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Review Article

Corrosion Inhibition of Carbon Steel in HCl Solution by Some Plant Extracts

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The strict environmental legislations and increasing ecological awareness among scientists have led to the development of "green" alternatives to mitigate corrosion. In the present work, literature on green corrosion inhibitors has been reviewed, and the salient features of our work on green corrosion inhibitors have been highlighted. Among the studied leaves, extract *Andrographis paniculata* showed better inhibition performance (98%) than the other leaves extract. *Strychnos nuxvomica* showed better inhibition (98%) than the other seed extracts. *Moringa oleifera* is reflected as a good corrosion inhibitor of mild steel in 1 M HCl with 98% inhibition efficiency among the studied fruits extract. *Bacopa monnieri* showed its maximum inhibition performance to be 95% at 600 ppm among the investigated stem extracts. All the reported plant extracts were found to inhibit the corrosion of mild steel in acid media.

1. Introduction

Among the several methods of corrosion control and prevention, the use of corrosion inhibitors is very popular. Corrosion inhibitors are substances which when added in small concentrations to corrosive media decrease or prevent the reaction of the metal with the media. Inhibitors are added to many systems, namely, cooling systems, refinery units, chemicals, oil and gas production units, boiler, and so forth. Most of the effective inhibitors are used to contain heteroatom such as O, N, and S and multiple bonds in their molecules through which they are adsorbed on the metal surface. It has been observed that adsorption depends mainly on certain physicochemical properties of the inhibitor group, such as functional groups, electron density at the donor atom, π-orbital character, and the electronic structure of the molecule. Though many synthetic compounds showed good anticorrosive activity, most of them are highly toxic to both human beings and environment. The use of chemical inhibitors has been limited because of the environmental threat, recently, due to environmental regulations. These inhibitors may cause reversible (temporary) or irreversible (permanent) damage to organ system, namely, kidneys or liver, or disturbing a biochemical process or disturbing an enzyme system at some site in the body. The toxicity may be manifest either during the synthesis of the compound or during its applications. These known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products as corrosion inhibitors. Plant extracts have become important because they are environmentally acceptable, inexpensive, readily available and renewable sources of materials, and ecologically acceptable. Plant products are organic in nature, and some of the constituents including tannins, organic and amino acids, alkaloids, and pigments are known to exhibit inhibiting action. Moreover, they can be extracted by simple procedures with low cost. In the present work, the authors have reviewed literature on green corrosion inhibitors. Many authors such as E. E. Ebenso, B. Hammouti, A. Y. El Etre, P. C. Okafor, E. Oguzie, and P. B. Raja, have contributed significantly to the green mitigation by investigating several plants and their different body parts as corrosion inhibitors. The reviews of the literature along with salient features are summarised in Table 1.

In a previous work, the authors have investigated the extract of plants, namely, *Azadirachta indica* (leaves), *Punica*

Table 1: Plant extracts investigated as corrosion inhibitors by other authors.

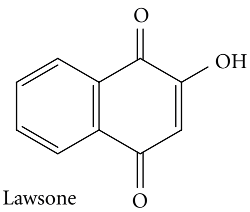
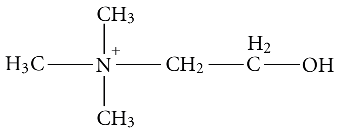
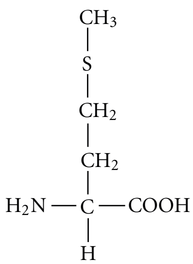
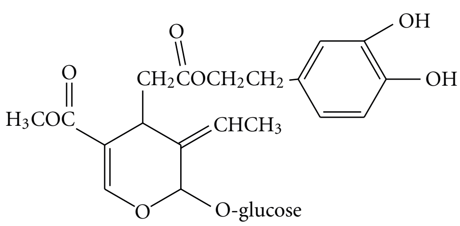
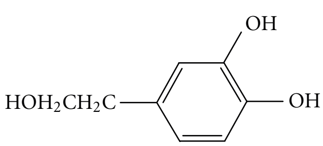
S. no.	Inhibitors used	Active constituents	Inhibition efficiency (%)	Remarks
(1)	*Lawsonia*	 Lawsone	95.0	The aqueous extract of the leaves of henna (lawsonia) as the corrosion inhibitor was reported in C steel, nickel and zinc in acidic, neutral and alkaline solutions, using the polarization technique [1]
(2)	*Fenugreek*	 Choline  Methionine	92.2	The temperature effects were investigated on mild steel corrosion in 2.0 M of HCl and H_2SO_4 in the absence and presence of aqueous extract of fenugreek leaves (AEFLs) with the help of gravimetric method [2]
(3)	*Olea europaea*	 Oleuropein  Hydroxytyrosol	93.0	The inhibitive action of the aqueous extract of olive leaves was reported towards the corrosion of C-steel in 2 M HCl solution using weight loss measurements, Tafel polarization, and cyclic voltammetry [3]
(4)	*Cotula cinerea, Retama retam,* and *Artemisia herba*	Anagyrine, cytisine	67.0	Plant extracts were investigated on the corrosion of X52 mild steel in aqueous 20% (2.3 M) sulphuric acid. Weight loss determinations and electrochemical measurements were also performed [4]

Table 1: Continued.

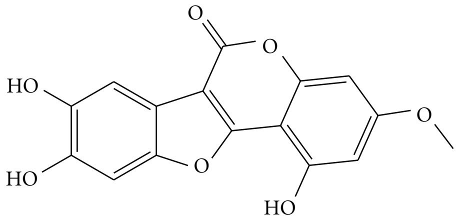
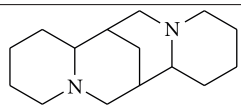
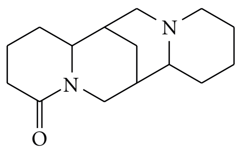
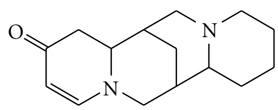
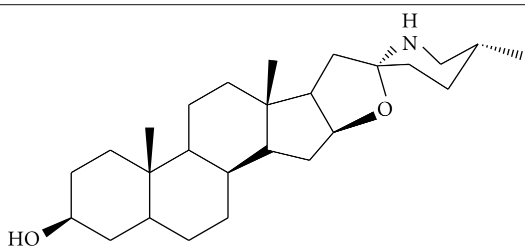
S. no.	Inhibitors used	Active constituents	Inhibition efficiency (%)	Remarks
(5)	*Eclipta alba*	 Wedelolactone	99.6	The inhibition effect of *Eclipta alba* in 1 N hydrochloric acid on corrosion of mild steel was investigated by weight loss, potentiodynamic polarization, and impedance methods, and the extracts of *Eclipta alba* were found to be effective corrosion pickling inhibitor [5]
(6)	*Rauvolfia serpentina*	Reserpine, ajmalicine, ajmaline, isoajmaline, ajmalinine, chandrine	94.0	*Rauvolfia serpentina* was tested as the corrosion inhibitor for mild steel in 1 M HCl and H_2SO_4 using weight loss method at three different temperatures, namely, 303, 313, and 323 K. Potentiodynamic polarization, electrochemical impedance spectroscopy, and scanning electron microscope (SEM) studies were also performed [4]
(7)	*Lupinus albus*	 Sparteine  Lupanine  Multiflorine	86.5	The behaviour of the inhibitive effect of lupine (*Lupinus albus* L.) extract on the corrosion of steel in aqueous solution of 1 M sulphuric, and 2 M hydrochloric acid was studied by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques [6]
(8)	*Solanum tuberosum*	 Solasodine	91.3	The acid extracts of *Solanum tuberosum* were studied as the corrosion inhibitor for mild steel in 1 M HCl and H_2SO_4 medium using different techniques. It was found to be a good corrosion inhibitor [7]
(9)	*Nauclea latifolia*	Monoterpene, triterpene indole alkaloid, saponins	76.0	The inhibitive action of ethanol extracts from leaves (LV), bark (BK), and roots (RT) of *Nauclea latifolia* on mild steel corrosion in H_2SO_4 solutions at 30° and 60°C was studied using weight loss and gasometric techniques [8]

Table 1: Continued.

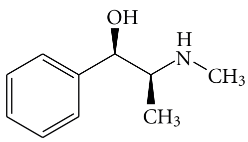
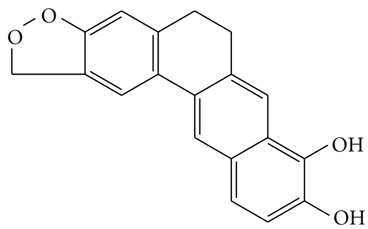
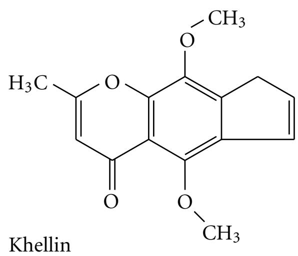
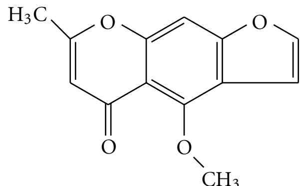
S. no.	Inhibitors used	Active constituents	Inhibition efficiency (%)	Remarks
(10)	*Sida rhombifolia*	 Ephedrine  Sida-rhombifolia alkaloid	97.4	The efficacy of an acid extracts of leaves of *Sida rhombifolia* L. as the corrosion inhibitor for mild steel in 1 M phosphoric acid medium using weight loss measurements, polarization, and electrochemical impedance spectral studies were investigated. It was found to be an effective corrosion inhibitor [9]
(11)	*Ammi visnaga*	 Khellin  Visnagin	99.3	The inhibitive effect of the extract of Khillah (*Ammi visnaga*) seeds, on the corrosion of SX 316 steel in HCl solution using weight loss measurements as well as potentiostatic technique, was assessed. Negative values were calculated for the energy of adsorption indicating the spontaneity of the adsorption process [10]
(12)	*Embilica uflicianalis, Terminalia chebula* and *Terminalia bellirica*	Emblicanin A&B, puniglucanin, pedunculagin, tannic acid, chebulinic acid, and gallic acid	80%	Extracts were used in 5% (w/v) commercial hydrochloric acid as corrosion inhibitors of mild steel exposed into 5% (w/v) hydrochloric acid at 328 K on mild steel. Both Tafel polarization and linear polarization resistance techniques were used. Remarkable decrease in corrosion current and increase in linear polarization resistance values were observed in the presence of the acid extracts [11]
(13)	*Carica papaya* and *Azadirachta indica*	Papain, carpaine, chymopapain, azadirachtin, salannin, gedunin, and azadirone	87%	Extracts were used as corrosion inhibitors for corrosion of mild steel. The percentage inhibition of efficiency was found to increase with the increase in concentration of both inhibitors [12]

Table 1: Continued.

S. no.	Inhibitors used	Active constituents	Inhibition efficiency (%)	Remarks
(14)	*Mentha pulegium*	Pulegone	80%	Natural oil extracted from pennyroyal mint (*Mentha pulegium*, PM) was evaluated as the corrosion inhibitor of steel in molar hydrochloric using weight loss measurements, electrochemical polarisation, and EIS methods. PM oil acted as an efficient cathodic inhibitor [13]
(15)	*Zanthoxylum alatum*	Terpineol, isoxazolidine, and imidazolinedione	85%	The inhibition effect of *Zanthoxylum alatum* plant extracts on the corrosion of mild steel in 5% and 15% aqueous hydrochloric acid solution was investigated by weight loss and electrochemical impedance spectroscopy (EIS) methods. The effect of temperature on the corrosion behaviour of mild steel in 5% and 15% HCl with the addition of plant extracts was studied in the temperature range 50–80°C. Surface analysis (SEM, XPS and FT-IR) was also carried out to establish the corrosion inhibitive property of this plant extract in HCl solution [14]
(16)	Thyme, Coriander, *Hibiscus,* Anis, Black Cumin and Garden Cress.	Thymol, malic acid, salicin, glutamic acid, leucine, and methionine	85%	Electrochemical impedance spectroscopy has been successfully used to evaluate the performance of these compounds. The ac measurements showed that the dissolution process is activation controlled. Potentiodynamic polarization curves indicate that the studied compounds are mixed-type inhibitors. Thyme, which contained the powerful antiseptic thymol as the active ingredient, offers excellent protection for steel surface [15]
(17)	*Phoenix dactylifera, Lawsonia inermis,* and *Zea mays*	Lawsone, esculetin, fraxetin, allantoin, sterols, and hordenine	90%	Extracts were used as corrosion inhibitors for steel, aluminum, copper, and brass in acid chloride and sodium hydroxide solutions using weight loss, solution analysis, and potential measurements. Only, *Phoenix dactylifera*, *Lawsonia inermis* extracts were found highly effective in reducing corrosion rate of steel in acid chloride solutions and aluminum in sodium hydroxide solutions [16]
(18)	*Datura metel*	Scopolamine, b-sitosterol, daturadiol, tropine, and daturilin	86%	Acid extract of the *D. metel* was studied for its corrosion inhibitive effect by electrochemical and weight loss methods. The results of AC impedance and polarisation studies correlate well with the weight loss studies [17]

Table 1: Continued.

S. no.	Inhibitors used	Active constituents	Inhibition efficiency (%)	Remarks
(19)	*Ricinus communis*	Ricinoleic or ricinic acid, ricinolein, and palmitin	84%	The corrosion behaviour of plant extract (*Ricinus communis*) was studied by means of electrochemical polarization, and impedance measurements. Results of study from polarization and electrochemical impedance measurements indicated that *Ricinus communis* might alleviate the corrosion process in mild steel [18]
(20)	*Mentha pulegium*	Pugelone, alpha-pinene, limonene, methone, and piperitone	80%	*Mentha* was used as the corrosion inhibitor of steel in molar hydrochloric using weight loss measurements, electrochemical polarisation and EIS methods. The increase in temperature leads to an increase in the inhibition efficiency of the natural substance [19]
(21)	*Carica papaya*	Chymopapain, pectin, carposide, carpaine, pseudocarpaine, dehydrocarpines, carotenoids, cryptoglavine, *cis*-violaxanthin, and antheraxanthin.	92%	Acid extracts of the different parts of *Carica papaya* were used as inhibitors in various corrosion tests. Gravimetric and gasometric techniques were used to characterize the mechanism of inhibition [20]
(22)	*Acacia seyal*	Catechu, dimethyltryptamine (DMT)	95%	The inhibitive effect of the gum exudate from *Acacia seyal* var. *seyal* was studied on the corrosion of mild steel in drinking water using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. The corrosion rates of steel and inhibition efficiencies of the gum exudates obtained from impedance and polarization measurements were in good agreement [21]
(23)	*Calotropis procera*	a-and b-Amyrins, cyanidin-3-rhamnoglucoside, cycloart-23-en-3b, 25-diol, cyclosadol	89%	Extract of the *C. procera* was studied for its corrosion inhibitive effect by weight loss, electrochemical, SEM, and UV methods. Using weight loss measurement data, mechanism of inhibitive action is probed by fitting in the adsorption isotherm [22]
(24)	*Centella asiatica*	Centellin, asiaticin, and centellicin	86%	*Centella asiatica* was studied as the corrosion inhibitor on mild steel in 1 N hydrochloric acid by weight loss method, gasometric method, potentiodynamic polarization method and AC impedance method [23]

Table 1: Continued.

S. no.	Inhibitors used	Active constituents	Inhibition efficiency (%)	Remarks
(25)	*Allium sativum, Juglans regia* and *Pogostemon cablin*	Allyl cysteine sulfoxide, methyl allyl thiosulfinate, allicin, diallyl disulfide, diallyl trisulfide, ajoene, pogostone, friedelin, epifriedelinol, pachypodol, retusine, and oleanolic acid	94%	Plant extracts on the corrosion of steel in aqueous solution of I N sulphuric acid were studied by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques [24]
(26)	*Combretum bracteosum*	Tannic acid	83%	Mature leaves of *Combretum bracteosum* were used for the corrosion inhibition of mild steel in H_2SO_4. Inhibition efficiency increases with the plant extracts concentration and decreases with temperature [25]
(27)	*Phyllanthus amarus*	Alkaloids, flavonoids, geraniin, hypophyllanthin, and phyllanthin		The inhibitive action of leaves (LV), seeds (SD), and a combination of leaves and seeds (LVSD) extracts of *Phyllanthus amarus* on mild steel corrosion in HCl and H_2SO_4 solutions was studied using weight loss and gasometric techniques. The results indicated that the extracts functioned as a good inhibitor in both environments and inhibition efficiency increased with extracts concentration. Temperature studies revealed an increase in inhibition efficiency with the rise in temperature, and activation energies decreased in the presence of the extract [26]
(28)	*Azadirachta indica*	azadirachtin, azadirone, gedunin, nimbin, nimbandiol, nimbinene, nimbolide, nimonol, nimbolin, salannin,margolone, melianol, vilasanin, and flavanoids	80%	The inhibitive action of leaves (LV), root (RT), and seeds (SD) extracts of *Azadirachta indica* on mildsteel corrosion in H_2SO_4solutions was studied using weight loss and gasometric techniques. The results obtained indicate that the extracts functioned as good inhibitors in H_2SO_4 solutions. Inhibition efficiency was found to increase with extracts concentration and temperature and followed the trend: SD > RT > LV. A mechanism of chemical adsorption of the phytochemical components of the plant extracts on the surface of the metal is proposed for the inhibition behaviour. The experimental data fitted into the Freundlich adsorption isotherm [27]

Table 1: Continued.

S. no.	Inhibitors used	Active constituents	Inhibition efficiency (%)	Remarks
(29)	*Musa sapientum* and banana peels	Gallocatechin and dopamine	71%	The inhibition of the corrosion of mild steel by ethanol extract of *Musa sapientum* peels in H_2SO_4 was studied using gasometric and thermometric methods. The results of the study reveal that the different concentrations of ethanol extract of *M. sapientum* peels inhibit mild steel corrosion [28]
(30)	*Murraya koenigii*		80%	The inhibitive action of extract of curry leaves (*Murraya koenigii*) on carbon steel in 1N HCl was studied using weight loss, gasometric studies electrochemical polarization, and AC impedance measurements [29]
(31)	*Medicago Sativa*	biotin, cytidine, inosine, guanine, guanosine, and riboflavin	90%	The inhibitive effect of water and alcoholic extracts of *Medicago Sativa* (*MS*) on the corrosion of steel in 2.0 M H_2SO_4 containing 10% EtOH has been studied using chemical (weight loss (ML), hydrogen evolution (HE)), electrochemical (potentiodynamic polarization (PDP) and impedance spectroscopy (EIS)) techniques [30].
(32)	*Oxandra asbeckii*	Liriodenine, azafluorenones alkaloids	86%	The inhibition effect of alkaloids extract from *Oxandra asbeckii* plant (OAPE) on the corrosion of C38 steel in 1 M hydrochloric acid solution was investigated by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The corrosion inhibition efficiency increases on increasing plant extracts concentration. Cathodic and anodic polarization curves showed that OAPE is a mixed-type inhibitor [31]
(33)	*Adhatoda vasica, Eclipta alba,* and *Centella asiatica*	Vasicine, vasicinone, asiaticoside, wedelolactone, β-sitosterol, and stigmasterol	99%	The inhibitive action of the extracts of *Adhatoda vasica, Eclipta alba,* and *Centella asiatica* on the corrosion of mild steel in 1N HCl was studied using weight loss method, electrochemical methods, and hydrogen permeation method. Polarization method indicated that the plant extracts are under mixed control, that is, promoting retardation of both anodic and cathodic reactions [32]

Table 1: Continued.

S. no.	Inhibitors used	Active constituents	Inhibition efficiency (%)	Remarks
(34)	*Ocimum sanctum, Aegle marmelos,* and *Solanum trilobatum*		99%	A comparative study of the inhibitory effect of plant extracts, *Ocimum sanctum*, *Aegle marmelos*, and *Solanum trilobatum*, on the Corrosion of mild steel in 1 N HCl medium was investigated using weight loss method, electrochemical methods, and hydrogen permeation method. Polarization method indicated that plant extracts behaved as mixed-type inhibitor [33]
(35)	*Anna squamosa*	Liriodenine and oxoanalobine	84%	Alkaloids extract from *Annona squamosa* plant has been studied as possible corrosion inhibitor for C38 steel in molar hydrochloric acid (1 M HCl). Potentiodynamic polarization and AC impedance methods have been used. The corrosion inhibition efficiency increases on increasing plant extract concentration [34]
(36)	*Heinsia crinita*			The paper provides information on the use of ethanol extract of *Heinsia crinita* as a corrosion inhibitor. Electrochemical studies such as polarisation and AC impedance spectra will throw more light on the mechanistic aspects of the corrosion inhibition [35]
(37)	*Dacryodis edulis*			The inhibition of low-carbon-steel corrosion in 1 M HCl and 0.5 M H_2SO_4 by extracts of *Dacryodis edulis* (DE) was investigated using gravimetric and electrochemical techniques. DE extract was found to inhibit the uniform and localized corrosion of carbon steel in the acidic media, affecting both the cathodic and anodic partial reactions [36]
(38)	*Emblica officinalis*		87%	Corrosion inhibition efficiency of acid extract of dry *Emblica officinalis* leaves for mild steel in 1 N HCl medium was investigated. Experimental methods include weight loss, potentiodynamic polarization, and impedance studies [37]
(39)	*Cyamopsis tetragonoloba*	3-epikatonic acid 7-o-beta-(2-rhamnosyl-glucosyl) myricetin, ash, astragalin, caffeic acid, and chlorogenic acid	92%	The role of seed extract of *Cyamopsis tetragonoloba* on corrosion mitigation of mild steel in 1 M HCl was investigated by weight loss method and potentiodynamic polarization technique. Experimental results were fitted into Langmuir and Temkin adsorption isotherm to study the process of inhibition [38]

granatum (shell), and *Momordica charantia* as corrosion inhibitors on mild steel in 3% NaCl solution by chemical and electrochemical methods. Maximum inhibition efficiency of 86%, 82%, and 79% was obtained at a concentration of 6 mL/L, 3 mL/L and 1.2 mL/L, respectively. *Azadirachta indica* showed 97% antiscaling properties [39].

Aqueous extracts of *Cordia latifolia* and *Curcumin* were investigated as corrosion inhibitors for mild steel in industrial cooling systems. The extracts showed maximum inhibition efficiency of 97.7% and 60%, respectively [40].

The inhibitive effect of the aqueous extract of Jasmin (*Jasminum auriculatum*) on corrosion of mild steel in 3% NaCl was investigated. It showed inhibition efficiency of 80%. It was found to be predominantly the anodic corrosion inhibitor [41].

The inhibitive effects of aqueous extracts of *Eucalyptus* (leaves), *Hibiscus* (flower), and *Agaricus* on the corrosion of mild steel for cooling-water systems, using tap water, have been investigated by means of weight loss (under static as well as dynamic conditions) and polarization methods. All the plant extracts were found to inhibit corrosion of mild steel following and their inhibitive efficiencies were in the order: *Agaricus* (85%), *Hibiscus* (79%), and *Eucalyptus* (74%) under the static test conditions. The inhibition efficiencies remain almost the same under the dynamic test conditions, which are nearer to field conditions. All the inhibitors (extracts) were found to follow Langmuir as well as Freundlich adsorption isotherms, that is, they inhibit corrosion through adsorption. Polarization measurements gave a similar order of inhibition efficiencies of plant extracts as that determined using the weight loss technique. *Agaricus* extract was found to be predominantly a cathodic inhibitor, while the extracts of *Eucalyptus* and *Hibiscus* were found to be mixed inhibitors [40].

Ascorbic acid in combination with DQ-2000 (aminotrimethyl phosphonic acid) and DQ-2010 (1-hydroxyethylidine 1,1-diphosphonic acid) was used to reduce the concentration of zinc in the blowdown of the cooling systems. All the inhibitors used were found to be effective. The maximum inhibition efficiency 99.2% was obtained with DQ-2010 100 ppm + Ascorbic acid 200 ppm concentration. Inhibitors follow Langmuir isotherm which showed that they inhibit corrosion through adsorption [42].

In present work, authors have used the extract of (Kalmegh) *Andrographis paniculata*, (Meethi Neem) *Murraya koenigii*, (Bael) *Aegle marmelos*, (Kuchla) *Strychnos nux-vomica*, (Karanj) *Pongamia pinnata*, (Jamun) *Syzygium cumini*, (Shahjan) *Moringa oleifera*, (Pipali) *Piper longum*, (Orange) *Citrus aurantium*, (Brahmi) *Bacopa monnieri*, (Pipal) *Ficus religiosa*, and (Arjun) *Terminalia arjuna* as corrosion inhibitors [43–48]. The active constituents and inhibition efficiencies of the extracts used are summarized in Table 2.

2. Experimental

Prior to all measurements, the mild steel specimens, having composition (in wt%) 0.076 C, 0.012 P, 0.026 Si, 0.192 Mn, 0.050 Cr, 0.135 Cu, 0.023 Al, 0.050 Ni, and the remainder iron, were polished successively with fine grade Emery papers from 600 to 1200 grades. The specimens were washed thoroughly with double-distilled water and finally degreased with acetone and dried at room temperature. The aggressive solution 1 M HCl was prepared by dilution of analytical grade HCl (37%) with double-distilled water, and all experiments were carried out in unstirred solutions.

AC impedance (EIS) measurements and potentiodynamic polarization studies were carried out using a GAMRY PCI 4/300 electrochemical work station based on ESA 400. Gamry applications include EIS 300 (for EIS measurements) and DC 105 software (for corrosion) and Echem Analyst (5.50 V) software for data fitting. All electrochemical experiments were performed in a Gamry three-electrodes electrochemical cell under the atmospheric conditions with a platinum counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode mild steel (7.5 cm long stem) with the exposed surface of 1.0 cm^2 was immersed into aggressive solutions with and without inhibitor, and then the open circuit potential was measured after 30 minutes. EIS measurements were performed at corrosion potentials, E_{corr}, over a frequency range of 100 kHz to 10 mHz with an AC signal amplitude perturbation of 10 mV peak to peak. Potentiodynamic polarization studies were performed with a scan rate of 1 mVs^{-1} in the potential range from 250 mV below the corrosion potential to 250 mV above the corrosion potential. All potentials were recorded with respect to the SCE.

3. Results and Discussion

3.1. Leaves Extract as Corrosion Inhibitors. The leaves extract of *Andrographis paniculata, Murraya koenigii*, and *Aegle marmelos* were investigated as corrosion inhibitors by weight loss and electrochemical methods in the present study. Among the studied leaves extract, *Andrographis paniculata* showed better inhibition performance than the other leaves extract. The result is summarized in Table 3 and Figure 1. The order of their inhibition efficiency has been found as follows:

$$\textit{Andrographis paniculata} > \textit{Murraya koenigii} > \textit{Aegle marmelos}. \quad (1)$$

The higher inhibitive performance of *Andrographis paniculata* is due to the presence of delocalized π-electrons. This extensive delocalized π-electrons favours its greater adsorption on the mild steel surface, thereby giving rise in very high inhibition efficiency (98.1%) at a concentration of 1200 ppm the relatively better performance of *Murraya koenigii* (96.7%) at 600 ppm than *Aegle marmelos* (96.2%) at 400 ppm. The most pronounced effect and the highest R_{ct} value (491.0 ohm cm^2) was obtained by inhibitor *Andrographis paniculata* at 1200 ppm concentration. The lowest R_{ct} value (264.8 ohm cm^2) was obtained by inhibitor *Aegle marmelos*. The high R_{ct} values are generally associated with a slower corroding system. These data revealed that R_{ct} values increased after the addition of inhibitors, and on the other hand, C_{dl} values decreased. This situation was a result of the adsorption of inhibitors at the metal/solution interface.

Table 2: Plant extracts used by us as corrosion inhibitors.

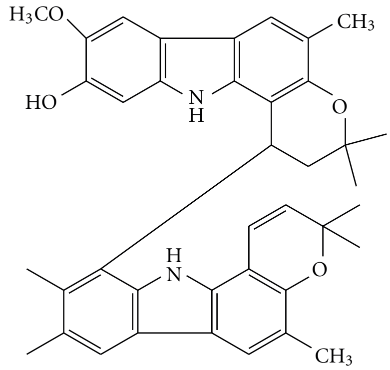
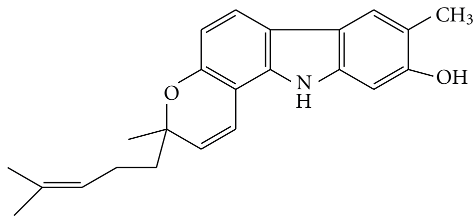
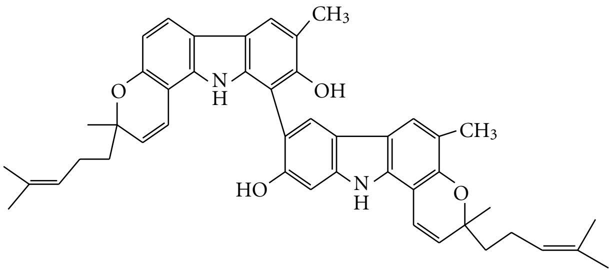
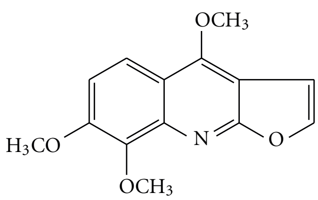
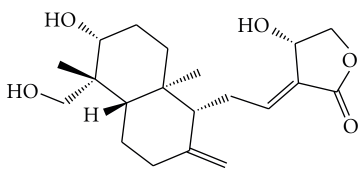
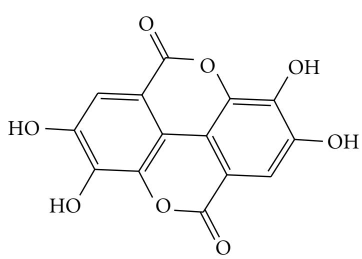
S. no.	Plant used	Active constituents	Common name	Inhibition efficiency (%)
(A)	*Murraya koenigii*			96.7
(1)			Murrafoline-I	
(2)			Pyrayafoline-D	
(3)			Mahabinine-A	
(B)	*Aegle marmelos*			96.2
(1)			Skimmianine	
(C)	*Andrographis paniculata*			98.1
(1)			Andrographolide	
(D)	*Syzygium cumini*			94.2
(1)			Ellagic acid	

Table 2: Continued.

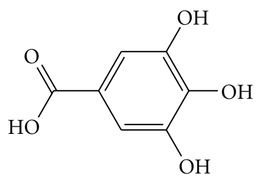
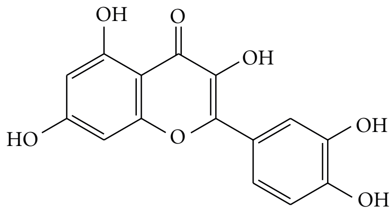
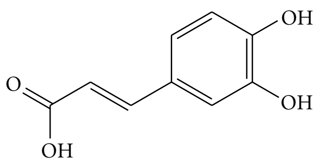
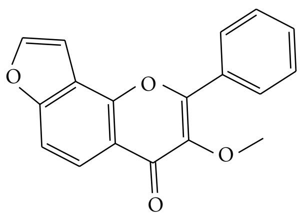
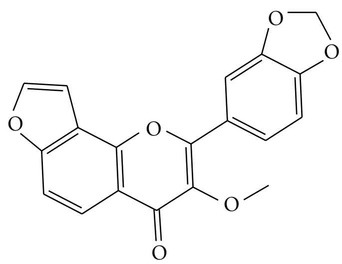
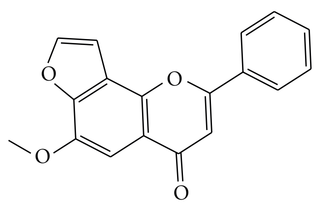
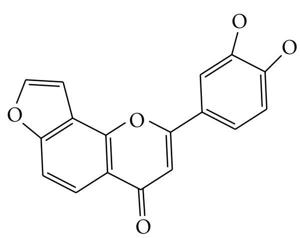
S. no.	Plant used	Active constituents	Common name	Inhibition efficiency (%)
(2)			Gallic acid	
(3)			Quercetin	
(4)			Cafeic acid	
(E)	*Pongamia pinnata*			97.6
(1)			Karanjin	
(2)			Pongapine	
(3)			Kanjone	
(4)			Pongaglabrone	

Table 2: Continued.

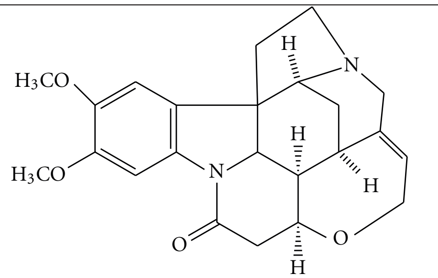
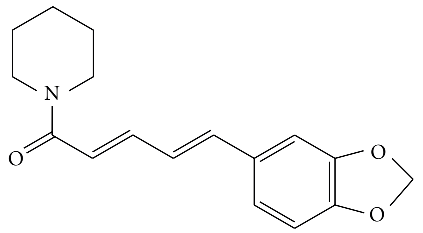
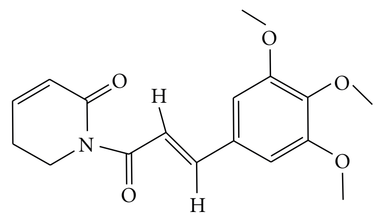
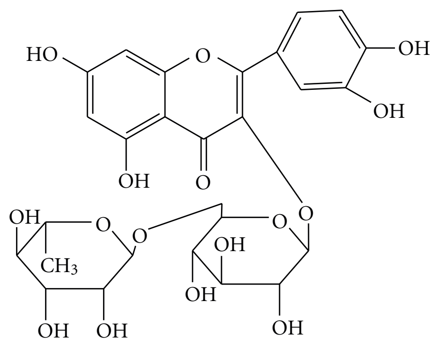
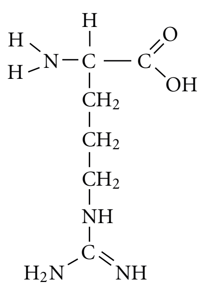
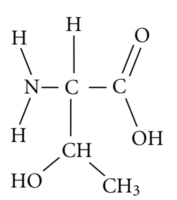
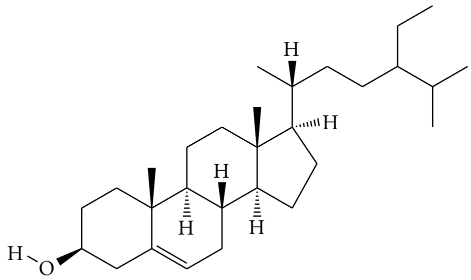
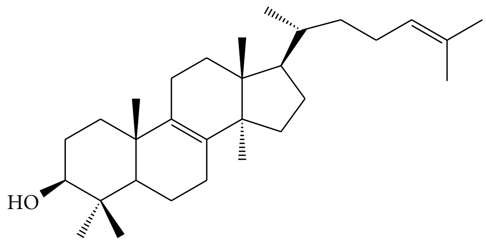
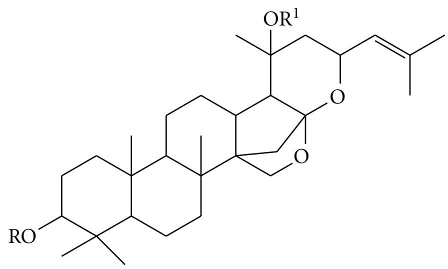
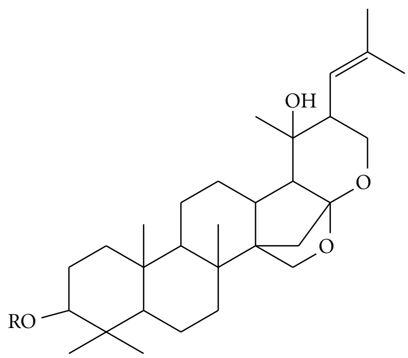
S. no.	Plant used	Active constituents	Common name	Inhibition efficiency (%)
(F)	*Strychnos nuxvomica*		Brucine	98.2
(G)	*Piper longum*			97.6
(1)			Piperine	
(2)			Piplartine	
(3)			Rutin	
(H)	*Moringa oleifera*			98.6
(1)			Arginine	
(I)	*Citrus Aurantium*			89.6
(1)			Threonine	

Table 2: Continued.

S. no.	Plant used	Active constituents	Common name	Inhibition efficiency (%)
(J)	*Terminalia arjuna*			88.9
(1)			b-Sitosterol	
(K)	*Ficus religiosa*			88.8
(1)			Lanosterol	
(L)	*Bacopa monnieri*			95.2
(1)			Bacoside A	
(2)			Bacoside B	

A decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer can cause this decrease in C_{dl} values, suggesting that the water molecules (having high dielectric constant) are replaced with inhibitor molecules (having low dielectric constant). It is worth noting that the percentage inhibition efficiencies obtained from impedance measurements were reasonably in a good agreement with those obtained from weight loss measurements.

3.2. Seed Extracts as Corrosion Inhibitors. We have used seed extracts of *Strychnos nuxvomica, Pongamia pinnata,* and *Syzygium cumini* in our present study. The result is concluded in Table 4 and Figure 2. The order of their inhibition efficiency has been found as follows:

$$\textit{Strychnos nuxvomica} > \textit{Pongamia pinnata} > \textit{Syzygium cumini}. \quad (2)$$

The best performance of *Strychnos nuxvomica* as the corrosion inhibitor can be attributed to the presence of three methoxy groups attached to the benzene nucleus. These extensive groups favor its greater adsorption on the mild steel surface, thereby giving rise to very high inhibition efficiency (98.2%) at a concentration as low as 350 ppm. The next

Table 3: Electrochemical impedance and Tafel data at 308 K.

Name of inhibitor	Inhibitor concentration	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	E (%)	-E_{corr} (mV versus SCE)	i_{corr} (mA/cm^2)	E (%)
1 M HCl	—	8.5	68.9	—	446	1540.0	—
Murraya koenigii	240.0	180.3	59.0	95.3	480	71.0	95.5
	300.0	256.2	58.2	96.6	469	48.0	96.9
	600.0	344.3	50.5	97.5	472	47.0	97.0
Aegle marmelos	200.0	101.9	59.2	91.7	457	159.0	89.3
	300.0	151.1	44.1	94.4	466	100.0	93.5
	400.0	264.8	30.7	96.7	499	60.0	96.0
Andrographis paniculata	300.0	99.0	56.9	91.4	489	82.0	94.6
	600.0	108.0	52.4	92.1	462	59.0	96.1
	1200.0	491.0	40.4	98.2	486	30.6	98.0

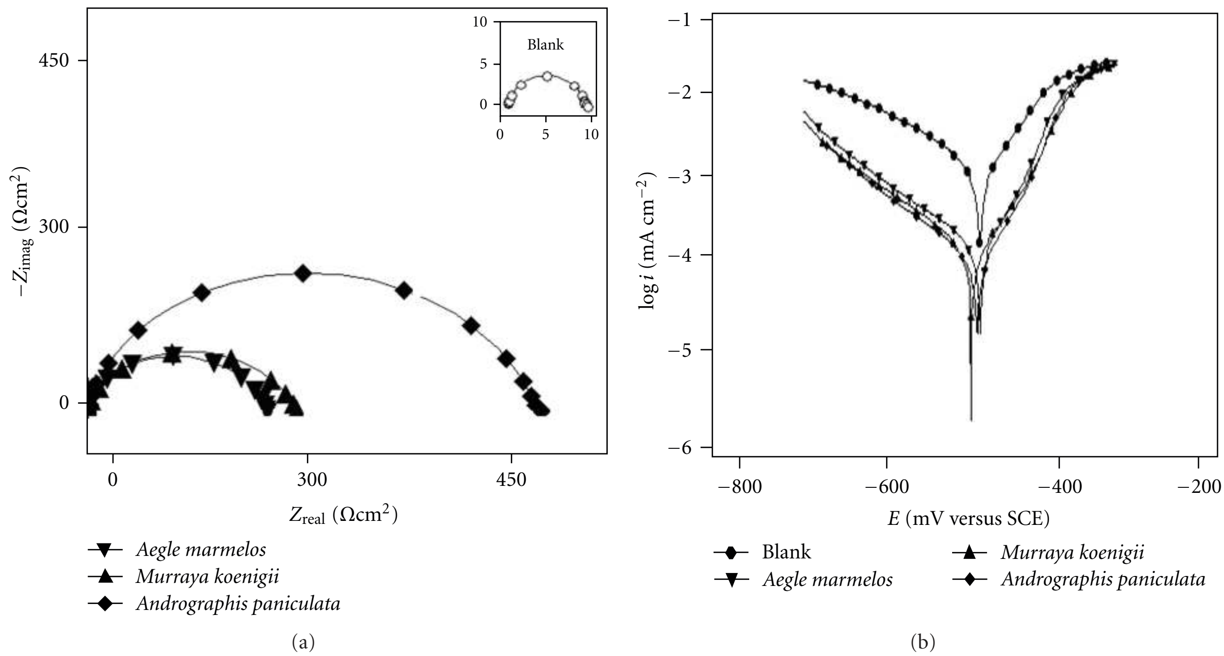


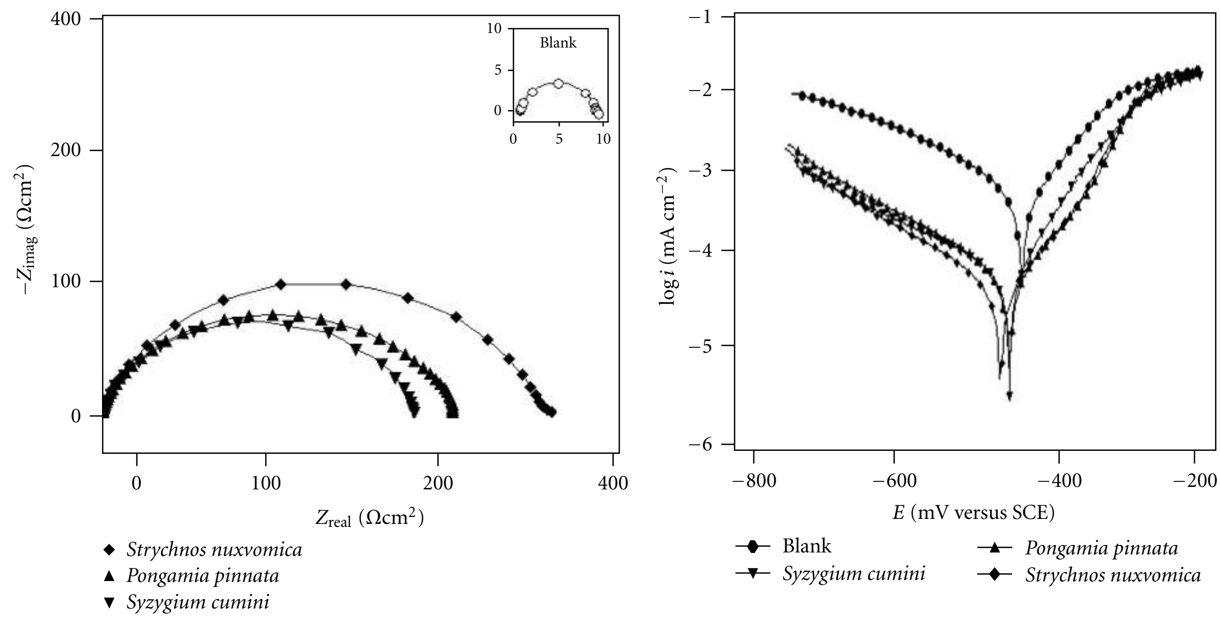
Figure 1: Nyquist plots and Tafel plots for mild steel in 1 M HCl in the absence and presence of different inhibitors at their optimum concentration.

best performance of *Pongamia pinnata* (97.6%) has been found at 400 ppm concentration. It was found that R_{ct} values increased to a maximum of 264 (Ω cm^2) at an optimum concentration of *Strychnos nuxvomica*. This situation was a result of the adsorption of inhibitors at the metal/solution interface. In the present study, maximum displacement was 48 mV, suggesting that tested seeds extract belonged to the mixed-type inhibitors.

3.3. Fruits Extracts as Corrosion Inhibitors. We have used fruits extract of *Moringa oleifera, Piper longum* and *Citrus aurantium* in our present study. The result is depicted in Table 5 and Figure 3. The inhibition efficiency of fruits extract follows the order

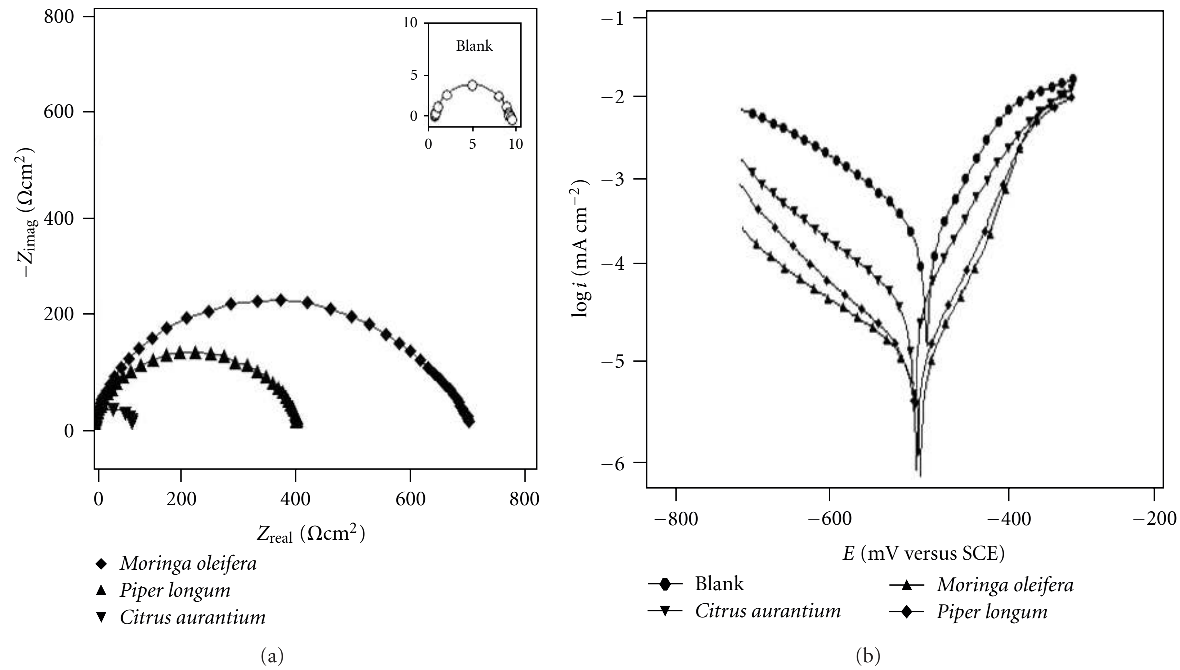
$$Moringa\ oleifera > Piper\ longum > Citrus\ aurantium \quad (3)$$

Good performance of fruits extract as corrosion inhibitors for mild steel in 1 M HCl solutions may be due to the presence of heteroatoms, π-electrons, and aromatic rings in their structures. The highest inhibition efficiency shown by *Moringa oleifera* is 98.2% at 300 ppm due to the presence of imine (C=N) group, four N atoms, and long alkyl chain and least efficiency of *Citrus aurantium* is 88.1% at 1200 ppm attributed to the presence of electron withdrawing COOH group. The R_{ct} values were found to increase, and on the other hand, C_{dl} values decreased in the presence of all fruits extract. This is due to the adsorption of these compounds at the metal/solution interface. The values of I_{corr} were found to decrease in the presence of inhibitors. The decrease in I_{corr} values can be due to the adsorption of fruits extract on the mild steel surface. It was observed that there is a small shift towards the cathodic region in the values of E_{corr}. In



(a) (b)

Figure 2: Nyquist plots and Tafel plots for mild steel in 1 M HCl in the absence and presence of different inhibitors at their optimum concentrations.



(a) (b)

Figure 3: Nyquist plots and Tafel plots for mild steel in 1 M HCl in the absence and presence of different inhibitors at their optimum concentrations.

the present study, maximum displacement in E_{corr} value was 69 mV, which indicates that all studied fruits extract were mixed-type inhibitors.

3.4. Stem Extracts as Corrosion Inhibitors. Stem extracts of *Bacopa monnieri, Ficus religiosa,* and *Terminalia arjuna* were used as corrosion inhibitors. *Bacopa monnieri* showed its maximum inhibition performance 95.2% at 600 ppm, while *Ficus religiosa* shows 88.7% at 1200 ppm. The better performance of *Bacopa monnieri* can be attributed to the presence of more O atoms in its structure. *Terminalia arjuna* has been found to give its maximum inhibition efficiency 83.4% at 1200 ppm. The R_{ct} values were found to increase and on the other hand, C_{dl} values decreased in the presence

Table 4: Electrochemical impedance, Tafel, and linear polarization resistance data at 308 K.

Name of inhibitor	Inhibitor concentration	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	E (%)	-E_{corr} (mV versus SCE)	i_{corr} (mA/cm^2)	E (%)
1 M HCl	—	8.5	68.9	—	446	1540.0	—
Syzygium cumini	240.0	97.1	67.6	91.2	443	165.0	89.2
	300.0	117.5	56.1	92.7	462	98.0	93.5
	600.0	238.5	53.7	96.4	469	60.0	96.0
Pongamia pinnata	300.0	129.5	39.6	92.9	461	84.0	94.0
	350.0	150.6	38.7	93.5	482	77.0	95.0
	400.0	239.8	35.7	96.5	471	49.0	97.0
Strychnos nuxvomica	250.0	130.3	52.0	93.5	461	132.0	91.4
	300.0	159.9	47.1	94.7	463	97.0	93.7
	350.0	263.9	43.3	96.7	494	27.5	98.2

Table 5: Electrochemical impedance, Tafel, and linear polarization resistance data at 308 K.

Name of inhibitor	Inhibitor concentration	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	E (%)	-E_{corr} (mV versus SCE)	i_{corr} (mA/cm^2)	E (%)
1 M HCl	—	8.5	68.9	—	446	1540.0	—
Piper longum	240.0	213.2.1	46.4	96.0	464	53.0	96.5
	300.0	273.3	33.1	96.9	469	46.0	96.9
	600.0	355.5	27.3	97.6	479	41.0	97.3
Moringa oleifera	200.0	215.0	43.0	96.0	503	59.0	96.1
	250.0	324.5	41.4	97.3	472	38.0	97.5
	300.0	644.9	32.4	98.6	493	28.0	98.1
Citrus aurantium	300.0	23.5	68.5	68.9	466	430.0	72.0
	600.0	58.2	65.4	85.4	515	212.0	86.2
	1200.0	65.2	56.3	87.0	464	160.0	89.6

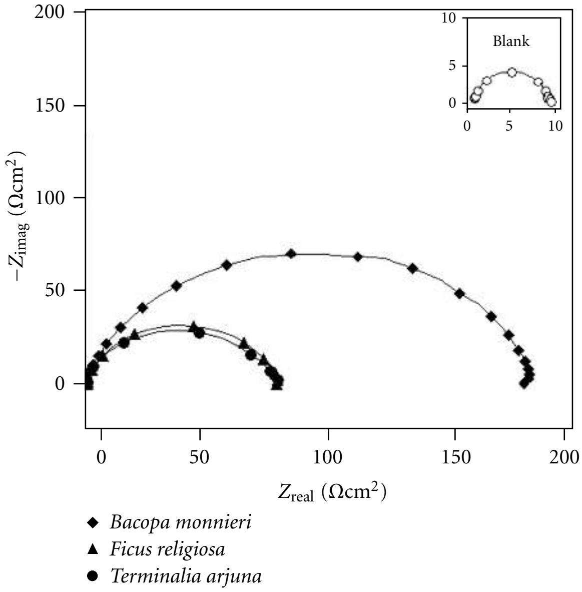
of all stem extract as in Table 6 and Figure 4. This may be due to the adsorption of these compounds at the metal/solution interface. Decrease in C_{dl} values, caused by a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the water molecules are replaced by inhibitor molecules. It was observed that the values of I_{corr} decrease in the presence of inhibitors. The decrease in I_{corr} values can be due to the adsorption of stems extract on the mild steel surface. The b_c and b_a values remained more or less identical in the absence and presence of stems extract studied, suggesting that the effect of inhibitors is not as large as to change the mechanism of corrosion.

All the studied plant extracts obtained from leaves, seeds, fruits, and stem showed good inhibition efficiency (>95%) at their optimum concentrations for mild steel in 1 M HCl. The optimum concentration is considered as a concentration beyond which increase in extract concentration showed no significant change in the inhibition efficiency. The good performance may be attributed to the synergism between the different compounds present in the extracts. *Andrographis paniculata* leaves extract showed 98% inhibition efficiency due to the presence of delocalized π-electrons as compared to those of *Strychnous nuxvomica* seed extract which can be attributed to the presence of three methoxy groups attached to the benzene nucleus favoring its greater adsorption on the mild steel surface, thereby giving rise to very high inhibition efficiency (98.2%) and *Moringa oleifera* fruit extract (98.1%) due to the presence of imine (C=N) group, four N atoms and long alkyl chain. Also, the low inhibition efficiency of *Bacopa monnieri* as compared to *Andrographis paniculata*, *Strychnous nuxvomica,* and *Moringa oleifera* can be attributed to the presence of O atoms in its structure.

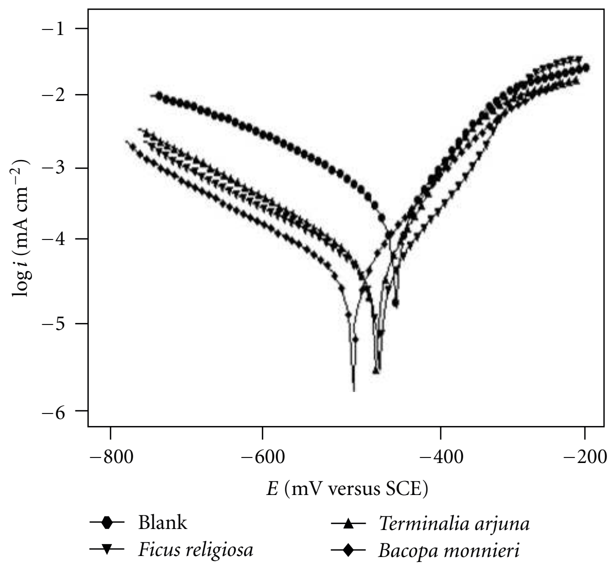
3.5. Mechanism of Corrosion Inhibition. In acidic solutions, transition of the metal/solution interface is attributed to the adsorption of the inhibitor molecules at the metal/solution interface, forming a protective film. The rate of adsorption is usually rapid, and hence, the reactive metal surface is shielded from the acid solutions [49]. The adsorption of an inhibitor depends on its chemical structure, its molecular size, the nature and charged surface of the metal, and distribution of charge over the whole inhibitor molecule. In fact, adsorption process can occur through the replacement of solvent molecules from the metal surface by ions and molecules accumulated near the metal/solution interface. Ions can accumulate at the metal/solution interface in excess of those required to balance the charge on the metal at the

Table 6: Electrochemical impedance, Tafel, and linear polarization resistance data at 308 K.

Name of inhibitor	Inhibitor concentration	R_{ct} (Ω cm^2)	C_{dl} (μF cm^{-2})	E (%)	-E_{corr} (mV versus SCE)	i_{corr} (mA/cm^2)	E (%)
1 M HCl	—	8.5	68.9	—	446	1540.0	—
	300.0	17.0	67.4	50.5	478	785.0	49.0
Terminalia arjuna	600.0	26.2	48.9	67.9	461	713.0	53.7
	1200.0	75.9	38.8	88.9	469	220.0	85.7
	300.0	28.7	63.9	70.7	444	407.0	54.0
Ficus religiosa	600.0	37.8	63.0	77.7	481	301.0	80.4
	1200.0	75.6	37.6	88.8	464	190.0	87.6
	240.0	41.9	53.5	79.9	464	518.0	66.3
Bacopa monnieri	300.0	74.2	44.2	88.6	486	218.0	85.8
	600.0	175.2	39.4	95.2	489	75.0	95.1



(a)



(b)

Figure 4: Nyquist plots and Tafel plots for mild steel in 1 M HCl in the absence and presence of different inhibitors at their optimum concentrations.

operating potential. These ions replace solvent molecules from the metal surface, and their centres reside at the inner Helmholtz plane. This phenomenon is termed specific adsorption, contact adsorption. The anions are adsorbed when the metal surface has an excess positive charge in an amount greater than that required to balance the charge corresponding to the applied potential. The exact nature of the interactions between a metal surface and an aromatic molecule depends on the relative coordinating strength towards the given metal of the particular groups present [50].

Generally, two modes of adsorption were considered. In one mode, the neutral molecules of leaves extract can be adsorbed on the surface of mild steel through the chemisorption mechanism, involving the displacement of water molecules from the mild steel surface and the sharing electrons between the heteroatoms and iron. The inhibitor molecules can also adsorb on the mild steel surface based on donor-acceptor interactions between π-electrons of the aromatic/heterocyclic ring and vacant d-orbitals of surface iron. In another mode, since it is well known that the steel surface bears the positive charge in acidic solutions [51], so it is difficult for the protonated leaves extract to approach the positively charged mild steel surface (H_3O^+/metal interface) due to the electrostatic repulsion. Since chloride ions have a smaller degree of hydration, thus they could bring excess negative charges in the vicinity of the interface and favour more adsorption of the positively charged inhibitor molecules, the protonated leaves extract adsorbed through electrostatic interactions between the positively charged molecules and the negatively charged metal surface.

Since all the different parts of plant extract possess several heteroatoms containing active constituents, therefore there may be a synergism between the molecules accounting for the good inhibition efficiencies.

4. Conclusions

(1) All the extracts studied showed good inhibition efficiency.

(2) *Andrographis paniculata*, *Strychnous nuxvomica*, and *Moringa oleifera* extracts showed inhibition efficiency above 98%.

(3) All the extracts were found to be the mixed type of inhibitors.

(4) All the results obtained from EIS, LPR, and weight loss are in good agreement with each other.

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