

## Review Article

# Green Inhibitors for Corrosion Protection of Metals and Alloys: An Overview

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Corrosion control of metals is of technical, economical, environmental, and aesthetical importance. The use of inhibitors is one of the best options of protecting metals and alloys against corrosion. The environmental toxicity of organic corrosion inhibitors has prompted the search for green corrosion inhibitors as they are biodegradable, do not contain heavy metals or other toxic compounds. As in addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable. Investigations of corrosion inhibiting abilities of tannins, alkaloids, organic amino acids, and organic dyes of plant origin are of interest. In recent years, sol-gel coatings doped with inhibitors show real promise. Although substantial research has been devoted to corrosion inhibition by plant extracts, reports on the detailed mechanisms of the adsorption process and identification of the active ingredient are still scarce. Development of computational modeling backed by wet experimental results would help to fill this void and help understand the mechanism of inhibitor action, their adsorption patterns, the inhibitor-metal surface interface and aid the development of designer inhibitors with an understanding of the time required for the release of self-healing inhibitors. The present paper consciously restricts itself mainly to plant materials as green corrosion inhibitors.

## 1. Introduction

Corrosion is the deterioration of metal by chemical attack or reaction with its environment. It is a constant and continuous problem, often difficult to eliminate completely. Prevention would be more practical and achievable than complete elimination. Corrosion processes develop fast after disruption of the protective barrier and are accompanied by a number of reactions that change the composition and properties of both the metal surface and the local environment, for example, formation of oxides, diffusion of metal cations into the coating matrix, local pH changes, and electrochemical potential. The study of corrosion of mild steel and iron is a matter of tremendous theoretical and practical concern and as such has received a considerable amount of interest. Acid solutions, widely used in industrial acid cleaning, acid descaling, acid pickling, and oil well acidizing, require the use of corrosion inhibitors in order to restrain their corrosion attack on metallic materials.

## 2. Corrosion Inhibitors

Over the years, considerable efforts have been deployed to find suitable corrosion inhibitors of organic origin in various corrosive media [1–4]. In acid media, nitrogen-base materials and their derivatives, sulphur-containing compounds, aldehydes, thioaldehydes, acetylenic compounds, and various alkaloids, for example, papaverine, strychnine, quinine, and nicotine are used as inhibitors. In neutral media, benzoate, nitrite, chromate, and phosphate act as good inhibitors. Inhibitors decrease or prevent the reaction of the metal with the media. They reduce the corrosion rate by

- (i) adsorption of ions/molecules onto metal surface,
- (ii) increasing or decreasing the anodic and/or cathodic reaction,
- (iii) decreasing the diffusion rate for reactants to the surface of the metal,

- (iv) decreasing the electrical resistance of the metal surface.
- (v) inhibitors that are often easy to apply and have *in situ* application advantage.

Several factors including cost and amount, easy availability and most important safety to environment and its species need to be considered when choosing an inhibitor.

**2.1. Organic Inhibitors.** Organic inhibitors generally have heteroatoms. O, N, and S are found to have higher basicity and electron density and thus act as corrosion inhibitor. O, N, and S are the active centers for the process of adsorption on the metal surface. The inhibition efficiency should follow the sequence  $O < N < S < P$ . The use of organic compounds containing oxygen, sulphur, and especially nitrogen to reduce corrosion attack on steel has been studied in some detail. The existing data show that most organic inhibitors adsorbed on the metal surface by displacing water molecules on the surface and forming a compact barrier. Availability of nonbonded (lone pair) and p-electrons in inhibitor molecules facilitate electron transfer from the inhibitor to the metal. A coordinate covalent bond involving transfer of electrons from inhibitor to the metal surface may be formed. The strength of the chemisorption bond depends upon the electron density on the donor atom of the functional group and also the polarizability of the group. When an H atom attached to the C in the ring is replaced by a substituent group ( $-NH_2$ ,  $-NO_2$ ,  $-CHO$ , or  $-COOH$ ) it improves inhibition [4]. The electron density in the metal at the point of attachment changes resulting in the retardation of the cathodic or anodic reactions. Electrons are consumed at the cathode and are furnished at the anode. Thus, corrosion is retarded. Straight chain amines containing between three and fourteen carbons have been examined. Inhibition increases with carbon number in the chain to about 10 carbons, but, with higher members, little increase or decrease in the ability to inhibit corrosion occurs. This is attributed to the decreasing solubility in aqueous solution with increasing length of the hydrocarbon chain. However, the presence of a hydrophilic functional group in the molecule would increase the solubility of the inhibitors.

The performance of an organic inhibitor is related to the chemical structure and physicochemical properties of the compound like functional groups, electron density at the donor atom, p-orbital character, and the electronic structure of the molecule. The inhibition could be due to (i) Adsorption of the molecules or its ions on anodic and/or cathodic sites, (ii) increase in cathodic and/or anodic over voltage, and (iii) the formation of a protective barrier film. Some factors that contribute to the action of inhibitors are

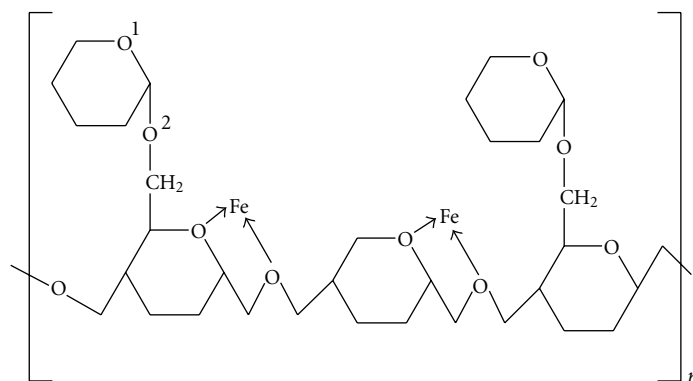
- (i) chain length,
- (ii) size of the molecule,
- (iii) bonding, aromatic/conjugate,
- (iv) strength of bonding to the substrate,
- (v) cross-linking ability,
- (vi) solubility in the environment.

The role of inhibitors is to form a barrier of one or several molecular layers against acid attack. This protective action is often associated with chemical and/or physical adsorption involving a variation in the charge of the adsorbed substance and transfer of charge from one phase to the other. Sulphur and/or nitrogen-containing heterocyclic compounds with various substituents are considered to be effective corrosion inhibitors. Thiophene, hydrazine derivatives offer special affinity to inhibit corrosion of metals in acid solutions. Inorganic substances such as phosphates, chromates, dichromates, silicates, borates, tungstates, molybdates, and arsenates have been found effective as inhibitors of metal corrosion. Pyrrole and derivatives are believed to exhibit good protection against corrosion in acidic media. These inhibitors have also found useful application in the formulation of primers and anticorrosive coatings, but a major disadvantage is their toxicity and as such their use has come under severe criticism. Among the alternative corrosion inhibitors, organic substances containing polar functions with nitrogen, sulphur, and/or oxygen in the conjugated system have been reported to exhibit good inhibiting properties. The inhibitive characteristics of such compounds derive from the adsorption ability of their molecules, with the polar group acting as the reaction center for the adsorption process. The resulting adsorbed film acts as a barrier that separates the metal from the corrosive, and efficiency of inhibition depends on the mechanical, structural, and chemical characteristics of the adsorption layers formed under particular conditions.

Inhibitors are often added in industrial processes to secure metal dissolution from acid solutions. Standard anti corrosion coatings developed till date passively prevent the interaction of corrosion species and the metal. The known hazardous effects of most synthetic organic inhibitors and the need to develop cheap, nontoxic and ecofriendly processes have now urged researchers to focus on the use of natural products. Increasingly, there is a need to develop sophisticated new generation coatings for improved performance, especially in view of Cr VI being banned and labeled as a carcinogen. The use of inhibitors is one of the best options of protecting metals against corrosion. Several inhibitors in use are either synthesized from cheap raw material or chosen from compounds having heteroatoms in their aromatic or long-chain carbon system. However, most of these inhibitors are toxic to the environment. This has prompted the search for green corrosion inhibitors.

### 3. Green Inhibitors

Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment. *Delonix regia* extracts inhibited the corrosion of aluminum in hydrochloric acid solutions [5], rosemary leaves were studied as corrosion inhibitor for the Al + 2.5Mg alloy in a 3% NaCl solution at 25°C [6], and El-Etre investigated natural honey as a corrosion inhibitor for copper [7] and investigated



SCHEME 1: Guar gum.

opuntia extract on aluminum [8]. The inhibitive effect of the extract of khillah (*Ammi visnaga*) seeds on the corrosion of SX 316 steel in HCl solution was determined using weight loss measurements as well as potentiostatic technique. The mechanism of action is attributed to the formation of insoluble complexes as a result of interaction between iron cations, and khellin [9] and Ebenso et al. showed the inhibition of corrosion with ethanolic extract of African bush pepper (*Piper guinensis*) on mild steel [10]; *Carica papaya* leaves extract [11]; neem leaves extract (*Azadirachta indica*) on mild steel in  $H_2SO_4$  [12]. Zucchi and Omar investigated plant extracts of *Papaia*, *Poinciana pulcherrima*, *Cassia occidentalis*, and *Datura stramonium* seeds and *Papaya*, *Calotropis procera B*, *Azadirachta indica*, and *Auforpio turkiale* sap for their corrosion inhibition potential and found that all extracts except those of *Auforpio turkiale* and *Azadirachta indica* reduced the corrosion of steel with an efficiency of 88%–96% in 1 N HCl and with a slightly lower efficiency in 2 N HCl. They attributed the effect to the products of the hydrolysis of the protein content of these plants [13]; Umoren et al. [14], studied the corrosion inhibition of mild steel in  $H_2SO_4$  in the presence of gum arabic (GA) (naturally occurring polymer) and polyethylene glycol (PEG) (synthetic polymer). It was found that PEG was more effective than gum arabic.

Yee [15] determined the inhibitive effects of organic compounds, namely, honey and *Rosmarinus officinalis* L on four different metals—aluminium, copper, iron, and zinc, each polarized in two different solutions, that is, sodium chloride and sodium sulphate. The experimental approach employed potentiodynamic polarization method. The best inhibitive effect was obtained when zinc was polarised in both honey-added sodium chloride and sodium sulphate solutions. Rosemary extracts showed some cathodic inhibition when the metal was polarized in sodium chloride solution. This organic compound, however, displayed less anodic inhibition when compared with honey. The main chemical components of rosemary include borneol, bornyl acetate, camphor, cineole, camphene, and alpha-pinene. Chalchat et al. [16], reported that oils of rosemary were found to be rich in 1,8-cineole, camphor, bornyl acetate, and high amount of hydrocarbons. Recently, work has

been emphasized on the use of *Rosmarinus officinalis* L as corrosion inhibitor for Al-Mg corrosion in chloride solution [6]. It is believed that the catechin fraction present in the rosemary extracts contributes to the inhibitive properties that act upon the alloy. Ouariachi et al. [17] also reported the inhibitory action of *Rosmarinus officinalis* oil as green corrosion inhibitors on C38 steel in 0.5 M  $H_2SO_4$ .

Odiogenyi et al. [18] reported that the ethanolic extract of *Vernonia amygdalina* appears to be a good inhibitor for the corrosion of mild steel in  $H_2SO_4$  and action is by classical Langmuir adsorption isotherm.

The effect of addition of halides (KCl, KBr, and KI) was also studied, and the results obtained indicated that the increase in efficiency was due to synergism [13]. Umoren et al. also investigated the corrosion properties of *Raphia hookeri* exudates gum—halide mixtures for aluminum corrosion in acidic medium [16]. *Raphia hookeri* exudates gum obeys Freundlich, Langmuir, and Temkin adsorption isotherms. Phenomenon of physical adsorption is proposed. Abdallah also tested the effect of guar gum on carbon steel. It is proposed that it acts as a mixed type inhibitor [14]. The mechanism of action of C-steel by guar gum is due to the adsorption at the electrode/solution interface. Guar gum is a polysaccharide compound containing repeated heterocyclic pyrane moiety as shown in Scheme 1. The presence of heterooxygen atom in the structure makes possible its adsorption by coordinate type linkage through the transfer of lone pairs of electron of oxygen atoms to the steel surface, giving a stable chelate five-membered ring with ferrous ions. The chelation between O1 and O2 with  $Fe^{++}$  seems to be impossible due to proximity factor presented as in Scheme 1:

The simultaneous adsorption of oxygen atoms forces the guar gum molecule to be horizontally oriented at the metal surface, which led to increasing the surface coverage and consequently protection efficiency even in the case of low inhibitor concentrations.

Okafor et al. looked into the extracts of onion (*Allium sativum*), *Carica papaya* extracts, *Garcinia kola*, and *Phyllanthus amarus* [19–22]. El-Etre, Abdallah M used Natural honey as corrosion inhibitor for metals and alloys. II C-steel in high saline water [23]. Jojoba oil has also been evaluated [24]. Artemisia oil has been investigated for it

is anticorrosion properties [25]. Oguzie and coworkers evaluated *Telfaria occidentalis*, *Occinum viridis*, *Azadirachta indica*, and *Sansevieria trifasciata* extracts [26–29]. Bendahou et al., studied using the extracts of rosemary in steel [27], and Sethuraman studied *Datura* [30]. Recently, studies on the use of some drugs as corrosion inhibitors have been reported by some researchers [31, 32]. Most of these drugs are heterocyclic compounds and were found to be environmentally friendly, hence, they have great potentials of competing with plant extracts. According to Eddy et al. drugs are environmentally friendly because they do not contain heavy metals or other toxic compound. In view of this adsorption and inhibitive efficiencies of ACPDQC (5-amino-1-cyclopropyl-7-[(3R, 5S) 3, 5-dimethylpiperazin-1-YL]-6,8-difluoro-4-oxo-quinoline-3-carboxylic acid), on mild steel corrosion have been studied and found to be effective.

Eddy et al. [33] studied inhibition of the corrosion of mild steel by ethanol extract of *Musa species* peel using hydrogen evolution and thermometric methods of monitoring corrosion. Inhibition efficiency of the extract was found to vary with concentration, temperature, period of immersion, pH, and electrode potentials. Adsorption of *Musa species* extract on mild steel surface was spontaneous and occurred according to Langmuir and Frumkin adsorption isotherms and also physical adsorption. Deepa Rani and Selvaraj [34] report the inhibition efficacy of *Punica granatum* extract on the corrosion of Brass in 1 N HCl evaluated by mass loss measurements at various time and temperature. Langmuir and Frumkin adsorption isotherms appear to be the mechanism of adsorption based on the values of activation energy, free energy of adsorption. Few researchers have summarized the effect of plant extracts on corrosion [35–38].

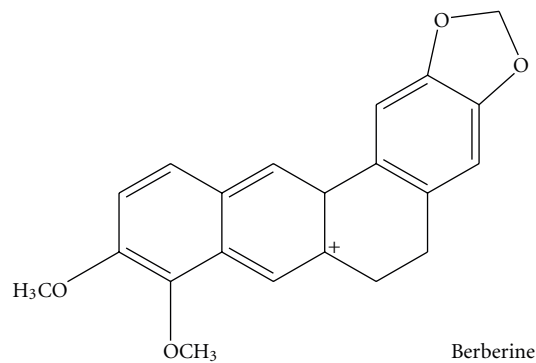
Efforts to find naturally organic substances or biodegradable organic materials to be used as corrosion inhibitors over the years have been intensified. Several reports are available on the various natural products used as green inhibitors as shown in Tables 1 and 2. Low-grade gram flour, natural honey, onion, potato, gelatin, plant roots, leaves, seeds, and flowers gums have been reported as good inhibitors. However, most of them have been tested on steel and nickel sheets. Although some studies have been performed on aluminum sheets, the corrosion effect is seen in very mild acidic or basic solutions (millimolar solutions).

### 3.1. Mechanism of Action of Green Inhibitors

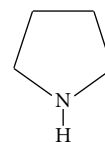
Many theories to substantiate the mode of action of these green inhibitors have been put forth by several workers. Mann has suggested that organic substances, which form onium ions in acidic solutions, are adsorbed on the cathodic sites of the metal surface and interfere with the cathodic reaction.

Various mechanisms of action have been postulated for the corrosion inhibition property of the natural products.

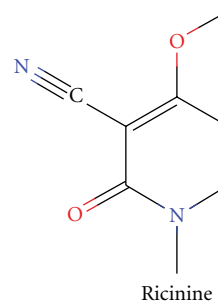
*Argemone mexicana*. It is a contaminant of mustard seeds contain an alkaloid berberine which has a long-chain of aromatic rings, an N atom in the ring, and, at several places



SCHEME 2: Berberine.



SCHEME 3: Pyrrolidine.



SCHEME 4: Ricinine.

H atoms attached to C are replaced by groups, –CH, –OCH<sub>3</sub>, and –O. The free electrons on the O and N atoms form bonds with the electrons on the metal surface. Berberine in water ionizes to release a proton, thus the now negatively charged O atom helps to free an electron on the N atom and forms a stronger bond with the metallic electrons. These properties confer good inhibition properties to *Argemone mexicana* (Scheme 2).

*Garlic*. It contains allyl propyl disulphide. Probably, this S-containing unsaturated compounds affects the potential cathodic process of steel.

*Carrot*. It contains pyrrolidine in aqueous media, pyrrolidine ionizes, and the N atom acquires a negative charge, and the free electrons on N possess still higher charge, resulting in stronger bond formation at N. Carrot does not ionize in acidic media and thus does not protect in acids (Scheme 3).

*Castor Seed*. They contain the alkaloid ricinine. The N atom is in the ring attachment of the –OCH<sub>3</sub> (Scheme 4).

TABLE 1: Green inhibitors used for corrosion inhibition of steel.

Sl. no.	Metal	Inhibitor source	Active ingredient	References
(1)	Steel	Tamarind		[39]
(2)	Steel	Tea leaves		[40]
(3)	Steel	Pomegranate juice and peels		[41]
(4)	Steel	<i>Emblica officinalis</i>		[42]
(5)	Steel	<i>Terminalia bellerica</i>		[43]
(6)	Steel	Eucalyptus oil	Monomtrene 1,8-cineole	[44]
(7)		Rosemary		[45]
(8)	C-steel, Ni, Zn	Lawsonia extract (Henna)	Lawson (2-hydroxy-1, 4-napthoquinone resin and tannin, coumarine, Gallic, acid, and sterols)	[46]
(9)	Mild steel	Gum exudate	Hexuronic acid, neutral sugar residues, volatile monoterpenes, canaric and related triterpene acids, reducing and nonreducing sugars	[47]
(10)	Mild steel	<i>Musa sapientum</i> peels (Banana peels)		[48]
(11)	Carbon steel	Natural amino acids—alanine, glycine, and leucine		[48]
(12)	Steel	Natural amino acids		[15]
(13)	Mild steel	<i>Garcinia kola</i> seed	Primary and secondary amines Unsaturated fatty acids and biflavnone	[49]
(14)	Steel	<i>Auforpio turkiale</i>	Protein hydrolysis	[50]
(15)	Steel	<i>Azydracta indica</i>	Protein hydrolysis	[51]
(16)	Steel	Aloe leaves		[52]
(17)	Steel	Mango/orange peels		[53]
(18)	Steel	<i>Hibiscus sabdariffa</i> (Calyx extract) in 1 M H <sub>2</sub> SO <sub>4</sub> and 2 M HCl solutions, Stock 10–50%	Molecular protonated organic species in the extract. Ascorbic acid, amino acids, flavonoids, Pigments and carotene	[54]

**Black Pepper.** Quraishi et al. [73] studied corrosion inhibition of mild steel in hydrochloric solution by black pepper extract (*Piper nigrum* family: *Piperaceae*) by mass loss measurements, potentiodynamic polarisation, and electrochemical impedance spectroscopy (EIS). Black pepper extract gave maximum inhibition efficiency (98%) at 120 ppm at 35°C for mild steel in hydrochloric acid medium. Electrochemical evaluation revealed it to be a mixed-type inhibitor and that charge transfer controls the corrosion process. The corrosion inhibition property was attributed to an alkaloid “Piperine”.

**3.1.1. Fennel Seeds.** Essential oil from *fennel* (*Foeniculum vulgare*) (FM) was tested as corrosion inhibitor of carbon steel in 1 M HCl using electrochemical impedance spectroscopy (EIS), Tafel polarisation methods, and weight loss measurements [74]. The increase of the charge-transfer resistance

( $R_{ct}$ ) with the oil concentration supports the molecules of oil adsorption on the metallic surface. The polarization plots reveal that the addition of natural oil shifts the cathodic and anodic branches towards lower currents, indicative of a mixed-type inhibitor. The analysis of FM oil, obtained by hydrodistillation, using Gas Chromatography (GC) and Gas Chromatography/Mass Spectrometry (GC/MS) showed that the major components were limonene (20.8%) and pinene (17.8%). Interestingly, the composition of FM oil was variable according to the area of harvest and the stage of development. The analysis allowed the identification of 21 components which accounted for 96.6% of the total weight. The main constituents were limonene (20.8%) and pinene (17.8%) followed by myrcene (15%) and fenchone (12.5%). The adsorption of these molecules could take place via interaction with the vacant d-orbitals of iron atoms

TABLE 2: Green Inhibitors used for corrosion inhibition of aluminum, aluminum alloys, and other metals and alloys.

Sl. no.	Metal	Inhibitor source	Active ingredient	References
(1)	Al	CeCl <sub>3</sub> and mercaptobenzothiazole (MBT)		[55]
(2)	Al, steel	Aqueous extract of tobacco plant and its parts	Nicotine	[56]
(3)	Al	Vanillin		[57]
(4)	Al-Mg alloy	Aqueous extract of <i>Rosmarinus officinalis</i> —Neutral phenol subfraction of the aqueous extract	Catechin	[58]
(5)	Al	Sulphates/molybdates and dichromates as passivators		[59]
(6)	Al	Amino and polyamino acids—aspartic acid		[6]
(7)	Al	Pyridine and its selected derivatives (symmetric collidine and 2,5-dibrompyridine)		[60]
(8)	Al	Citric acid		[61]
(9)	Fe, Al	Benzoic acid		[62]
(10)	Al	Rutin and quercetin		[63]
(11)	Al			US Patent 5951747
(12)	Al	Polybutadieonic acid		[64]
(13)	Al and Zn	Saccharides—mannose and fructose		[65]
(14)	Al, Al-6061 and Al-Cu	Neutral solutions using sulphates, molybdates, and dichromates		[66]
(15)	Al	<i>Vernonia amygdalina</i> (Bitter leaf)		[67]
(16)	Al	Prosopis—cineraria (khejari)		[60]
(17)	Al	Tannin beetroot		[68]
(18)	Al	Saponin		[69]
(19)	Al	Acacia concianna		[70]
(20)	Al and Zn	Saccharides		[71]
(21)	Al	Opuntia (modified stems cladodes)	Polysaccharide (mucilage and pectin)	[72]
(22)	Al-Mg alloy	<i>Rosmarinus officinalis</i>		[8]
(23)	Zn	Metal chelates of citric acid		[61]
(24)	Zn	Onion juice	S-containing acids (glutamyl peptides) S-(1-propenyl) L-cysteine sulfoxide, and S-2-carboxypropyl glutathione	[63]
(25)	Sn	Natural honey (acacia chestnut)		[64]
(26)	Sn	Black radish	120	[8]



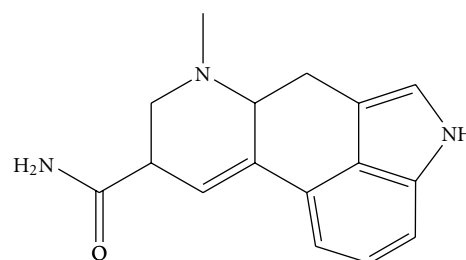
FIGURE 1: (a) Mangostana fruit. (b) Pericarp.

(chemisorption). It is logical to assume that such adsorption is mainly responsible for the good protective properties by a synergistic effect of various molecules [74–76].

**3.1.2. *Garcinia mangostana*.** Vinod Kumar et al. [77] studied the corrosion inhibition of acid extract of the pericarp of the fruit of *G. mangostana* on mild steel in hydrochloric acid medium. *G. mangostana*, colloquially known as “the mangosteen”, is a tropical evergreen tree. Mangosteen fruit, (Figure 1) on ripening the fruit, turns from green to purple in colour.

The extract of the pericarp of *G. mangostana* contains oxygenated prenylated xanthenes, 8-hydroxycudraxanthone G and mangostingone [7-methoxy-2-(3-methyl-2-butenyl)-8-(3-methyl-2-oxo-3-butenyl)-1,3,6-trihydroxyxanthone, along with other xanthenes such as cudraxanthone G, 8-deoxygartanin, garcimangosone B, garcinone D, garcinone E, gartanin, 1-isomangostin,  $\alpha$ -mangostin,  $\gamma$ -mangostin, mangostinone, smeathxanthone A, and tovophyllin A [77, 78]. Electrochemical parameters such as  $E_{corr}$ ,  $\beta_a$ , and  $\beta_c$  indicate the mixed mode of inhibition, but predominantly cathodic. IR analysis and impedance studies indicate that the adsorption on the metal surface is due to the heteroatoms present in the organic constituents of the extract of *G. mangostana*.

**3.1.3. *Ipomea involcrata*.** Obot et al. [79] studied the corrosion inhibition efficiency of *Ipomea involcrata* (IP) (family: Convolvulaceae) leaf extract on aluminium. It is a common ornamental vine with heart-shaped and bright white pink or purple flowers that has a long history of use in central to southern Mexico. The plant has been shown to contain mainly d-lysergic acid amide (LSA) (Figure 2) and small amounts of other alkaloids, namely, chanoclavine, elymoclavine, and ergometrine, and d-isolysergic acid amide [79]. D-lysergic acid amide (LSA) (Figure 2) contains N and O in their structure including  $\pi$ -electrons which are required for corrosion inhibiting effects. Probably, chanoclavine, elymoclavine, ergometrine, d-isolysergic acid amide, and



7-Methyl-4, 6.6a, 7, 8, 9-hexahydro-indolo[4, 3-fg]quinoline-9-carboxamide

FIGURE 2: Structure of lysergic acid.

other ingredients of the plant extracts synergistically increase the strength of the layer formed by the d-lysergic acid amide (LSA). Thus, the formation of a strong physisorbed layer between the metal surface and the phytoconstituents of the plant extract could be the cause of the inhibitive effect. The above authors have also reported that *Chromolaena odorata* as an excellent inhibitor for aluminium corrosion [80]. The environmentally friendly inhibitor could find possible applications in metal surface anodizing and surface coating in industries.

**3.1.4. *Soya Bean*.** It is rich in proteins, which are often good inhibitors in acidic media.

Most natural extracts constitute of oxygen- and nitrogen-containing compounds. Most of the oxygen-containing constituents of the extracts is a hydroxy aromatic compound, for example, tannins, pectins, flavonoids, steroids, and glycosides. Tannins are believed to form a passivating layer of tannates on the metallic surface. Similarly, it is postulated that a number of OH groups around the molecule lure them to form strong links with hydrogen and form complexes with metals. The complexes thus formed cause blockage of micro anodes and/or microanodes, which are generated on

the metal surfaces when in contact with electrolytes, and, hence, retard subsequent dissolution of the metal.

**3.1.5. Terminalia catappa.** The inhibitive and adsorption properties of ethanol extract of *Terminalia catappa* for the corrosion of mild steel in  $\text{H}_2\text{SO}_4$  were investigated using weight loss, hydrogen evolution, and infrared methods of monitoring corrosion. The inhibition potential of ethanol extract of *T. catappa* is attributed to the presence of saponin, tannin, phlobatin, anthraquinone, cardiac glycosides, flavanoid, terpene, and alkaloid in the extract. The adsorption of the inhibitor on mild steel surface is exothermic, spontaneous, and best described by Langmuir adsorption model [81] similar results were reported for *Gnetum Africana* [82].

**Caffeic Acid.** de Souza and Spinelli [83] studied the inhibitory action of caffeic acid as a green corrosion inhibitor for mild steel. The inhibitor effect of the naturally occurring biological molecule caffeic acid on the corrosion of mild steel in 0.1 M  $\text{H}_2\text{SO}_4$  was investigated by weight loss, potentiodynamic polarization, electrochemical impedance, and Raman spectroscopy. The different techniques confirmed the adsorption of caffeic acid onto the mild steel surface and consequently the inhibition of the corrosion process. Caffeic acid acts by decreasing the available cathodic reaction area and modifying the activation energy of the anodic reaction.

**3.1.6. Gossypium hirsutum.** The corrosion inhibition properties of *Gossypium hirsutum* L leave extracts (GLE) and seed extracts (GSE) in 2 M sodium hydroxide (NaOH) solutions were studied using chemical technique. *Gossypium* extracts inhibited the corrosion of aluminium in NaOH solution. The inhibition efficiency increased with increasing concentration of the extracts. The leave extract (GLE) was found to be more effective than the seed extract (GSE). The GLE gave 97% inhibition efficiency while the GSE gave 94% at the highest concentration [83].

It is found that ethanol extract of *M. sapientum* peels (banana) can be used as an inhibitor for mild steel corrosion. The inhibitor acts by being adsorbed on mild steel surface according to classical adsorption models of Langmuir and Frumkin adsorption isotherms. Adsorption characteristics of the inhibitor follow physical adsorption mechanism. It is found that temperature, pH, period of immersion, electrode potential, and concentration of the inhibitor basically control the inhibitive action of *M. sapientum* peels.

**3.1.7. Carmine and Fast Green Dyes.** The use of dyes such as azo compounds methyl yellow, methyl red, and methyl orange [84] as inhibitors for mild steel has been reported [85–87]. The inhibition action of carmine and fast green dyes on corrosion of mild steel in 0.5 M HCl was investigated using mass loss, polarization, and electrochemical impedance (EIS) methods. Fast green showed inhibition efficiency of 98% and carmine 92%. The inhibitors act as mixed type with predominant cathodic effect.

Corrosion inhibition of mild steel in acidic solution by the dye molecules can be explained on the basis of adsorption

on the metal surface, due to the donor-acceptor interaction between  $\pi$  electrons of donor atoms N, O and aromatic rings of inhibitors, and the vacant d-orbitals of iron surface atoms [88, 89]. The fast green molecules possess electroactive nitrogen, oxygen atoms, and aromatic rings, favouring the adsorption while the carmine molecules possess electroactive oxygen atoms and electron rich paraquinanoid aromatic rings. In addition, the large and flat structure of the molecules occupies a large area of the substrate and thereby forming a protective coating. The inhibitors were adsorbed on the mild steel surface according to the Temkin adsorption isotherm (Figure 3).

Torres et al. [90] studied the effects of aqueous extracts of spent coffee grounds on the corrosion of carbon steel in a 1 mol  $\text{L}^{-1}$  HCl. Two methods of extraction were studied: decoction and infusion. The inhibition efficiency of C-steel in 1 mol  $\text{L}^{-1}$  HCl increased as the extract concentration and temperature increased. The coffee extracts acted as a mixed-type inhibitor with predominant cathodic effectiveness. In this study, the adsorption process of components of spent coffee grounds extracts obeyed the Langmuir adsorption isotherm. The chlorogenic acids isolated do not appear to be the active ingredient.

**3.2. Biocorrosion and Prevention by Green Inhibitors.** Biocorrosion relates to the presence of micro organisms that adhere to different industrial surfaces and damage the metal. Bacterial cells encase themselves in a hydrated matrix of polysaccharides and protein and form a slimy layer known as biofilm. The biofilm is a gel consisting of approximately 95% water, microbial metabolic products like enzymes, extracellular polymeric substances, organic and inorganic acids, and also volatile compounds such as ammonia or hydrogen sulphide and inorganic detritus [90–92]. Extracellular polymeric substances play a crucial role in biofilm development. Inhibition of biofilm formation is the simplest way of biocorrosion prevention. Use of naturally produced compounds such as plant extracts could be used as effective biocides [34].

## 4. Sol-Gel Coatings

In recent years, the sol-gel coatings doped with inhibitors developed to replace chromate conversion coatings show real promise [93]. Results show that the corrosion resistance of the sol-gel coatings containing  $\text{CeCl}_3$  proves to be better than that of the pure and MBT-added sol-gel coatings by the electrochemical methods. However, unlike chromium, silane-based sol-gel coatings mainly act as physical barrier rather than form chemical bond with substrate. Inhibitors are necessary to release in the coating film to slow the corrosion process through self-healing effect [57, 89, 94–96]. Among the inhibitors, rare-earth elements are generally considered to be effective and nontoxic in sol-gel coatings. Additionally, some organic inhibitors, especially heterocyclic compounds, are effective as slowly released inhibitors in sol-gel coating [97, 98]. Andreeva et al. suggested self-healing anticorrosion coatings based on pH [99, 100]. The approach



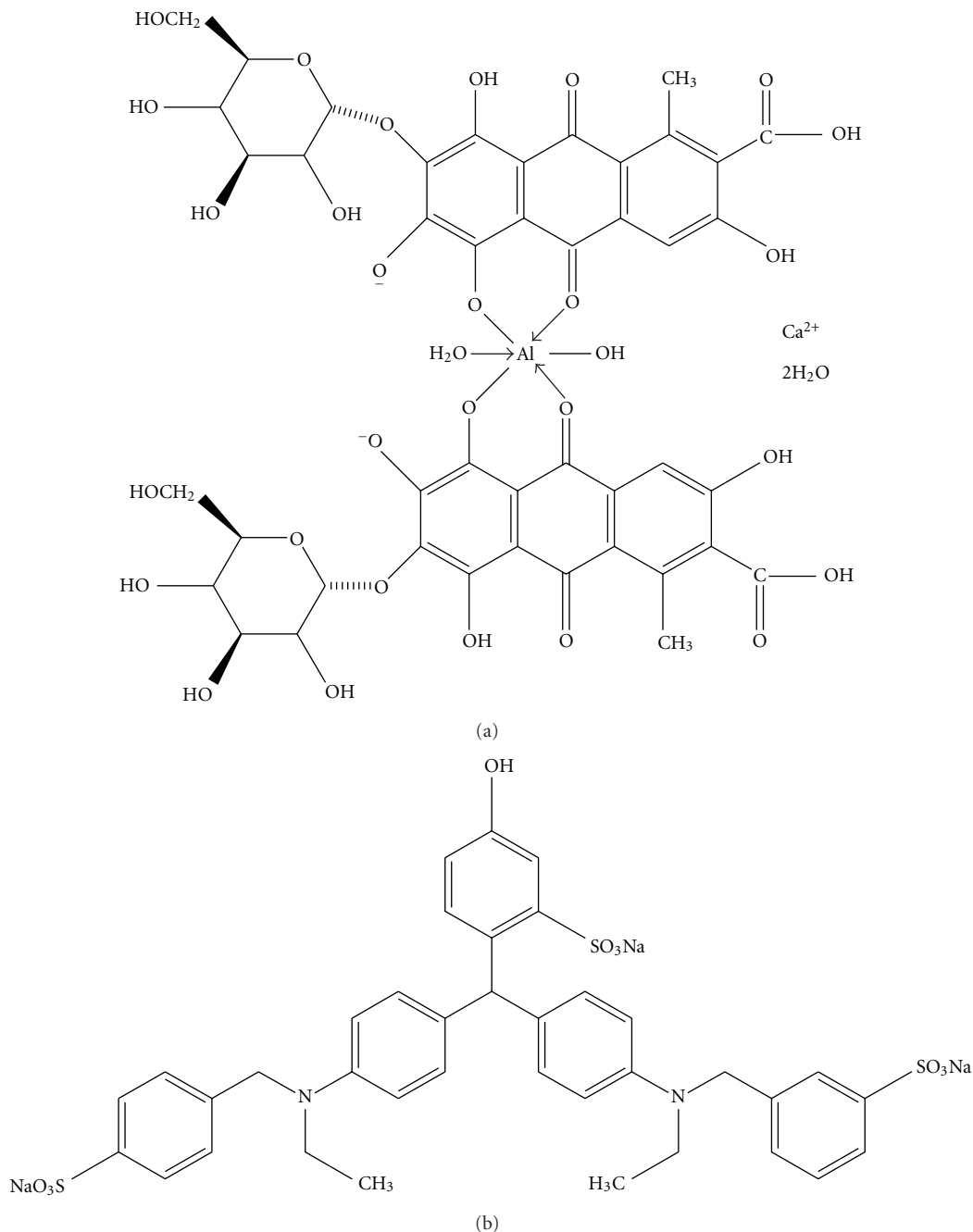


FIGURE 3: Structure of (a) carmine and (b) fast green.

to prevention of corrosion propagation on metal surfaces achieving the self-healing effect is based on suppression of accompanying physicochemical reactions. The corrosion processes are followed by changes of the pH value in the corrosive area and metal degradation. Self-healing or self-curing of the areas damaged by corrosion can be performed by three mechanisms: pH neutralization, passivation of the damaged metal surface by inhibitors entrapped between polyelectrolyte layers, and repair of the coating. The corrosion inhibitor incorporated as a component of the layer-by-layer film into the protective coating is responsible for

the most effective mechanism of corrosion suppression. Quinolines are environmentally friendly corrosion inhibitors that are attracting more and more attention as alternatives to the harmful chromates.

Recent awareness of the corrosion inhibiting abilities of tannins, alkaloids, organic and amino acids, as well as organic dyes has resulted in sustained interest on the corrosion inhibiting properties of natural products of plant origin. Such investigation is of much importance because in addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available,

and renewable sources of materials. Although a number of insightful papers have been devoted to corrosion inhibition by plant extracts, reports on the detailed mechanisms of the adsorption process are still scarce. The drawback of most reports on plant extracts as corrosion inhibitors is that the active ingredient has not been identified.

In recent years, sol-gel coatings doped with green inhibitors show real promise for corrosion protection of a variety of metals and alloys.

## 5. Computational Modeling for Corrosion

Simulation is a prognostic computational tool for complex scientific and engineering problems. The simplest simulation methods have been used for decades, but, with the increase in computational memory and speed simulation, have become the prevalent tool for analysis [101–103]. Simulation turns probability models into statistics problems where the results can be analyzed using standard statistical methods. The challenge of a simulation is to implement a procedure that efficiently captures the desired model characteristics. Often the goal of probability computations is the evaluation of high reliability. In fact, computation of high reliabilities itself is an ongoing research concern. Hence, there is no one way in which to do the computation. Monte Carlo simulation is the traditional and powerful method if computational complexity and time are not limiting. The Box-Muller method is also well known. A variety of techniques have been developed to reduce the number of simulations without compromising accuracy.

The study of corrosion involves the study of the chemical, physical, metallurgical, and mechanical properties of materials as it is a synergistic phenomenon in which the environment is as equally important as the materials involved. Computer modeling techniques can handle the study of complex systems such as corrosion and thus are appropriate and powerful tools to study the mechanism of action of corrosion and its inhibitors.

In the recent past, computer modeling techniques have been successfully applied to corrosion problems as summarized in review articles by Zamani et al. [104] and Munn [105]. The application of computer modeling techniques to corrosion systems requires an understanding of the physical phenomenon of corrosion and the mathematics which govern the corrosion process. In addition, knowledge of the numerical procedures which are the basis of computer modeling techniques is essential for accurate computational analyses. In addition, validation of the computer analysis results with experimental data is mandatory. Without a reasonably accurate description of the damage process at a scale that is pertinent to the desired application, probabilistic computations have minimal value for prognosis and life-cycle assessment.

For corrosion modeling, the materials characterization depends on the orientation of the material. Figure 4 is a composite of three optical micrographs of the perpendicular faces of a typical specimen of 7075-T6 aluminum alloy, where LT, LS, and TS are the rolling, long-transverse, and short-transverse planes, respectively. Visually, there is a difference

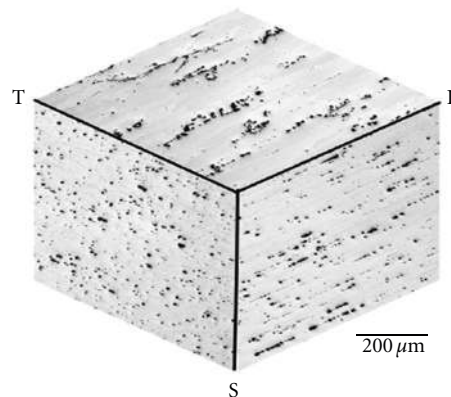


FIGURE 4: Three optical micrographs of the perpendicular faces of a typical specimen of 7075-T6 aluminum alloy.

in the three surfaces, and the variability in the location, size, and density of the particles is apparent. Thus, for example when modeling for aircraft wings, the LS surface is the most significant surface to characterize because it is the surface in fastener holes subjected to high-stress loading.

### 5.1. Some Examples of Computational Modeling in Corrosion Inhibition

**5.1.1. Tryptophan.** According to the description of frontier orbital theory, HOMO is often associated with the electron donating ability of an inhibitor molecule. High EHOMO values indicate that the molecule has a tendency to donate electrons to the metal with unoccupied molecule orbitals. ELUMO indicates the ability of the molecules to accept electrons. The lower value of ELUMO is the easier acceptance of electrons from metal surface. The gap between the LUMO and HOMO energy levels of the inhibitor molecules is another important index, and the low absolute values of the energy band gap ( $DE = ELUMO - EHOMO$ ) means good inhibition efficiency. Studies indicated that L-tryptophan has high value of EHOMO and low value of ELUMO with low-energy band gap. Adsorption energy calculated for the adsorption of L-tryptophan on Fe surface in the presence of water molecules equals  $-29.5 \text{ kJ mol}^{-1}$ , which implies that the interaction between L-tryptophan molecule and Fe surface is strong [105, 106]. Molecule dynamics simulation results showed that L-tryptophan molecules assumed a nearly flat orientation with respect to the Fe (1 1 0) surface. The calculated adsorption energy between a L-tryptophan molecule and Fe surface is  $-29.5 \text{ kJ mol}^{-1}$ .

The optimized molecule structure, the highest occupied molecule orbitals, the lowest unoccupied molecule orbital, and the charge distribution of L-tryptophan molecule using DFT functional (B3LYP/6-311\*G) are shown in Figure 5. The figure shows that in L-tryptophan molecule, C5, C12, C13, C14, C15, N7, N10, O2, and O4 carry more negative charges, while C8 and C6 carry more positive charges.

This means that C5, C12, C13, C14, C15, N7, N10, O2, and O4 are the negative charge centers, which can offer

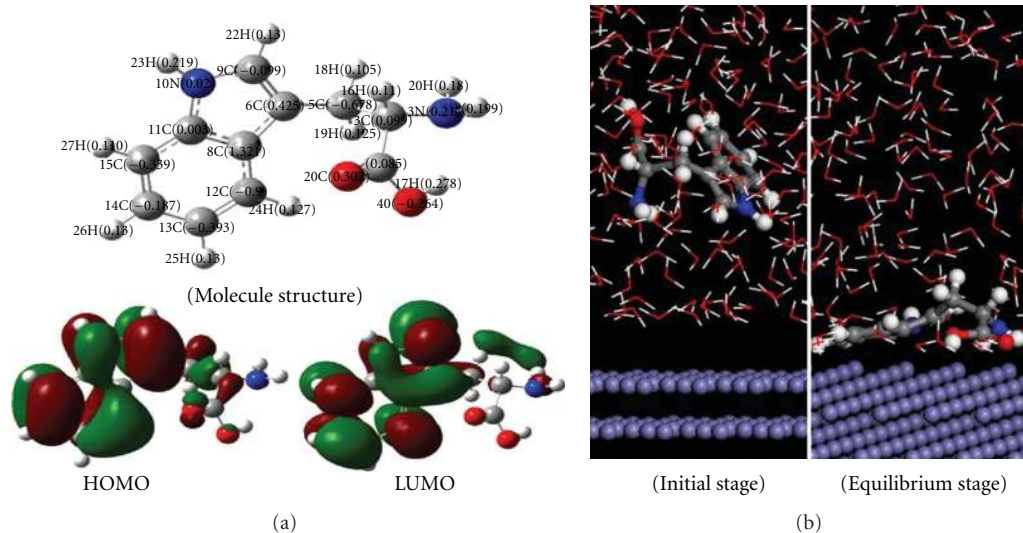


FIGURE 5: (a) Optimised molecule structure and charge density distribution of L-tryptophan. (b) L-tryptophan adsorbed on Fe surface in water solution.

electrons to the Fe atoms to form coordinate bond, and C8 and C6 are the positive charge centers, which can accept electrons from orbital of Fe atoms to form feedback bond. The optimized structure is in accordance with the fact that excellent corrosion inhibitors cannot only offer electrons to unoccupied orbital of the metal, but also accept free electrons from the metal. Therefore, it can be inferred that indole ring, nitrogen, and oxygen atoms are the possible active adsorption sites.

Presuel-Moreno et al. [107] modeled the chemical throwing power of an Al-Co-Ce metallic coating under thin electrolyte films representative of atmospheric conditions. An Al-Co-Ce alloy coating was developed for an AA2024-T3 substrate that can serve as barrier, sacrificial anode, and reservoir to supply soluble inhibitor ions to protect any defect sites or simulated scratches exposing the substrate. The model calculates the time necessary to accumulate Ce +3 and Co +2 inhibitors over the scratch when released from the Al-Co-Ce coating under different conditions such as the pH-dependent passive dissolution rate of an Al-Co-Ce alloy to define the inhibitor release flux. Transport by both electromigration and diffusion was considered. The effects of scratch size, initial pH, chloride concentration, and electrochemical kinetics of the material involved were studied. Studies indicated that sufficient accumulation of the released inhibitor (i.e., the Ce +3 concentration surpassed the critical inhibitor concentration over AA2024-T3 scratches) was achieved within a few hours (e.g., ~4 h for scratches of  $S = 1500 \mu\text{m}$ ) when the initial solution pH was 6 and the coating was adjacent to the AA2024-T3.

Pradip and Rai [108] modeled design of phosphonic-acid-based corrosion inhibitors using a force field approach.

**5.1.2. Piperidine and Derivatives.** Khaled and Amin [109] studied the adsorption and corrosion inhibition behaviour of four selected piperidine derivatives, namely, piperidine (pip),

2-methylpiperidine (2mp), 3-methylpiperidine (3mp), and 4-methylpiperidine (4mp) at nickel in 1.0 M  $\text{HNO}_3$  solution computationally by the molecular dynamics simulation and quantum chemical calculations and electrochemically by Tafel and impedance methods. The molecular dynamics (MD) simulations were performed using the commercial software MS Modeling from Accelrys using the amorphous cell module to create solvent piperidines cells on the nickel substrate. The behaviour of the inhibitors on the surface was studied using molecular dynamics simulations, and the condensed phase optimized molecular potentials for atomistic simulation studies (COMPASS) force field. COMPASS is an ab initio powerful force field which supports atomistic simulations of condensed phase materials [102]. Molecular simulation studies were applied to optimize the adsorption structures of piperidine derivatives. The nickel/inhibitor/solvent interfaces were simulated, and the charges on the inhibitor molecules as well as their structural parameters were calculated in the presence of solvent effects. Quantum chemical calculations based on the ab initio method were performed to determine the relationship between the molecular structure of piperidines and their inhibition efficiency. Results obtained from Tafel and impedance methods are in good agreement and confirm theoretical studies.

Khaled and Amin [110] also conducted studies on the molecular dynamics simulation on the corrosion inhibition of aluminum in molar hydrochloric acid using some imidazole derivatives. They also adapted Monte Carlo simulations technique incorporating molecular mechanics and dynamics to simulate the adsorption of methionine derivatives, namely, L-methionine, L-methionine sulphoxide, and L-methionine sulphone on iron (110) surface in 0.5 M sulphuric acid. Results show that methionine derivatives have a very good inhibitive effect for corrosion of mild steel in 0.5 M sulphuric acid solution.

5.1.3. *Aniline and Its Derivatives.* The inhibiting action of aniline and its derivatives on the corrosion of copper in hydrochloric acid has been investigated by Henriquez et al. [39], with emphasis on the role of substituents. With this purpose five different anilines were selected: aniline, p-chloroaniline, p-nitro aniline, p-methoxy, and p-methylaniline. A theoretical study using molecular mechanic and ab initio Hartree Fock methods, to model the adsorption of aniline on copper (100) showed results in good agreement with the experimental data. Aniline adsorbs parallel to the copper surface, showing no preference for a specific adsorption site. On the other hand, from ab initio Hartree Fock calculations, adsorption energy between 2 kcal/mol and 5 kcal/mol is obtained, which is close to the experimental value, confirming that the adsorption of aniline on the metal substrate is rather weak. In view of these results, the orientation of the aniline molecule with respect to the copper surface is considered to be the dominant effect. Mechanic molecular calculations were carried out using the Insight II, a comprehensive graphic molecular modeling program, to obtain configurations of minimum energy.

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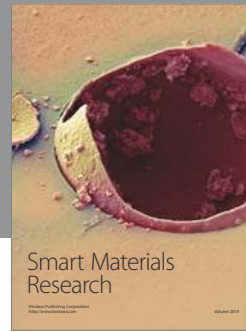
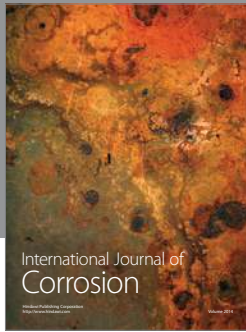
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