Green Approaches to Corrosion Mitigation

Guest Editors: Peter C. Okafor, Eno E. Ebenso, Ali Y. El-Etre, and Mumtaz Ahmad Quraishi
Green Approaches to Corrosion Mitigation
Green Approaches to Corrosion Mitigation

Guest Editors: Peter C. Okafor, Eno E. Ebenso, Ali Y. El-Etre, and Mumtaz Ahmad Quraishi
# Editorial Board

| Country       | Name                                      | Country       | Name                                      |
|---------------|-------------------------------------------|---------------|-------------------------------------------|
| Australia     | Raman Singh                               | Italy         | Flavio Deflorian                          |
| Spain         | Carmen Andrade                            | Spain         | José Maria Bastidas                       |
| USA           | Ksenija Babic                             | Poland        | Marek Danielewski                         |
| Italy         | Pier Luigi Bonora                         | Italy         | Flavio Deflorian                          |
| Spain         | Sebastian Feliu                           | China         | W. Ke, China                             |
| Australia     | Wei Gao, New Zealand                      | Japan         | H. K. Kwon, Japan                        |
| Germany       | Karl Ulrich Kainer                        | Canada        | Dongyang Y. Li, Canada                   |
| Germany       | Karl Ulrich Kainer                        | China         | Chang-Jian Lin                           |
| Ireland       | Weiqian Yang                               | Canada        | Efstathios I. Meletis, USA                |
| USA           | Ramana M. Pidaparti                       | Serbia        | Vesna Mišković-Stanković, Serbia         |
| UK            | Michael I. Ojovan                          | China         | Rokuro Nishimura, Japan                   |
| Spain         | F. J. M. Pérez                            | Germany       | Willem J. Quadakkers, Germany             |
| USA           | Ramana M. Pidaparti                       | USA           | Aravamudhan Raman                        |
| Germany       | Michael J. Schütze                        | USA           | Aravamudhan Raman                        |
| Canada        | Jerzy A. Szpunar                           | China         | Yanjing Su, China                       |
| China         | Michael J. Schütze                        | China         | Yu Zuo, China                           |
| USA           | Aravamudhan Raman                         | Canada        | Yanjing Su, China                       |
| USA           | Michael J. Schütze                        | USA           | Yu Zuo, China                           |
## Contents

**Green Approaches to Corrosion Mitigation**, Peter C. Okafor, Eno E. Ebenso, Ali Y. El-Etre, and Mumtaz Ahmad Quraishi  
Volume 2012, Article ID 908290, 2 pages

**Corrosion Inhibition of Carbon Steel in HCl Solution by Some Plant Extracts**, Ambrish Singh, Eno E. Ebenso, and M. A. Quraishi  
Volume 2012, Article ID 897430, 20 pages

**Evaluation of Corrosion Behavior of Galvanized Steel Treated with Conventional Conversion Coatings and a Chromate-Free Organic Inhibitor**, Laura A. Hernandez-Alvarado, Luis S. Hernandez, and Sandra L. Rodriguez-Reyna  
Volume 2012, Article ID 368130, 8 pages

**Interesting Behavior of *Pachycormus discolor* Leaves Ethanol Extract as a Corrosion Inhibitor of Carbon Steel in 1 M HCl: A Preliminary Study**, Ramses Garcia Inzunza, Benjami’n Valdez Salas, Rita Kharshan, Alla Furman, and Michael Schorr Wienner  
Volume 2012, Article ID 980654, 8 pages

**Inhibitory Action of Artemisia annua Extracts and Artemisinin on the Corrosion of Mild Steel in H₂SO₄ Solution**, P. C. Okafor, V. E. Ebiekpe, C. F. Azike, G. E. Egbug, E. A. Brisibe, and E. E. Ebenso  
Volume 2012, Article ID 768729, 8 pages

**Green Inhibitors for Corrosion Protection of Metals and Alloys: An Overview**, B. E. Amitha Rani and Bharathi Bai J. Basu  
Volume 2012, Article ID 380217, 15 pages

**Development of Novel Corrosion Techniques for a Green Environment**, Zaki Ahmad and Faheemuddin Patel  
Volume 2012, Article ID 982972, 8 pages

**The Inhibitory Action of the Extracts of *Adathoda vasica, Eclipta alba,* and *Centella asiatica* on the Corrosion of Mild Steel in Hydrochloric Acid Medium: A Comparative Study**, M. Shyamala and P. K. Kasthuri  
Volume 2012, Article ID 852827, 13 pages
Editorial
Green Approaches to Corrosion Mitigation

Peter C. Okafor,1 Eno E. Ebenso,2 Ali Y. El-Etre,3 and Mumtaz Ahmad Quraishi4

1 Corrosion and Electrochemistry Research Group, Department of Pure and Applied Chemistry, University of Calabar, PMB. 1115, Cross River State, Calabar, Nigeria
2 Department of Chemistry, Faculty of Agriculture, Science & Technology, North West University, Mafikeng Campus, Private Bag X2046, Mmabatho 2735, South Africa
3 Department of Chemistry, Faculty of Science, Benha University, Benha 13518, Egypt
4 Department of Applied Chemistry, Institute of Technology, Banaras Hindu University, Varanasi 221005, India

Correspondence should be addressed to Peter C. Okafor, peter.okafor@fulbrightmail.org

Received 2 November 2011; Accepted 2 November 2011

Copyright © 2012 Peter C. Okafor et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Owing to the increasing ecological awareness, as well as the strict environmental regulations, and consequently the need to develop environmentally friendly processes, attention is currently focused on the development of “green” alternatives to mitigating corrosion. Green approaches to corrosion mitigation entail the use of substances, techniques, and methodologies that reduce or eliminate the use of feedstocks, products, byproducts, solvents, reagents, and so forth that are hazardous to human health or the environment in combating corrosion. They include the use of plant extracts, ionic liquids, biochemicals, and biodegradable organic and green inorganic inhibitors; the development of corrosion inhibitors based on waste products; protection against corrosion by corrosion byproducts, ionexchange pigments, and coatings; the development of mitigation techniques that enable the detection and prevention of the early stages of corrosion, and so forth.

Of all these methods, the use of plant extracts in corrosion inhibition studies has continued to attract patronage as evident in the papers published in this special issue. Four papers present the inhibition behaviour of plant extracts in the corrosion of metals in acidic media, and another one gives an overview of plant extracts used as corrosion inhibitors in aqueous media. It is interesting to note that in the field of corrosion inhibition we are going back to the past as a result of the fact that increasing awareness of health and ecological risks is drawing attention to finding more suitable nontoxic inhibitors, which are found mostly among the class of natural products. In the Middle Ages (i.e., from the 5th century to the 15th century), the use of plant extracts (flour, bran, yeast, a mixture of molasses and vegetable oil, and starch) for pickling of metal articles by master armourers has been reported [1, 2]. However, the available information indicates that the earliest documented use of corrosion inhibitors appears to be that described by Marangoni and Stephanelli [3], who used extracts of bran among other substances to inhibit the corrosion of iron in acids. Few years later, the first patent in corrosion inhibition was given to Baldwin in 1895 [2] who specified the use of natural plant product, molasses and vegetable oils, for pickling sheet steel in acids. In US Patent 640491 in 1900 given to Robinson and Sutherland, they used starch, a biodegradable material.

In 1930, plant extracts (dried stems, leaves, and seeds) of celandine (Chelidonium majus) and other plants were used in H2SO4 pickling baths [2]. In the 1970s and 80s, the study of plant extracts as corrosion inhibitors became more extensive.

Based on previous works in the 70s and 80s, one would have thought that there will be an upsurge in the publications and application of plant extracts as metallic corrosion inhibitors in the 90s. This was not the case, as the literature search indicated the contrary. The reason is not unconnected with the difficulties in isolating and purifying the active ingredients of the extracts as most reviewers insisted that the active principles responsible for the inhibition be identified and tested, coupled with the mild enforcement of the laws on the use of ecofriendly inhibitors.

At the inception of this new millennium, various research groups showed an increased interest in the use of natural products as corrosion inhibitor resulting in enormous data on plant extract as corrosion inhibitors. The reason for this
uninterrupted interest can undoubtedly be ascribed to an increased awareness of the environmental requirements that is currently imposed on the development of cleaner chemical inhibitors, of the health risks associated with the use of unsafe and toxic inorganic inhibitors, and of the great contribution that these data can give to developing eco-friendly corrosion inhibitors. This clearly shows that the era of green inhibitors is here.

Green approaches to corrosion mitigation also involve the use of green chromate-free organic inhibitors as explored by L. A. Hernandez-Alvarado et al. and the development of techniques that enable the detection and prevention of corrosion as presented in this special issue.

Peter C. Okafor
Eno E. Ebenso
Ali Y. El-Etre
Mumtaz Ahmad Quraishi

References

[1] I. N. Putilova, S. A. Balezin, and V. P. Barannik, Metallic Corrosion Inhibitors, Translated from the Russian by Ryback, Pergamon Press, New York, NY, USA, 1960, As cited by D. V. Gupta and S. Green, Inhibitor—where are we, Proceedings of Corrosion 2004, Paper no. 04406, NACE International, Houston, Tex, USA 2004.

[2] B. Sanyal, “Organic compounds as corrosion inhibitors in different environments—a review,” Progress in Organic Coatings, vol. 9, no. 2, pp. 165–236, 1981.

[3] J. O’M. Bockris and B. E. Conway, “Hydrogen overpotential and the partial inhibition of the corrosion of iron,” Journal of Physical Chemistry, vol. 53, no. 4, pp. 527–539, 1949.
Corrosion Inhibition of Carbon Steel in HCl Solution by Some Plant Extracts

Ambrish Singh,¹ Eno E. Ebenso,² and M. A. Quraishi¹

¹ Department of Applied Chemistry, Institute of Technology, Banaras Hindu University, Varanasi 221005, India
² Department of Chemistry, Faculty of Agriculture, Science & Technology, North West University (Mafikeng Campus), Mmabatho 2735, South Africa

Correspondence should be addressed to M. A. Quraishi, maquraishi.apc@itbhu.ac.in

Received 30 July 2011; Revised 13 October 2011; Accepted 17 October 2011

Academic Editor: Peter C. Okafor

Copyright © 2012 Ambrish Singh et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

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 anticrosive 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*               | ![Lawsonia Structure](image) | 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*              | ![Fenugreek Structure](image) | 92.2                      | The temperature effects were investigated on mild steel corrosion in 2 M HCl and H₂SO₄ in the absence and presence of aqueous extract of fenugreek leaves (AEFLs) with the help of gravimetric method [2] |
| (3)   | *Olea europaea*          | ![Olea europaea Structure](image) | 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,*        | ![Cotula cinerea Structure](image) | 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] |

*Note: The structures of the active constituents are not fully readable due to image quality issues.*
| S. no. | Inhibitors used       | Active constituents                               | Inhibition efficiency (%) | Remarks                                                                                                                                 |
|-------|-----------------------|--------------------------------------------------|---------------------------|-----------------------------------------------------------------------------------------------------------------------------------------|
| (5)   | **Eclipta alba**      | [Chemical structure image]                        | 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$_2$SO$_4$ 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**     | [Chemical structure image]                        | 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** | [Chemical structure image]                        | 91.3                      | The acid extracts of *Solanum tuberosum* were studied as the corrosion inhibitor for mild steel in 1 M HCl and H$_2$SO$_4$ 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$_2$SO$_4$ 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*                     |                    | 97.4                      | The efficacy of an acid extract 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*                         |                    | 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    | *Emblica officinalis,* *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] |
| 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* | Lawsonsone, 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 1 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 H2SO4. 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 H2SO4 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, nimboline, nimbolin, salannin, margolone, melianol, vilasalin, and flavanoids | 80%                       | The inhibitive action of leaves (LV), root (RT), and seeds (SD) extracts of *Azadirachta indica* on mild steel corrosion in H2SO4 solutions was studied using weight loss and gasometric techniques. The results obtained indicate that the extracts functioned as good inhibitors in H2SO4 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] |
| 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$_2$SO$_4$ 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$_2$SO$_4$ 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, azfluorenones 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 vatica*, *Eclipta alba*, and *Centella asiatica* | Vasicine, vasicinone, asiaticoside, wedelolactone, β-sitosterol, and stigmasterol | 99%                        | The inhibitive action of the extracts of *Adhatoda vatica*, *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)   | Annona 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 H₂SO₄ 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-α-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 Monordica 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 cm² 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, Ecorr, 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:

\[\text{Andrographis paniculata} > \text{Murraya koenigii} > \text{Aegle marmelos}.\] (1)

The higher inhibitive performance of Andrographis paniculata is due to the presence of delocalized \(\pi\)-electrons. This extensive delocalized \(\pi\)-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 cm²) was obtained by inhibitor Andrographis paniculata at 1200 ppm concentration. The lowest \(R_{ct}\) value (264.8 ohm cm²) 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*        | ![Murraya koenigii](attachment) | Murrafoline-I     | 96.7                      |
| (1)    |                           | ![Murraya koenigii](attachment) |                   |                           |
| (2)    |                           | ![Murraya koenigii](attachment) | Pyrayfoline-D     |                           |
| (3)    |                           | ![Murraya koenigii](attachment) | Mahabinine-A      |                           |
| (B)    | *Aegle marmelos*          | ![Aegle marmelos](attachment) | Skimmianine       | 96.2                      |
| (1)    |                           | ![Aegle marmelos](attachment) |                   |                           |
| (C)    | *Andrographis paniculata* | ![Andrographis paniculata](attachment) | Andrographolide    | 98.1                      |
| (1)    |                           | ![Andrographis paniculata](attachment) |                   |                           |
| (D)    | *Syzygium cumini*         | ![Syzygium cumini](attachment) | Ellagic acid      | 94.2                      |
| (1)    |                           | ![Syzygium cumini](attachment) |                   |                           |
| S. no. | Plant used       | Active constituents | Common name   | Inhibition efficiency (%) |
|-------|------------------|---------------------|---------------|---------------------------|
| (2)   | Pongamia pinnata | Gallic acid         |               | 97.6                      |
| (3)   | Pongamia pinnata | Quercetin           |               |                           |
| (4)   | Pongamia pinnata | Cafeic acid         |               |                           |
| (1)   | Pongamia pinnata | Karanjin            |               |                           |
| (2)   | Pongamia pinnata | Pongapine           |               |                           |
| (3)   | Pongamia pinnata | Kanjone             |               |                           |
| (4)   | Pongamia pinnata | Pongaglabrone       |               |                           |
| S. no. | Plant used               | Active constituents | Common name | Inhibition efficiency (%) |
|--------|--------------------------|---------------------|-------------|---------------------------|
| (F)    | *Strychnos nuxvomica*    | Brucine             | 98.2        |
| (G)    | *Piper longum*           | Piperine            | 97.6        |
| (1)    |                          |                     |             |
| (3)    |                          | Rutin               |             |
| (H)    | *Moringa oleifera*       | Arginine            | 98.6        |
| (1)    |                          |                     |             |
| (1)    | *Citrus Aurantium*       | Threonine           | 89.6        |
| (1)    |                          |                     |             |
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:

$$\text{Strychnos nuxvomica} > \text{Pongamia pinnata} > \text{Syzygium cumini.}$$

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 | $R_{ct}$ ($\Omega$ cm$^2$) | $C_{dl}$ ($\mu$F 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                        | 95.5    | 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 ($\Omega$ 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

Good performance of fruits extract as corrosion inhibitors for mild steel in 1 M HCl solutions may be due to the presence of heteroatoms, $\pi$-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
the present study, maximum displacement in $E_{\text{corr}}$ 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...
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 $\pi$-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 4: Electrochemical impedance, Tafel, and linear polarization resistance data at 308 K.**

| Name of inhibitor | Inhibitor concentration | $R_{ct}$ ($\Omega \text{cm}^2$) | $C_{dl}$ ($\mu\text{F cm}^{-2}$) | $E$ (%) | $-E_{corr}$ (mV versus SCE) | $i_{corr}$ (mA/cm²) | $E$ (%) |
|-------------------|-------------------------|-----------------|----------------|--------|----------------|-----------------|--------|
| 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 | $R_{ct}$ ($\Omega \text{cm}^2$) | $C_{dl}$ ($\mu\text{F cm}^{-2}$) | $E$ (%) | $-E_{corr}$ (mV versus SCE) | $i_{corr}$ (mA/cm²) | $E$ (%) |
|-------------------|-------------------------|-----------------|----------------|--------|----------------|-----------------|--------|
| 1 M HCl           | —                       | 8.5             | 68.9           | —      | 446            | 1540.0          | —      |
| Piper longum      | 240.0                   | 213.2           | 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            | 56.4           | 85.4   | 515            | 212.0           | 86.2   |
|                   | 1200.0                  | 65.2            | 56.3           | 87.0   | 464            | 160.0           | 89.6   |
Table 6: Electrochemical impedance, Tafel, and linear polarization resistance data at 308 K.

| Name of inhibitor                  | Inhibitor concentration | $R_{ct}$ (Ω cm²) | $C_{dl}$ (μF cm⁻²) | -$E_{corr}$ (mV versus SCE) | $i_{corr}$ (mA/cm²) | $E$ (%) |
|------------------------------------|-------------------------|------------------|--------------------|----------------------------|---------------------|---------|
| 1 M HCl                             | —                       | 8.5              | 68.9               | —                          | 446                 | 1540.0  | —       |
| *Terminalia arjuna*                | 300.0                   | 17.0             | 67.4               | 50.5                       | 478                 | 785.0   | 49.0    |
|                                    | 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    |
| *Ficus religiosa*                  | 300.0                   | 28.7             | 63.9               | 70.7                       | 444                 | 407.0   | 54.0    |
|                                    | 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    |
| *Bacopa monnieri*                  | 240.0                   | 41.9             | 53.5               | 79.9                       | 464                 | 518.0   | 66.3    |
|                                    | 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    |

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 $\pi$-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 ($\text{H}_3\text{O}^+$/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*, *Strychnos 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.

References

[1] A. Y. El-Etre, M. Abdallah, and Z. E. El-Tantawy, “Corrosion inhibition of some metals using Lawsonia extract,” *Corrosion Science*, vol. 47, no. 2, pp. 385–395, 2005.

[2] E. A. Noor, “Temperature effects on the corrosion inhibition of mild steel in acidic solutions by aqueous extract of fenugreek leaves,” *International Journal of Electrochemical Science*, vol. 2, pp. 996–1017, 2007.

[3] A. Y. El-Etre, “Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves,” *Journal of Colloid and Interface Science*, vol. 314, no. 2, pp. 578–583, 2007.

[4] P. B. Raja and M. G. Sethuraman, “Natural products as corrosion inhibitor for metals in corrosive media—A review,” *Materials Letters*, vol. 62, no. 1, pp. 113–116, 2008.

[5] M. Shyamala and A. Arulanantham, “Eclipta alba as corrosion pickling inhibitor on mild steel in hydrochloric acid,” *Journal of Materials and Science and Technology*, vol. 25, no. 5, pp. 633–636, 2009.

[6] A. M. Abdel-Gaber, B. A. Abd-El-Nabey, and M. Saadawy, “The role of acid anion on the inhibition of the acidic corrosion of steel by lupine extract,” *Corrosion Science*, vol. 51, no. 5, pp. 1038–1042, 2009.

[7] P. Both Raja and M. G. Sethuraman, “Solanum tuberosum as an inhibitor of mild steel corrosion in acid media,” *Iranian Journal of Chemistry and Chemical Engineering*, vol. 28, no. 1, pp. 77–84, 2009.

[8] I. E. Uwah, P. C. Okafor, and V. E. Ebieke, “Inhibitive action of ethanol extracts from *Nauclea latifolia* on the corrosion of mild steel in *H*₂*S*₄ solutions and their adsorption characteristics,” *Arabian Journal of Chemistry*. In press.

[9] S. Saratha and R. Meenakshi, “Corrosion inhibitor-A plant extract,” *Der Pharma Chemica*, vol. 2, pp. 287–294, 2010.

[10] A. Y. El-Etre, “Khillah extract as inhibitor for acid corrosion of SX 316 steel,” *Applied Surface Science*, vol. 252, no. 24, pp. 8521–8525, 2006.

[11] M. J. Sanghvi, S. K. Shukla, A. N. Misra, M. R. Padh, and G. N. Mehta, “Inhibition of hydrochloric acid corrosion of mild steel by aid extracts of *emblica officinalis*, *terminalia bellirica* and *terminalia chebula*,” *Bulletin of Electrochemistry*, vol. 13, no. 8-9, pp. 358–361, 1997.

[12] E. E. Ebenso, J. Udofot, J. Ekpe, and U. J. Iboke, “Studies on the inhibition of mild steel corrosion by some plant extracts in acidic medium,” *Discovery and Innovation*, vol. 10, no. 1-2, pp. 52–59, 1998.

[13] A. Bouyanzer, B. Hammouti, and L. Majidi, “Pennyroyal oil from *Mentha pulegium* as corrosion inhibitor for steel in 1 M HCl,” *Materials Letters*, vol. 60, no. 23, pp. 2840–2843, 2006.

[14] L. R. Chauhan and G. Gunasekaran, “Corrosion inhibition of mild steel by plant extract in dilute HCl medium,” *Corrosion Science*, vol. 49, no. 3, pp. 1143–1161, 2007.

[15] E. Khamis and N. Alandis, “Herbs as new type of green inhibitors for acidic corrosion of steel,” *Materialwissenschaft und Werkstofftechnik*, vol. 33, no. 9, pp. 550–554, 2002.

[16] H. H. Rehan, “Corrosion control by water-soluble extracts from leaves of economic plants,” *Materialwissenschaft und Werkstofftechnik*, vol. 34, no. 2, pp. 232–237, 2003.

[17] M. G. Sethuraman and P. B. Raja, “Corrosion inhibition of mild steel by *Datura metel* in acidic medium,” *Pigment and Resin Technology*, vol. 34, no. 6, pp. 327–331, 2005.

[18] R. A. L. Sathiyanathan, M. M. Essa, S. Maruthamuthu, M. Selvanayagam, and N. Palaniswamy, “Inhibitory effect of *Ricinus communis* (Castor-oil plant) leaf extract on corrosion of mild steel in low chloride medium,” *Journal of the Indian Chemical Society*, vol. 82, no. 4, pp. 357–359, 2005.

[19] E. Chaib, A. Bouyanzer, B. Hammouti, and M. Benkaddour, “Inhibition of the corrosion of steel in 1 M HCl by eugenol derivatives,” *Applied Surface Science*, vol. 246, no. 1–3, 1998–2005.

[20] P. C. Okafor and E. E. Ebenso, “Inhibitive action of *Carica papaya* extracts on the corrosion of mild steel in acidic media and their adsorption characteristics,” *Pigment and Resin Technology*, vol. 36, no. 3, pp. 134–140, 2007.

[21] J. Buchweishajja and G. S. Mhizni, “Natural products as a source of environmentally friendly corrosion inhibitors: the case of gum exudate from *Acacia seyal* var. *seyal*,” *Portugaliae Electrochemica Acta*, vol. 26, no. 3, pp. 257–265, 2008.

[22] P. B. Raja and M. G. Sethuraman, “Inhibition of corrosion of mild steel in sulphuric acid medium by *Calotropis procera*,” *Pigment and Resin Technology*, vol. 38, no. 1, pp. 33–37, 2009.

[23] M. Shyamala and A. Arulanantham, “Corrosion inhibition effect of *centella asiatica* (*Vallarai*) on mild steel in hydrochloric acid,” *Asian Journal of Chemistry*, vol. 21, no. 8, pp. 6102–6110, 2009.

[24] C. Anca, M. Ioana, D. I. Vaireanu, L. Isosif, L. Carmen, and C. Simona, “Estimation of inhibition efficiency for carbon steel corrosion in acid media by using natural plant extracts,” *Revista de Chimie*, vol. 60, no. 11, pp. 1175–1180, 2009.

[25] P. C. Okafor, I. E. Uwah, O. O. Ekeream, and U. J. Ekpe, “*Combretum bracteatum* extracts as eco-friendly corrosion inhibitor for mild steel in acidic medium,” *Pigment and Resin Technology*, vol. 38, no. 4, pp. 236–241, 2009.

[26] P. C. Okafor, M. E. Ikpi, I. E. Uwah, E. E. Ebenso, U. J. Ekpe, and S. A. Umoren, “Inhibitory action of *Phyllanthus amarus* extracts on the corrosion of mild steel in acidic media,” *Corrosion Science*, vol. 50, no. 8, pp. 2310–2317, 2008.

[27] P. C. Okafor, E. E. Ebenso, and U. J. Ekpe, “Azadirachta indica extracts as corrosion inhibitor for mild steel in acid medium,” *International Journal of Electrochemical Science*, vol. 5, no. 7, pp. 978–993, 2010.

[28] N. O. Eddy and E. E. Ebenso, “Adsorption and inhibitive properties of ethanol extracts of *Musa sapientum* peels as a green corrosion inhibitor for mild steel in H₂SO₄,” *African Journal of Pure and Applied Chemistry*, vol. 2, pp. 046–054, 2008.

[29] A. Sharmila, A. A. Prema, and P. A. Sahayaraj, “Influence of *Murraya koenigii* (curry leaves) extract on the corrosion inhibition of carbon steel in HCL solution,” *Rasayan Journal of Chemistry*, vol. 3, no. 1, pp. 74–81, 2010.

[30] A. M. Al-Turkustani, S. T. Arab, and L. S. S. Al-Qarni, “Medicago Sativa plant as safe inhibitor on the corrosion of steel in 2.0 M *H*₂*S*₄ solution,” *Journal of Saudi Chemical Society*, vol. 15, no. 1, pp. 73–82, 2011.
[31] M. Lebrini, F. Robert, A. Lecante, and C. Roos, “Corrosion inhibition of C38 steel in 1M hydrochloric acid medium by alkaloids extract from *Oxandra asbeckii* plant,” *Corrosion Science*, vol. 53, no. 2, pp. 687–695, 2011.

[32] M. Shyamala and P. K. Kasthuri, “The inhibitory action of the extracts of *Adhatoda vasica*, *Eclipta alba*, and *Centella asiatica* on the corrosion of mild steel in hydrochloric acid medium: a comparative study,” *International Journal of Corrosion*, vol. 2012, Article ID 852827, 13 pages, 2012.

[33] M. Shyamala and P. K. Kasthuri, “A comparative study of the inhibitory effect of the extracts of *Ocimum sanctum*, *Aegle marmelos*, and *Solanum trilobatum* on the corrosion of mild steel in hydrochloric acid medium,” *International Journal of Corrosion*, vol. 2011, Article ID 129647, 11 pages, 2011.

[34] M. Lebrini, F. Robert, and C. Roos, “Inhibition effect of alkaloids extract from *Annona squamosa* plant on the corrosion of C38 steel in normal hydrochloric acid medium,” *International Journal of Electrochemical Science*, vol. 5, no. 11, pp. 1698–1712, 2010.

[35] N. O. Eddy and A. O. Odiongenyi, “Corrosion inhibition and adsorption properties of ethanol extract of *Heinsia crinata* on mild steel in *H*2*SO*4, “*Pigment and Resin Technology*, vol. 39, no. 5, pp. 288–295, 2010.

[36] E. E. Oguzie, C. K. Enenebeaku, C. O. Akalezi, S. C. Okoro, A. A. Ayuk, and E. N. Ejike, “Adsorption and corrosion-inhibiting effect of *Dacryodis edulis* extract on low-carbon-steel corrosion in acidic media,” *Journal of Colloid and Interface Science*, vol. 349, no. 1, pp. 283–292, 2010.

[37] R. Saratha and V. G. Vasudha, “*Emblica Officinalis* (Indian Gooseberry) leaves extract as corrosion inhibitor for mild steel in 1N HCL medium,” *E-Journal of Chemistry*, vol. 7, no. 3, pp. 677–684, 2010.

[38] S. Subhashini, R. Rajalakshmi, A. Prithiba, and A. Mathina, “Corrosion mitigating effect of *Cyanopsis Tetragonoloba* seed extract on mild steel in acid medium,” *E-Journal of Chemistry*, vol. 7, no. 4, pp. 1133–1137, 2010.

[39] M. A. Quraishi, “Investigation of some green compounds as corrosion and scale inhibitors for cooling systems,” *Corrosion*, vol. 55, no. 5, pp. 493–497, 1999.

[40] A. Minhaj, P. A. Saini, M. A. Quraishi, and I. H. Farooqi, “A study of natural compounds as corrosion inhibitors for industrial cooling systems,” *Corrosion Prevention and Control*, vol. 46, no. 2, pp. 32–38, 1999.

[41] I. H. Farooqi, M. A. Quraishi, and P. A. Saini, “Corrosion prevention of mild steel in 3% NaCl water by some naturally-occurring substances,” *Corrosion Prevention and Control*, vol. 46, no. 4, pp. 93–96, 1999.

[42] I. H. Farooqi, M. A. Nasir, and M. A. Quraishi, “Environmentally-friendly inhibitor formulations for industrial cooling systems,” *Corrosion Prevention and Control*, vol. 44, no. 5, pp. 129–134, 1997.

[43] M. A. Quraishi, A. Singh, V. K. Singh, D. K. Yadav, and A. K. Singh, “Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of *Murraya koenigii* leaves,” *Materials Chemistry and Physics*, vol. 122, no. 1, pp. 114–122, 2010.

[44] A. Singh, I. Ahamad, V. K. Singh, and M. A. Quraishi, “Inhibition effect of environmentally benign Karanj (*Pongamia pin- nata*) seed extract on corrosion of mild steel in hydrochloric acid solution,” *Journal of Solid State Electrochemistry*, vol. 15, pp. 1087–1097, 2011.

[45] A. Singh, V. K. Singh, and M. A. Quraishi, “Aqueous extract of Kalmegh (*Andrographis paniculata*) leaves as green inhibitor for mild steel in hydrochloric acid solution,” *International Journal of Corrosion*, vol. 2010, Article ID 275983, 10 pages, 2010.

[46] A. Singh, V. K. Singh, and M. A. Quraishi, “Effect of fruit extracts of some environmentally benign green corrosion inhibitors on corrosion of mild steel in hydrochloric acid solution,” *Journal of Materials and Environmental Science*, vol. 1, no. 3, pp. 162–174, 2010.

[47] A. Singh, V. K. Singh, and M. A. Quraishi, “Inhibition effect of environmentally benign Kuchla (*Strychnos nuxvomica*) seed extract on corrosion of mild steel in hydrochloric acid solution,” *Kasayan Journal of Chemistry*, vol. 3, pp. 811–824, 2010.

[48] A. Singh, I. Ahamad, D. K. Yadav, V. K. Singh, and M. A. Quraishi, “The effect of environmentally benign fruit extract of Shahjan (*Moringa oleifera*) on the corrosion of mild steel in hydrochloric acid solution,” *Chemical Engineering Communications*, vol. 199, no. 1, pp. 63–77, 2012.

[49] C. Y. Chao, L. F. Lin, and D. D. Macdonald, “A point defect model for anodic passive films,” *Journal of the Electrochemical Society*, vol. 128, no. 6, pp. 1187–1194, 1981.

[50] I. M. Ritchie, S. Bailey, and R. Woods, “Metal-solution interface,” *Advances in Colloid and Interface Science*, vol. 80, no. 3, pp. 183–231, 1999.

[51] G. N. Mu, T. P. Zhao, M. Liu, and T. Gu, “Effect of metallic cations on corrosion inhibition of an anionic surfactant for mild steel,” *Corrosion*, vol. 52, no. 11, pp. 853–856, 1996.
Evaluation of Corrosion Behavior of Galvanized Steel Treated with Conventional Conversion Coatings and a Chromate-Free Organic Inhibitor

Laura A. Hernandez-Alvarado,1 Luis S. Hernandez,2 and Sandra L. Rodriguez-Reyna3

1 Faculty of Chemical Sciences, Universidad Autonoma de San Luis Potosi, Avenida Salvador Nava No. 6, 78290 San Luis Potosi, SLP, Mexico
2 Institute of Metallurgy, Universidad Autonoma de San Luis Potosi, Avenida Sierra Leona No. 550, 78210 San Luis Potosi, SLP, Mexico
3 Faculty of Engineering, Universidad Autonoma de San Luis Potosi, Avenida Salvador Nava No. 8, 78290 San Luis Potosi, SLP, Mexico

Correspondence should be addressed to Luis S. Hernandez, hersal@uaslp.mx

Received 1 June 2011; Accepted 29 August 2011

Academic Editor: Peter C. Okafor

Conventional weight loss tests and both DC and AC electrochemical techniques were used to study if an organic inhibitor containing an alkanolamine salt of a polycarboxylic acid can substitute toxic coatings as chromating and certain phosphating procedures in the protection of galvanized steel. The electrolyte used was a 0.5 M aerated NaCl solution. All tests gave concordant results, indicating that the chromate-free organic inhibitor does protect galvanized steel in this environment, even though the provided protection was less than that of the chromate conversion coating. It was observed that, after a moderate initial attack, the corrosion rate diminishes due to the appearance and growth of passivating corrosion products layers, mainly constituted by zinc hydroxychloride (Zn₅(OH)₈Cl₂·H₂O) and two varieties of zinc hydroxide, among other crystalline compounds.

1. Introduction

Conversion coatings are applied to galvanized steel to improve adhesion of additional protective coatings and for corrosion protection of the zinc coating. Phosphate conversion coatings (PCCs) provide adhesion but do not provide substantial corrosion protection. PCCs provide uniform surface texture and increased surface area, and, when used as a base for paint, they promote good adhesion, increase the resistance of the paint to humidity and water soaking, and eventually increase the corrosion resistance of the painted system [1]. Most galvanized steel used in manufacturing industries (car, household appliances, etc.) is phosphate coated and painted. However, some authors [2] have reported the harmful effects of phosphating, mainly those compositions that contain nickel. Chromate conversion coatings (CCCs) for zinc have been the most widely used, as they enhance bare or painted corrosion resistance, improve the adhesion of paint or other organic finishes, and provide the metallic surface with a decorative finish. CCCs are distinguished by their easy application, their applicability to a wide range of alloys and, in many cases, their ability to improve the galvanized corrosion resistance by virtue of a built-in inhibitor reservoir [3]. Although chromate is an excellent corrosion inhibitor, it is highly toxic; it has carcinogenic effects and must be handled and disposed of with extreme care. Therefore, there are severe restrictions on its use.

Much effort has been devoted to replace chromate chemicals with safe, nontoxic alternatives that are environmentally benign, and many environmental friendly coating systems are under development [4–7]. However, preparation and corrosion behavior of these alternatives is not clear and their practical usage is doubtful. The purpose of this paper is to evaluate the corrosion protection provided by a chromate-free organic inhibitor that is suggested as a nontoxic alternative to chromate and phosphate conversion coatings on galvanized steel. The water-soluble organic inhibitor is based on an alkanolamine salt of a polycarboxylic acid.
2. Experimental Procedure

Test specimens of $5 \times 10$ cm were cut from a mild steel sheet of 1 mm thickness and subsequently submerged in a molten zinc bath to obtain a galvanized coating of 1450 g/m$^2$, according to ASTM A 90 standard. The specimens were degreased in trichloroethylene, rinsed in distilled water, coated, rinsed again in distilled water, and then dried for seven days prior to submit them to the tests. The chemical composition and other characteristics of the tested coatings are described in Table 1.

The corrosion resistance and paint adhesion characteristics may generally be determined, in addition to the coating weight, by a characteristic color imparted by the chromium compounds formed on the surface of the zinc. After the chromating, the galvanized surface had a dark orange, almost brown, transparent color that made possible to see the zinc grains on the surface. These colored hexavalent chromium conversion coatings are generally considered to give the best overall corrosion protection, as well as poor electrical conductivity and excellent paint adhesion properties [5]. The samples treated with the phosphating solution got a dull black color with granular appearance. Surfaces treated with the inhibitor did not show any visible change at all. The water-soluble corrosion inhibitor contains an alkanolamine salt of a polycarboxylic acid. The tested concentration, according to ASTM A 90 standard. The specimens were degreased in trichloroethylene, rinsed in distilled water, and then dried for seven days prior to submit them to the tests. The chemical composition and other characteristics of the tested coatings are described in Table 1.

The corrosion protection and paint adhesion characteristics may generally be determined, in addition to the coating weight, by a characteristic color imparted by the chromium compounds formed on the surface of the zinc. After the chromating, the galvanized surface had a dark orange, almost brown, transparent color that made possible to see the zinc grains on the surface. These colored hexavalent chromium conversion coatings are generally considered to give the best overall corrosion protection, as well as poor electrical conductivity and excellent paint adhesion properties [5]. The samples treated with the phosphating solution got a dull black color with granular appearance. Surfaces treated with the inhibitor did not show any visible change at all. The water-soluble corrosion inhibitor contains an alkanolamine salt of a polycarboxylic acid. The tested concentration, application procedures, and elimination of corrosion products of the samples treated with this commercial product were made in strict accordance with the instructions of the manufacturer. For example, a borax solution (35 gL$^{-1}$ at 65°C) was used for elimination of corrosion products. It is claimed that the inhibitor protects galvanized steel by sealing pores and other discontinuities present in the zinc coating. It is also suggested as a replacement of sodium nitride to protect ferrous metallic materials.

The protective effect of these treatments on galvanized steel was studied by immersion tests conducted in a naturally aerated 0.5 M NaCl solution, pH = 6.0, during 134 days and at room temperature. Panels in triplicate were withdrawn from the solution at different periods of time. In all tests, there were included untreated galvanized panels as blanks. The corrosion weight loss parameter was obtained after cleaning the surface of the panels in an acetic acid solution. Other specimens were examined after the same test periods, without stripping the corrosion products, by X-ray diffraction (XRD). The XRD patterns of the corroded samples were recorded using a diffractometer with a Cu K$\alpha$ radiation of 1.54056 Å operated at 36 kV/30 mA. The samples were step-scanned in the 2θ range of 5° to 35° with a step size of 0.02 and a time step of 3 s.

In order to perform the electrochemical techniques, glass tubes were attached to the panel surface with a silicone sealer. The tube, that defined an interior exposed area of 10.3 cm$^2$, was filled with the 0.5 M NaCl solution. The cell contained a graphite electrode as the counter electrode and a saturated calomel electrode (sce) as reference. The open circuit potential ($E_{ocp}$) and the polarization resistance ($R_p$) were determined throughout the immersion time. $E_{ocp}$ and $R_p$ measurements were carried out previously to $R_p$. The $R_p$ values were determined by imposing a pulse of ± 10 mV and recording the current system response. In addition, potentiodynamic polarization measurements were carried out at a scan rate of 120 mV/min, from −250 to +500 mV with respect to $E_{ocp}$. AC impedance measurements were made at the $E_{ocp}$ by using a frequency response analyzer (FRA) operated under microcomputer control. The FRA was connected to the electrochemical cell through a potentiostat. A sinusoidal signal of 10 mV was applied over the frequency range from 100 kHz to 5 mHz. Impedance data were analyzed using a complex nonlinear least-squares program (CNLS). All electrochemical measurements were carried out in triplicate, at room temperature and with no deaeration or stirring of the electrolyte.

### Table 1: Some characteristics of the tested coatings.

| Coating   | Chemical composition                                                                 | pH  | Application method          |
|-----------|---------------------------------------------------------------------------------------|-----|-----------------------------|
| chromate  | 200 g potassium dichromate + 6 cc sulphuric acid in 1 L of water                       | 0.8 | dipping for 20 sec at room temperature |
| phosphate | 21.0 g acidic zinc phosphate + 1.2 g sodium nitrite + 1.8 g triethanolamine oleate in 1 L of water | 5.0 | dipping for 600 sec at room temperature |
| inhibitor 5.0% | water-soluble corrosion inhibitor containing an alkanolamine salt of a polycarboxylic acid | 8.0 | dipping for 40 sec at 75°C    |

3. Results

3.1. Microstructural Characterization of the Coatings. The zinc coating weight of 1450 g/m$^2$ corresponds to an approximate thickness of 101 μm per side (Figure 1). Figures 2(a) through 2(c) show the backscattered scanning electron micrographs of the untreated and treated galvanized steel samples. The characteristic aspect of microcracking due to dehydration and the shrinkage of the coating during drying are visible in the chromated samples (Figure 2(a)). The surface of the phosphated samples appeared totally covered by a compact layer of small crystals (hopeite) that favors a firm anchorage of organic coatings (Figure 2(b)). Untreated galvanized samples had a very smooth surface and only appeared the limits of the zinc grains, scratches, and white points that correspond to lead particles (Figure 2(c)). The surfaces of the samples treated with the inhibitor (not included here) did not show any difference in comparison with the untreated galvanized ones.
3.2. Weight Loss and Electrochemical Measurements. Figure 3 shows the gravimetric results of the considered materials immersed in a 0.5 M NaCl solution up to 134 days. Untreated and treated galvanized steel showed very low corrosion rates, less than 10 mg/cm² (~38 μm/y), which are within a range considered as excellent (25–100 μm/y) according to a widely used classification [8]. Furthermore, the corrosion rate values obtained for untreated galvanized steel are approximate to those previously reported by other authors using similar NaCl solutions [9]. It is clearly observed that the inhibitor and the phosphating protected in a moderate way the galvanized steel, although the highest protection is shown by the chromated samples. It is worth mentioning the less steep curve slope of the chromated samples. Regarding the process kinetics, in the early immersion days the four curves show a moderate corrosion rate that diminished as the exposure time elapsed, indicating that corrosion rate was governed by diffusion processes. As the immersion time increased, a white layer of corrosion products appeared over the sample’s surfaces, except for the chromate ones; it restricted the access of the solution to the metallic zinc. The chromated samples did not show any visible deterioration.

Regarding the \( R_p \) variation as function of time (Figure 4), there is an evident difference between the higher values of the chromated samples and the lower values of the other surface conditions. Even at the end of the immersion period, the chromated samples values are still very high compared to those of the other surface conditions (<2500 Ω·cm²). In general, all samples depicted a very similar performance. In the case of phosphated samples, the \( R_p \) values were initially low, later they increased with the immersion time, and finally, after 110 days of immersion, they decreased again. This indicates that corrosion exists at the beginning of the immersion and later the \( R_p \) values increase due to the plugging of the spaces among the hopeite crystals with corrosion products. Afterwards, the movement of the electrolyte during the measurements uncovers the holes again. This behavior was congruent with the evolution of the \( E_{ocp} \) values. The \( R_p \) data were obtained in triplicate; the tendency shown in Figure 4 is representative of the three samples tested for each surface condition.

The \( E_{ocp} \) of the four surface conditions exhibited initial values around the known free open circuit potential of uncoated zinc in aerated saline solutions (~900 to ~1100 mV_{sc})}, presenting afterwards two trends (not shown): a permanency (plateau) in this potential range until the 134th day (chromated and inhibitor-treated samples) or a displacement towards nobler potentials as time elapses (phosphated and untreated samples). For these last two surface conditions, the increase of the \( E_{ocp} \) was due to the fact that the system evolved towards the uncoated steel \( E_{ocp} \) in this environment, as was demonstrated by the presence of abundant rust on the samples at the end of the immersion test.
Figure 3: Corrosion performance of galvanized steel with various surface conditions immersed in a 0.5 M NaCl solution during 134 days.

Figure 4: Evolution of $R_p$ of galvanized steel with the exposure time with various surface conditions immersed in a 0.5 M NaCl solution.

Figure 5: Potentiodynamic polarization curves of galvanized steel with various surface conditions immersed in a 0.5 M NaCl solution during 1 h.

Figure 6(a) to 6(c) for the phosphated, chromated and untreated galvanized samples after 1 h, respectively, whereas Figure 6(d) depicted the diagram for an untreated sample after 168 h. In these figures, the experimental diagrams are curves. The anodic branches show active zinc dissolution and a monotonically increase of current up to very steep slopes, which indicates a diffusion-controlled reaction rate. These branches also show that the different surface treatments increased the anodic dissolution rate with respect to untreated galvanized. This unexpected behavior may be due to the untreated sample's air drying after immersion in the NaCl solution the day previous to the potentiodynamic polarization measurements. It has been reported that air drying after immersion in a 5% NaCl solution drastically reduces the corrosion current of a zinc material. This decrease is attributed to the formation of a more compact corrosion products film as a result of drying [10]. In the cathodic curves, however, there exist a clear reduction in the values of the current density, from the untreated sample to the chromated one, which is exactly of an order of magnitude and that can be confirmed with the $i_{corr}$ values from Table 2, calculated with the potentiostat software. It is worth mentioning the low $i_{corr}$ values of all surface conditions and the fact that anodic slopes values decrease with corrosion rate.

The inhibitive action of chromating is manifested in this decrease of the oxygen rate reduction and has been previously reported by some authors [11, 12]. Moreover, the position of the extreme surface conditions, corresponding to the fastest and the slowest oxygen rate reduction (untreated and chromating, respcting) coincide with the results of weight loss test (Figure 3).

The impedance measurements were taken 1 and 168 h after the electrolyte had made contact with the sample surface. Typical Nyquist impedance diagrams are shown in Figures 6(a) to 6(c) for the phosphated, chromated and untreated galvanized samples after 1 h, respectively, whereas Figure 6(d) depicted the diagram for an untreated sample after 168 h. In these figures, the experimental diagrams are
Table 2: Electrochemical data of the tested materials after immersion in 0.5 M NaCl for 1 h.

| Condition     | $\beta_a$ (mV/decade) | $\beta_c$ (mV/decade) | $i_{corr}$ ($\mu$A/cm$^2$) | $E_{oc}/E_{corr}$ (mV SCE) | Corrosion rate (mpy) | Ch Sq  |
|---------------|-----------------------|------------------------|-----------------------------|-----------------------------|----------------------|--------|
| Untreated     | 88                    | 367                    | 11.9                        | $-1033/-1050$               | 7.0                  | $3.67e^{-6}$     |
| Inhibitor 5%  | 44                    | 224                    | 6.9                         | $-1046/-1080$               | 4.0                  | $3.75e^{-6}$     |
| Phosphated    | 52                    | 201                    | 1.8                         | $-1010/-1020$               | 1.0                  | $4.07e^{-6}$     |
| Chromated     | 35                    | 278                    | 1.1                         | $-1050/-1040$               | 0.7                  | $4.09e^{-6}$     |

Figure 6: Experimental and simulated Nyquist impedance diagrams of galvanized steel with various surface treatments immersed in a 0.5 M NaCl solution during 1 h (a) phosphated, (b) chromated, (c) untreated, and (d) untreated immersed during 168 h.

Figure 7: Equivalent electric circuit model used to fit the impedance data for treated and untreated galvanized samples.

The diagrams have different shapes and values at the low frequency limit. The phosphated and chromated samples exhibited larger values than the untreated ones. The samples treated with the organic inhibitor showed impedance diagrams very similar to those of untreated samples and are not shown. In general, the impedances measured after 1 h decreased after 168 h of contact with the electrolyte, except for the chromated condition.
According to the interpretation of this type of complex plane plots, the samples after one hour of immersion showed two frequency-dependent components: an initial high frequency semicircle, less defined for the untreated sample (Figure 6(c)), and a second component clearly defined in the low frequency range. This component is a greater second semicircle for phosphated and untreated surfaces and seemingly a diffusion tail (Warburg impedance) for chromate sample. It is generally accepted that both second components (semicircle or diffusion tail) appear as a consequence of a diffusion controlled corrosion process, related mainly with the oxygen reduction. An equivalent electric circuit for plots like these assumes that the diffusion process is much slower than the charge-transfer reaction and that diffusion is rate-controlling [14].

For untreated galvanized steel samples, the size of the second semicircle decreases as the immersion time increases and a capacitive branch appears in the low frequency range. Concerning the low frequency end observed in Figures 6(b) and 6(c), this behavior has been attributed, namely, to a potential drift [15]; this “tail back” is due probably to the effect of changing potential on the impedance response.

3.3. XRD of Corrosion Products and Salt Spray Test. Figure 8 presents the XRD spectra of corrosion products, the chemical composition of the detected compounds and the periods when they appeared. In all the samples, was identified zinc hydroxychloride \((\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O})\), known as Simonkolleite, and in most of the samples at least two varieties of \(\text{Zn(OH)}_2\) were detected.
Hopeite ($\text{Zn}_3(\text{PO}_4)_2 \cdot 4\text{H}_2\text{O}$) was detected in all the phosphated samples analyzed. Bracewellite (CrO(OH)) appeared only after 33 and 60 days of immersion on the surfaces of the chromated samples. It is a compound supposed to exist in accelerated chromium chromate coatings [16]. The peaks displacement in de XRD spectra are due to an inadequate sample alignment.

The presence of CrO(OH) after 33 days of immersion is due to the dissolution of the coating’s amorphous hexavalent compounds, remaining an insoluble trivalent chromium compounds layer. Composition depth profiles indicate that the hexavalent chromium compounds exist predominantly in the outer portion of the coating [16, 17]. The $\beta$-Zn(OH)$_2$ seems also to be present only in two specific periods, since the composition of zinc corrosion products in chloride solutions depends on the exposure time, so the hydroxides exists just temporarily, becoming hydroxychlorides as immersion time elapses, as it will be explained later.

Samples of the different surface conditions of galvanized steel were submitted to a salt spray test applying the ASTM B 117 method, which was carried out in triplicate. The appearance of the samples was evaluated at different time intervals with a maximum of 168 hours. By then all samples, except the chromated ones, were totally covered by white corrosion products and also presented incipient red corrosion. The chromated samples, on the other hand, appeared lustrous and only in one of them the dark orange color had disappeared (Figure 9).

### 4. Discussion

In the immersion test, the high initial corrosion rates, except for the chromated samples, are a consequence of the anodic dissolution of treated or untreated galvanized steel before forming the corrosion products. As long as immersion time increased, a white layer of corrosion products appeared over all samples’ surfaces, except on the chromated ones, and the high initial values of corrosion rate decreased. These white films, which resulted in being protector, got thicker with time, causing the corrosion rate to decrease even more.

Regarding the chromate samples, it has been reported that, as far as the surface preserves its dark orange, almost brown aspect, Cr$^{6+}$ ions have not been leached and the coating is still protecting the zinc substrate [18].

With regard to this white corrosion products layer, Feitknecht [19] previously reported the presence of zinc hydroxychloride and zinc hydroxide in immersion tests in a NaCl solution of the same concentration as that used in this study, and they also appear in the reaction sequence for zinc exposed in natural marine atmospheres [20]:

$$\text{Zn} \rightarrow \text{Zn(OH)}_2 \rightarrow \text{ZnCl}_2 \cdot n\text{Zn(OH)}_2$$  \hspace{1cm} (1)

with $n = 4$ for Simonkolleite. Several explanations for the apparent corrosion-inhibiting nature of Simonkolleite have been proposed, trying to justify the fact that the higher the amount of Simonkolleite in the corrosion products, the higher the resistance to corrosion [21]: (1) it has been considered that it is a more compact corrosion product than ZnO because the $c$ axis of the hexagonal close-packed structure of Simonkolleite is parallel to the film corrosion products growth direction, (2) it probably decreases the oxygen reduction rate on itself, (3) that is due to its low solubility product ($8.2 \times 10^{-76}$). On the other hand, crystalline and amorphous varieties of Zn(OH)$_2$ have been detected using cyclic voltammetry in chloride containing electrolytes [22]. It has been reported that the amorphous variety has a higher solubility product and is metastable.

The impedance diagrams, whose low frequency semi-circle or tail may indicate a finite thickness layer diffusion process, related mainly with the oxygen reduction, confirmed that the corrosive process is governed by diffusion, as it is also indicated by the weight loss and DRX results. According to Barranco et al. [23], it is likely that a complex mass transport mechanism intervenes in the system formed by the corrosive medium/corrosion products/metal, both in the liquid phase and through the corrosion products layer that coats the metallic surface.

Finally, the $R_p$ values of the samples, except for the chromated ones, were too low to ensure an acceptable protection. These values were inferior to 2500 $\Omega \cdot \text{cm}^2$ during
the test period and did not increase at the end of the test in spite of the rust presence in the phosphated and untreated galvanized samples.

5. Conclusions

The organic inhibitor does protect galvanized steel in a 0.5 M NaCl solution, even though the higher protection was provided by the chromate conversion coating. So, if the organic inhibitor will substitute chromating, other considerations should be kept in mind. The quiescent nature of the electrolyte definitely contributed to this protection, because it allowed the corrosion product layers to remain on the surface during the immersion time.

The corrosion rate of galvanized steel, with the different surface conditions, decreased with time. This decrease was associated with the formation and growth of adherent, white corrosion products layers on the metallic surface, mainly composed of zinc hydroxylchloride and zinc hydroxide. These layers limited the dissolved oxygen access to the treated or untreated surfaces of galvanized steel, causing the processes in the surface to be controlled by diffusion.

Regarding the chromate conversion coating, even though there was not a great amount of white corrosion products films, they were detected in XRD spectra. The higher protection provided by the this conversion coating to galvanized steel was mainly due to its own nature and it was confirmed by the polarization resistance results, and by the notable inhibition of the oxygen reduction reaction observed in the cathodic potentiodynamic polarization branches.

References

[1] X. G. Zhang, Corrosion and Electrochemistry of Zinc, Plenum Press, New York, NY, USA, 1996.

[2] J. F. McIntyre and R. J. Brent, "Tendencies of the pretreatment technology in next millennium," Pinturas y Acabados Industriales, vol. 42, no. 261, pp. 36–44, 2000.

[3] R. G. Buchheit, S. B. Mamidipally, P. Schmutz, and H. Guan, "Active corrosion protection in Ce-modified hydrotalcite conversion coatings," Corrosion, vol. 58, no. 1, pp. 3–14, 2002.

[4] S. A. Furman, "Novel coating technology replaces chromate in zinc galvanizing process," Materials Performance, vol. 49, no. 1, pp. 10–12, 2010.

[5] J. W. Bibber, "Chromium-free conversion coatings for zinc and its alloys," Journal of Applied Surface Finishing, vol. 2, no. 4, pp. 273–275, 2009.

[6] T. Peng and R. Man, "Rare earth and silane as chromate replacers for corrosion protection on galvanized steel," Journal of Rare Earths, vol. 27, no. 1, pp. 159–163, 2009.

[7] A. D. King and J. R. Scully, "Sacrificial anode-based galvanic and barrier corrosion protection of 2024-T351 by a Mg-rich primer and development of test methods for remaining life assessment," Corrosion, vol. 67, no. 5, Article ID 055004, 22 pages, 2010.

[8] M. G. Fontana, Corrosion Engineering, McGraw-Hill, Singapore, 3rd edition, 2008.

[9] M. Toga, P. Moyo, and D. J. Simbi, "Corrosion of galvanized steel in simulated mine water environments," in Proceedings 15th International Corrosion Congress, paper 231, 9 pages, Granada, Spain, 2002.

[10] M. Sagiyama, A. Hiraya, and T. Watanabe, "Electrochemical behavior of electrodeposited zinc-iron alloys in 5% NaCl solution," Journal of the Iron and Steel Institute of Japan, vol. 77, no. 2, pp. 244–250, 1991.

[11] R. L. Zeller and R. F. Savinell, "Interpretation of A.C. impedance response of chromated electrogalvanized steel," Corrosion Science, vol. 26, no. 5, pp. 389–399, 1986.

[12] A. A. O. Magalhaes, I. C. P. Margarit, and O. R. Mattos, "Electrochemical characterization of chrome coatings on galvanized steel," in Proceedings of the International Symposium on Electrochemical Impedance Spectroscopy (EIS '98), pp. 239–241, Rio de Janeiro, Brazil, 1998.

[13] F. De Florian, V. B. Miskovic-Stankovic, P. L. Bonora, and L. Fedrizzi, "Degradation of epoxy coatings on phosphatized zinc-electroplated steel," Corrosion, vol. 50, no. 6, pp. 438–446, 1994.

[14] C. Lin, T. Nguyen, and M. E. McNight, "Relation between A.C. impedance data and degradation of coated steel. 1. Effects of surface roughness and contamination on the corrosion behavior of epoxy-coated steel," Progress in Organic Coatings, vol. 20, no. 2, pp. 169–186, 1992.

[15] L. M. Callow and J. D. Scantlebury, "Electrochemical impedance on coated metal electrodes. Part 1: Polarization effects," JOCCA, vol. 64, no. 2, pp. 83–87, 1981.

[16] R. G. Buchheit and A. E. Hughes, "Chromate and chromate-free conversion coatings," in Corrosion: Fundamentals, Testing and Protection, vol. 13A of ASM Handbook, pp. 720–35, ASM International, Materials Park, Ohio, USA, 2003.

[17] I. Suzuki, Corrosion-Resistant Coatings Technology, Marcel Dekker, New York, NY, USA, 1989.

[18] W. Zhang and R. G. Buchheit, "Effect of ambient aging on inhibition of oxygen reduction by chromate conversion coatings," Corrosion, vol. 59, no. 4, pp. 356–362, 2003.

[19] W. Feitknecht, "Studies on the influence of chemical factors on the corrosion of metals," Chemistry and Industry, vol. 36, pp. 1101–1109, 1959.

[20] V. Kucera and E. Mattsson, "Atmospheric corrosion," in ASTM Manual on Corrosion Mechanisms, F. Mansfeld, Ed., pp. 211–284, Marcel Dekker, New York, NY, USA, 1987.

[21] X. G. Zhang, Corrosion and Electrochemistry of Zinc, Plenum Press, New York, NY, USA, 1996.

[22] C. M. Rangel and L. F. Cruz, "Zinc dissolution in lisbon tap water," Corrosion Science, vol. 33, no. 9, pp. 1479–1493, 1992.

[23] V. Barranco, S. Feliu Jr., and S. Feliu, "EIS study of the corrosion behaviour of zinc-based coatings on steel in quiescent 3% NaCl solution. Part 1: directly exposed coatings," Corrosion Science, vol. 46, no. 9, pp. 2203–2220, 2004.
Research Article

Interesting Behavior of *Pachycormus discolor* Leaves Ethanol Extract as a Corrosion Inhibitor of Carbon Steel in 1 M HCl: A Preliminary Study

Ramses Garcia Inzunza,1 Benjamin Valdez Salas,1 Rita Kharshan,2 Alla Furman,2 and Michael Schorr Wienner1

1 Laboratory of Corrosion and Material, Institute of Engineering, Autonomous University of Baja California, Blvd. Benito Juárez y Calle de la Normal, S/N, 21280 Mexicali, BC, Mexico
2 Cortec Corporation, 4119 White Bear Parkway, St. Paul, MN 55110, USA

Correspondence should be addressed to Ramses Garcia Inzunza, ramses.garcia@uabc.edu.mx

Received 27 June 2011; Accepted 30 August 2011

Academic Editor: Peter C. Okafor

Copyright © 2012 Ramses Garcia Inzunza et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The purpose of this paper is to evaluate the inhibitive action of an ethanol extract from the leaves of *Pachycormus discolor* (EEPD) on the corrosion of carbon steel in 1 M HCl at different temperatures; gravimetric method and electrochemical tests were conducted. Potentiodynamic polarization was used at room temperature and resistance polarization at different temperatures. Thermodynamic adsorption parameters are shown in order to demonstrate the spontaneous adsorption. The inhibition of EEPD was performed via adsorption of the extract species on the carbon steel surface. The ethanol extract obeys Langmuir adsorption isotherm. Potentiodynamic polarization results indicate that the ethanol extract acts as a mixed type inhibitor. The results revealed that the inhibition efficiency (IE) of EEPD increases (when the concentration is increased). Phytochemical and FTIR analyses are also presented in this work. It was found that the IE increases with the temperature in a 2.0% v/v solution which showed 94.52% IE at 25°C and 97.89% at 75°C.

1. Introduction

Acid pickling is an accepted treatment of a metallic surface to remove impurities, stains, and steel rust with an acid solution, such as hydrochloric acid (HCl) and sulphuric acid (H₂SO₄), usually before subsequent processing such as extrusion, rolling, painting, galvanizing or plating with zinc, aluminum, and so forth. However, inhibitor application is required since the corrosive media impairs the metal used [1].

Another important treatment is the well acidizing that is achieved by pumping hydrochloric acid into the well which is useful to dissolve limestone, dolomite, and calcite cement between the sediment grains of the reservoir rocks. In order to protect the integrity of the already completed well, inhibitor additives are introduced to the well to prohibit the well steel casting corroding with the acid.

Today the use of corrosion inhibitors have been expanded, they range from rare earth elements [2–4] to organic compounds [5–9] since they are ecofriendly and harmless to the environment.

There are natural antioxidants used as organic corrosion on inhibitor or extract from aromatic herbs, species, and medicinal plants [10, 11].

The purpose of the present work is to show an alternative corrosion inhibitor based on endemic plant of Baja California, Mexico that will control the corrosion problem and will not damage the environment due to its biodegradable properties.

2. Experimental Procedure

2.1. Preparation of Carbon Steel Specimen. Specimens of carbon steel 1018 (AISI) were mechanically cut into coupons of size 5 cm × 1.2 cm × 0.2 cm and were provided with a hole of a uniform diameter to facilitate the suspension of
the coupons in the test solution for the application of the weight loss method. For electrochemical studies, cylindrical carbon steel 1018 were used as a working electrode, with a 1 cm² area exposed and the rest being covered. The chemical composition of this steel is 0.15–0.20% C, 0.60–0.90% Mn, 0.04 (max) P, 0.05 (max) S and the remainder is Fe. The working electrode was polished with sand papers from 100 to 600 grades and subsequently washed with methanol and then stored in a desiccator [12]. Accurate weight of the samples was obtained using an electronic balance METTLER TOLEDO.

2.2. Preparation of the Plant Extract. The leaves of the Pachycormus discolor were taken, dried in a desiccator SECADOR, and then well grounded into powder. Then 70 gr of this dry plant material remains in maceration with n-hexane, three times, at a rate of 20 volumes of solvent per 1 gr mass of plant material, kept stirred at room temperature for at least 4 hours each time. Filtering was met on the three portions of the extract. The distillation of solvents leads to a waxy mass, which was discarded for the study of corrosion inhibition. Immediately after, the same plant material was kept under stirring three times for 6 hours at room temperature (25°C) at a rate of 10 volume of Ethanol (80% v/v) per 1 gr of dry and shattered leaves in order to extract the active components. The three portions were mixed, and then most of the solvent was eliminated by azeotropic distillation of ethanol at reduced pressure, prolonging the necessary distillation and/or increasing depression as possible. Do not exceed 45°C.

Concentrated solutions of corrosion inhibitor were prepared from the ethanol extract and were added to 1 M HCl at the range of 0.005% to 2.0% (v/v).

2.3. Infrared Analysis. IR analysis was carried out using a PERKIN-ELMER100 FTIR spectrometer to determine the functional groups of the ethanol extract.

2.4. Phytochemical Screening. Phytochemical screening was carried out on the ethanol extract of the leaves of Pachycormus discolor [13]. The plant extract were screened for various compounds.

2.5. Weight Loss Method. The polished and preweighed carbon steel coupons of uniform size were tied with threads and suspended in 50 mL test solutions (in duplicate), with and without the inhibitor at 1% and 2% (v/v) concentrations for various time intervals. The coupons were washed, dried, and weighed. Then the weight loss was calculated.

The parameters used in this study are the following:

(1) Time: 1.5 h, 4.5 h, 6.5 h, 21 h, 48 h, 109 h.
(2) Inhibitor concentration: 1%, 2% (v/v).

The corrosion rate of the coupon of carbon steel 1018 was determined according to the loss in weight as a function of time.

\[
\rho_{corr} = \frac{m_1 - m_2}{At},
\]

Where, \(m_1\) and \(m_2\) are the weight before and after the corrosion, respectively. \(A\) is the total area of the coupon and \(t\) the corrosion time. From this data, inhibition efficiency (IE) was calculated.

The inhibition efficiency is given by the following:

\[
IE(\%) = \left(\frac{\rho_{corr}^* - \rho_{corr}}{\rho_{corr}}\right) \times 100,
\]

where, \(\rho_{corr}\) is the corrosion rate without inhibitor. \(\rho_{corr}^*\) is the corrosion rate with inhibitor.

2.6. Electrochemical Measurements. The electrochemical analysis was performed using a three electrode system [14]. The carbon steel working electrode, saturated calomel (SCE) reference electrode, and high purity graphite counter electrodes were used in the corrosion cell. Measurements were performed using a Gamry Instrument Potentiostat/Galvanostat/ZRA PC 4/300 and DC 105 Corrosion Technique software.

The working electrode was polished with 120 to 600 grit sand paper, washed with methanol, and dried. Instead of a salt bridge, a Luggin capillary arrangement was used to keep SCE on the working electrode to avoid the ohmic contribution. The polarization plots were obtained 10 minutes after the working electrode was immered in the solution using Tafel Technique at room temperature (23°C). Applying a scan rate of 1 mV/s in a range from −250 mV to +250 mV versus corrosion potential \(E_{corr}\) of the working electrode measured against SCE.

The inhibition efficiency was calculated using the formula [15]

\[
IE(\%) = \left(\frac{I_{corr} - I_{corr}^*}{I_{corr}}\right) \times 100,
\]

where \(I_{corr}\) is corrosion current without inhibitor. \(I_{corr}^*\) is corrosion current with inhibitor.

Values of linear polarization resistance \(R_p\) were obtained using the polarization resistance technique at 23°C, 40°C, 60°C, and 75°C. The scan rate was 0.125 mV/s in a range from −0.20 to 0.20 mV versus corrosion potential \(E_{corr}\) of the working electrode measured against SCE.

The inhibition efficiency was calculated using the formula [16]

\[
IE(\%) = \left(\frac{R_{p_{blank}} - R_{p_{nh}}}{R_{p_{nh}}^*}\right) \times 100,
\]

where \(R_{p_{nh}}\) is the polarization resistance in the presence of inhibitor at each temperature. \(R_{p_{blank}}^*\) is the polarization resistance in the absence of inhibitor at each temperature.

The gravimetric and electrochemical corrosion tests were conducted in accordance with the practices recommended in ASTM standards G3 and G31 [17, 18].

3. Results and Discussion

3.1. Weight Loss Studies. The inhibitor was tested at two different concentrations 1% and 2% (v/v); their corresponding
Table 1: Corrosion rates as a function of immersion time with and without *Pachycormus discolor* ethanol extract.

| Inhibitor concentration % (v/v) | Immersion time (hr) | Corrosion rates (mg·cm\(^{-2}\)·hr\(^{-1}\)) |
|---------------------------------|---------------------|---------------------------------------------|
|                                 | 1.5                 | 4.5                                         | 6.5 | 21  | 48  | 109 |
| Blank                           | 0.78                | 0.51                                        | 0.57| 0.57| 0.48| 0.57|
| 1.0                             | 0.47                | 0.17                                        | 0.14| 0.08| 0.06| 0.05|
| 2.0                             | 0.18                | 0.12                                        | 0.09| 0.04| 0.03| 0.03|

Table 2: Inhibition efficiency as a function of immersion time and concentration of *Pachycormus discolor* ethanol extract.

| Inhibitor concentration % (v/v) | Immersion time (hr) | Inhibition efficiency (%) |
|---------------------------------|---------------------|---------------------------|
|                                 | 1.5                 | 4.5                       | 6.5 | 21 | 48  | 109 |
| 1.0                             | 39.59               | 66.09                     | 74.34|84.61|86.59|89.88|
| 2.0                             | 76.07               | 77.40                     | 83.79|92.47|93.50|93.50|

corrosion rates and inhibition efficiencies are presented in Tables 1 and 2, respectively. The corrosion rate decreases as the inhibitor concentration increases.

The corrosion rate diminishes 6 to 9 times after about 109 hours of immersion time, and the data are shown in Table 1.

The addition of inhibitors increases the IE, irrespective of the time of immersion. This may be due to the adsorption of phytochemical constituents of the extracts on the metal surface. The results related with the effect of time of different inhibitor concentrations for carbon steel 1018 immersed in 1 M HCl are also shown in Table 2. The inhibition efficiency is higher when the immersion time is increasing. The highest efficiency (93.50%) was obtained with the 2% v/v of inhibitor concentration after 109 hr testing.

3.2. Polarization Studies. The effect of the inhibitor concentration is shown in Figure 1 which presents the anodic and cathodic potentiodynamic polarization measurements of carbon steel 1018 in 1 M HCl solution at room temperature with EEPD. The electrochemical corrosion parameters: current density ($i_{corr}$), cathodic and anodic Tafel slopes ($\beta_c$ and $\beta_a$), and the percentage efficiency (IE) for the corrosion inhibition of carbon steel 1018 in 1 M HCl at room temperature at different concentrations of the plant extract are given in Table 3.

Polarization studies revealed that the corrosion current density ($i_{corr}$) decreased noticeably with the addition of the extract. Further, there was an anodic shift of the $E_{corr}$ value from $-471$ mV (blank) to $-432$ mV at 2% v/v indicating that the *Pachycormus discolor* leaves extracts acted as an anodic inhibitor [19] for carbon steel 1018 in 1 M HCl, which was supported by the gradual and significant decrease of the anodic Tafel slope, $\beta_a$ is 113.9 mV/decade of blank to 71.0 mV/decade at 2% v/v. In lower inhibitor concentrations, the values of the cathodic Tafel slopes were decreasing too, though not markedly. This means that the extract must have acted by blocking anodic sites and also cathodic site to some extent, and the extract contained the active molecules which behaved as mixed type of inhibition.

Figure 1: Anodic and cathodic plots of carbon steel 1018 in 1 M HCl solution in the absence and presence of various concentrations of *Pachycormus discolor* ethanol extract.

Figure 2: Langmuir adsorption isotherm of EEPD on carbon steel 1018 surface in 1 M HCl.
Table 3: Polarization parameters for carbon steel in 1 M HCl at room temperature containing various concentrations of *Pachycormus discolor* ethanol extract.

| Concentration (v/v) % | $E_{corr}$ (mV/SCE) | $\beta_c$ (mV/dec) | $\beta_a$ (mV/dec) | $i_{corr}$ ($\mu$A/cm$^2$) | IE % |
|-----------------------|----------------------|---------------------|---------------------|-----------------------------|------|
| Blank                 | −471.0               | 125.8               | 113.9               | 442.0                       | —    |
| 0.005                 | −495.0               | 136.7               | 129.1               | 284.0                       | 35.7 |
| 0.001                 | −490.0               | 116.9               | 111.0               | 237.0                       | 46   |
| 0.1 0                 | −492.0               | 108.3               | 94                  | 139                         | 68.55|
| 0.5 0                 | −465.0               | 119.2               | 80.9                | 114.0                       | 74.20|
| 1.0                   | −484.0               | 108.8               | 78.4                | 69.20                       | 84.34|
| 2.0                   | −432.0               | 167.5               | 71.0                | 24.20                       | 94.52|

Table 4: Polarization resistance values for carbon steel in 1 M HCl at different temperatures obtained by electrochemical measurements in the absence and presence of EEPD in various concentrations.

| Inhibitor concentration (v/v) % | Temperature (°C) | Polarization resistance (Ω) | Inhibition efficiency (%) |
|---------------------------------|------------------|-----------------------------|--------------------------|
| Blank                           | 23               | 43.865                      |                          |
|                                 | 40               | 17                          |                          |
|                                 | 60               | 5.16                        |                          |
|                                 | 75               | 2.067                       |                          |
| 0.005                           | 23               | 68.22                       | 35.70                    |
|                                 | 40               | 21.03                       | 19.14                    |
|                                 | 60               | 6.008                       | 14.11                    |
|                                 | 75               | 2.989                       | 30.86                    |
| 0.01                            | 23               | 85.60                       | 48.70                    |
|                                 | 40               | 31.07                       | 45.28                    |
|                                 | 60               | 7.346                       | 29.75                    |
|                                 | 75               | 3.174                       | 34.87                    |
| 0.1                             | 23               | 99.88                       | 56.08                    |
|                                 | 40               | 32.19                       | 47.18                    |
|                                 | 60               | 8.353                       | 38.22                    |
|                                 | 75               | 3.395                       | 39.11                    |
| 0.5                             | 23               | 153.6                       | 71.44                    |
|                                 | 40               | 34.86                       | 51.23                    |
|                                 | 60               | 9.527                       | 45.83                    |
|                                 | 75               | 4.591                       | 54.97                    |
| 1.0                             | 23               | 236.2                       | 81.42                    |
|                                 | 40               | 101.4                       | 83.23                    |
|                                 | 60               | 19.54                       | 73.59                    |
|                                 | 75               | 5.56                        | 62.82                    |
| 2.0                             | 23               | 620.2                       | 92.95                    |
|                                 | 40               | 574.4                       | 97.00                    |
|                                 | 60               | 148.4                       | 96.52                    |
|                                 | 75               | 115.5                       | 97.89                    |

3.3. Effect of Temperature. The effect of the temperature on the corrosion rate of carbon steel 1018 in the absence and in the presence of various inhibitors concentrations was studied at a temperature range from 23°C to 75°C, using the polarization resistance electrochemical measurement (Table 4). It was found that the polarization resistance in the absence and in the presence of inhibitor decreases with the increase in temperature, but the polarization resistance value is much greater for an inhibited acid solution than the uninhibited acid solution.

Regarding the 2% v/v inhibitor concentration, it shows an interesting behavior since the values of polarization resistance increase with the increase in temperature.
3.4. Adsorption Isotherms. The primary step in the mechanism of action of the inhibitors in acid solutions is generally the adsorption on the metal surface, which is usually oxide free in acid solutions. Bockris states that [24] the adsorption of an organic substance onto the metal surface can be expressed in the following exchanger reaction:

\[
\text{Org}_{\text{sol}} + n\text{H}_2\text{O}_{\text{ads}} \leftrightarrow \text{Org}_{\text{ads}} + n\text{H}_2\text{O}_{\text{sol}},
\]

where \( n \) is the number of water molecules displaced of the metal surface by one molecule of the adsorbed inhibitor; the value of \( n \) depends on the transversal section of the organic molecule area with respect to the water molecule. The adsorption of the organic molecules occurs because the interaction between the energy on the metal surface and the inhibitor is greater than the interaction of the energy on the metal surface and the water molecules. When the equilibrium of the process described in (5) is reached, it is possible to obtain diverse expressions of the adsorption isotherm plots, and thus, the degree of surface coverage (\( \theta = \text{IE(\%)} / 100 \)) can be plotted as a function of the inhibitor concentration under test.

From Table 4, it can be concluded that \( \theta \) increases with the inhibitor concentration; this is attributed to more adsorption of inhibitor molecules onto the carbon steel surface. The surface coverage values (\( \theta \)) for different concentrations of the inhibitor in an acid medium have been evaluated from the polarization resistance data. The data was plotted graphically to obtain a suitable adsorption isotherm (Figure 2). The Langmuir adsorption isotherm [25] was applied to analyze its mechanism by the following:

\[
\frac{C}{\theta} = \frac{1}{K} + C,
\]

where \( C \) is the inhibitor concentration in mL L\(^{-1}\) in the electrolyte, and \( K \) (mL\(^{-1}\) L) is the equilibrium constant for the adsorption/desorption process.

The adsorption parameters from Langmuir adsorption isotherms are estimated and given in Table 5. It indicates that the inhibitor obeys the Langmuir model since the experimental data presents adequate curve fittings for the applied adsorption isotherms; the correlation coefficients \( (r^2) \) were in the range: \( 0.993 \geq r^2 \geq 0.923 \) and also the slopes tend to be close to a unit.

The \( K \) value demonstrates that it is affected by the temperature; when the temperature increases from 23°C to 40°C, \( K \) decreases as a result, on the other hand, when the temperature increased from 65 to 75, the value of \( K \) increased as well; however, the value \( K \) that is obtained at room temperature (23°C) is much greater than the values at other temperatures. This means that the strength of adsorption is higher.

3.5. Thermodynamic Adsorption Isotherms. Thermodynamic adsorption data, such as change in free energy (\( \Delta G_{\text{ads}} \)), enthalpy of adsorption (\( \Delta H_{\text{ads}} \)), and the entropy of adsorption (\( \Delta S_{\text{ads}} \)), can be calculated depending on the estimated values of \( K \) from adsorption isotherms [26] at different temperatures as follows.

The \( \Delta G_{\text{ads}} \) values at all studied temperatures can be calculated from the following [27]:

\[
K = \frac{1}{C_{\text{H}_2\text{O}}} \exp \left( \frac{\Delta G_{\text{ads}}}{RT} \right),
\]

where \( C_{\text{H}_2\text{O}} \) is the concentration of water molecules (in mL L\(^{-1}\)) at the metal/solution interface. Then, the \( \Delta G_{\text{ads}} \) obtained values are plotted versus \( T \) (Figure 3) in accordance with the basic equation [28]:

\[
\Delta G_{\text{ads}} = \Delta H_{\text{ads}} - T\Delta S_{\text{ads}}.
\]

A straight line of interception represents the \( \Delta H_{\text{ads}} \) values. By introducing the values in (8), the \( \Delta S_{\text{ads}} \) values are calculated at all studied temperatures. As it can be observed in Figure 3,
a segmented straight line of three opposite slopes was obtained in 1 M HCl indicating the existence of three sets of adsorption sites with different energetic enthalpies of adsorption, leading to the occurrence of a comprehensive adsorption.

The negative values of $\Delta G_{\text{ads}}$ indicate that the adsorption of EEPD on the carbon steel 1018 surface is an spontaneous process [29, 30].

The most negative value of $\Delta G_{\text{ads}}$ occurs at room temperature ($23^\circ C$); furthermore, the negative value of $\Delta H_{\text{ads}}$ indicates that the adsorption of the inhibitor’s molecules is an exothermic reaction.

In addition, $\Delta G_{\text{ads}}$ decreases (becomes more negative) with an increasing temperature in the range from 60\(^\circ\)C to 75\(^\circ\)C; it also shows the positive value of $\Delta H_{\text{ads}}$, indicating the occurrence of an endothermic process at which increasing the temperature facilitates the adsorption of the molecules.

The negative values of $\Delta S_{\text{ads}}$ (Table 6) are accompanied with the exothermic adsorption process, which agrees with the expected event; when the adsorption is an exothermic process, it must be accompanied by a decrease (becomes more negative) in the entropy change [31].

Moreover, the value of the adsorption heat ($\Delta H_{\text{ads}}$) gives valuable information about the mechanism of the inhibitor adsorption. According to the listed values of $\Delta H_{\text{ads}}$ (Table 6) it can be explained by the following.

Both endothermic ($\Delta H_{\text{ads}} = 7.6593\text{ kJ mol}^{-1}$) and exothermic ($\Delta H_{\text{ads}} = -36.649\text{ kJ mol}^{-1}$) adsorption behaviors were determined depending on the exact range of the applied temperatures. The average of $\Delta H_{\text{ads}}$ is about $-22.15\text{ kJ mol}^{-1}$ which is larger than the common physical adsorption heat, but smaller than the common chemical adsorption heat [32]; it probably indicates that both physical and chemical adsorption took place.

3.6. Infrared Analysis. The IR spectra (Figure 4) of the extract of Pachycormus discolor contain bands which correspond to: phenolic hydroxyl groups (3379.39 cm\(^{-1}\)); carbonyl groups (1715 cm\(^{-1}\)), aromatic C=C bending (1613 cm\(^{-1}\)), C=H out of plane bending (878.79 and 750.78 cm\(^{-1}\)), two bands appear for the C–O stretching vibrations in esters in 1324 and 1205 cm\(^{-1}\).

3.7. Phytochemical Screening. Phytochemical screening was carried out on the ethanol extract of the leaves of Pachycormus discolor. The plant extracts were screened for various compounds (Table 7).

Several papers that have been published show that compounds such as alkaloids may be responsible for the corrosion inhibitive effect in a hydrochloric acid medium [33, 34]. Other corrosion inhibitors [35, 36] contain lactones, saponins, polyphenols, and they are also effective.

In the present case, the mixture of the different compounds can be responsible for the corrosion inhibitive effect. There is no data about the main compound on the ethanol extract of the leaves of Pachycormus discolor.

4. Conclusions

(i) The Ethanol extract of the leaves of Pachycormus discolor acts as a mixed type inhibitor for the corrosion of carbon steel 1018 in 1 M HCl.
(ii) Weight loss studies, polarization studies, electrochemical and polarization resistance measurements are in good agreement.

(iii) The effect of immersion time of EEPD showed maximum efficiency in 109 hours at room temperature at 2% v/v inhibitor concentration.

(iv) The polarization resistance increases with the amount of the inhibitor.

(v) The adsorption of *Pachycormus discolor* on the carbon steel 1018 surface in hydrochloric acid obeys the Langmuir adsorption isotherm model.

(vi) The effect of temperature revealed that both physical and chemical adsorption take place.

(vii) The negative value of free energy change of adsorption indicates that the adsorption of the inhibitor on carbon steel 1018 surface was spontaneous.

(viii) The inhibition efficiency of EEPD at room temperature is greater than at higher temperatures, except at 2% v/v inhibitor concentration.

References

[1] H. H. Uhlig, “Corrosión y control de corrosión,” Urmo, 1979.

[2] B. T. Kilbourn, “Ressources en lanthanides et yttrium, production de composés de ces éléments, utilisations dans les céramiques de haute technologie,” *Ceramic Engineering and Science Proceedings*, vol. 6, no. 9-10, pp. 1331–1341, 1985.

[3] M. Bethencourt, F. J. Botana, J. J. Calvino, M. Marcos, and M. A. Rodríguez-Chacón, “Lanthanide compounds as environmentally-friendly corrosion inhibitors of aluminium alloys: a review,” *Corrosion Science*, vol. 40, no. 11, pp. 1803–1819, 1998.

[4] M. A. Arenas, A. Conde, and J. I. de Damborenea, “Cerium: a suitable green corrosion inhibitor for tinplate,” *Corrosion Science*, vol. 44, no. 3, pp. 511–520, 2002.

[5] S. M. El-Sawy, Y. M. Abu-Ayana, and F. A. Abdel-Mohdy, “Some chitin/chitosan derivatives for corrosion protection and waste water treatments,” *Anti-Corrosion Methods and Materials*, vol. 48, no. 4, pp. 227–234, 2001.

[6] E. Cano, P. Pinilla, J. L. Polo, and J. M. Bastidas, “Copper corrosion inhibition by fast green, fuchsin acid and basic compounds in citric acid solution,” *Materials and Corrosion*, vol. 54, no. 4, pp. 222–228, 2003.

[7] D. J. Choi, Y. W. Kim, and J. G. Kim, “Development of a blended corrosion, scale, and microorganism inhibitor for open recirculating cooling systems,” *Materials and Corrosion*, vol. 52, no. 9, pp. 697–704, 2001.

[8] G. Moretti, F. Guidi, and G. Grion, “Tryptamine as a green iron corrosion inhibitor in 0.5 M deaerated sulphuric acid,” *Corrosion Science*, vol. 46, no. 2, pp. 387–403, 2004.

[9] S. A. Abd El-Maksoud, “The effect of organic compounds on the electrochemical behaviour of steel in acidic media. A review,” *International Journal of Electrochemical Science*, vol. 3, pp. 528–555, 2005.

[10] P. B. Raja and M. G. Sethuraman, “Natural products as corrosion inhibitor for metals in corrosive media—a review,” *Materials Letters*, vol. 62, no. 1, pp. 113–116, 2008.

[11] C. Chandler, M. Khodash, and A. Furman, “Sugar beets against corrosion,” *Corrosion Reviews*, vol. 20, no. 4-5, pp. 379–390, 2002.

[12] A. Y. El-Etre and Z. El-Tantawy, “Inhibition of metallic corrosion using ficus extract,” *Portugaliae Electrochimica Acta*, vol. 24, pp. 347–356, 2006.

[13] A. Lourenço, L. Cruz Lopez, and A. San Feliciano, “Extracción, Fraccionamiento y Aislamiento de Compuestos Activos,” in *Programa Iberoamericano de Ciencia y Tecnología para el desarrollo (CYTED ’10)*, Universidade Nova de Lisboa, Portugal. Universidade Metodista de Piracicaba, Brasil. Universidad de Salamanca, España, 2010.

[14] ASTM G5-94, “Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements,” 2004.

[15] M. Scendo, “Inhibition of copper corrosion in sodium nitrate solutions with nontoxic inhibitors,” *Corrosion Science*, vol. 50, no. 6, pp. 1584–1592, 2008.

[16] M. Bouklah and B. Hammouti, “Thermodynamic characterisation of steel corrosion for the corrosion inhibition of steel in sulphuric acid solutions by Artemisia,” *Portugaliae Electrochimica Acta*, vol. 24, pp. 461, 2006.

[17] ASTM G3-89, “Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing,” 2010.

[18] ASTM G31-72, “Standard Practice for Laboratory Immersion Corrosion Testing of Metals,” 2004.

[19] O. L. Rigg Jr., *Corrosion Inhibitors*, Edited by C. C. Nathan, NACE, Houston, Tex, USA, 1973.

[20] B. I. Ita and O. E. Offiong, “The study of the inhibitory properties of benzoil, benzil, benzoin-(4-phenylthiolicarbazone) and benzil-(4-phenylthiosmicarbazone) on the corrosion of mild steel in hydrochloric acid,” *Materials Chemistry and Physics*, vol. 70, no. 3, pp. 330–335, 2001.

[21] S. N. Raicheva, E. Sokolova, and A. E. Stoyanova, “Some factor of the inhibitory effect of nitrogen-and sulphur-containing organic compounds on steel corrosion,” *Bulgarian Chemical Communications*, vol. 27, p. 363, 1994.

[22] M. M. Singh and A. Gupta, “Inhibition of mild steel corrosion in formic acid solution,” *Bulletin of Electrochemistry*, vol. 12, no. 9, pp. 511–516, 1996.

[23] M. H. Wahdan, A. A. Hermas, and M. S. Morad, “Corrosion inhibition of carbon-steel by propargytriphenylphosphonium bromide in H2SO4 solution,” *Materials Chemistry and Physics*, vol. 76, no. 2, pp. 111–118, 2002.

[24] J. O. M. Rockris and D. A. J Swinkel, “Adsorption of naphtalene on solid metal electrodes,” *Journal of The Electrochemical Society*, vol. 111, p. 735, 1964.

[25] I. Langmuir, “The constitution and fundamental properties of solids and liquids. II. Liquids,” *Journal of the American Chemical Society*, vol. 39, p. 1848, 1947.

[26] E. A. Noor, “Temperature effects on the corrosion inhibition of mild steel in acidic Solutions by aqueos extract of Fenugreek leaves,” *International Journal of Electrochemical Science*, vol. 2, pp. 996–1017, 2007.

[27] E. Khamsi, “Effect of temperature on the acidic dissolution of steel in the presence of inhibitors,” *Corrosion*, vol. 46, no. 6, pp. 476–484, 1990.

[28] A. A. El-Awady, B. A. Abd-El-Nabey, and S. G. Aziz, “Kinetic-thermodynamic and adsorption isotherms analyses for the inhibition of the acid corrosion of steel by cyclic and open-chain amines,” *Journal of The Electrochemical Society*, vol. 139, no. 8, pp. 2149–2154, 1992.

[29] M. Elachouri, M. S. Hajji, M. Salem et al., “Some nonionic surfactants as inhibitors of the corrosion of iron in acid chloride solutions,” *Corrosion*, vol. 52, no. 2, pp. 103–108, 1996.
[30] B. V. Savithri and S. M. Mayanna, “Tetrabutyl ammonium iodide, cetyl pyridinium bromide and cetyl trimethyl ammonium bromide as corrosion inhibitors for mild steel in sulphuric acid,” *Indian Journal of Chemical Technology*, vol. 3, no. 5, pp. 256–258, 1996.

[31] J. M. Thomas and W. J. Thomas, *Introduction to the Principles of Heterogeneous Catalysis*, Academic Press, London, UK, 5th edition, 1981.

[32] G. Mu, X. Li, and G. Liu, “Synergistic inhibition between tween 60 and NaCl on the corrosion of cold rolled steel in 0.5 M sulfuric acid,” *Corrosion Science*, vol. 47, no. 8, pp. 1932–1952, 2005.

[33] P. B. Raja and M. G. Sethuraman, “Studies on the inhibitive effect of Datura stramonium extract on the acid corrosion of mild steel,” *Surface Review and Letters*, vol. 14, no. 6, pp. 1157–1164, 2007.

[34] M. Lebrini, F. Robert, and C. Roos, “Alkaloids extract from Palicourea guianensis plant as corrosion inhibitor for C38 steel in 1 M hydrochloric acid medium,” *International Journal of Electrochemical Science*, vol. 6, no. 3, pp. 847–859, 2011.

[35] M. Shyamala and P. K. Kasthuri, “The inhibitory action of the extracts of Adathodavasica, Eclipsa alba and Centellaasiatica on the Corrosion of Mild Steel in Hydrochloric acid medium—a comparative study,” *International Journal of Corrosion*, vol. 2012, Article ID 852827, 13 pages, 2012.

[36] I. E. Uwah, P. C. Okafor, and V. E. Ebiekpe, “Inhibitive action of ethanol extracts from Nauclea latifolia on the corrosion of mild steel in H₂SO₄ solutions and their adsorption characteristics,” *Arabian Journal of Chemistry*. In press.
Research Article

Inhibitory Action of *Artemisia annua* Extracts and Artemisinin on the Corrosion of Mild Steel in H$_2$SO$_4$ Solution

P. C. Okafor, V. E. Ebiekpe, C. F. Azike, G. E. Egbung, E. A. Brisibe, and E. E. Ebenso

1 Corrosion and Electrochemistry Research Group, Department of Pure and Applied Chemistry, University of Calabar, PMB 1115, Calabar, Nigeria
2 Headquarters Eastern Naval Command, Navy Road, Calabar, Nigeria
3 Department of Biochemistry, University of Calabar, PMB 1115, Calabar, Nigeria
4 Department of Genetics and Biotechnology, University of Calabar, PMB 1115, Calabar, Nigeria
5 Department of Chemistry, North-West University, Mafikeng Campus, Private Bag X2046, Mmabatho 2735, South Africa

Correspondence should be addressed to P. C. Okafor, peter.okafor@fulbrightmail.org

Received 24 June 2011; Accepted 9 August 2011

1. Introduction

Present trend in research on environmentally friendly corrosion inhibitors is taking us back to exploring the use of natural products as possible sources of cheap, nontoxic, and ecofriendly corrosion inhibitors. These natural products are either synthesized or extracted from aromatic herbs, spices, and medicinal plants. Of increasing interest is the use of medicinal plant extracts as corrosion inhibitors for metals in acid solutions. This is because these plants serve as incredibly rich sources of naturally synthesized chemical compounds that are environmentally acceptable, inexpensive, readily available, and renewable sources of materials [1, 2]. These chemicals include alkaloids, flavonoids, terpenoids, glycosides, tannins, saponins, fats and oils, and carbohydrates, and so forth [3–11]. The complex composition of phytochemicals in plant extracts makes it difficult to attempt to assign the inhibition ability to a particular constituent. Some researchers have, however, ascribed the inhibition efficiency of these medicinal plants to their active components used for medical purposes [3]. We have recently attempted to assign the inhibition ability to some constituents by studying the inhibitive effect of different parts of a given plant with variable concentrations of the phytochemicals on acid corrosion [4–7]. Another most probable method would be the use of different solvents in the extraction process and comparing their inhibition efficiencies. This is yet to be explored in most of the reported work on corrosion inhibition of plant extracts.

*Artemisia annua* is native to Asia, most probably China, but is currently cultivated in many countries including Nigeria, mainly as a source of artemisinin, an important natural sesquiterpene lactone with antimalarial effect against susceptible and multidrug resistant *Plasmodium* spp. The plant is a large shrub often reaching more than 2.0 m in height, usually single-stemmed with alternate branches. The leaves are deeply dissected and range from 2.5 to 5 cm in length.

*A. annua* contains at least 20 known sesquiterpenes including artemisinin (arteannuin A), arteannuin B, artemisitene, and artemisinin acid. Artemisinin content varies from as low as 0.01 to 1.5% of plant dry weight depending
on various factors such as the plant’s origin, its stage of development, and the cultivation conditions [12–14]. This compound, isolated more than 50 years ago from *A. annua* by Chinese scientists searching for novel antimalarial drugs, has an unusual trioxane structure with seven stereogenic centers and tetracyclic framework (Figure 1) but lacks a nitrogen containing heterocyclic ring which is found in most antimalarial compounds. *A. annua* has also been shown to have a high content of flavonoid compounds, including the newly reported C-glycosyl flavonoids as a possible component of the antioxidant and antiviral activity [15].

In view of our interest in environmentally friendly corrosion inhibitor, the present study reports the inhibitory effect of acid (AEAA), ethanol (EEAA), and toluene (TEAA) extracts from *A. annua* and artemisinin (ATS) on mild steel corrosion in *H*2*SO*4 solutions using the weight loss and gasometric techniques.

### 2. Experimental Methods

The mild steel sheets used in this present work have the composition presented in Table 1. Before measurements, the mild steel coupons were mechanically polished with series of emery paper of variable grades starting with the coarsest and proceeding in steps to the finest (600) grade, degreased with absolute ethanol, dipped into acetone, and air-dried. The hydrogen evolution experiments were conducted on mild steel coupons of dimension 1.33 × 0.08 × 5.0 cm (with a surface area of 14.008 cm²), and, for the weight loss study, mild steel specimens of size 4.0 × 0.08 × 5.0 cm (with a surface area of 41.44 cm²) were used.

**2.1. Preparation of Inhibitor Solutions.** Dried leaves of *Artemisia annua* and artemisinin (ATS) used for this work were gotten from the Department of Genetics and Biotechnology, University of Calabar, Calabar, Nigeria. The leaves were ground into powder form. 80.0 g of the powder was extracted continually with 250 cm³ of the appropriate solvent (ethanol and toluene for the ethanol and toluene extracts, resp.) in a soxhlet extractor for 24 hours. After recovering most of the solvents, the extracts were heated on a water bath (at 60°C) until most of the solvents evaporated. 4.0 g of the extracts were soaked in 1 liter of 5 M *H*2*SO*4 and 1 M *H*2*SO*4 solutions for hydrogen evolution and weight loss measurements, respectively. The resultant solutions were kept for 24 hours, filtered, and stored. From the stock solutions (4.0 gL⁻¹), test solutions (concentrations of 0.1, 0.5, 1.0, 2.0 and 4.0 gL⁻¹) were prepared. Similar procedure was also carried out with 4.0 g of the powdered form of the leaves. For the ATS-*H*2*SO*4 solutions, 20, 50, 100, 200, and 400 mgL⁻¹ ATS solutions were prepared in 5.0 M *H*2*SO*4 and 1.0 M *H*2*SO*4 solutions for hydrogen evolution and weight loss measurements, respectively.

**2.2. Phytochemical Screening.** Phytochemical screening was carried out on the extracts from *A. annua* following the methods described by Harbone [16], Sofowora [17], and Trease and Evans [18]. The plant extracts were screened for alkaloids, saponins, tannins, flavonoids, cardiac glycosides, and anthraquinones.

**2.3. Weight Loss and Gasometric Measurements.** The weight loss and gasometric measurements were carried out as previously described [19, 20]. However, experiments were conducted at 30°C for weight loss, and at 30°, 40°, 50°, and 60°C for gasometric measurements.

For the weight loss measurements, the mild steel coupons were each suspended and completely immersed in the test solutions (1 M *H*2*SO*4) with and without different concentrations of the plant extracts and artemisinin (ATS) with the help of glass hooks and rods for 7 days at 30 ± 1°C. The coupons were retrieved at 24-hour intervals, washed several times in 20% sodium hydroxide solution containing 200 gL⁻¹ of zinc dust until clean, dipped into acetone, air-dried, and reweighed [19, 20].

Gasometric technique is based on the principle that corrosion reactions in aqueous media are characterized by the evolution of gas resulting from the cathodic reaction of the corrosion process, which is proportional to the rate of corrosion [21]. The rate of evolution of the gas (*R*H*) was determined from the slope of the graph of volume of gas evolved per surface area versus immersion time and efficiencies (%IE) determined using

\[
%IE = \left( \frac{R_{H} - R_{H}^{e}}{R_{H}^{e}} \right) \times 100, \tag{1}
\]

where *R*H and *R*H are the rates of hydrogen evolution per surface area in the absence and presence of the inhibiting molecules, respectively.

| Element | C  | Si | Mn | S  | P  | Ni | Cr | Mo | Cu | Fe  |
|---------|----|----|----|----|----|----|----|----|----|-----|
| Composition | 0.19 | 0.26 | 0.64 | 0.05 | 0.06 | 0.09 | 0.08 | 0.02 | 0.27 | Balance |

**Table 1: Chemical composition of the mild steel.**

---

**Figure 1: Structure of artemisinin.**
In determining the rate of hydrogen evolution per surface area, the contribution of other gases, including water vapor at especially higher temperature is assumed to be insignificant. This gasometric technique has been corroborated by other well-established corrosion rate determination techniques, including weight loss, thermometric, and electrochemical techniques [22–24]. The data presented in this work represents the average of two to three measurements from the weight loss and gasometric techniques.

3. Results and Discussion

3.1. Weight Loss Results. The variation of the weight loss (in mg cm\(^{-2}\)) of mild steel with immersion time in 1 M H\(_2\)SO\(_4\) solutions in the absence and presence of ATS and EEAA at 30°C is as shown in Figure 2. The weight loss was observed to increase with increase in time but decrease with increase in the concentration of the inhibitors. This behavior reflects the inhibitive effect of the inhibitors toward the acid corrosion of the steel. Similar trend was observed in the presence of the other plant extracts. The rate of corrosion (in mg cm\(^{-2}\)h\(^{-1}\)) of the mild steel in the acid medium determined from the slope of the plots is given in Table 2. It is clearly seen that the corrosion rate decreases with increase in the inhibitors concentration. This observed trend may result from the fact that adsorption and surface coverage increase with the increase in concentration; thus, the surface is separated from the medium. From the corrosion rate values, the inhibition efficiency (%IE) was determined using

\[
%\text{IE} = \frac{R_o - R_i}{R_o} \times 100, \quad (2)
\]

where \(R_o\) and \(R_i\) are the corrosion rates in the absence and presence of the inhibiting molecules, respectively. The data are given in Table 2. It is observed that the inhibition efficiency increases as the added inhibitors concentrations are increased. It reaches 96% for 4.0 gL\(^{-1}\) EEAA, 93% for, 4.0 gL\(^{-1}\) AEAA, and 24% for 400 mgL\(^{-1}\) ATS.

3.2. Gasometric Technique. The effect of addition of the tested extracts (EEAA, AEAA, and TEAA) and ATS at different concentrations and temperatures on the corrosion of mild steel in 5 M H\(_2\)SO\(_4\) was studied in more detail using the gas evolution method. The gas evolution technique is more suitable at a high corrodent concentration, while the weight loss method suffices for a low corrodent concentration [19].

Table 3 groups the corresponding values of rate of hydrogen evolved per surface area of the mild steel and the inhibition efficiencies. It is clear that the presence of all tested extracts and ATS reduced the rate of hydrogen evolution per surface area and consequently the corrosion attack is inhibited. It is clearly seen that the rate of hydrogen evolution per surface area decreases with increase in the extracts and ATS concentrations. This trend as noted earlier may result from the fact that adsorption and surface coverage increases with the increase in the inhibitors concentration, thus, separating the surface of the metal from the medium [25–27]. It is also observed from Table 3 that the inhibition efficiencies follow the trend: EEAA > AEAA > TEAA > ATS. Similar trend was obtained at lower concentration of the acid via the weight loss method. The inhibition efficiency increases with the extracts and ATS concentrations to reach 96.73, 94.01, 86.10 and 44.41% for EEAA, AEAA, TEAA, and ATS, respectively. Figure 3 illustrates the comparison of the inhibition efficiencies of the extracts and ATS on the corrosion of mild steel in H\(_2\)SO\(_4\) at 30°C.

3.3. Activation Parameters. Temperature can affect mild steel corrosion in acidic media in the presence and absence of inhibitor. To determine the action energy of the corrosion process, gasometric measurements were taken at various temperatures (30–60°C) in the presence and absence of the extracts and ATS. The corresponding results are also given in Table 3. From these results, we can deduce that the rate of
Table 2: Calculated values of the corrosion rate and inhibition efficiency for mild steel coupons in 1.0 M H₂SO₄ solutions in the absence and presence of inhibitors (using the weight loss technique).

| Inhibitor | System                                      | Corrosion rates (mg cm⁻² hr⁻¹) | Inhibition efficiency (%) |
|-----------|---------------------------------------------|-------------------------------|---------------------------|
| Blank     | 1.406                                       | —                             | —                         |
| EEAA      | 0.1 gL⁻¹ EEAA + 5 M H₂SO₄                 | 1.040                         | 26.00                     |
|           | 0.5 gL⁻¹ EEAA + 5 M H₂SO₄                 | 0.886                         | 37.02                     |
|           | 1.0 gL⁻¹ EEAA + 5 M H₂SO₄                 | 0.703                         | 50.01                     |
|           | 2.0 gL⁻¹ EEAA + 5 M H₂SO₄                 | 0.366                         | 74.00                     |
|           | 4.0 gL⁻¹ EEAA + 5 M H₂SO₄                 | 0.064                         | 95.48                     |
| AEAA      | 0.1 gL⁻¹ AEAA + 5 M H₂SO₄                 | 0.886                         | 37.02                     |
|           | 0.5 gL⁻¹ AEAA + 5 M H₂SO₄                 | 0.515                         | 63.35                     |
|           | 1.0 gL⁻¹ AEAA + 5 M H₂SO₄                 | 0.414                         | 70.55                     |
|           | 2.0 gL⁻¹ AEAA + 5 M H₂SO₄                 | 0.206                         | 85.36                     |
|           | 4.0 gL⁻¹ AEAA + 5 M H₂SO₄                 | 0.105                         | 92.54                     |
| ATS       | 20 mgL⁻¹ ATS + 5 M H₂SO₄                  | 1.266                         | 9.97                      |
|           | 50 mgL⁻¹ ATS + 5 M H₂SO₄                  | 1.172                         | 16.61                     |
|           | 100 mgL⁻¹ ATS + 5 M H₂SO₄                 | 1.159                         | 17.55                     |
|           | 200 mgL⁻¹ ATS + 5 M H₂SO₄                 | 1.153                         | 17.98                     |
|           | 400 mgL⁻¹ ATS + 5 M H₂SO₄                 | 1.071                         | 23.81                     |

Figure 3: Variation of inhibition efficiency with extract concentration for mild steel in 5 M H₂SO₄ containing the inhibitors at 30°C.

Hydrogen evolution per surface area increases with the rise of temperature. The inhibitive efficiencies of the inhibitors decrease with the rise of temperature.

Figure 4 shows Arrhenius plots for the mild steel in 5 M H₂SO₄ solutions in the absence and presence of EEAA. Similar plots were obtained in the presence of AEAA, TEAA, and ATS. The activation energies (ΔEₐ) can be expressed by the Arrhenius equation:

\[ k = A \exp \left( \frac{-E_a}{RT} \right), \]  

where \( T \) is the absolute temperature, \( A \) is the Arrhenius constant, and \( R \) is the universal gas constant. The values of \( k \) were taken to be equal to the rate of hydrogen evolution per surface area [4, 28–30]. The activation energies are given in Table 3. It is evident that the presence of inhibitor increases the activation energy. This may indicate the physical nature of adsorption mechanism [31, 32].

The enthalpy (ΔH*) and entropy of activation (ΔS*) were determined using the Eyring transition state equation (Figure 5 for EEAA):

\[ k = \frac{RT}{Nh} \exp \left( \frac{\Delta S^*}{R} \right) \exp \left( -\frac{\Delta H^*}{RT} \right), \]

where \( N \) is the Avogadro's number, \( h \) is the Plank's constant, and \( \Delta H^* \) and \( \Delta S^* \) are the standard enthalpy and entropy.
of activation, respectively. The data are given in Table 3. Inspection of Table 3 shows higher values for ΔH° in the presence of the inhibitors, indicative of the higher protection efficiency observed for the system [28]. The ΔS° values in the absence and presence of the inhibitors are negative. This implies that the activation complex in the rate determining step represents association rather than dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [33].

3.4. Adsorption Parameters. The inhibitive action of the plant extracts toward the acid corrosion of steel is attributed to the adsorption of ATS and the other components of the plant on the surface of the mild steel. The adsorbed layer acts as a barrier for mass and charge transfers, leading to a decrease in the corrosion rate. Thus, it follows that the inhibition efficiency (%IE) is directly proportional to the fraction of the surface covered by the adsorbed molecules (θ). Therefore, θ is calculated using the relation \( \theta = \%IE/100 \) [3]. The mode of variation of θ with the extract concentration specifies the adsorption isotherm that describes the system. The obtained θ values were applied to different adsorption isotherm equations and found to fit the Langmuir adsorption isotherm (Figure 6 for AEAA) with \( R^2 \) values of up to 0.9962 for EEAA, 0.9995 for AEAA, 0.9688 for TEAA, and 0.9026 for ATS. The Langmuir adsorption isotherm may be formulated as

\[
\frac{c}{\theta} = \frac{1}{Kc}
\]

(5)
Table 4: Thermodynamic parameters for the adsorption of EEAA, AEAA, TEAA, and ATS on mild steel in 5 M H2SO4 (using the gasometric technique).

| Inhibitor | 30°C | 40°C | 50°C | 60°C | ΔH°_{ads} (KJmol⁻¹) | ΔS°_{ads} (Jmol⁻¹) |
|-----------|------|------|------|------|---------------------|--------------------|
| EEAA      | 3.97 | 3.31 | 2.48 | 1.94 | -20.37             | -55.51             |
| AEAA      | 5.92 | 4.42 | 3.27 | 2.03 | -29.41             | -81.89             |
| TEAA      | 1.35 | 1.08 | 0.97 | 0.50 | -25.50             | -81.01             |
| ATS       | 0.32 | 0.23 | 0.24 | 0.16 | -17.22             | -66.45             |

Figure 6: Langmuir adsorption isotherm for AEAA on mild steel in 5 M H2SO4.

Figure 7: Curve fitting of log K data against 1/T.

where \( c \) is inhibitor concentration, \( \theta \) is the fraction of the surface covered by the adsorbed molecules, and \( K \) equals the equilibrium constant. The values of \( K \) obtained from the intercept of the isotherm plots are given in Table 4. \( K \) values are seen to decrease with increase in temperature suggesting that the inhibitors are physically adsorbed on the surface of the metal. From the dependence of the \( K \) values on temperature, the thermodynamic parameters \( \Delta H_{ads} \) and \( \Delta S_{ads} \) were obtained by linear least squares fits of the log \( K \) data against \( 1/T \) (Figure 7):

\[
\log K = -\frac{\Delta H_{ads}^o}{RT} + \frac{\Delta S_{ads}^o}{R}.
\]  

The resultant values are given in Table 4. Generally, negative values of \( \Delta H_{ads}^o \) were obtained indicating an exothermic adsorption process. The exothermic adsorption process signifies either physical or chemical adsorption, while endothermic adsorption process is attributable to chemisorption. In an exothermic process, physical adsorption is distinguished from chemisorption by considering the absolute value of adsorption enthalpy. Typically, enthalpy of physical adsorption process is lower than 80 KJmol⁻¹, while the enthalpy of chemisorption process approaches 100 KJmol⁻¹ [32]. The values of the obtained enthalpy therefore suggest physical adsorption of the inhibitors on the surface of the metal. Comparing the values of \( \Delta H_{ads}^o \) obtained in this work with the values of \( \Delta H^* \) (enthalpy of activation), it is observed that the latter are very much larger than those of \( \Delta H_{ads}^o \). This has been interpreted to indicate physical adsorption rather than chemisorption [28].

3.5. Mechanism of Inhibition. The adsorption of an organic adsorbate on a metal surface is generally regarded as a substitutional adsorption process between the organic molecule in the aqueous solution (\( \text{Org}_{(sol)} \)) and water molecules adsorbed on the metallic surface (\( \text{H}_2\text{O}_{(ads)} \)) [34]:

\[
\text{Org}_{(sol)} + x\text{H}_2\text{O}_{(ads)} = \text{Org}_{(ads)} + x\text{H}_2\text{O}_{(sol)},
\]  

where \( x \) is the size ratio representing the number of water molecules replaced by one molecule of organic adsorbate. The adsorption of organic compounds can be described by two main types of interaction: physical adsorption and chemisorption. In general, the proceeding of physical adsorption requires the presence of both electrically charged surface of the metal and charged species in the bulk of the solution. Chemisorption process involves charge sharing or charge-transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond. This is possible in case of a positive as well as a negative charge on the surface. The presence of a transition metal, having vacant, low-energy electron orbital and of an inhibitor with molecules having relatively loosely bound electrons or heteroatoms with lone pair of electrons is necessary [35, 36].

The plant extracts under investigation contain ATS in variable concentrations (0.01 to 1.5% of plant dry weight) [12–15]. The compound inhibits the corrosion reaction to
an appreciable extent as shown in Tables 2 and 3. ATS is a slightly polar compound [12] and can adsorb directly on the positively charged mild steel surface. ATS has an unusual trioxane structure with seven stereogenic centers and tetracyclic framework (Figure 1). It is probable that the adsorbed molecule is oriented with three of the tetracyclic ring structures parallel to the metal surface, thereby creating a barrier for mass and charge transfers. This situation leads to the protection of the mild steel from the acid corrosive ions. Comparing the inhibition efficiencies of ATS with those of the plant extracts, it is evident that ATS has the least efficiency. In addition to ATS, the plant extracts contain other known sesquiterpenes (over 20) including artemannuin B, artemisitene and artemisinin acid, flavonoid compounds, and other naturally occurring organic compounds [12–15]. This large number of different chemical compounds may form adsorbed intermediates which may either inhibit (forming insoluble Fe-phytochemical complex) or catalyse further metal dissolution. From the observed results, it can be inferred that the insoluble Fe-phytochemical complexes dominate the adsorbed intermediates and thus the resultant inhibitive effects. Synergistic inhibition of the components of the plant extracts may also contribute to the enhanced inhibition efficiency when compared to that of ATS. In addition to the physical adsorption mechanism of inhibition of ATS and other components of the extracts, there could be chemical adsorption of some components of the extracts which may also enhance the inhibition ability of the plant extracts. However, from the study, it is evident that physical adsorption is the dominant mechanism of inhibition.

The results from the phytochemical screening of the extracts are shown in Table 5. It revealed that the composition of the extracts is dependent on the type of solvents used for the extraction process. EEAA is observed to contain alkaloids, appreciable quantities of flavonoids, tannins, and glycosides. Flavonoids and glycosides were detected in AEAA while tannins and glycosides were present in TEAA. The presence of more phytochemicals in EEAA, especially the alkaloids (which are nitrogen containing organic bases) and flavonoids compared to the other extracts may be responsible for the observed highest inhibition efficiency of EEAA. Comparing the phytochemical components of AEAA and TEAA, and relating them to their inhibition efficiencies, it could be inferred that the flavonoids inhibit better than the tannins thus the higher efficiency observed for AEAA. From the observed phytochemical screening results and inhibition efficiencies, it could be concluded that the flavonoids are the principal phytochemicals in the extracts responsible for the inhibition ability of the plant. Synergism effects with other components of the plants, especially the alkaloids and tannins, may increase the inhibition efficiency to an appreciable extent, as observed for EEAA.

### 4. Conclusions

The ethanol (EEAA), acid (AAEE), and toluene (TEAA) extracts from the leaves of *Artemisia annua* and artemisinin (ATS) act as inhibitors for the corrosion of mild steel in H2SO4 solutions and the maximum inhibition efficiencies followed the trend: EEAA > AEAA > TEAA > ATS. The inhibition efficiency values increase with increase in concentration of the inhibitors and decrease with increase in temperature. The composition of the extracts as well as its inhibition efficiency is dependent on the type of solvents used for the extraction process. Synergistic inhibition of the components of the plant extracts with ATS is attributed to the enhanced inhibition efficiencies of the extracts. The adsorption of the inhibitors molecules was consistent with Langmuir adsorption isotherm, and physical adsorption is proposed as the dominant mechanism of inhibition.

### References

[1] R. M. Saleh, A. A. Ismail, and A. H. El Hosary, “Corrosion inhibition by naturally occurring substances. vii. the effect of aqueous extracts of some leaves and fruit peels on the corrosion of steel, Al, Zn and Cu in acids,” *British Corrosion Journal*, vol. 17, no. 3, pp. 131–135, 1982.

[2] O. K. Abiola and A. O. James, “The effects of Aloe vera extract on corrosion and kinetics of corrosion process of zinc in HCl solution,” *Corrosion Science*, vol. 52, no. 2, pp. 661–664, 2010.

[3] A. Y. El-Etre, “Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves,” *Journal of Colloid and Interface Science*, vol. 314, no. 2, pp. 578–583, 2007.

[4] P. C. Okafor and E. E. Ebenso, “Inhibitive action of Carica papaya extracts on the corrosion of mild steel in acidic media and their adsorption characteristics,” *Pigment and Resin Technology*, vol. 36, no. 3, pp. 134–140, 2007.

[5] P. C. Okafor, M. E. Ikpi, I. E. Uwah, E. E. Ebenso, U. J. Ekpe, and S. A. Umoren, “Inhibitory action of Phyllanthus amarus extracts on the corrosion of mild steel in acidic media,” *Corrosion Science*, vol. 50, no. 8, pp. 2310–2317, 2008.

[6] I. E. Uwah, P. C. Okafor, and V. E. Ebiekpe, “Inhibitive action of ethanol extract from Nauclea latifolia on the corrosion of mild steel in H2SO4 solutions and their adsorption characteristics,” *Arabian Journal of Chemistry*. In press.

[7] P. C. Okafor, E. E. Ebenso, and U. J. Ekpe, “Azadirachta indica extracts as corrosion inhibitor for mild steel in acid medium,” *International Journal of Electrochemical Science*, vol. 5, no. 7, pp. 978–993, 2010.

[8] I. B. Obot, S. A. Umoren, and N. O. Obi-Egbedi, “Corrosion inhibition and adsorption behaviour for aluminium by extract of *Aningeria robusta* in HCl solution: synergistic effect of iodide ions,” *Journal of Materials and Environmental Science*, vol. 2, no. 1, pp. 60–71, 2011.
[9] M. Lebrini, F. Robert, and C. Roos, “Alkaloids extract from Palicourea guianensis plant as corrosion inhibitor for C38 steel in 1 M hydrochloric acid medium,” International Journal of Electrochemical Science, vol. 6, no. 3, pp. 847–859, 2011.

[10] M. Lebrini, F. Robert, P. A. Blandinières, and C. Roos, “Corrosion inhibition by Isertia cocinea plant extract in hydrochloric acid solution,” International Journal of Electrochemical Science, vol. 6, no. 7, pp. 2443–2460, 2011.

[11] A. O. James and O. Akaranta, “Inhibition of corrosion of zinc in hydrochloric acid solution by red onion skin acetone extract,” Research Journal of Chemical Sciences, vol. 1, no. 1, pp. 31–37, 2011.

[12] M. Kohler, W. Haerdi, P. Christen, and J.-L. Veuthey, “Extraction of artemisinin and artemisinic acid from Artemisia annua L. using supercritical carbon dioxide,” Journal of Chromatography A, vol. 785, no. 1-2, pp. 353–360, 1997.

[13] P. S. Covello, “Making artemisinin,” Phytochemistry, vol. 69, no. 17, pp. 2881–2885, 2008.

[14] J. Ferreira and J. Janick, “Annual Wormwood (Artemisia annua L.) New Crop FactSHEET,” 2009, http://www.hort.purdue.edu/newcrop/cropfactsheets/artemisia.pdf, 23rd March, 2010.

[15] J. Han, M. Ye, X. Qiao, M. Xu, B.-R. Wang, and D.-A. Guo, “Characterization of phenolic compounds in the Chinese herbal drug Artemisia annua by liquid chromatography coupled to electrospray ionization mass spectrometry,” Journal of Pharmaceutical and Biomedical Analysis, vol. 47, no. 3, pp. 516–525, 2008.

[16] J. B. Harbone, Phytochemical Methods: A Guide to Modern Techniques of Plant Analysis, Chapman and Hill, London, UK, 1973.

[17] E. R. Sofowora, “Guidelines for research promotion and development in traditional medicine,” Nigeria Journal of Pharmacy, vol. 11, pp. 117–118, 1980.

[18] G. E. Trease and W. C. Evans, A Textbook of Pharmacology, Baillier Tidally, London, UK, 1996.

[19] U. J. Ekpe, U. J. Ibok, B. I. Ita, O. E. Offiong, and E. E. Ebenso, “Inhibitory action of methyl and phenyl thiosemicarbazone derivatives on the corrosion of mild steel in hydrochloric acid,” Materials Chemistry and Physics, vol. 40, no. 2, pp. 87–93, 1995.

[20] B. I. Ita and O. E. Offiong, “Inhibition of steel corrosion in hydrochloric acid by pyridoxal, 4-methylthiosemicarbazide, pyridoxal-(4-methylthiosemicarbazone) and its Zn(II) complex,” Materials Chemistry and Physics, vol. 48, no. 2, pp. 164–169, 1997.

[21] P. C. Okafor, U. J. Ekpe, E. E. Ebenso, E. M. Umoron, and K. E. Leizou, “Inhibition of mild steel corrosion in acidic medium by Allium sativum extracts,” Bulletin of Electrochemistry, vol. 21, no. 8, pp. 347–352, 2005.

[22] A. Y. El-Elte, “The inhibitive action of the mucilage extracted from the modified stems of prickly pears, toward acid corrosion of aluminum,” Corrosion Science, vol. 45, no. 11, pp. 2485–2495, 2003.

[23] M. Abdallah, “Antibacterial drugs as corrosion inhibitors for corrosion of aluminum in hydrochloric solution,” Corrosion Science, vol. 46, no. 8, pp. 1981–1996, 2004.

[24] P. C. Okafor, U. J. Ekpe, E. E. Ebenso, E. E. Oguzie, N. S. Umo, and A. R. Etor, “Extract of Allium cepa and Allium sativum as corrosion inhibitors of mild steel in HCl solution,” Transactions of the SAEST, vol. 41, no. 2, pp. 82–87, 2006.

[25] T. Zhao and G. Mu, “The adsorption and corrosion inhibition of anion surfactants on aluminium surface in hydrochloric acid,” Corrosion Science, vol. 41, no. 10, pp. 1937–1944, 1999.

[26] M. Abdallah, E. A. Helal, and A. S. Fouda, “Aminopyrimidine derivatives as inhibitors for corrosion of 1018 carbon steel in nitric acid solution,” Corrosion Science, vol. 48, no. 7, pp. 1639–1654, 2006.

[27] S. S. Rehim, O. A. Hazzazi, M. A. Amin, and K. F. Khaled, “On the corrosion inhibition of low carbon steel in concentrated sulphuric acid solutions. Part I: chemical and electrochemical (AC and DC) studies,” Corrosion Science, vol. 50, no. 8, pp. 2258–2271, 2008.

[28] A. A. El-Awady, B. A. Abd-El-Nabey, and S. G. Aziz, “Kinetic-thermodynamic and adsorption isotherms analyses for the inhibition of the acid corrosion of steel by cyclic and open-chain amines,” Journal of the Electrochemical Society, vol. 139, no. 8, pp. 2149–2154, 1992.

[29] P. C. Okafor, V. I. Osabor, and E. E. Ebenso, “Eco-friendly corrosion inhibitors: inhibitive action of ethanol extracts of Garcinia kola for the corrosion of mild steel in H2SO4 solutions,” Pigment and Resin Technology, vol. 36, no. 5, pp. 299–305, 2007.

[30] E. E. Oguzie, G. N. Onuoha, and A. I. Onuchukwu, “The inhibition of aluminium corrosion in potassium hydroxide by “Congo Red” dye, and synergistic action with halide ions,” Anti-Corrosion Methods and Materials, vol. 52, no. 5, pp. 293–298, 2005.

[31] K. Gomma and M. H. Wahdan, “Effect of temperature on the acidic dissolution of copper in the presence of amino acids,” Materials Chemistry and Physics, vol. 32, no. 2, pp. 142–148, 1994.

[32] S. Martinez and I. Stern, “Thermodynamic characterization of metal dissolution and inhibitor adsorption processes in the low carbon steel/mimosas tannin/sulfuric acid system,” Applied Surface Science, vol. 199, no. 1–4, pp. 83–89, 2002.

[33] S. S. Abd El Rehim, M. A. M. Ibrahim, and K. F. Khalid, “The inhibition of 4-(2’-amino-5’-methylphenylazo) antipyrine on corrosion of mild steel in HCl solution,” Materials Chemistry and Physics, vol. 70, no. 3, pp. 268–273, 2001.

[34] B. B. Damaskin, O. A. Petrii, and B. Batrakov, Adsorption of Organic Compounds on Electrodes, Plenum Press, New York, NY, USA, 1971.

[35] A. Le Mahaute and G. Grepy, “Introduction to transfer and motion in fractal media: the geometry of kinetics,” Solid State Ionics, vol. 9–10, no. 17, pp. 17–30, 1983.

[36] G. Reinhard and U. Rammet, in Proceedings of the Proceedings of the 6th European Symposium on Corrosion Inhibitors, p. 831, Ferrara, Italy, 1985.
Review Article

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

B. E. Amita Rani and Bharathi Bai J. Basu

Surface Engineering Division, CSIR-National Aerospace Laboratories, Bangalore 560037, India

Correspondence should be addressed to B. E. Amita Rani, amitharani@nal.res.in

Received 31 March 2011; Revised 17 June 2011; Accepted 17 June 2011

Copyright © 2012 B. E. A. Rani and B. B. J. Basu. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

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 (–NH2, –NO2, –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 corroden, 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
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 H2SO4 [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 Auporpio turkiale sap for their corrosion inhibition potential and found that all extracts except those of Auporpio 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 H2SO4 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 H2SO4.

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 H2SO4 and action is by classical Langmuir adsorption isotherm. The effect of addition of halides (KCI, 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 pyran 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 Sanseviera trifasciata extracts [26–29]. Benda-hou 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, SS)-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 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 H atoms attached to C are replaced by groups, –CH, –OCH3, 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 –OCH3 (Scheme 4).
| 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          | *Emblica officinalis*        |                                                                                  | [42]       |
| (5)    | Steel          | *Terminalia bellerica*       |                                                                                  | [43]       |
| (6)    | Steel          | Eucalyptus oil               | Monomtréne 1,8-cineole                                                           | [44]       |
| (7)    | Steel          | Rosemary                     |                                                                                  | [45]       |
| (8)    | C-steel, Ni, Zn| Lawsonia extract (Henna)     | Lawsone (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     | *Musa sapientum* peels (Banana peels) |                                                                                  | [48]       |
| (11)   | Carbon steel   | Natural amino acids—alanine, glycine, and leucine |                                                                                  | [48]       |
| (12)   | Steel          | Natural amino acids          |                                                                                  | [15]       |
| (13)   | Mild steel     | *Garcinia kola* seed         | Primary and secondary amines, Unsaturated fatty acids and biflavnone              | [49]       |
| (14)   | Steel          | *Auforpio turkiale*          | Protein hydrolysis                                                               | [50]       |
| (15)   | Steel          | *Azzydracta indica*          | Protein hydrolysis                                                               | [51]       |
| (16)   | Steel          | Aloe leaves                  |                                                                                  | [52]       |
| (17)   | Steel          | Mango/orange peels           |                                                                                  | [53]       |
| (18)   | Steel          | *Hibiscus sabdariffa* (Calyx extract) in 1 M H₂SO₄ 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.
| Sl. no. | Metal          | Inhibitor source                                                                 | Active ingredient                                                                 | References |
|--------|----------------|---------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|------------|
| (1)    | Al             | CeCl₃ 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 *Rosmarinus officinalis*—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             | *Vernonia amygdalina* (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    | *Rosmarinus officinalis*                                                          |                                                                                  | [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]        |
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 xanthones, 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 xanthones such as cudraxanthone G, deoxygartanin, garcinanosone B, garcinone D, garcinone E, gartanin, 1-isomangostin, α-mangostin, γ-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 *Ipomoea involcrata* (IP) (family: Convolulaceae) 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-lysergic 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 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 H$_2$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, phlobatins, antraquinone, cardiac glycosides, flavonoid, 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 H$_2$SO$_4$ was investigated using 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. leaf 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 leaf 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 pararquianoid 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 L$^{-1}$ HCl. Two methods of extraction were studied: decoction and infusion. The inhibition efficiency of C-steel in 1 mol 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 microorganisms 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 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
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 lifecycle 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 in the three surfaces, and the variability in the location, size, and density of the particles is apparent. Thus, for e.g., 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 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 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...
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 μm) 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 HNO₃ 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 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.

Acknowledgments

The encouragement and cooperation received from Dr. Upadhya, Director, NAL, Bangalore, Dr. Ranjan Moodithaya, KTMD, and Dr. K.S. Rajam, Head, SED are gratefully acknowledged. Patents used in the paper are: (1) US Patent 5951747—Non-chromate corrosion inhibitors for aluminum alloys; (2) United States Patent 5286357—Corrosion sensors; (3) WO/2002/008345—CORROSION INHIBITORS; and (4) British patent, 2327,1895.

References

[1] M. Bouklah, B. Hammouti, T. Benhadda, and M. Benkadour, “Thiophene derivatives as effective inhibitors for the corrosion of steel in 0.5 M H2SO4,” Journal of Applied Electrochemistry, vol. 35, no. 11, pp. 1095–1101, 2005.
[2] A. S. Fouda, A. A. Al-Sarawy, and E. E. El-Katori, “Pyrazolone derivatives as corrosion inhibitors for C-steel HCl solution,” Desalination, vol. 201, pp. 1–13, 2006.
[3] A. Fiala, A. Chibani, A. Darchen, A. Bouakkam, and K. Djebbar, “Investigations of the inhibition of copper corrosion in nitric acid solutions by ketene dithioacetals derivatives,” Applied Surface Science, vol. 253, no. 24, pp. 9347–9356, 2007.
[4] U. R. Evans, The Corrosion and Oxidation of Metals, Hodder Arnold, 1976.
[5] O. K. Abiola, N. C. Oforka, E. E. Ebenson, and N. M. Nwinnuka, “Eco-friendly corrosion inhibitors: The inhibitive action of Delonix Regia extract for the corrosion of aluminium in acidic media,” Anti-Corrosion Methods and Materials, vol. 54, no. 4, pp. 219–224, 2007.
[6] M. Kliskic, J. Radoservic, S. Gudic, and V. Katalinic, “Aquous extract of Rosmarinus officinalis L as inhibitor of Al-Mg alloy corrosion in chloride solution,” Journal of Applied Electrochemistry, vol. 30, no. 7, pp. 823–830, 2000.
[7] A. Y. El-ETre, “Natural honey as corrosion inhibitor for metals and alloys. I. Copper in neutral aqueous solution,” Corrosion Science, vol. 40, no. 11, pp. 1845–1850, 1998.
[8] A. Y. El-ETre, “Inhibition of aluminium corrosion using Opuntia extract,” Corrosion Science, vol. 45, no. 11, pp. 2485–2495, 2003.
[9] A. Y. El-ETre, “Khillah extract as inhibitor for acid corrosion of SX 316 steel,” Applied Surface Science, vol. 252, no. 24, pp. 8521–8525, 2006.
[10] E. E. Ebenson, U. J. Ibok, U. J. Ekpe et al., “Corrosion inhibition studies of some plant extracts on aluminium in acidic medium,” Transactions of the SAEST, vol. 39, no. 4, pp. 117–123, 2004.
[11] E. E. Ebenson and U. J. Ekpe, “Kinetic study of corrosion and corrosion inhibition of mild steel in H2SO4 using Parica papaya leaves extract,” West African Journal of Biological and Applied Chemistry, vol. 41, pp. 21–27, 1996.
[12] U. J. Ekpe, E. E. Ebenson, and U. J. Ibok, “Inhibitory action of Azadirachta indica leaves extract on the corrosion of mild steel in H2SO4,” West African Journal of Biological and Applied Chemistry, vol. 37, pp. 13–30, 1994.
[13] F. Zucchi and I. H. Omar, “Plant extracts as corrosion inhibitors of mild steel in HCl solutions,” Surface Technology, vol. 24, no. 4, pp. 391–399, 1985.
[14] S. A. Umoren, O. Ogbofe, I. O. Igwe, and E. E. Ebenson, “Inhibition of mild steel corrosion in acidic medium using synthetic and naturally occurring polymers and synergistic halide additives,” Corrosion Science, vol. 50, no. 7, pp. 1998–2006, 2008.
[15] Y. J. Yee, “Green inhibitors for corrosion control: a Study on the inhibitive effects of extracts of honey and rosmarinus officinalis L. (Rosemary),” M.S. thesis, University of Manchester, Institute of Science and Technology, 2004.
[16] J. C. Chalchat, R. P. Garry, A. Michet, B. Benjilali, and J. L. Chabart, “Essential oils of Rosemary (Rosmarinus officinalis L.). The chemical composition of oils of various origins (Morocco, Spain, France),” Journal of Essential Oil Research, vol. 5, no. 6, pp. 613–618, 1993.
[17] E. El Ouariachi, J. Paolini, M. Bouklah et al., “Adsorption properties of Rosmarinus of ficinalis oil as green corrosion inhibitors on C38 steel in 0.5 M H2SO4,” Acta Metallurgica Sinica, vol. 23, no. 1, pp. 13–20, 2010.
[18] A. O. Odiomgenyi, S. A. Odoemelam, and N. O. Eddy, “Corrosion inhibition and adsorption properties of ethanol extract of Vernonia Amygdalina for the corrosion of mild steel in H2SO4,” Portuguese Electrochimica Acta, vol. 27, no. 1, pp. 33–45, 2009.
[19] S. A. Umoren and E. E. Ebenson, “Studies of the anti-corrosive effect of Raphia hookeri exudate gum-halide mixtures for aluminium corrosion in acidic medium,” Pigment and Resin Technology, vol. 37, no. 3, pp. 173–182, 2008.
[20] M. Abdallah, “Guar gum as corrosion inhibitor for carbon steel in sulphuric acid solutions,” Portuguese Electrochimica Acta, vol. 22, pp. 161–175, 2004.
[21] P. C. Okafor, U. J. Ekpe, E. E. Ebenson, E. M. Umoren, and K. E. Leizou, “Inhibition of mild steel corrosion in acidic medium using Allium sativum extracts,” Journal of Essential Oil Research, vol. 24, no. 4, pp. 309–314, 2012.
[22] P. C. Okafor and E. E. Ebenson, “Inhibitive action of Carica papaya extracts on the corrosion of mild steel in acidic media and their adsorption characteristics,” Pigment and Resin Technology, vol. 36, no. 3, pp. 134–140, 2007.
[23] P. C. Okafor, V. I. Osabor, and E. E. Ebenson, “Eco-friendly corrosion inhibitors: Inhibitive action of ethanolic extracts of Garcinia kola for the corrosion of mild steel in H2SO4 solutions,” Pigment and Resin Technology, vol. 36, no. 5, pp. 299–305, 2007.
[24] P. C. Okafor, M. E. Ikpi, I. E. Uwah, E. E. Ebenso, U. J. Ekpe, and S. A. Umorden, "Inhibitory action of Phyllanthus amarus extracts on the corrosion of mild steel in acidic media," Corrosion Science, vol. 50, no. 8, pp. 2310–2317, 2008.

[25] A. Y. El-Etre and M. Abdallah, "Natural honey as corrosion inhibitor for metals and alloys. II. C-steel in high saline water," Corrosion Science, vol. 42, no. 4, pp. 731–738, 2000.

[26] A. Chetouani, B. Hammouti, and M. Benkaddour, "Corrosion inhibition of iron in hydrochloric acid solution by jojoba oil," Pigment and Resin Technology, vol. 33, no. 1, pp. 26–31, 2004.

[27] A. Bouyanzer and B. Hammouti, "A study of anti-corrosive effects of Artemisia oil on steel," Pigment and Resin Technology, vol. 33, no. 5, pp. 287–292, 2004.

[28] E. E. Oguzie, "Inhibition of acid corrosion of mild steel by Telfaria occidentalis extract," Pigment and Resin Technology, vol. 34, no. 6, pp. 321–326, 2005.

[29] E. E. Oguzie, "Studies on the inhibitive effect of Occimum viridis extract on the acid corrosion of mild steel," Materials Chemistry and Physics, vol. 99, pp. 441–446, 2006.

[30] E. E. Oguzie, "Corrosion inhibition of aluminum in acidic and alkaline media by Susevieria trifasciata extract," Corrosion Science, vol. 49, no. 3, pp. 1527–1539, 2007.

[31] M. A. Bendahou, M. B. E. Benadellah, and B. B. Hammouti, "A study of rosemary oil as a green corrosion inhibitor for steel in 2 M H_{2}PO_{4}," Pigment and Resin Technology, vol. 35, no. 2, pp. 95–100, 2006.

[32] M. G. Sethuraman and P. B. Raja, "Corrosion inhibition of mild steel by Datura metel in acidic medium," Pigment and Resin Technology, vol. 34, no. 6, pp. 327–331, 2005.

[33] N. O. Eddy, S. A. Odoemelam, and A. O. Odiongenyi, "Ethanol extract of musa species peels as a green corrosion inhibitor for mild steel: Kinetics, adsorption and thermodynamic considerations," Electronic Journal of Environmental, Agricultural and Food Chemistry, vol. 8, no. 4, pp. 243–255, 2009.

[34] P. Deepa Rani and S. Selvaraj, "Inhibitive and adsorption properties of punica granatum extract on brass in acid media," Journal of Phytochemistry, vol. 2, no. 11, pp. 58–64, 2010.

[35] S. Rajendran, V. Ganga Sri, J. Arockiaselvi, and A. J. Amalraj, "Corrosion inhibition by plant extracts—an overview," Bulletin of Electrochemistry, vol. 21, no. 8, pp. 367–377, 2005.

[36] K. Srivastava and P. Srivastava, "Studies on plant materials as corrosion inhibitors," British Corrosion Journal, vol. 16, no. 4, pp. 221–223, 1981.

[37] R. M. Saleh, A. A. Ismail, and A. A. El Hosary, "Corrosion inhibition by naturally occurring substances. vii. the effect of aqueous extracts of some leaves and fruit peels on the corrosion of steel, Al, Zn and Cu in acids," British Corrosion Journal, vol. 17, no. 3, pp. 131–135, 1982.

[38] P. B. Raja and M. G. Sethuraman, "Natural products as corrosion inhibitor for metals in corrosive media—a review," Materials Letters, vol. 62, no. 1, pp. 113–116, 2008.

[39] J. H. Henriquez-Román, M. Sancy, M. A. Páez et al., “The influence of aniline and its derivatives on the corrosion behaviour of copper in acid solution,” Journal of Solid State Electrochemistry, vol. 9, no. 7, pp. 504–511, 2005.

[40] A. A. El Hosary, R. M. Saleh, and A. M. Shams El Din, "Corrosion inhibition by naturally occurring substances. I. The effect of Hibiscus sabdariffa (karkade) extract on the dissolution of Al and Zn," Corrosion Science, vol. 12, no. 12, pp. 897–904, 1972.

[41] R. M. Saleh and A. M. Shams El Din, "Efficiency of organic acids and their anions in retarding the dissolution of aluminium," Corrosion Science, vol. 12, no. 9, pp. 689–697, 1972.

[42] M. J. Sanghvi, S. K. Shuklan, A. N. Misra, M. R. Padh, and G. N. Mehta, "Inhibition of hydrochloric acid corrosion of mild steel by aid extracts of Emblica officinalis, Terminalia bellirica and Terminalia chebula," Bulletin of Electrochemistry, vol. 13, no. 8–9, pp. 358–361, 1997.

[43] M. J. Shangvi, S. K. Shuklan, A. N. Misra, M. R. Padh, and G. N. Mehta, "Corrosion inhibition of mild steel in hydrochloric acid by aid extracts of Sapindus trifoliatus, Acacia concina and Trillia," Transactions of the Metal Finishers Association of India, vol. 5, no. 3, pp. 143–147, 1996.

[44] A. Chetouani and B. Hammouti, "Corrosion inhibition of iron in hydrochloric acid solutions by naturally henna," Bulletin of Electrochemistry, vol. 19, no. 1, pp. 23–25, 2003.

[45] B. Muller, W. Klager, and G. Kubitzki, "Metal chelates of citric acid as corrosion inhibitors for zinc pigment," Corrosion Science, vol. 39, no. 8, pp. 1481–1485, 1997.

[46] A. Bouyanzer, L. Majidi, and B. Hammouti, "Effect of eucalyptus oil on the corrosion of steel in 1M HCl," Bulletin of Electrochemistry, vol. 22, no. 7, pp. 321–324, 2006.

[47] A. Y. El-Etre, "Natural onion juice as inhibitor for zinc corrosion," Bulletin of Electrochemistry, vol. 22, no. 2, pp. 75–80, 2006.

[48] I. Radojic, K. Berković, S. Kovač, and J. Vorkapić-Furač, "Natural honey and black radish juice as tin corrosion inhibitors," Corrosion Science, vol. 50, no. 5, pp. 1498–1504, 2008.

[49] A. Y. El-Etre, M. Abdallah, and Z. E. El-Tantawy, "Corrosion inhibition of some metals using lawsonia extract," Corrosion Science, vol. 47, no. 2, pp. 385–395, 2005.

[50] S. A. Umorden, I. B. Obot, and E. E. Ebenso, "Corrosion inhibition of aluminium using exudate gum from Pachylobus edulis in the presence of halide ions in HCl," E-Journal of Chemistry, vol. 5, no. 2, pp. 355–364, 2008.

[51] N. O. Eddy and E. E. Ebenso, "Adsorption and inhibitive properties of ethanol extracts of Musa sapientum peels as a green corrosion inhibitor for mild steel in H_{2}SO_{4}," African Journal of Pure and Applied Chemistry, vol. 2, no. 6, pp. 046–054, 2008.

[52] S. Lyon, "A natural way to stop corrosion," Nature, vol. 427, no. 406, p. 407, 2004.

[53] E. E. Oguzie, K. L. Iyeh, and A. I. Onuchukwu, "Inhibition of mild steel corrosion in acidic media by aqueous extracts from Garcinia kola seed," Bulletin of Electrochemistry, vol. 22, no. 2, pp. 63–68, 2006.

[54] R. M. Saldo, A. A. Ismail, and A. A. El Hosary, "Corrosion Inhibition by naturally occurring substances. v. the effect of aqueous extracts of some leaves and fruit peels on the corrosion of steel, Al, Zn and Cu in acids," British Corrosion Journal, vol. 17, no. 3, pp. 131–135, 1982.

[55] E. E. Oguzie, "Corrosion inhibitive effect and adsorption behaviour of Hibiscus Sabdariffa extract on mild steel in acidic media," Portugaliae Electrlochimica Acta, vol. 26, pp. 303–314, 2008.

[56] E. E. Oguzie, "Corrosion inhibitive effect and adsorption behaviour of Hibiscus sabdariffa extract on mild steel in acidic media," Portugaliae Electrochimica Acta, vol. 26, no. 3, pp. 303–314, 2008.

[57] H. W. Shi, F. C. Liu, E. H. Han, and M. C. Sun, "Investigation on a sol-gel coating containing inhibitors on 2024-T3 aluminum alloy," Chinese Journal of Aeronautics, vol. 19, pp. S106–S112, 2006.

[58] G. D. Davis, "The Use of Extracts of Tobacco Plants as Corrosion Inhibitors," http://www.electrochem.org/dl/ma/202/pdfs/0340.PDF.
N. Lahhit, A. Bouyanzer, J.-M. Desjobert et al., "Fennel (Foeniculum vulgare) essential oil as green corrosion inhibitor of carbon steel in hydrochloric acid solution," *Portugaliae Electrochimica Acta*, vol. 29, no. 2, pp. 127–138, 2011.

A. El-Etre, "Inhibition of acid corrosion of aluminum using vanillin," *Corrosion Science*, vol. 43, no. 6, pp. 1031–1039, 2001.

W. A. Badawy, F. M. Alhara, and A. S. ElAzab, "Electrochemical behaviour and corrosion inhibition of Al, Al-6061 and Al-Cu in neutral aqueous solutions," *Corrosion Science*, vol. 41, no. 4, pp. 709–727, 1999.

B. Müller, "Amino and polyamino acids as corrosion inhibitors for aluminium and zinc pigments," *Pigment and Resin Technology*, vol. 31, no. 2, pp. 84–87, 2002.

M. Kliskic, J. Radosevi, and S. Gudic, "Pyridine and its derivatives as inhibitors of aluminium corrosion in chloride solution," *Journal of Applied Electrochemistry*, vol. 27, no. 6, pp. 947–952, 1997.

R. Solmaz, G. Kardaş, B. Yazıcı, and M. Erbil, "Citric acid as natural corrosion inhibitor for aluminium protection," *Corrosion Engineering Science and Technology*, vol. 43, no. 2, pp. 186–191, 2008.

Z. Sibel, "The effects of benzoic acid in chloride solutions on the corrosion of iron and aluminium," *Turkish Journal of Chemistry*, vol. 26, no. 3, pp. 403–408, 2002.

K. Berkovic, S. Kovac, and J. Vorkapić-Furac, "Natural compounds as environmentally friendly corrosion inhibitors of aluminium," *Acta Alimentaria*, vol. 33, no. 3, pp. 237–247, 2004.

Y. Tao, X. Zhang, and Z. Gu, "The inhibition of corrosion of aluminium in acid environment by situ electrocoagulation of polybutadienonic acid," *Wuhan University Journal of Natural Sciences*, vol. 3, no. 2, pp. 221–225, 1998.

B. Müller and M. Kurreff, "Saccharide und deren Derivate als Korrosionsinhibitoren für Aluminiumpigmente in wäbrigen Medien," *Materials and Corrosion*, vol. 44, no. 9, pp. 373–378, 2004.

G. O. Awwiri and F. O. Igbo, "Inhibitive action of Vernonia amygdalina on the corrosion of aluminium alloys in acidic media," *Materials Letters*, vol. 57, no. 22–23, pp. 3705–3711, 2003.

S. Manish Kumar, K. Sudesh, R. Ratnani, and S. P. Mathur, "Corrosion inhibition of Aluminium by extracts of Prosopis juliflora in acidic media," *Bulletin of Electrochemistry*, vol. 22, no. 2, pp. 69–74, 2006.

A. A. Hossary, M. M. Gauish, and R. M. Saleh, "Corrosion inhibitor formulations from coal-tar distillation products for acid cleaning of steel in HCl," in *Proceedings of the 2nd International Symposium on Industrial and Oriented Basic Electrochemistry*, pp. 6–18, SAEST, CECRI, Madras, India, 1980.

R. A. Tupikov, Y. G. Dragunov, I. L. Kharina, and D. S. Zmienko, "Protection of carbon steels against atmospheric corrosion in a wet tropical climate using gas-plasma metalization with aluminum," *Protection of Metals*, vol. 44, no. 7, pp. 673–682, 2008.

P. Arora, T. Jain, and S. P. Mathur, *Chemistry*, vol. 1, p. 766, 2005.

M. A. Quraishi, D. K. Yadav, and I. Ahamad, "Green approach to corrosion inhibition by black pepper extract in hydrochloric acid solution," *Open Corrosion Journal*, vol. 2, pp. 56–60, 2009.

N. Lahhit, A. Bouyanzer, J.-M. Desjobert et al., "Fennel (Foeniculum vulgare) essential oil as green corrosion inhibitor of carbon steel in hydrochloric acid solution," *Portugaliae Electrochimica Acta*, vol. 29, no. 2, pp. 127–138, 2011.

E. E. Ougzie, "Corrosion inhibition of mild steel in hydrochloric acid solution by methylene blue dye," *Materials Letters*, vol. 59, no. 8–9, pp. 1076–1079, 2005.

A. Zarrouk, I. Warad, B. Hammouti, A. Dafali, S. S. Al-Deyab, and N. Benchet, "The effect of temperature on the corrosion of Cu/HNO₃ in the Presence of organic inhibitor: Part-2," *International Journal of Electrochemical Science*, vol. 5, no. 10, pp. 1516–1526, 2010.

K. P. Vinod Kumar, M. S. Narayanan Pillai, and G. Rexin Thusnavis, "Pericarp of the fruit of garcinia mangostana as corrosion inhibitor for mild steel in hydrochloric acid medium," *Portugaliae Electrochimica Acta*, vol. 28, no. 6, pp. 373–383, 2010.

H. A. Jung, B. N. Su, W. J. Keller, R. G. Mehta, and A. D. Kinghorn, "Antioxidant xanthones from the pericarp of Garcinia mangostana (Mangosteen)," *Journal of Agricultural and Food Chemistry*, vol. 54, no. 6, pp. 2077–2082, 2006.

I. B. Obot and O. O. Obi-Egbedi, S. A. Umoren, and E. E. Akenye, "Synergistic and antagonistic effects of anions and ipomeoa invulcata as green corrosion inhibitor for aluminium dissolution in acidic medium," *International Journal of Electrochemical Science*, vol. 5, no. 7, pp. 994–1007, 2010.

I. B. Obot and N. O. Obi-Egbedi, "Ipomoea invulcata as an ecofriendly inhibitor for aluminium in alkaline medium," *Portugaliae Electrochimica Acta*, vol. 27, no. 4, pp. 517–524, 2009.

I. B. Obot and N. O. Obi-Egbedi, "An interesting and efficient green corrosion inhibitor for aluminium from extracts of Chlomolaena odorata L. in acidic solution," *Journal of Applied Electrochemistry*, vol. 40, no. 11, pp. 1977–1983, 2010.

N. O. Eddy, P. A. Ekumemgbo, and P. A. P. Mamza, "Ethanol extract of Terminalia catappa as a green inhibitor for the corrosion of mild steel in H₂SO₄," *Green Chemistry Letters and Reviews*, vol. 2, no. 4, pp. 223–231, 2009.

F. A. de Souza and A. Spinelli, "Caffeic acid as a green corrosion inhibitor for mild steel," *Corrosion Science*, vol. 51, no. 3, pp. 642–649, 2008.

O. K. Abiola, J. O. E. Otaigbe, and O. J. Kio, "Gossypium hirsutum L. extracts as green corrosion inhibitor for aluminium in NaOH solution," *Corrosion Science*, vol. 51, no. 8, pp. 1879–1881, 2009.

F. Tirbonod and C. Fiaud, "Inhibition of the corrosion of aluminium alloys by organic dyes," *Corrosion Science*, vol. 18, no. 2, pp. 139–149, 1978.

J. D. Talati and J. M. Daraji, "Inhibition of corrosion of B26S aluminium in phosphoric acid by some azo dyes," *Journal of the Indian Chemical Society*, vol. 68, no. 2, pp. 67–72, 1991.

P. Gupta, R. S. Chaudhary, T. K. G. Namboodhiri, B. Prakash, and B. B. Prasad, "Effect of mixed inhibitors on dezincification and corrosion of 63/37 brass in 1% sulfuric acid," *Corrosion*, vol. 40, no. 1, pp. 33–36, 1984.

P. B. Tandel and B. N. Oza, "Performance of some dyestuffs as inhibitors during corrosion of mild-steel in binary acid mixtures (HCl + HNO₃)," *Journal of the Electrochemical Society of India*, vol. 49, pp. 49–128, 2000.

M. L. Zheludkevich, R. Serra, M. F. Montemor, and M. G. S. Ferreira, "Oxide nanoparticle reservoirs for storage and prolonged release of the corrosion inhibitors," *Electrochemistry Communications*, vol. 7, no. 8, pp. 836–840, 2005.

V. V. Torres, R. S. Amado, C. Faia de Sá et al., "Inhibitory action of aqueous coffee ground extracts on the corrosion of..."
carbon steel in HCl solution,” *Corrosion Science*, vol. 53, no. 7, pp. 2385–2392, 2011.

[91] G. G. Geesey, “Microbial exopolymers: ecological and economic considerations,” *American Society Microbiology News*, vol. 48, pp. 9–14, 1982.

[92] I. B. Beech and C. C. Gaylarde, “Recent advances in the study of biocorrosion—an overview,” *Revista de Microbiologia*, vol. 30, no. 3, pp. 177–190, 1999.

[93] P. S. Guiamet and S. G. Gomez De Saravia, “Laboratory studies of biocorrosion control using traditional and environmentally friendly biocides: an overview,” *Latin American Applied Research*, vol. 35, no. 4, pp. 295–300, 2005.

[94] M. F. Montemor, W. Trabelsi, M. Zheludevich, and M. G. S. Ferreira, “Modification of bis-silane solutions with rare-earth cations for improved corrosion protection of galvanized steel substrates,” *Progress in Organic Coatings*, vol. 57, no. 1, pp. 67–77, 2006.

[95] A. Pepe, M. Aparicio, S. Ceré, and A. Durán, “Preparation and characterization of cerium doped silica sol-gel coatings on glass and aluminum substrates,” *Journal of Non-Crystalline Solids*, vol. 348, pp. 162–171, 2004.

[96] X. W. Yu, C. N. Cao, Z. M. Yao, Z. Derui, and Y. Zhongda, “Corrosion behavior of rare earth metal (REM) conversion coatings on aluminum alloy LY12,” *Materials Science and Engineering A*, vol. 284, no. 1-2, pp. 56–63, 2000.

[97] A. N. Khramov, N. N. Voevodin, V. N. Balbyshev, and M. S. Donley, “Hybrid organo-ceramic corrosion protection coatings with encapsulated organic corrosion inhibitors,” *Thin Solid Films*, vol. 447-448, pp. 549–557, 2004.

[98] E. M. Sherif and S. M. Park, “Effects of 1,4-naphthoquinone on aluminum corrosion in 0.50 M sodium chloride solutions,” *Electrochimica Acta*, vol. 51, no. 7, pp. 1313–1321, 2006.

[99] M. S. Donley, R. A. Mantz, A. N. Khramov, V. N. Balbyshev, L. S. Kasten, and D. J. Gaspar, “The self-assembled nanophase particle (SNAP) process: a nanoscience approach to coatings,” *Progress in Organic Coatings*, vol. 47, no. 3-4, pp. 401–415, 2003.

[100] D. V. Andreeva, D. Fix, H. Möhwald, and D. G. Shchukin, “Self-healing anticorrosion coatings based on pH-sensitive polyelectrolyte/inhibitor sandwichlike nanostructures,” *Advanced Materials*, vol. 20, no. 14, pp. 2789–2794, 2008.

[101] M. L. Zheludkevich, D. G. Shchukin, K. A. Yasakau, H. Möhwald, and M. G. S. Ferreira, “Anticorrosion coatings with self-healing effect based on nanocontainers impregnated with corrosion inhibitor,” *Chemistry of Materials*, vol. 19, no. 3, pp. 402–411, 2007.

[102] V. DeGiorgi, “Corrosion basics and computer modeling,” in *Industrial Applications of the BEM*, chapter 2, pp. 47–79, 1986.

[103] H. Sun, P. Ren, and J. R. Fried, “The compass force field: parameterization and validation for polyphosphazenes,” *Computational and Theoretical Polymer*, vol. 8, pp. 229–246, 1998.

[104] N. G. Zamani, J. F. Porter, and A. A. Mufﬁ, “Survey of computational efforts in the ﬁeld of corrosion engineering,” *International Journal for Numerical Methods in Engineering*, vol. 23, no. 7, pp. 1295–1311, 1986.

[105] R. S. Munn, “A review of the development of Computational Corrosion analysis for special corrosion modelling through its maturity in the Mid 1980’s-Computer modelling in Corrosion,” ASTM STP 1154 American Study for Testing and Materials, Philadelphia, pp 215–228, 1991.
Review Article

Development of Novel Corrosion Techniques for a Green Environment

Zaki Ahmad and Faheemuddin Patel

Mechanical Engineering Department, King Fahd University of Petroleum & Minerals (KFUPM), Dhahran 31261, Saudi Arabia

Correspondence should be addressed to Faheemuddin Patel, faheemmp@kfupm.edu.sa

Received 4 March 2011; Accepted 3 July 2011

Academic Editor: Peter C. Okafor

Copyright © 2012 Z. Ahmad and F. Patel. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The synergistic effect of air pollution, brown clouds and greenhouse gasses is deleterious to human health and industrial products. The use of toxic inhibitors, chemicals in water treatment plants, and anti-fouling agents in desalination plants has contributed to the greenhouse effect. Conventional anti-corrosion techniques such as paints, coatings, inhibitor treatments, and cathodic protection paid no regard to greenhouse effect. Work on eco-friendly anti-corrosion techniques is scanty and largely proprietary. The use of nano-TiO$_2$ particles introduced in alkyds and polyurethane-based coatings showed a higher corrosion resistance compared to conventional TiO$_2$ coatings with significant photocatalytic activity to kill bacteria. The use of UV radiations for photo-inhibition of stainless steel in chloride solution can replace toxic inhibitors. Corrosion inhibition has also been achieved by using natural materials such as polymers instead of toxic chemical inhibitors, without adverse environmental impact. TiO$_2$ films exposed to UV radiation have shown the capability to protect the steel without sacrificing the film. Self-healing materials with encapsulated nanoparticles in paints and coatings have shown to heal the defects caused by corrosion. These innovative techniques provide a direction to the corrosion scientists, engineers, and environmentalists who are concerned about the increasing contamination of the planet and maintaining a green environment.

1. Introduction

The deterioration of materials and equipment by atmospheric pollution is not a new phenomenon and the corrosion engineers developed appropriate strategies to combat atmospheric corrosion. However, in the last decade global warming has placed heavy responsibilities on engineers and scientists to transform the conventional production processing techniques into eco-friendly techniques to control the greenhouse effect, which is slowly, but surely, inflicting an irreversible damage to materials and mankind on this planet. Whereas air pollution commonly refers to aerosols containing suspended impurities of particles such as sulfates, nitrates, organic compounds, and fly-ash particles, the green house gases contain mainly carbon dioxide (CO$_2$), methane (CH), nitric oxide and nitrogen dioxide (NO$_x$), sulfur (S), and chlorofluorocarbons (CFCs). Typical aerosols contain 25% sulfate, 11% organic, 9% BC, 6% nitrates, and 18% other materials. The Indian Ocean Experiment (INDOEX) conducted during 1996–1999 showed that the aerosols over the oceans show typically 1% sea salts and 10% mineral dust (Figure 1).

Brown clouds containing dangerous levels of aerosols observed in Asia have a tendency to increase global warming by as much as 50% [1]. The atmosphere is reported to be warming at a rate of 0.25°C per decade since 1950 at altitudes higher than 2–5 Km above sea level [2]. These brown clouds appear to have the same effect as green house gases. In context of corrosion, both green house gases and brown clouds have a deleterious effect on the integrity of buildings, vehicles, cultural monuments, and all engineered products. In the Euro-zone, 12 billion Euros are lost annually by deterioration of buildings [3]. The corrosion prevention practices are like a double-edged weapon; they stop corrosion, but the chemicals and materials used in corrosion prevention techniques interact with the atmosphere and add to environmental pollution. Corroded objects act synergistically to elevate pollution. Several metal ions interact with organic
compounds like humic acid and retard photocatalytic oxidation [4]. Corrosion prevention practices applied to power plants, desalination plants, transportation, aerospace, gas, oil, petrochemical and construction industries need to be modified to keep the environment green. No formal eco-friendly corrosion protection techniques have been reported by professional corrosion organizations. The results obtained by the authors from their previous work and some work reported in the literature have prompted them to present an overview of some eco-friendly corrosion techniques which could be improved further to save the planet from the green house carbon footprints by energy-efficient design, clean corrosion protection techniques, use of CO₂ for water production, CO₂ sequestration, and using warm water sources. By using warm cooling water, additional electrical energy savings of 12,208 MWH/yr and carbon dioxide footprint of 30,565 tons/year are predicted to be achieved. Clean water and superhydrophobic surfaces in heat exchanger tubes would have the capabilities to keep the tube surface ultraclean. Waste CO₂ releasing from chemical or other industries may be used in the desalination plants to make the design more eco-friendly. The above measures would reduce pollution in an area inflicted by one of the harshest environments with dangerous levels of aerosols.

2. Water Filtration. Water quality directly affects the magnitude of corrosion. Replacement of old techniques by new technologies such as vibratory shear enhanced technology (VSEP) has made it possible to produce clean water from reverse osmosis rejects by removing TOC (total organic compounds), TSS (total suspended solids), and TDS (total dissolved solids) content which induces corrosion and biofouling by formation of colloidal suspension [7]. A fluid dynamics comparison between crossflow filtration and vibratory shear enhanced process (VSEP) is shown in Figure 2, and a schematic of VSEP is shown in Figure 3. The VSEP technology is mature, proven, and cost-effective [8].

2.3. New Eco-Friendly Surface Modification Techniques. In corrosion prevention methods, coating is most widely practiced but it has aroused serious concerns because of its effect on environmental pollution. New environmental regulations focus on reducing the volatile organic compounds (VOCs) in paints which have the highest ozone-forming potential. The breakdown of coating under ultraviolet radiation and harsh environment necessitated the development of nanocoatings. Lotus flower, which remains clean in polluted water, provided a stimulus for the development of nanocoatings, which are corrosion resistant with dust and water repulsion properties. In a recent work by authors [9], nanoparticles of TiO₂ were introduced in alkyd resin binder in a ratio of 21:37 and blended in a high-speed dispersion mill. These paints were subjected to UV radiation, salt spray, and dust and water repulsion tests as specified by ASTM. After exposure to the above tests, it was observed that the nanotitanium dioxide coatings (Figure 4) showed a higher corrosion resistance with excellent water and dust repulsion properties and an outstanding resistance to ultraviolet radiation. These coatings showed a 90% reduction in coliform bacterial population due to their photocatalytic activity.

Most of the work on nanocoatings is proprietary and still in developing stages. The nanocoatings have opened a new gateway to contribute to a clean environment. Corrosion studies on nanostructured plasma-sprayed titanium dioxide and nanoalumina/titania coatings showed that these coatings offer an excellent barrier to erosion-corrosion in harsh environments such as encountered in pulp and paper industry [10]. A recent work has showed a high resistance to erosion-corrosion in 3.5 wt% NaCl containing polystyrene particles.
and a good photocatalytic activity [11]. The behavior of these coatings is dictated by the geometry of splat lamellae, volume percentage of unmelted particles, degree of residual porosity, and interlamellar spacing. A narrow interlamellar spacing prevents water penetration, and hence, erosion corrosion. Schematic of erosion-corrosion phenomenon in nanostructured coating is shown in Figure 5. The nanostructured TiO2 plasma-sprayed coatings are eco-friendly and showed a higher corrosion resistance than their conventional counterparts [12]. Table 1 shows the advantages of nanocoatings over conventional coatings.

2.4. Development of Innovative Surfaces. Environmental consideration is a prerequisite to an eco-friendly design. Galvanizing was a global choice because of longer life of steel; however, with the advances in nanocoatings with photoreactivity the choices have been broadened. A marked progress has been observed in recent years in fabrication of engineered surfaces, for example, hydrophobic surfaces. The authors have recently published a comprehensive review on fabrication of superhydrophobic surfaces [13]. The superhydrophobic surfaces possess excellent photocatalytic, water and dust repulsion, and corrosion resistance characteristics, and they represent the state-of-art eco-friendly corrosion protection techniques.

Two methods have been utilized to fabricate hydrophobic surfaces, modifying a rough surface with low energy compounds and roughening low surface energy materials. The water and dust repellency properties of such surfaces make them highly promising for a wide spectrum of applications in paints, coatings, photovoltaic cells, lubricants, electronic devices, biomaterials, prostheses implants and a host of micro/nano-electromechanical devices. The secret of superhydrophobicity lies in its unique two-level hierarchical surface comprising of nanobumps and microhills (valleys and troughs) embedded with epicuticular nanowax crystals as shown in Figure 6. Figure 7 shows the water drop rolling on lotus leaves without sticking and taking the dirt away due to superhydrophobicity.

Water contact angles are formed between the water droplets and substrate as shown in Figure 8. For a superhydrophobic surface the water contact angles must be between 150 and 180°. Maximum angle of 180° has been obtained by different techniques. At angles greater than 120° the water drops roll through the troughs and carry away the dust particles from the surface as shown in Figure 9.

Low-surface materials such as tetrafluoroethylene (Teflon), polydimethylsiloxane (PDMS), polyamides, polycarbonates, ZnO, and TiO2, have been used to fabricate superhydrophobic surfaces. Techniques such as laser etching [14], sol-gel [15, 16], and chemical etching [17] have been used to modify rough surface. These superhydrophobic surfaces keep corrosion at bay by not allowing a large volume of water to interact with the active surface. These surfaces can also be made to switch from a hydrophobic to a hydrophilic state. A hydrophilic surface can be used to separate oil from water. A stainless steel mesh coated with

Table 1: Comparison of conventional and nano coatings.

| Properties         | Conventional alumina/titania | Nanostructured alumina/titania | Improvement        |
|--------------------|------------------------------|--------------------------------|-------------------|
| Toughness          | Poor                         | Excellent                     | Dramatic          |
| Hardness (VHN)     | 1,000                        | 1,000                          | —                 |
| Wear resistance    | $7.5 \times 10^3$            | $40 \times 10^3$               | $\sim$5X          |
| Corrosion resistance| Good                        | Exceptional                   | Significant       |
| Grindability       | Poor                         | Excellent                     | Dramatic          |
| Fatigue life       | $<1$ million cycles          | $>10$ million cycles          | $>10$X            |
| Flex tolerance     | Result in coating spallation | Can be bent over 180 degrees with out spallation | Dramatic |
| Bond strength (psi)| 1,900                        | $\sim$8000                     | $\sim$4X          |
2.5. Self-Healing Materials and Surfaces. Recent attempts to create self-healing surfaces are directed to increase the life of engineered structures, which do not require periodic repairs or replacements over a long period of designed service life. An electroplated coating can be made more durable by encapsulating healing agents like chromium and zinc. In principle, capsules containing a healing agent (Figure 10) are embedded in a polymer. When the material is damaged, the capsules rupture and release the repairing agent (Figure 11).

One serious problem, which contributes to environmental pollution, is concrete corrosion. To tackle this problem, hollow and porous fibers filled with adhesive liquids are embedded in concrete. As soon as a crack appears the liquid is released to heal the crack. Delivering a healing agent from a remote reservoir to the damaged region via a vascular network housed in a honeycombed structure offers the potential of robust and sustainable system. Aeronautical and automobile companies are developing autonomous system that triggers the repair mechanism upon the onset of damage to retain the structural integrity and the service life without hurting the environment. A schematic of controlled release is shown in Figure 12.
2.6 Corrosion Inhibition and Cathodic Systems. Severe damage to environment has been caused over the years by the use of organic and inorganic inhibitors in oil and gas and water treatment plants. Inorganic inhibitors like chromates, nitrates, phosphates, and silicates, organic inhibitors like monoamines and diamines, synthetic inhibitors like chromophosphates, and scavengers like sodium sulfate have been indiscriminately used without regard to environmental pollution. Recent eco-friendly methods used in this regard include photo-induced inhibition of 304SS in sodium chloride by UV radiations. It has been shown that UV radiation has a significant effect in corrosion prevention [19]. Ultraviolet radiation has also been utilized to provide cathodic protection of steel structures in the presence of semiconductor films like TiO₂. Recently, the authors of [20] have designed a cathodic protection system by overlay of a thin TiO₂ film on steel substrate and exposing the system to UV radiation. The system is attached to a solar panel to store the electrons during bright and sunny days and regenerate the electrons at night and cloudy days. Because of a wide band gap of 3.2 eV, TiO₂ serves as an anode without sacrificing itself unlike the zinc and magnesium. While protecting the steel, the film of titanium dioxide surface generates hydroxyl radicals (OH⁻), superoxide anions (O₂⁻), and hydrogen peroxide (H₂O₂) which clean the organic
contamination by their photocatalytic activity as shown in Figure 13. This nonsacrificial galvanic cathodic protection system with added environmental and antibacterial properties offers an alternative to the conventional galvanic cathodic protection system where anodes are consumed and need periodic replacement. The eco-friendly techniques described above need further development; however, they offer a promise of clean corrosion prevention practices without hurting the environment.

3. Conclusion

With the revolutionary progress in industrialization and urbanization witnessed in recent years the intensity of air pollution and greenhouse gases has increased in alarming proportion. Both materials and mankind are therefore exposed to enhanced risk. New strategies to preserve materials and other resources need to be developed to enhance the life of materials while maintaining the environment green.
The existing corrosion solutions need to be transformed to green solutions by developing eco-friendly techniques. It has been shown how the corrosion protection methods such as inhibitor treatment, metallic-nonmetallic coatings, paints, and cathodic protection can be made greener by utilizing emerging techniques such as nano- and microtechnologies. Some work on eco-friendly techniques reported in the paper has shown how some of the traditional corrosion protection techniques can be transformed to eco-friendly techniques. It is just the beginning for a hopeful tomorrow.

Acknowledgment

The authors would like to acknowledge the support provided for this work by King Abdulaziz City for Science and Technology (KACST), Saudi Arabia, at King Fahd University of Petroleum & Minerals (KFUPM), Saudi Arabia, under National Science, Technology and Innovation Plan (NSTIP) with the Project no. 08-NAN93-4.

References

[1] “The Asian Brown Cloud: Climate and Other Environmental Impacts,” UNEP Assessment Report, 2002, http://www.rrcap.unep.org/issues/air/impactstudy/index.cfm/.
[2] V. Ramanathan, M. V. Ramana, G. Roberts et al., “Warming trends in Asia amplified by brown cloud solar absorption,” Nature, vol. 448, no. 7153, pp. 575–578, 2007.
[3] “Other effects on mankind: Air pollution speeds up corrosion,” Air Quality, Air Pollution & Climate Secretariat, Sweden, 2011, http://www.airclim.org/airQuality/sub4_3.php.
[4] C. S. Uyguner and M. Bekbolet, “Contribution of metal species to the heterogeneous photocatalytic degradation of natural organic matter,” International Journal of Photoenergy, vol. 2007, Article ID 23156, 8 pages, 2007.
[5] http://earthtrends.wri.org/pdf_library/country_profiles/cli_cou_682.pdf/.
[6] “Desalination Project Heads to Final Coastal Commission Hearing,” Poseidon Resources, Desalination Update, no. 14, 2008, http://www.workingwithwater.net/.
[7] G. Johnson, L. Stowell, and M. Monroe, “A Comparison of conventional treatment methods and VSEP, a vibrating membrane filtration system,” in Proceedings of the El Paso Desalination Conference, El Paso Texas, VSEP Treatment of RO Reject from Brackish Well Water, New Logic Research, March 2006.
[8] http://www.vsep.com/downloads/index.html.
[9] Z. Ahmad and M. Ahsan, “Nanopaint for desert environments,” Materials Performance, vol. 45, no. 11, pp. 30–33, 2006.
[10] Z. Ahmad and M. Ahsan, “Corrosion studies on the plasma-sprayed nanostructured titanium dioxide coatings,” Anti-Corrosion Methods and Materials, vol. 56, no. 4, pp. 187–195, 2009.
[11] Z. Ahmad and B. J. Aleem, “Erosion-corrosion behavior of DAS titanium dioxide coatings on neutral sodium chloride solution,” Nace Corrosion, vol. 65, no. 9, 2009.
[12] B. Qian and Z. Shen, “Fabrication of superhydrophobic surfaces by dislocation-selective chemical etching on aluminum, copper, and zinc substrates,” Langmuir, vol. 21, no. 20, pp. 9007–9009, 2005.
[13] Z. Ahmad, S. Rehman, and M. Ahsan, “Methods of fabrication of superhydrophobic engineering surfaces: a review,” International Review of Mechanical Engineering, vol. 3, no. 3, pp. 312–321, 2009.
[14] M. H. Jin, X. J. Feng, J. M. Xi et al., “Super-hydrophobic PDMS surface with ultra-low adhesive force,” Macromolecular Rapid Communications, vol. 26, no. 22, pp. 1805–1809, 2005.
[15] B. Qian and Z. Shen, “Fabrication of superhydrophobic surfaces by dislocation-selective chemical etching on aluminum, copper, and zinc substrates,” Langmuir, vol. 21, no. 20, pp. 9007–9009, 2005.
[16] Z. G. Guo, F. Zhou, J. C. Hao, and W. M. Liu, “Stable biomimetic super-hydrophobic engineering materials,” Journal of the American Chemical Society, vol. 127, no. 45, pp. 15670–15671, 2005.
[17] X. Wu, G. L. Zheng, and D. Wu, “Fabrication of superhydrophobic surfaces from micro structured ZnO-based surfaces via a wet-chemical route,” Langmuir, vol. 21, no. 7, pp. 2663–2667, 2005.
[18] L. Feng, Z. Zhang, Z. Mai et al., “A super-hydrophobic and super-oleophilic coating mesh film for the separation of oil and water,” *Angewandte Chemie*, vol. 43, no. 15, pp. 2012–2014, 2004.

[19] S. O. Moussa and M. G. Hocking, “The photo-inhibition of localized corrosion of 304 stainless steel in sodium chloride environment,” *Corrosion Science*, vol. 43, no. 11, pp. 2037–2047, 2001.

[20] I. Ahmed, Z. Ahmad, F. Patel, and M. Shuja Khan, “A photo-cathodic protection system utilizing UV radiations,” *International Journal of Engineering and Technology*, vol. 11, no. 1, pp. 197–202, 2011.
Research Article

The Inhibitory Action of the Extracts of Adathoda vasica, Eclipta alba, and Centella asiatica on the Corrosion of Mild Steel in Hydrochloric Acid Medium: A Comparative Study

M. Shyamala¹ and P. K. Kasthuri²

¹ Department of Chemistry, Government College of Technology, Tamil Nadu, Coimbatore 641013, India
² Department of Chemistry, L.R.G. Government Arts College for Women, Tamil Nadu, Tirupur 638604, India

Correspondence should be addressed to M. Shyamala, shyam786.399@rediffmail.com

Received 28 March 2011; Accepted 10 June 2011

Academic Editor: Ali Y. El-Etre

Copyright © 2012 M. Shyamala and P. K. Kasthuri. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The inhibitive action of the extracts of Adathoda vasica, Eclipta alba, and Centella asiatica on the corrosion of mild steel in 1N HCl has been studied using weight loss method, electrochemical methods, and hydrogen permeation method. Polarization method indicates that the plant extracts are under mixed control, that is, promoting retardation of both anodic and cathodic reactions. The impedance method reveals that charge-transfer process controls the corrosion of mild steel. The plant extracts obey Langmuir adsorption isotherm. Theoretical fitting of the corrosion data to the kinetic-thermodynamic model was tested to show the nature of adsorption. Physisorption mechanism has been proposed for the inhibition action of these plant extracts. The protective film formed on the surface was confirmed by SEM. From hydrogen permeation method, all the plant extracts were able to reduce the permeation current. Results obtained in all three methods were very much in good agreement in the order Eclipta alba > Adathoda vasica > Centella asiatica, and, among the three plant extracts studied, the maximum inhibition efficiency was found in Eclipta alba which showed 99.6% inhibition efficiency at 8.0% v/v concentration of the extract.

1. Introduction

Mild steel was the material of choice due to its characteristics of wide application in motor car bodies, machines, gears, pipes, tanks, and so forth and in most of the chemical industries. Hydrochloric acid and sulphuric acids are the medium generally being used for pickling mild steel. About 90% of pickling problems can be solved by introducing appropriate pickling inhibitor to the medium. The recent and growing trend is using plant extracts as corrosion inhibitor. Owing to strict environmental legislation, emphasis is being focused on development of naturally occurring substances as corrosion inhibitors [1]. Recently, many plant extracts have been reported to be very effective corrosion inhibitors for the protection of mild steel in acidic media [2–19]. In this study, the inhibition effect of the leaf extracts of Adathoda vasica (Adathodai), Eclipta alba (Karisalankanni), and Centella asiatica (Valarai) on the corrosion of mild steel in 1N hydrochloric acid was investigated using weight loss method, electrochemical methods, and hydrogen permeation method. There was no literature report on the studies of corrosion inhibition effect of the above plant extracts on mild steel in hydrochloric acid medium previously. From literature survey, it was found that the six plants selected for investigation was found to contain some alkaloids or hydroxyl organic compounds like sterols, tannins, and so forth. The aqueous extracts of these plants were prepared because alkaloids or hydroxyl organic compounds are easily soluble in water, and moreover due to the biodegradability, ecofriendliness, less toxicity, cost-effectiveness, easy availability, environmentally safe, and highly stable nature in acidic solutions, it was used to study the corrosion inhibition effect on mild steel in acid medium.

2. Experimental Procedure

2.1. Preparation of Mild Steel Specimen. Mild steel strips were mechanically cut into strips of size 4.5 cm × 2 cm × 0.2 cm
containing the composition of 0.14% C, 0.35% Mn, 0.17% Si, 0.025% S, 0.03% P, and the remainder Fe and provided with a hole of uniform diameter to facilitate suspension of the strips in the test solution for weight loss method. For electrochemical studies, mild steel strips of the same composition but with an exposed area of 1 cm² were used. For electrochemical studies, mild steel strips of the same

2.2. Preparation of the Plant Extract. The leaves of the *Adathoda vasica*, *Eclipta alba*, and *Centella asiatica* were taken and cut into small pieces, and they were dried in an air oven at 80 °C for 2 h and ground well into powder. From this, 10 g of the sample was refluxed in 100 mL distilled water for 1 h. The refluxed solution was then filtered carefully, the stock solution was prepared from the collected filtrate and prepared the desired concentrations by dilution with 1 N HCl and the concentration of the stock solution is expressed in terms of % (v/v). From the stock solution, 2%–10% concentration of the extract was prepared using 1 N hydrochloric acid. The aqueous extracts of these plants were prepared because alkaloids/hydroxyl organic compounds present in the leaves of these plants are easily hydrolysable and moreover have highly stable nature in acidic solutions. Similar kind of preparation has been reported in studies using aqueous plant extracts in the recent years [20–28].

2.3. Weight Loss Method. The pretreated specimens’ initial weights were noted and were immersed in the experimental solution (in triplicate) with the help of glass hooks at 30 °C for a period of 3 h. The experimental solution used was 1N HCl in the absence and presence of various concentrations of the plant extracts. After three hours, the specimens were taken out, washed thoroughly with distilled water, and dried completely, and their final weights were noted. From the initial and final weights of the specimen, the loss in weight was calculated and tabulated. From the weight loss, the corrosion rate (mpmy), inhibition efficiency (%), and surface coverage (θ) of plant extracts was calculated using the formula

\[
\text{Corrosion rate (mpmy)} = \frac{KW}{ATD},
\]

where \( K = 8.76 \times 10^4 \) (constant), \( W \) is weight loss in g, \( A \) is area in cm², \( t \) is time in hours and \( D \) is density in gm/cm³ (7.86),

\[
\text{Inhibition efficiency} \times 100, \quad (2)
\]

\[
\text{Surface coverage} = \frac{CR_\theta - CR_I}{CR_\theta} 
\]

where \( CR_\theta \) and \( CR_I \) are corrosion rates in the absence and presence of the inhibitors.

2.4. Potentiodynamic Polarization Method. Potentiodynamic polarization measurements were carried out using electrochemical analyzer. The polarization measurements were made to evaluate the corrosion current, corrosion potential, and Tafel slopes. Experiments were carried out in a conventional three-electrode cell assembly with working electrode as mild steel specimen of 1 sq.cm.area which was exposed and the rest being covered with red lacquer, a rectangular Pt foil as the counter electrode, and the reference electrode as SCE. Instead of salt, bridge a luggin capillary arrangement was used to keep SCE close to the working electrode to avoid the ohmic contribution. A time interval of 10–15 minutes was given for each experiment to attain the steady-state open-circuit potential. The polarization was carried from a cathodic potential of −800 mV (versus SCE) to an anodic potential of −200 mV (versus SCE) at a sweep rate of 1 mV per second. From the polarization curves, Tafel slopes, corrosion potential, and corrosion current were calculated. The inhibitor efficiency was calculated using the formula,

\[
\text{IE}(\%) = \frac{I_{\text{corr}}^* - I_{\text{corr}}}{I_{\text{corr}}} \times 100, \quad (3)
\]

where \( I_{\text{corr}} \) and \( I_{\text{corr}}^* \) are corrosion current in the absence and presence of inhibitors.

2.5. Electrochemical Impedance Method. The electrochemical AC-impedance measurements were also performed using electrochemical analyzer. Experiments were carried out in a conventional three-electrode cell assembly as that used for potentiodynamic polarization studies. A sine wave with amplitude of 10 mV was superimposed on the steady open circuit potential. The real part (\( Z' \)) and the imaginary part (\( Z'' \)) were measured at various frequencies in the range of 100 KHz to 10 MHz. A plot of \( Z' \) versus \( Z'' \) was made. From the plot, the charge transfer resistance (\( R_t \)) was calculated, and the double layer capacitance was then calculated using

\[
C_{dl} = \frac{1}{2\pi f_{\text{max}} R_t}, \quad (4)
\]

where \( R_t \) is charge transfer resistance, and \( C_{dl} \) is double layer capacitance. The experiments were carried out in the absence and presence of different concentrations of inhibitors. The percentage of inhibition efficiency was calculated using

\[
\text{IE}(\%) = \frac{R_t^* - R_t}{R_t} \times 100, \quad (5)
\]

where \( R_t^* \) and \( R_t \) are the charge transfer resistance in the presence and absence of inhibitors.

2.6. Hydrogen Permeation Method. The behaviour of the inhibitors with regard to hydrogen permeation can be understood by measuring the permeation current with and without inhibitors. An inhibitor can be considered as completely effective only if it simultaneously inhibits metal dissolution and hydrogen penetration into the metal [29]. Hydrogen permeation study has been taken up with an idea of screening the inhibitors with regard to their effectiveness...
on the reduction of hydrogen uptake. Hence, the hydrogen permeation study was carried out using an adaptation of the modified Devanathan-Stachurski two compartment cell assembly [30, 31] in 1N HCl medium in the absence and presence of optimum concentration of the extracts. Similar kind of study is reported in the works of Quraishi and Rawat [32].

2.7. Surface Examination Studies. Surface examination of mild steel specimens in the absence and presence of the optimum concentration of the extracts immersed for 3 h at 30°C was studied using JEOL-Scanning electron microscope (SEM) with the magnification of 1000x specimens.

3. Results and Discussion

3.1. Weight Loss Studies. The various corrosion parameters such as corrosion rate (CR), inhibition efficiency (IE), and surface coverage (θ) were obtained from weight loss method 1N hydrochloric acid in the absence and presence of various concentrations of the plant extracts ranging from 2% to 10% v/v and listed in Table 1.

It was found that the optimum concentration for *Adathoda vasica* was found to be 6% v/v with maximum inhibition efficiency of 99.0%, *Eclipta alba*, at 8% v/v with maximum inhibition efficiency of 99.6% and *Centella asiatica* at 10% v/v with maximum inhibition efficiency of 85.3% for a period of 3 hours of immersion time. This result indicates that the plant extracts could act as good corrosion inhibitors.

3.1.1. Effect of Immersion Time at 30°C. The effect of immersion time on corrosion rate and inhibition efficiency of the plant extracts with an optimum concentration at 30°C studied as given in Table 2 shows that the inhibition efficiency of the extract slightly decreased with the increase of immersion time from 3 to 24 h and reveals that the plant extracts showed maximum efficiency at 3 h of immersion time which is sufficient for the pickling process.

3.2. Potentiodynamic Polarization Studies. Electrochemical corrosion kinetic parameters such as corrosion potential (E_corr), corrosion current (I_corr), anodic and cathodic Tafel slopes (b_a and b_c), and percentage efficiency (IE) for the corrosion of mild steel in 1N HCl at 30°C in the absence and presence of different concentrations of the plant extract are given in Table 3, and its corresponding polarization curves are shown in Figure 1. Potentiodynamic polarization studies revealed that the corrosion current density (I_corr) markedly decreased with the addition of the extract and the corrosion potential shifts to less negative values upon addition of the plant extract. Moreover, the values of anodic and cathodic Tafel slopes (b_a and b_c) are slightly changed indicating that this behavior reflects the plant extracts ability to inhibit the corrosion of mild steel in 1N HCl solution via the adsorption of its molecules on both anodic and cathodic sites, and, consequently, the extracts act through mixed mode of inhibition [20, 21]. It was observed that with increase in concentration of the plant extract from 2% to 10%, the maximum inhibition efficiency of 99.2% was observed for *Adathoda vasica* at an optimum concentration of 6% in v/v, for *Eclipta alba* extract with 99.7% at 8% v/v, and *Centella asiatica* with 85.7% at 10% v/v of the extract.

3.3. Electrochemical Impedance Studies. Impedance measurements were studied to evaluate the charge-transfer resistance (R_t) and double-layer capacitance (C_dl), and through these parameters the inhibition efficiency was calculated. Figure 2 shows the Impedance diagrams for mild steel in 1N HCl with different concentrations of the plant extract, and the impedance parameters derived from these investigations are given in Table 4.

From Figure 2, the obtained impedance diagrams are almost in a semicircular appearance, indicating that the charge-transfer process mainly controls the corrosion of mild steel. Deviations of perfect circular shape are often referred to the frequency dispersion of interfacial impedance. This anomalous phenomenon may be attributed to the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena. In fact, in the presence of the plant extracts, the values of R_t have enhanced and the values of double-layer capacitance are also brought down to the maximum extent. The decrease in C_dl shows that the adsorption of the inhibitors takes place on the metal surface in acidic solution.

For *Adathoda vasica* extract, the maximum R_t value of 285.23 Ω cm² and minimum C_dl value of 7.65 μF/cm² are obtained at an optimum concentration of 6% in v/v with a maximum inhibition efficiency of 97.3%. For *Eclipta alba* extract, the maximum R_t value of 358.80 Ω cm² and minimum C_dl value of 6.00 μF/cm² are obtained at an optimum concentration of 8% in v/v with a maximum inhibition efficiency of 97.9%. For *Centella asiatica* extract, the maximum R_t value of 54.32 Ω cm² and minimum C_dl value of 39.88 μF/cm² are obtained at an optimum concentration of 10% in v/v with a maximum inhibition efficiency of 86.0%. A good agreement is observed between the results of weight loss method and electrochemical methods (potentiodynamic polarization method and impedance method) in the order *Eclipta alba > Adathoda vasica > Centella asiatica*.

3.4. Effect of Temperature. The effect of temperature on the corrosion rate of mild steel in free acid and in the presence of the optimum concentration of the inhibitors (plant extracts) was studied in the temperature range of 30°C to 80°C, using the weight loss measurements and given in Table 5. It was found that the rates of mild steel corrosion, in free and inhibited acid solutions, increase with increase in temperature, but the corrosion rate is much decreased for inhibited acid solution than the uninhibited acid solution. Consequently, the inhibition efficiency of the extract decreases with the increasing temperature. This result suggests a physical adsorption of the extract compounds on the mild steel surface. It also revealed that the extract was adsorbed on the mild steel surface at all temperatures.
Table 1: Corrosion parameters obtained from weight loss measurements for mild steel in 1N HCl containing various concentrations of the plant extracts.

| Name of the plant extract | Conc. of the extract (% in v/v) | Corrosion rate (mmpy) | Inhibition efficiency (%) | Surface coverage (θ) |
|---------------------------|---------------------------------|-----------------------|--------------------------|----------------------|
| Blank                     | 30.67                           | —                     | —                        | —                    |
|                          | 2.0                              | 1.78                  | 94.2                     | 0.9419               |
|                          | 4.0                              | 1.17                  | 96.2                     | 0.9618               |
| Adathoda vasica          | 6.0                              | 0.30                  | 99.0                     | 0.9902               |
|                          | 8.0                              | 0.35                  | 98.8                     | 0.9885               |
|                          | 10.0                             | 0.58                  | 98.1                     | 0.9811               |
| Eclipta alba             | Blank                            | 30.67                 | —                        | —                    |
|                          | 2.0                              | 2.90                  | 90.5                     | 0.9054               |
|                          | 4.0                              | 1.98                  | 93.5                     | 0.9354               |
|                          | 6.0                              | 0.98                  | 96.8                     | 0.9680               |
|                          | 8.0                              | 0.12                  | 99.6                     | 0.9960               |
|                          | 10.0                             | 0.12                  | 99.6                     | 0.9960               |
| Centella asiatica        | Blank                            | 30.67                 | —                        | —                    |
|                          | 2.0                              | 12.82                 | 58.2                     | 0.5820               |
|                          | 4.0                              | 10.79                 | 64.8                     | 0.6482               |
|                          | 6.0                              | 8.55                  | 72.1                     | 0.7212               |
|                          | 8.0                              | 6.56                  | 78.6                     | 0.7861               |
|                          | 10.0                             | 4.50                  | 85.3                     | 0.8532               |

Table 2: Effect of immersion time on percentage inhibition efficiency of mild steel in 1N HCl at 30°C in the presence of optimum concentration of the plant extracts.

| Name of the plant extract with optimum conc. | Time (h) | 3  | 6  | 9  | 12 | 15  | 18 | 21  | 24  |
|---------------------------------------------|----------|----|----|----|----|-----|----|-----|-----|
| 6% v/v of Adathoda vasica                   |          | 99.0| 98.2| 96.6| 96.2| 95.5| 94.4| 93.6| 92.7|
| 8% v/v of Eclipta alba                      |          | 99.6| 98.5| 98.0| 97.3| 96.5| 96.0| 95.3| 94.8|
| 10% v/v of Centella asiatica               |          | 85.3| 84.8| 84.3| 78.6| 71.4| 70.8| 68.3| 67.1|

Table 3: Potentiodynamic polarization parameters for mild steel in 1N HCl containing various concentrations of the plant extracts.

| Name of the plant extract | Conc. of extract (% in v/v) | $E_{corr}$ (V) | $I_{corr}$ (mA/cm²) | Tafel slope mV/decade | Inhibition efficiency (%) |
|---------------------------|-----------------------------|----------------|----------------------|-----------------------|--------------------------|
| Blank                     | —                           | −0.510         | 3.57                 | 78                    | 122                      | —                        |
|                          | 2.0                         | −0.512         | 0.21                 | 78                    | 124                      | 94.1                     |
| Adathoda vasica          | 4.0                         | −0.491         | 0.14                 | 76                    | 122                      | 96.1                     |
|                          | 6.0                         | −0.493         | 0.02                 | 74                    | 120                      | 99.2                     |
|                          | 8.0                         | −0.493         | 0.02                 | 74                    | 120                      | 99.2                     |
|                          | 10.0                        | −0.508         | 0.06                 | 76                    | 122                      | 97.2                     |
| Eclipta alba             | 2.0                         | −0.494         | 0.32                 | 80                    | 126                      | 91.0                     |
|                          | 4.0                         | −0.502         | 0.20                 | 78                    | 124                      | 94.4                     |
|                          | 6.0                         | −0.494         | 0.10                 | 76                    | 126                      | 97.2                     |
|                          | 8.0                         | −0.496         | 0.01                 | 74                    | 122                      | 99.7                     |
|                          | 10.0                        | −0.482         | 0.06                 | 78                    | 124                      | 98.3                     |
| Centella asiatica        | 2.0                         | −0.492         | 1.47                 | 76                    | 128                      | 58.8                     |
|                          | 4.0                         | −0.491         | 1.22                 | 78                    | 126                      | 65.8                     |
|                          | 6.0                         | −0.493         | 0.97                 | 80                    | 122                      | 72.8                     |
|                          | 8.0                         | −0.470         | 0.74                 | 74                    | 126                      | 79.3                     |
|                          | 10.0                        | −0.492         | 0.51                 | 76                    | 124                      | 85.7                     |
studied. A similar observation was seen in the studies of El-
Etre [3].

3.5. Kinetics and Mechanism of Corrosion Inhibition. The major phytochemical constituents present in *Adathoda vasica* are the alkaloids *Vasicine and Vasicinone* (Figure 3), the major phytochemical constituent present in *Centella asiatica* is *Asiaticoside*, a triterpene glycoside (Figure 4), and the major phytochemical constituent present in *Eclipta alba* are *Wedelolactone, β-sitosterol, Stigmasterol* (Figures 5(a), 5(b), and 5(c)), and also an alkaloid *Ecliptine* [33–35]. Inspection of the chemical structures of the phytochemical constituents reveals that these compounds are easily hydrolysable and the compounds can adsorb on the metal surface via the lone pair of electrons present on their oxygen atoms and make a barrier for charge and mass transfer leading to decreasing the interaction of the metal with the corrosive environment. As a result, the corrosion rate of the metal was decreased. The formation of film layer essentially blocks discharge of H⁺ and dissolution of metal ions. Due to electrostatic interaction, the protonated constituent’s molecules are adsorbed (physisorption) and high inhibition is expected. Acid pickling inhibitors containing organic N, S, and OH groups behave similarly to inhibit corrosion [36, 37].
Figure 2: (1) Blank, (2) 2.0 (% in v/v), (3) 4.0 (% in v/v), (4) 6.0 (% v/v), (5) 8.0 (% v/v), (6) 10.0 (% in v/v). Impedance diagrams for mild steel in 1N HCl solution in the absence and presence of various concentrations of the plant extract (a) *Adathoda vasica*, (b) *Eclipta alba*, and (c) *Centella asiatica*.

Table 4: Impedance parameters for the corrosion of mild steel in 1N HCl in the absence and presence of various concentrations of the plant extracts at 30°C.

| Name of the plant extract | Conc. of extract (% in v/v) | $R_z$ (Ω cm$^2$) | $C_{di}$ (μF/cm$^2$) | Inhibition efficiency (%) |
|---------------------------|----------------------------|------------------|----------------------|--------------------------|
| Blank                     | —                          | 7.58             | 285.34               |                          |
|                           | 2.0                        | 126.51           | 17.01                | 94.0                     |
|                           | 4.0                        | 200.34           | 10.72                | 96.2                     |
|                           | 6.0                        | 285.23           | 7.65                 | 97.3                     |
|                           | 8.0                        | 255.35           | 8.44                 | 97.0                     |
|                           | 10.0                       | 208.34           | 10.25                | 96.4                     |
| *Adathoda vasica*         | 2.0                        | 87.86            | 24.52                | 91.4                     |
|                           | 4.0                        | 136.49           | 15.86                | 94.4                     |
|                           | 6.0                        | 207.32           | 10.45                | 96.3                     |
|                           | 8.0                        | 358.80           | 6.00                 | 97.9                     |
|                           | 10.0                       | 356.80           | 6.00                 | 97.9                     |
| *Eclipta alba*            | 2.0                        | 18.32            | 118.02               | 58.6                     |
|                           | 4.0                        | 22.35            | 96.61                | 66.1                     |
| *Centella asiatica*       | 6.0                        | 27.54            | 78.50                | 72.5                     |
|                           | 8.0                        | 35.12            | 61.51                | 78.4                     |
|                           | 10.0                       | 54.32            | 39.88                | 86.0                     |
Table 5: Corrosion rate for the mild steel in 1N HCl at different temperatures obtained by weight loss method in the absence of the inhibitor and presence of the optimum concentration of the plant extracts.

| Name of the plant | Temperature (°C) | Corrosion rate (mmpy) | Inhibition efficiency (%) |
|-------------------|------------------|------------------------|---------------------------|
| Blank             | 30               | 30.67                  |                           |
|                   | 40               | 50.12                  |                           |
|                   | 50               | 70.79                  |                           |
|                   | 60               | 108.43                 |                           |
|                   | 70               | 125.89                 |                           |
|                   | 80               | 177.82                 |                           |
| 6% in v/v of Adathoda vasica | 30 | 0.30                   | 99.0                      |
|                   | 40               | 0.60                   | 98.8                      |
|                   | 50               | 1.26                   | 98.2                      |
|                   | 60               | 2.63                   | 97.6                      |
|                   | 70               | 5.25                   | 95.8                      |
|                   | 80               | 10.02                  | 94.4                      |
| 8% in v/v of Eclipta alba | 30 | 0.12                   | 99.6                      |
|                   | 40               | 0.62                   | 98.7                      |
|                   | 50               | 1.78                   | 97.5                      |
|                   | 60               | 4.47                   | 95.8                      |
|                   | 70               | 11.22                  | 93.7                      |
|                   | 80               | 23.00                  | 87.1                      |
| 10% in v/v of Centella asiatica | 30 | 4.50                   | 85.32                     |
|                   | 40               | 7.32                   | 85.39                     |
|                   | 50               | 10.40                  | 85.30                     |
|                   | 60               | 15.91                  | 85.32                     |
|                   | 70               | 18.52                  | 85.28                     |
|                   | 80               | 28.21                  | 84.14                     |

Figure 3: (1) Vasicine (2) Vasicinone.

The inhibition of the corrosion of mild steel in 1N HCl medium with addition of different concentrations of the extract can be explained by the adsorption of the components of the plant extracts on the metal surface. Inhibition efficiency (IE) is directly proportional to the fraction of the surface covered by the adsorbed molecules (θ). Therefore, (θ) with the extract concentration specifies the adsorption isotherm that describes the system and gives the relationship between the coverage of an interface with the adsorbed species and the concentration of species in solution. The values of the degree of surface coverage (θ) were evaluated at different concentrations of the inhibitors in 1N HCl solution. Attempts were made to fit θ values to various adsorption isotherm. An inhibitor is found to obey Langmuir, if a plot of log θ/1-θ versus log C is linear. Similarly, for Temkin plot θ versus log C, for BDM plot (log C + log θ/1-θ) versus θ^{3/2} and for Frumkin plot log θ/(1-θ)C versus θ will be linear. On examining, the adsorption of different concentrations of Adathoda vasica, Eclipta alba, and Centella asiatica extracts on the surface of mild steel in 1N hydrochloric acid was found to obey Langmuir adsorption isotherm. The Langmuir adsorption isotherm plot for the adsorption of various concentrations of the plant extracts is shown in Figure 6.

Theoretical fitting of the corrosion data to the kinetic-thermodynamic model was tested to show the nature of adsorption. The standard free energy of adsorption ΔG_{ads} which can characterize the interaction of adsorption molecules and metal surface was calculated

$$\ln K = \ln \frac{1}{55.5} - \frac{\Delta G_{ads}}{RT}, \quad (6)$$

where one molecule of water is replaced by one molecule of inhibitor and the numerical value (1/55.5) in the equation stands for the molarity of water.

The value of K can be calculated using

$$K = \frac{\theta}{(1-\theta)C}. \quad (7)$$
The enthalpy of adsorption ($\Delta H$) was calculated

$$\Delta H = E_a - RT,$$

and the entropy of adsorption ($\Delta S$) was calculated using

$$\Delta G = \Delta H - T\Delta S.$$  

The calculated values of activation energy ($E_a$), enthalpy of adsorption ($\Delta H$), free energy of adsorption ($\Delta G$), and entropy of adsorption ($\Delta S$) are shown in Table 6.

The activation energy $E_a$ was found to be 31.38 KJ mol$^{-1}$ for (1N HCl) and increased to 62.41 KJ mol$^{-1}$ in the presence of the Adathoda vasica extract and 93.48 KJ mol$^{-1}$ for Eclipta alba which shows that the adsorbed organic matter has provided a physical barrier to charge and mass transfer, leading to reduction in corrosion rate. The higher value of $E_a$ in the presence of the inhibitor compared to that in the absence of the inhibitor was attributed to physisorption [4]. For Centella asiatica, $E_a$ was found to be 31.33 KJ mol$^{-1}$ and remained almost same as blank suggesting inhibition efficiency had not changed with temperature variation for Centella asiatica.

The values of $\Delta G_{ads}$ around $-20$ KJ mol$^{-1}$ or lower are consistent with the electrostatic interaction between organic charged molecules, and the charged metal (physisorption) and those around $-40$ KJ mol$^{-1}$ or higher involved charge sharing or transfer from the organic molecules to the metal surface to form a coordinate type of bond (chemisorption) as discussed by Moretti et al. [38]. In this case, the negative sign of free energy of adsorption for the plant extracts indicates that the adsorption of the plant extracts on mild steel surface was a spontaneous process and the adsorption could be physisorption. Studies of El-Etre [3] and Li et al. [5] reported similar kind of results. The positive value of enthalpy of adsorption ($\Delta H$) suggests that the reaction was endothermic and the adsorption of the inhibitor on the metal surface has taken place. Positive value of entropy of adsorption ($\Delta S$) indicates that the reaction was spontaneous and feasible. Earlier work of Bhajiwala and Vashi [39] supports this.
3.6. Surface Examination Studies. Surface examination of the mild steel specimens was made using JEOL—scanning electron microscope (SEM) with the magnification of 1000x. The mild steel specimens after immersion in 1N HCl solution for three hours at 30°C in the absence and presence of optimum concentration of the plant extracts were taken out, dried, and kept in a dessicator. The protective film formed on the surface of the mild steel was confirmed by SEM studies. The SEM images of mild steel immersed in 1N HCl in the absence and presence of the optimum concentration of the plant extracts are shown in Figures 7, 8, 9, and 10. From the SEM images, it was found that more grains were found in SEM image of mild steel immersed in 1N HCl solution in the absence of the inhibitor, whereas no grains were found in the SEM image of mild steel immersed in 1N HCl solution in the presence of the plant extracts, which shows the presence of a protective film over the surface of the mild steel in the presence of the inhibitors and the protective film is uniform in the order *Eclipta alba* > *Adathoda vasica* > *Centella asiatica*. The SEM morphology of the adsorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the plant extracts.

3.7. Hydrogen Permeation Studies. When metals are in contact with acids, atomic hydrogen is produced. Before they combine to produce hydrogen molecules, a fraction may diffuse into the metal. Inside the metal, the hydrogen atoms may combine to form molecular hydrogen. Thus,
Table 6: Calculated values of activation energy ($E_a$), enthalpy of adsorption ($\Delta H$), free energy of adsorption ($\Delta G$), and entropy of adsorption ($\Delta S$) in the absence and presence of the optimum concentration of the plant extracts.

| System          | Temp ($T$) in K | $E_a$ (KJ mol$^{-1}$) | $\Delta H$ (KJ mol$^{-1}$) | $\Delta G$ (KJ mol$^{-1}$) | $\Delta S$ (KJ mol$^{-1}$) |
|-----------------|----------------|-----------------------|-----------------------------|----------------------------|----------------------------|
| Blank           | 303            | 28.86                 |                             |                            |                            |
|                 | 313            | 28.78                 |                             |                            |                            |
|                 | 323            | 28.69                 |                             |                            |                            |
|                 | 333            | 28.61                 |                             |                            |                            |
|                 | 343            | 28.53                 |                             |                            |                            |
|                 | 353            | 28.45                 |                             |                            |                            |
| Adathoda vasica | 303            | 59.89                 | $-17.18$                    | $0.2544$                   |
|                 | 313            | 59.81                 | $-17.27$                    | $0.2463$                   |
|                 | 323            | 59.72                 | $-16.71$                    | $0.2367$                   |
|                 | 333            | 59.64                 | $-16.42$                    | $0.2284$                   |
|                 | 343            | 59.56                 | $-15.26$                    | $0.2181$                   |
|                 | 353            | 59.48                 | $-14.82$                    | $0.2105$                   |
| Eclipta alba    | 303            | 90.96                 | $-18.78$                    | $0.3622$                   |
|                 | 313            | 90.88                 | $-16.31$                    | $0.3425$                   |
|                 | 323            | 90.79                 | $-15.04$                    | $0.3277$                   |
|                 | 333            | 90.71                 | $-14.02$                    | $0.3145$                   |
|                 | 343            | 90.63                 | $-13.22$                    | $0.3028$                   |
|                 | 353            | 90.55                 | $-11.29$                    | $0.2885$                   |
| Centella asiatica | 303          | 28.81                 | $-8.75$                     | $0.1240$                   |
|                 | 313            | 28.73                 | $-9.04$                     | $0.1207$                   |
|                 | 323            | 28.64                 | $-9.28$                     | $0.1174$                   |
|                 | 333            | 28.56                 | $-9.68$                     | $0.1148$                   |
|                 | 343            | 28.48                 | $-9.88$                     | $0.1118$                   |
|                 | 353            | 28.40                 | $-10.19$                    | $0.1093$                   |

Table 7: Values of hydrogen permeation current for the corrosion of mild steel in 1N HCl alone and in the presence of inhibitors.

| Inhibitor       | Conc. of the extract (% in v/v) | Permeation current (μA) | Reduction in permeation current (%) |
|-----------------|---------------------------------|-------------------------|-------------------------------------|
| Blank           | —                               | 23.0                    | —                                   |
| Adathoda vasica | 6.0                             | 3.1                     | 86.52                               |
| Eclipta alba    | 8.0                             | 2.2                     | 90.43                               |
| Centella asiatica | 10.0                      | 19.4                    | 15.65                               |

Figure 9: SEM photograph of mild steel immersed in 1N HCl solution containing an optimum conc. (6% v/v) of Adathoda vasica.

Figure 10: SEM photograph of mild steel immersed in 1N HCl solution containing an optimum conc. (10% v/v) of Centella asiatica.

A very high internal pressure is built up. This leads to heavy damage of the metal. This is known as “hydrogen embrittlement”. This phenomenon of hydrogen entry into the metals can occur in industrial processes like pickling, plating, phosphating, and so forth. An inhibitor can be considered as completely effective only if it simultaneously
inhibits metal dissolution and hydrogen penetration into the metal [40]. Hydrogen permeation study has been taken up with an idea of screening the inhibitors with regard to their effectiveness on the reduction of hydrogen uptake. The behaviour of the inhibitors with regard to hydrogen permeation can be understood by measuring the permeation current with and without inhibitors [30].

There are basically two reaction schemes. Common to both schemes, the first step is the diffusion of few hydrogen atoms that get onto the electrode surface. Hydrated protons are reduced to form neutral hydrogen atoms upon those areas of the surface, which are unoccupied. One can say protons are discharged on to free sites on the electrode to form adsorbed hydrogen atoms

\[ M(e) + H_3O^+ \rightarrow MH_{ads} + H_2O, \quad (10) \]

where \( M \) is the cathodic metal surface. The second step is the desorption step. The two basic reaction paths are

(i) discharge \( D \), followed by chemical desorption, \( CD \),

\[ MH_{ads} + MH_{ads} \rightarrow 2M + H_2 \uparrow \quad (11) \]

(ii) discharge \( D \), followed by electrolytic desorption, \( ED \),

\[ MH_{ads} + H_3O^+ + M(e) \rightarrow 2M + H_2O + H_2 \uparrow . \quad (12) \]

For transition metals, it has been reported that the electrolytic desorption is the rate determining step. A part of the atomic hydrogen liberated during these processes enters the metal, when the remainder is evolved as hydrogen gas [40]. From the hydrogen permeation studies on mild steel in 1N HCl in the absence and presence of inhibitors, it was observed that all the prepared extracts were able to reduce the permeation current compared to the control. The decrease in the permeation current follows the order Eclipta alba > Adathoda vasica > Centella asiatica. Permeation current versus time curves for mild steel in 1N HCl in the absence and presence of inhibitors are shown in Figure 11, and their corresponding permeation are given in Table 7.

The reason for the reduced permeation currents in presence of the inhibitors can be attributed to the slow discharge step followed by fast electrolytic desorption step

\[ M(e) + H_3O^+ \rightarrow MH_{ads} + H_2O, \quad (13) \]

The reduction of hydrogen uptake could be attributed to adsorption of the phytochemical constituents present in the plant extracts on the mild steel surface, which prevented permeation of hydrogen into metal.

4. Conclusion

(1) The leaf extracts of Adathoda vasica, Eclipta alba, and Centella asiatica act as good and efficient inhibitors for corrosion of mild steel in 1N Hydrochloric acid.

(2) The maximum inhibition efficiency for Eclipta alba extract was found to be 99.6% in the optimum concentration 8% in v/v, for Adathoda vasica extract, 99.0% in the optimum concentration 6% in v/v, and for Centella Asiatica extract, 85.3% in the optimum concentration 10% in v/v.

(3) The effect of immersion time of all the plant extracts at the optimum concentration showed maximum efficiency in 3 h immersion time at 30°C and found sufficient for pickling process.

(4) Potentiodynamic polarization studies revealed that the extracts act through mixed mode of inhibition.

(5) The impedance method revealed that charge-transfer process mainly controls the corrosion of mild steel.

(6) The adsorption of different concentrations of the plant extracts on the surface of mild steel in 1N hydrochloric acid followed Langmuir adsorption isotherm.

(7) The effect of temperature revealed physical adsorption for the inhibition action of these plant extracts.

(8) The value of activation energy \( E_a \) revealed that the adsorbed organic matter provided a physical barrier to charge and mass transfer, leading to reduction in corrosion rate.

(9) The negative sign of free energy of adsorption suggests that the adsorption action of the inhibitor on mild steel surface was a spontaneous process and the adsorption was found to be physisorption.

(10) The positive value of enthalpy of adsorption \( \Delta H \) suggests that the reaction was endothermic and the adsorption of the inhibitors on the metal surface takes place.

(11) A positive value of entropy of adsorption \( \Delta S \) indicates that the reaction was spontaneous and feasible.
(12) The SEM morphology of the adsorbed protective film on the mild steel surface has confirmed the high performance of inhibitive effect of the plant extracts.

(13) From hydrogen permeation method, it was observed that all the plant extracts were able to reduce the permeation current compared to the control.

(14) Results obtained in weight loss method were very much in good agreement with the electrochemical methods and Hydrogen permeation method in the order Eclipta alba > Adathoda vasica > Centella asiatica, and among the three plant extracts studied, the maximum inhibition efficiency was found in Eclipta alba which showed 99.6% inhibition efficiency at 8.0% v/v concentration of the extract.

References

[1] M.A. Quraishi and D. K. Yadav, “Corrosion and its control by some green Inhibitors,” in Proceedings of the 14th National Congress on Corrosion Control, 2008.

[2] A. Bouyander, B. Hammouti, and L. Majidi, “Pennyroyal oil from Mentha pulegium as corrosion inhibitor for steel in 1 M HCl,” Materials Letters, vol. 60, no. 23, pp. 2840–2843, 2006.

[3] A. Y. El-Etre, “Inhibition of aluminum corrosion using Opuntia extract,” Corrosion Science, vol. 45, no. 11, pp. 2485–2495, 2003.

[4] K. O. Orubite and N. C. Oforka, “Inhibition of the corrosion of mild steel in hydrochloric acid solutions by the extracts of leaves of Nypa fruticans Wurmb,” Materials Letters, vol. 58, no. 11, pp. 1768–1772, 2004.

[5] Y. Li, P. Zhao, Q. Liang, and B. Hou, “Berberine as a natural source inhibitor for mild steel in 1 M H2SO4,” Applied Surface Science, vol. 252, no. 5, pp. 1245–1253, 2005.

[6] A. Y. El-Etre, M. Abdallah, and Z. E. El-Tantawy, “Corrosion inhibition of some metals using lawsonia extract,” Corrosion Science, vol. 47, no. 2, pp. 385–395, 2005.

[7] E. Emeka and Oguzie, “Studies on the inhibitive effect of Ocimum viride extract on the corrosion of mild steel,” Materials Chemistry and Physics, vol. 99, no. 2-3, pp. 441–446, 2006.

[8] G. Gunasekaran and L. R. Chauhan, “Eco friendly inhibitor for corrosion inhibition of mild steel in phosphoric acid medium,” Electrochimica Acta, vol. 49, no. 25, pp. 4387–4395, 2004.

[9] I. B. Obot, S. A. Umorn, and N. O. Obi-Egbeli, “Corrosion inhibition and adsorption behaviour for aluminium by extract of Aningeria robusta in HCl solution: synergistic effect of iodide ions,” Journal of Materials and Environmental Science, vol. 2, no. 1, pp. 60–71, 2011.

[10] H. Al-Sehaibani, “Evaluation of Henna leaves as environmentally friendly corrosion inhibitors for metals,” Materialwissenschaft and Werkstofftechnik, vol. 31, no. 2, pp. 1060–1063, 2009.

[11] M. Lebrini, F. Robert, and C. Roos, “Inhibition effect of alkaloids extract from Anonna squamosa plant on the corrosion of C38 steel in normal hydrochloric acid medium,” International Journal of Electrochemical Science, vol. 5, no. 11, pp. 1698–1712, 2010.

[12] C. A. Loto and A. I. Mohammed, “The effect of Anacardium Occidentale (cashew) juice extract on the corrosion of mild steel in hydrochloric acid,” Corrosion Prevention and Control Journal, vol. 47, no. 2, pp. 5056–5063, 2000.

[13] G. D. Davis, The Use of Extracts of Tobacco Plants as Corrosion Inhibitors, DACCO SCI, INC, Columbia, Md, USA, 2000.

[14] O. K. Abiola, “The inhibition of mild steel corrosion in an acidic medium by fruit juice of citrus paradisi,” Journal of Corrosion Science and Engineering, vol. 5, no. 10, 2006.

[15] A. O. James and E. O. Ekpe, “Inhibition of corrosion of mild steel in 2M hydrochloric acid by Aloe Vera,” International Journal of Pure and Applied Chemistry, vol. 35, no. 10, 2002.

[16] M. Lebrini, F. Robert, and C. Roos, “Alkaloids extract from Palicourea guianensis plant as corrosion inhibitor for C38 steel in 1 M hydrochloric acid medium,” International Journal of Electrochemical Science, vol. 6, no. 3, pp. 847–859, 2011.

[17] J. Bruneton, Pharmacognosie-Phytochimie, Plantes Médicinales, Médicales Internationales, Tec&Doc, Paris, France, 4eme edition, 2009.

[18] E. E. Ebenso, N. O. Eddy, and A. O. Odiongenyi, “Corrosion inhibitive properties and adsorption behaviour of ethanol extract of Piper guineensis as a green corrosion inhibitor for mild steel in H2SO4,” African Journal of Pure and Applied Chemistry, vol. 2, no. 11, pp. 107–115, 2008.

[19] I. M. Mejeha, A. A. Uroh, K. B. Okeoma, and G. A. Alozie, “The inhibitive effect of Solanum melongena L. leaf extract on the corrosion of aluminium in tetraoxosulphate (VI) acid,” African Journal of Pure and Applied Chemistry, vol. 4, no. 8, pp. 158–165, 2010.

[20] A. Y. El-Etre, “Inhibition of acid corrosion of carbon steel using aqueous extract of olive leaves,” Journal of Colloid and Interface Science, vol. 314, no. 2, pp. 578–583, 2007.

[21] A. M. Abdel-Gaber, B. A. Abd-El-Nabey, I. M. Sidahmed, A. M. El-Zayady, and M. Saadawy, “Inhibitive action of some plant extracts on the corrosion of steel in acidic media,” Corrosion Science, vol. 48, no. 9, pp. 2765–2779, 2006.

[22] A. M. Abdel-Gaber, B. A. Abd-El-Nabey, and M. Saadawy, “The role of acid anion on the inhibition of the acidic corrosion of steel by lupine extract,” Corrosion Science, vol. 51, no. 5, pp. 1038–1042, 2009.

[23] B. Anand and V. Balasubramanian, “Corrosion behaviour of mild steel in acidic medium in presence of aqueous extract of Allamanda blanchetti,” E-Journal of Chemistry, vol. 8, no. 1, pp. 226–230, 2011.

[24] M. H. Hussin and M. J. Kassim, “Electrochemical studies of mild steel corrosion inhibition in aqueous solution by Uncaria gambir extract,” Journal of Physical Sciences, vol. 21, pp. 1–13, 2010.

[25] A. M. Al-Turkustani, “Aloe plant extract as environmentally friendly inhibitor on the corrosion of aluminium in hydrochloric acid in absence and presence of iodide ions,” Modern Applied Science, vol. 4, pp. 105–124, 2010.

[26] S. Rajendran, M. Agasta, R. B. Devi, B. S. Devi, K. Rajam, and J. Jeyasundari, “Corrosion inhibition by an aqueous extract of Henna leaves ( Lawsonia Inermis L),” Zaštita Materijala, vol. 50, pp. 77–84, 2009.

[27] J. A. Selvi, S. Rajendran, V. G. Sri, A. J. Amalraj, and B. Narayanasamy, “Corrosion inhibition by beet root extract,” Portugaliae Electrochimica Acta, vol. 27, pp. 1–11, 2009.

[28] G. Ilayaraja, A. R. Sasiekkhumar, and P. Dhanakodi, “Inhibition of mild steel corrosion in acidic medium by aqueous extract of Tridax procumbens L.,” E-Journal of Chemistry, vol. 8, no. 2, pp. 685–688, 2011.
[29] M.A.V. Devanathan and Z. Stachurski, “The Adsorption and
diffusion of electrolytic hydrogen in palladium,” Proceedings
of Royal Society, vol. 70, p. 10, 1962.
[30] J. O. M. Bockris, J. McBreen, and L. Nanis, “The hydrogen
evolution kinetics and hydrogen entry into a-iron,” Journal of
The Electrochemical Society, vol. 112, no. 10, pp. 1025–1031,
1965.
[31] M. J. Danielson, “Use of the Devanathan-Stachurski cell to
measure hydrogen permeation in aluminum alloys,” Corrosion
Science, vol. 44, no. 4, pp. 829–840, 2002.
[32] M. A. Quraishi and J. Rawat, “Influence of iodide ions
on inhibitive performance of tetraphenyl-dithia-octaaza-
cyclotetradeca-hexaene (PTAT) during pickling of mild steel
in hot sulfuric acid,” Materials Chemistry and Physics, vol. 70,
no. 1, pp. 95–99, 2001.
[33] www.himalayahealthcare.com/herbfinder/english.htm.
[34] K. K. Bhargava, “Himalaya herbal monograph,” Indian Journal
of Chemistry, vol. 8, p. 664, 1970.
[35] M. J. Sanghavi, S. K. Shukla, A. N. Misra, M. R. Padh, and G. N.
Mehta, “Inhibition of hydrochloric acid corrosion of mild steel
by aid extracts of Emblica officinalis, Terminalia bellirica and
Terminalia chebula,” Bulletin of Electrochemistry, vol. 13, no.
8-9, pp. 358–361, 1997.
[36] A. A. El Hosary, R. M. Saleh, and A. M. Shams-Eldin,
“Corrosion inhibition by naturally occurring substances-1.
The effect of hibiscus subdarifia (karkade) extract on the
dissolution of Al and Zn,” Corrosion Science, vol. 12, pp. 897–
904, 1972.
[37] M. Ajmal, A. S. Mideen, and M. A. Quraishi, “2-hydrazino-
6-methyl-benzothiazole as an effective inhibitor for the corro-
sion of mild steel in acidic solutions,” Corrosion Science, vol.
36, no. 1, pp. 79–84, 1994.
[38] G. Moretti, F. Guidi, and G. Grion, “Tryptamine as a green
iron corrosion inhibitor in 0.5 M deaerated sulphuric acid,”
Corrosion Science, vol. 46, no. 2, pp. 387–403, 2004.
[39] H. M. Bhajiwala and R. T. Vashi, “Ethylamines as corrosion
inhibitors for zinc in HNO3 / HCl binary mixture,” Bulletin of
Electrochemistry, vol. 18, no. 6, pp. 261–266, 2002.
[40] K. N. Srinivasan, M. Selvam, and S. Venkata Krishna Iyer,
“Hydrogen permeation during zinc-manganese alloy plating,”
Journal of Applied Electrochemistry, vol. 23, no. 4, pp. 358–363,
1993.