ct} = The charge-transfer resistances. Equation (2) was utilized to calculate the values of the double layer capacitance. (Cdl). [74]

$$C_{dl} = \frac{1}{\omega R_{ct}} = \frac{1}{2\pi f_{max} R_{ct}} \text{----- (2)}$$

in the Nyquist plot, where,

f_{\max} = frequency at the maximum.

Charge transfer resistance values are denoted by R_{ct} .

C_{dl} = Double layer capacitance

7. Quantum chemical calculations

Complete geometry optimization of the inhibitor molecules was carried out using Gaussian 03 software and the DFT-Density functional theory techniques Beck's three-parameter exchange functional and LeeYangeParr non-local correlation functional (B3LYP) using 6-1G* basis set. [75]. Using frontier molecular orbital models (HOMO and LUMO), the adsorption of the inhibitor chemicals on the metal surface was interpreted. According to DFTKoopman's theorem, the electron affinity (A) is equivalent to the negative of the lowest unoccupied molecular orbital energy (ELUMO), and the ionization potential (I) is roughly equal to the negative of the highest occupied molecular orbital energy (EHOMO).

$$I = -EHOMO$$

$$A = -ELUMO$$

To assess the electron density distributions, natural bond orbital (NBO) analysis [78] was used. Calculating the chemical reactivity parameters requires knowledge of the electron density. The, global hardness (η) and the global softness (σ) global reactivities include electronegativity (χ). They can be calculated from the following equations:

$$\chi = \frac{I + A}{2}$$

$$\eta = \frac{I - A}{2}$$

$$\sigma = \frac{1}{\eta} = -\frac{2}{E_{HOMO} - E_{LUMO}}$$

8. Research Gap

This study shows how acidic conditions may successfully inhibit mild steel. Researchers have already demonstrated the value of inhibitors. High-temperature research has not received much attention from scientists generally. Quantum mechanics and molecular dynamics are useful in understanding the link between structure and property and how it influences the efficacy of corrosion inhibition.

9. Conclusions

A number of publications have addressed the research on different kinds of drugs with regard to corrosion inhibition. Their chemical structure, molecular structure, and affinities for metal surfaces all have an impact on how effectively they suppress corrosion. As corrosion inhibitors, the compounds containing aromatic rings as well as heteroatoms like nitrogen, oxygen, and phosphorus perform well. The table in this paper contains a quick list of the organic corrosion inhibitors. As the dosages are increased, all of these inhibitors show improved inhibitory activity. An improvement in inhibitory efficiency was seen at temperatures between 303 K and 333 K. Weight loss, electrochemical impedance spectroscopy, and linear polarization resistance all produce comparable outcomes. For researchers starting their corrosion research, this publication will offer extra benefits.

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