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RESEARCH

Applicability of Drugs as Sustainable Corrosion Inhibitors

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ABSTRACT

This review highlights the overview of recent trends in the usage of drugs as corrosion inhibitor for metal/alloy surfaces, particularly mild steel, aluminum, and copper in acidic, basic, or saline medium. The drug molecules generally containing atom having lone pair of electrons such as nitrogen (N), oxygen (O), Sulphur (S) and phosphorus (P) as well as a hydrophobic moiety that will repel aqueous corrosive species away from the metal surface and a mediately with an aromatic ring, unsaturation that are observed to be a significant component of extremely efficient inhibitors. The efficacy of various drugs, including antipyretics, analgesics, antibiotics, anti-depressants, and anti-histamines, is studied using weight loss, electrochemical impedance spectroscopy, potentiodynamic polarization and surface analysis techniques. Drugs molecules work by producing a layer on the metal's surface and can serve as anodic, cathodic, or mixed inhibitors. This protective film formed results of strong interactions such as free-orbital adsorption, chemisorption, and electrostatic adsorption, which prevent corrosive species from attacking the metal surface. Recent concerns and future prospective for further research and development to achieve more efficient and environmentally friendly inhibitors are additionally highlighted.

KEYWORDS

Drugs, corrosion, inhibitor, inhibition efficiency.

INTRODUCTION

Corrosion is generally perceived in terms of the degradation of a metal due to the consequences of a corrosive medium and is attracting considerable interest in the destructive result of a chemical reaction between a metal or metal alloy and its environment. Corrosion is an undesirable natural anomaly that badly affects the properties and beauty of the industrially important metals and their alloys, thereby decreases their life span. Corrosion has affected the exterior shell of various infrastructures for instance highways, bridges, buildings, chemical processing sections, waste water treatment and almost on all metallic objects, including our routine life use. Apart from the material loss, corrosion also adversely affects the environment as well as the human safety along with industrial operations. Corrosion highly affects the three main areas of concern: safety, economics, and environmental damage so, there is need to be controlled by some inhibition mechanism or with the help of some appropriate anti-corrosive agents in small concentrations [**1**]. Corrosion can be prevented up to some extent by using corrosion preventive methods. Several corrosion experiments and preventative measures technologies have been created and utilised in many laboratory and industrial domains during the recent decades. Corrosion inhibition serves as the most practicable, cost-effective, and efficient approach to managing deterioration on surface of the metal in different mediums by preventing metal dissolution and acid consumption. Inhibitors can be applied as a solution or as a protective coating using different techniques. Corrosion inhibitors are those chemicals that react with the surface of metal or surrounding gases to suppress the corrosion process's electrochemical reactions and are used to reduce the effect of a corrosive environment on metals. In different industries, the various compounds including organic and inorganic substances are used as inhibitors. The compounds generally containing atom having lone pair of electrons such as nitrogen (N), oxygen (O), Sulphur (S) and phosphorus (P) as well as a hydrophobic moiety that will repel aqueous corrosive species away from the metal surface and a mediately with an aromatic ring, unsaturation

that are observed to be a significant component of extremely efficient inhibitors to minimize the corrosion rate of metals in acidic environment [**2**]. Usage of drugs as corrosion inhibiting substance is the sustainable way to control the corrosion as these can be used in even in expired form because main component remains active even after expiry [**3–7**] Drugs molecules work by producing a layer on the metal's surface and can serve as anodic, cathodic, or mixed inhibitors. This protective film formed results of strong interactions such as free- orbital adsorption, chemisorption, and electrostatic adsorption, which prevent corrosive species from attacking the metal surface. This adsorption is generally one molecule layer thick and is unable to access the bulk of metals [**8**]. The adsorption process is governed by physicochemical variables such as functional groups, steric factors, aromaticity, π-orbital character of donating electrons, electron density at donor atoms, and the electronic structure of the molecules [**9**]. The present review is focused on applicability of various categories of drugs as corrosion inhibitor in various media and for various metals and alloys using different efficient analytical techniques to calculate inhibition efficiencies.

QUALITIES OF COMPOUNDS TO ACT AS SUSTAINABLE CORROSION INHIBITOR

Compound with following properties act as ideal inhibitor for application:

- Non-toxic nature
- Capable of working at high temperature
- Non requirement of specially designed storage facilities
- Long time protection of metal
- Complete surface protection of metal

DRUGS AS CORROSION INHIBITORS

Various techniques are available for the investigation of drugs as corrosion inhibitory compounds. Electrochemical Impedance spectroscopy (EIS) is used to calculate polarization resistance for determination of inhibition efficiency. Potentiodynamic polarization (PDP) measurements calculate corrosion current and corrosion potential through Tafel slope for the inhibition efficiency. The shift in corrosion potential (E_{corr}) is a measure of the mechanism of inhibition and drug may be categorized as cathodic, anodic or mixed type [**10**]. Mass loss measurement calculates corrosion rate and inhibition efficiency at particular temperature, concentration and immersion time [**11**]. Scanning Electron Microscopy (SEM), Transmission Electron microscopy (TEM) and Atomic Force Microscopy (AFM) are used to study surface morphology of metal outer surface before and after inhibition [**12-13**]. FTIR and FTIR-ATR detect the type of functional group and bonding between metal surface and inhibitor. Kinetic and thermodynamic parameters evaluate the feasibility of corrosion. Quantum Chemical Calculation Method and Density Functional Theory (DFT) with high accuracy are used for the determination of the optimized structure of inhibitors, electronegativity, frontier orbitals (HOMO and LUMO), chemical hardness, chemical softness. X-ray fluorescence (XRF) is helpful in finding composition analysis of materials [**14**]. EDAX (Energy Dispersive X-Ray Analysis) is employed to identify elemental composition of material [**15**]. UV-VIS spectroscopy helps in determination of type of transition in inhibitor molecule and to ensure formation of protective layer [**16**]. Drugs of various categories have been investigated to be successful corrosion inhibitors by using these techniques.

Corrosion protection by antipyretic drugs

The antipyretic drugs are primarily used to bring down body temperature. Due to environmentally benign nature and favorable structural properties, these can be used as corrosion inhibitors. Ibuprofen triazole has been investigated for its anticorrosive characteristics in sulphuric acid with inhibition efficiency of 97% by using gravimetric, electrochemical techniques and quantum chemical [**17**]. Ibuprofen protected the metal at cathode as well as anodic sites showing mixed type behaviour. Ibuprofen was investigated as corrosion inhibitor for various metals in different media [**18-19**] using electrochemical, weight loss, quantum chemical studies. Paracetamol was also studied for its anticorrosive behaviour and its efficiency was found to be high for carbon steel, copper and mild steel in acidic media. Aspirin is also found to be effective for mild steel, copper and aluminum corrosion inhibition. Many antipyretic drugs have been mentioned in the Table 1.

Corrosion protection by analgesic drugs

The analgesic drugs are primarily used to relieve pain but due to its similar structural properties as that of corrosion inhibitors, these can be used to control corrosion. Various analgesic medications have been used to control corrosion and have been employed successfully for prevention of corrosion in widely used industrially important mild steel. Voltaren was found to be efficient inhibitor in HCl with the performance of 96.1 using weight loss, electrochemical techniques, scanning electron microscopy, electron dispersive X ray technique. Etricoxib was examined for corrosion inhibitory characteristics for carbon steel in phosphoric acid with high efficiency. Many analgesic drugs have been mentioned in the table 1.

Corrosion protection by Psychotherapeutic / antidepressant drugs

The Psychotherapeutic drugs are used to control depression and anxiety. Fluxamine along with its blends with polyethylene glycol and glutathione were successfully assessed for the prevention of corrosion in hydrochloric acid with the inhibitory performance of 85.6% and the

methodology used was electrochemical and weight loss method. SEM micrographs were also used to justify the inhibitory action of [**20**]. Alprazolam was found to be effective for prevention of corrosion in mild steel with the inhibition efficiency of 86% as estimated by weight loss, electrochemical experimentation. Venlafaxine, Bezodiazpam, Lorazepam and barbiturates were also estimated as excellent corrosion inhibitors using various corrosion testing techniques. Many antidepressant drugs have been mentioned in the **Table 1**.

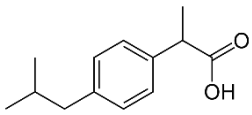
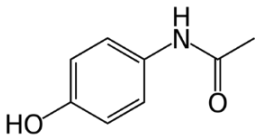
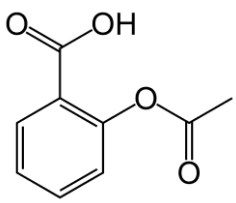
Corrosion protection by Antibiotic drugs

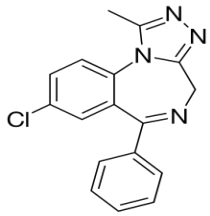
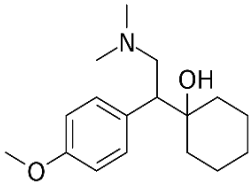
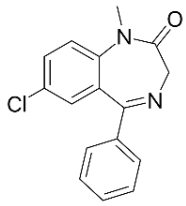
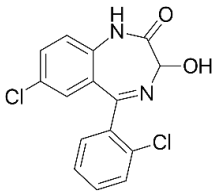
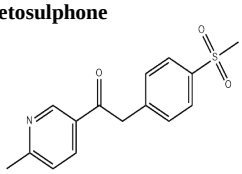
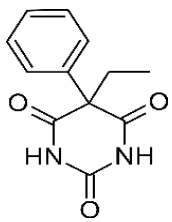
Antibiotic medicines are effective to fight infections caused by micro-organisms like bacteria. As these drugs have hetero atoms and pi electrons, so these may also act as corrosion inhibitors. Streptomycin was studied for corrosion inhibition of mild steel in HCl corrosive medium using weight loss and electrochemical measurements and showed inhibition efficacy of 88.5%. Studies revealed protection against corrosion through adsorption of the drug on metal surface without modifying the mechanism of corrosion phenomenon. Ampicillin antibiotic drugs was investigated for corrosion inhibition properties for mild steel in sulphuric acid as well as hydrochloric acid for mild steel with high [**21-22**]. Ampicillin was also effective for corrosion inhibition in zinc and stainless steel [**23-24**]. Cetoxamine, Ethambutol, Fluconazole, Clotrimazole were also tested for their anticorrosive behaviour for various materials in different aggressive media and were found effective corrosion inhibitors. Some of antibiotic drugs have been mentioned in the **Table 1**.

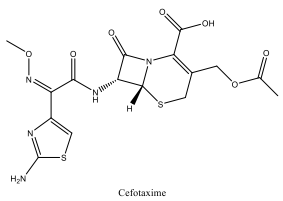
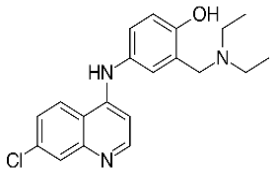
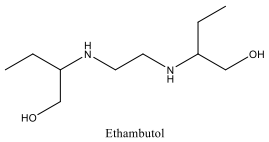
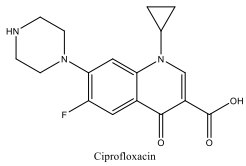
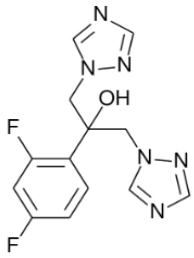
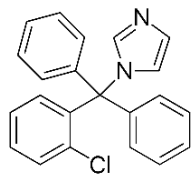
Corrosion protection by Antihistamine drugs

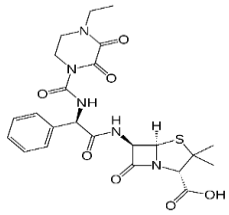
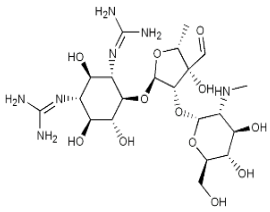
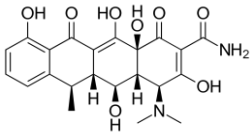
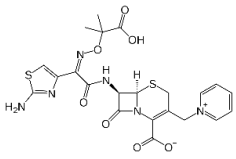
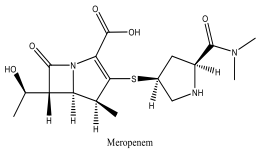
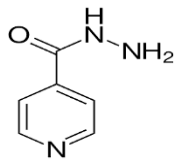
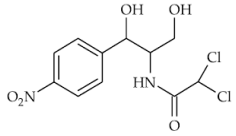
Antihistamines medications are effective against allergy [**25**]. Many antihistamine drugs show great potential to act as corrosion inhibitor. Cetirizine have been investigated as efficient corrosion inhibitor with the inhibition efficacy of 95% using gravimetric, electrochemical method and quantum chemical calculations. Cetirizine protected the mild steel at cathodic as well as anodic sites and formed monolayer on the metal surface. Promethazine and dioxopromethaxime were also found to be effective for corrosion prevention in copper in sulphuric acid showing mixed type of behaviour with the efficacy of 93.43% and 96.98% respectively. Some of the antihistamine drugs have been mentioned in **Table 1**.

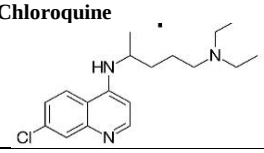
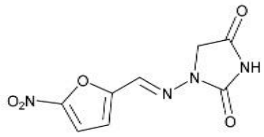
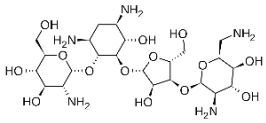
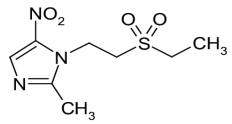
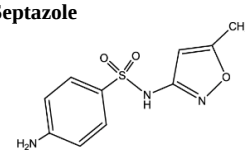
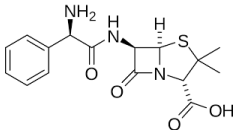
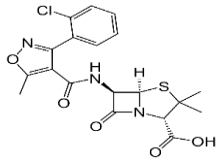
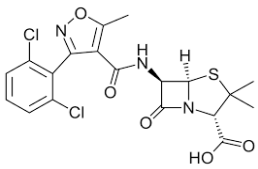
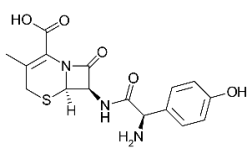
Table 1. Drugs of various categories in different acids for various metals.

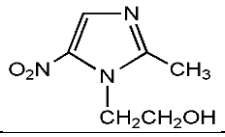
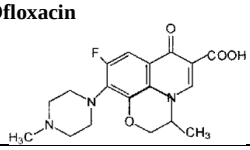
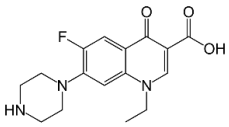
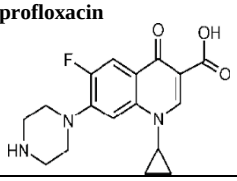
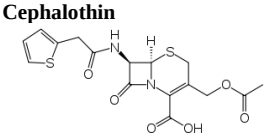
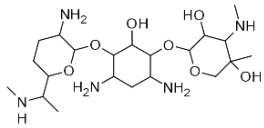
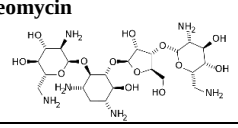
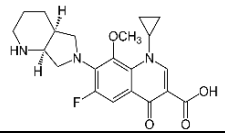
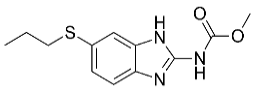
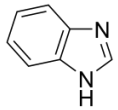
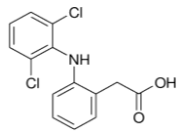
Name of Drug and structure	Material and Medium	Techniques used	Isotherm	Mode of inhibition	Inhibition efficacy (%)	Ref.
Antipyretics Drugs						
Ibuprofen 	Mild Steel in 0.5M H_2SO_4	Electrochemical, Weight loss	Langmuir	Mixed	63.2	[19]
	Al 6063 in 0.5M H_2SO_4	Electrochemical, Weight loss	Langmuir	Mixed	80.58	[18]
	430T1 Stainless Steel in 0.5M H_2SO_4	Electrochemical, Weight loss	Langmuir	Mixed	60.69	[26]
	Cu in Acid mixture	Electrochemical, Weight loss, Quantum chemical study	Langmuir	Mixed	97.2	[17]
Paracetamol 	Cu in Acid mixture	Electrochemical, Weight loss, Quantum chemical study, SEM	Langmuir	Mixed	96.3	[27]
	Low Carbon Steel in 1M H_2SO_4	SEM, Weight loss, Electrochemical, Quantum chemical study	Langmuir	Mixed	94	[28]
	Carbon Steel in 0.5M H_2SO_4	Electrochemical, Weight loss	Langmuir	Mixed	94	[29]
	Carbon Steel in 1M HCl	Electrochemical, Weight loss study	Langmuir	Mixed	86	[29]
Aspirin 	MS in 1M HCl	SEM, Electrochemical, Weight loss	Langmuir	Mixed	80	[30]
	MS in 1M H_2SO_4	Weight Loss Study, Computational Study, SEM	Langmuir	-	79.2	[31]
	Cu in 0.5M HCl	Electrochemical, Weight loss, Quantum chemical study	Langmuir	Mixed	67	[32]

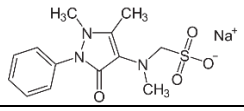
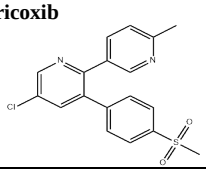
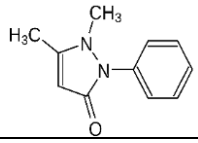
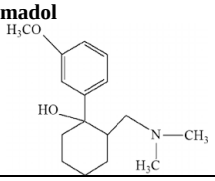
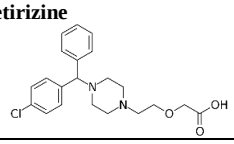
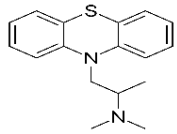
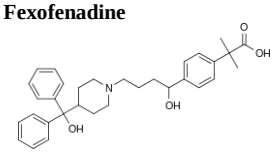
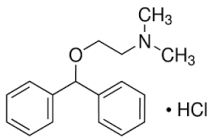
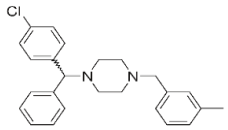
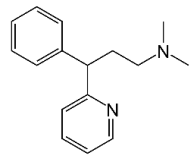
Anti-depressants Drugs						
Alprazola 	Al in 3M HCl	Electrochemical, Quantum Chemical study	Langmuir	Mixed	98.9	[33]
Venlafaxine 	MS in 0.5M HCl	Electrochemical, Weight loss, Quantum chemical study, Atomic Force Microscopy	Langmuir	Mixed	86.1	[34]
Benzodiazepine 	MS in 1M HCl	Electrochemical Study, Weight loss Study	Langmuir	Mixed	91	[35]
Lorezepam 	MS in 1M HCl	SEM, Electrochemical, Weight loss, Quantum chemical study	Langmuir	Mixed	90	[36]
Ketosulphone 	Zn in 0.1M HCl	Electrochemical study, SEM	Langmuir	Mixed	96	
Barbiturates 	MS in 1M H_3PO_4	Electrochemical Study, Weight loss Study, Quantum chemical study	Langmuir	Mixed	89.3	[37]

Antibiotics Drugs						
Cefotaximess  Cefotaxime	MS in 0.1M HCl	Electrochemical study, Weight Loss	Langmuir	Mixed	95.8	[38]
Amodiaquinine 	MS in 0.1M HCl	Electrochemical study, Weight Loss Study	Langmuir	Mixed	44.33	[39]
Ethambutol  Ethambutol	2205 Duplex Stainless Steel in 0.5M HCl	Weight Loss study, Electrochemical study	Langmuir	Mixed	98.3	[40]
	MS in 2M HCl	Quantum Chemical, Electrochemical, SEM, Weight Loss	Langmuir	Mixed	91.30	[41]
	MS in 0.5M HCl	Electrochemical study, Weight Loss study, MD simulations	Langmuir	Mixed	95	[42]
Ciprofloxacin  Ciprofloxacin	Carbon steel in 1M HCl	Electrochemical study, Hydrogen evolution, EFM, SEM, Weight loss	Langmuir	Mixed	91	[43]
Fluconazole 	Al in 0.1M HCl	Quantum Chemical Study, Weight loss	Langmuir	Mixed	82	[44]
Clotrimazole 	Al in 1M HCl	Quantum Chemical Study, Weight loss	Langmuir	-	90.9	[45]

Piperacillin 	MS in 1M HCl	Electrochemical Study, Weight loss	Langmuir	Mixed	93	[46]
Sreptomycin 	MS in 1M HCl	Electrochemical Study, Weight loss, Atomic Force Microscopy	EI Awady	Mixed	88.5	[47]
Doxocyclin 	MS in 1M HCl	Weight Loss study, Electrochemical Study, AFM	Langmuir	Mixed	95	[48]
Ceftazidime 	Mild steel in 1M HCl	Weight Loss study, Electrochemical Study, SEM, EDX, EFM Quantum Chemical Study	Langmuir	Mixed	94.2	[49]
Meropenum 	Cu in 1M HNO_3	Weight loss Study, Electrochemical Study, EFM, SEM, EDX, Quantum Chemical Study	Tempkin	Mixed	98.7	[50]
Isoniazid 	MS in 1M HCl	Weight loss, Electrochemical Study, Atomic Force Microscopy, XPS,	Langmuir	Mixed	96	[51]
Chloraphenicol 	A315MS in 0.1M HCl	Weight loss Study, LPR, OCP	Langmuir	Mixed	85.3	[52]

Chloroquine 	Al in 1M HCl	Quantum Chemical Study, Weight Loss	Freundlich	Mixed	74.99	[53]
Nitrofurantoin 	MS in 1M HCl	Electrochemical Study, Weight loss, SEM, EDX	Langmuir	Mixed	97.6	[54]
Paromomycin 	Zn in 1M HCl	Electrochemical Study, Weight loss	Tempkin	Mixed	91.96	[55]
Tinidazole 	MS in 3% HCl	Electrochemical Study, Quantum Chemical Study, Weight Loss	Langmuir	Mixed	62	[56]
Septazole 	Cu in 0.1M HCl	Electrochemical Study, Quantum Chemical Study, Weight Loss, EFM, SEM	Langmuir	Mixed	97	[57]
Ampicillin 	Al in 0.5 M HNO_3	Electrochemical Study, Quantum Chemical Study, Weight Loss, SEM	Langmuir	Mixed	85	[58]
Cloxacillin 	MS in 1N HCl	Electrochemical Study, Weight Loss, Hydrogen permeation measurement, Diffused reflectance Spectroscopy	Tempkin	Mixed	81	[59]
Dicloxacillin 	Al in 0.5M HNO_3	Electrochemical Study, Quantum Chemical Study, Weight Loss, Optical Microscopy, SEM	Langmuir	Mixed	58.9	[60]
Cefadroxyl 	Al in 1M HCl	Electrochemical Study, Quantum Chemical Study, Weight Loss, SEM	Adsorption	Mixed	93.22	[61]

Metronidazole 	MS in Aqueous	Weight Loss Study, Electrochemical Study, FTIR	Langmuir	Mixed	84	[62]
Ofloxacin 	MS in 1N HCl	Weight Loss Study	Langmuir	-	92.13	[63]
Norfloxacin 	MS in 1N HCl	Weight Loss Study	Langmuir	-	91.54	[63]
Ciprofloxacin 	304 Stainless Steel in 1.5% NaCl	Electrochemical Study	Adsorption	Anodic	93	[64]
Cephalothin 	API 5L X52 in 1M HCl	Weight Loss study, Electrochemical Study, SEM	Langmuir	Mixed	92	[65]
Gentamicin 	MS in 1M HCl	Electrochemical Study, Weight Loss, SEM	Langmuir	Mixed	89.3	[66]
Neomycin 	Carbon Steel in 0.1M H_2SO_4	Electrochemical Study, Weight Loss, AFM	Langmuir	Mixed	76.4	[67]
Moxifloxacin 	Carbon Steel in 1M HCl	Weight loss Study, Electrochemical Study, Hydrogen Evolution, SEM	Langmuir	Mixed	92	[68]
Albendazole 	MS in 0.1M HCl	Electrochemical Study, Weight Loss	Langmuir	Mixed	96	[69]
Benzimidazole 	MS in HCl	Weight Loss study, Electrochemical Study, SEM	Langmuir	Mixed	92	[70]
Analgesics Drug						
Voltaren 	Al in 1M HCl	Weight Loss study, Electrochemical Study	Langmuir	Mixed	89.7	[71]

Analgin 	MS in 1M HCl	Quantum Chemical Study, Electrochemical Study, Weight Loss	Langmuir	Mixed	96.1	[72]
Etoricoxib 	Carbon Steel in 0.5M H_3PO_4	Electrochemical Study, Weight Loss, SEM, EDX	Langmuir	Anodic	80.6	[73]
Phenazone 	Al in 3M HCl	Electrochemical Study, Gasometry, Quantum Chemical Study, SEM	Tempkin	Mixed	82	[74]
Tramadol 	Al in 1M HCl	Weight Loss study, Electrochemical Study, Quantum Chemical Study	Langmuir	Mixed	98	[75]
Anti-Histamine Drugs						
Cetirizine 	Cu in 0.5M H_2SO_4	Weight Loss study, Electrochemical Study, Quantum Chemical Study, XPS	Langmuir	Mixed	95	[76]
Promethazine 	Cu in 0.5M H_2SO_4	Electrochemical Study, Weight Loss, Quantum Chemical Study, SEM	Langmuir	Mixed	96.98	[77]
Fexofenadine 	MS in 1M HCl	Quantum Chemical Study, Electrochemical Study, Weight Loss	Langmuir	Mixed	97	[78]
Diphenahydraminehydrochloride 	MS in 1M HCl	Electrochemical Study, Weight Loss, SEM	Langmuir	Mixed	91.4	[79]
Meclizine 	Al in 1M HCl	Weight Loss study, Electrochemical Study, SEM	Langmuir	Mixed	95.4	[80]
Pheniramine 	MS in 1M HCl	Weight Loss study, Electrochemical Study, SEM	Langmuir	Mixed	98.1	[81]

GENERAL MECHANISM OF ACTION OF DRUG INHIBITOR

Corrosion inhibition mechanism of drug on metal in acid can be explained on the basis of thermodynamic, electrochemical and quantum chemical studies. Inhibitor molecules get adsorbed on metal surface by displacing water molecules already adsorbed on metal by displacement reaction.

$$Drug_{(sol)} + yH_2O_{(ads)} \longrightarrow Drug_{(ads)} + yH_2O_{(sol)}$$

Gravimetric measurements justify physical/chemical adsorption mechanism of inhibition. The drug molecules get protonated at active sites (N, O) having maximum charge density which in turn adsorb negative ions and generate charge in acidic media. Negative ions of acid gets adsorbed on charged metal surface to generate negative charge thereby causing electrostatic attraction between negatively charged metal and protonated inhibitor hence, physical adsorption.

$$[Drug] + H^+ \longrightarrow [DrugH]^+$$

$$M + X^- \longrightarrow [MX]^-$$

$$[DrugH]^+ + [MX]^- \longrightarrow \text{Electrostatic interaction}$$

Chemical adsorption occurs by transfer of electrons from drug molecule to metal to form coordinate bond. Electrochemical measurements suggest mixed/cathode/ anodic type behavior of inhibitor for materials in acids. Inhibitor prevents corrosion at anodic site by reducing evolution of hydrogen and at cathodic site by adsorbing directly on metal surface.

FUTURE PROSPECTIVE

In order to ensure the continuity of the shipping, the processing process, and manufacturing processes in the petroleum sector, the application of corrosion inhibitors is nowadays essential. The use of used drugs as corrosion inhibitors is an additional option to already-available pharmaceutical and additionally available natural compounds. The wide range of research results on drug-induced corrosion control shown above, supports the ability of these bio-inspired compounds to be superior corrosion inhibitors. But in order to materialize this choice as a scalable commercial solution, it is noteworthy to validate previous discoveries and fully explore the rich potential in the domain. As per the in-depth study of the corrosion inhibition procedure, molecules are needed to develop a strong foundation, and a thorough scale- up disquisition in the artificial environment is also prominently significant. However, the experimental gap continues to have potential for developing research utilizing discussed-about expired medications. Additionally, several types of medicines that are expired, such as medical and herbal products, have not been examined yet. There is currently little literature available on the research of expired medications as corrosion inhibitors in CO_2-saturated solution. Therefore, there are many interesting possibilities for study on this subject.

CONCLUSION

In this study, every type of medication used as a corrosion inhibitor was successful in reducing the rate at which metals corroded. The inhibition efficacy of drug molecules is affected by its molecular structure, affinity with metal surface, and chemical composition. Drugs with active components that preserve metallic surfaces from chemicals that are corrosive by having heteroatoms, lone pair electrons, conjugations, and moiety of aromatic rings. The drugs can only be utilized in acidic solutions due to their limited solubility in neutral/brine solutions. By comparing the experimental findings of various approaches, it is possible to determine the reliability and dependability of the inhibition measurement. The adsorption of a substantial fraction of the plant components on metallic surfaces followed the Langmuir adsorption isotherm; nevertheless, Temkin and Freundlich's adsorption was also reported in a number of observations. Weight loss measurements, as well as several electrochemical techniques such as potentiodynamic polarisation, electrochemical impedance spectroscopy, quantum chemical analysis, gravimetric analysis, and the surface analysis approach, are the most useful strategies in investigating corrosion inhibition.

CONFLICTS OF INTEREST

There are no conflicts to declare.

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