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# Potential of *Azadirachta indica* as a green corrosion inhibitor against mild steel, aluminum, and tin: a review

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## Abstract

*Azadirachta indica* (AZI, commonly recognized as "Neem") is noteworthy both for its chemical and for its biological actions. It is one of the most fruitful sources of secondary metabolites in nature. To date, more than 300 natural products have been isolated from different sections of the tree, with new compounds added to the list every year. As a contribution to the current interest on green corrosion inhibitors, the present study aims at broadening the application of plant extracts for metallic corrosion inhibition by investigating the inhibiting properties of *A. indica* especially for mild steel, aluminum, and tin. In the present article, we discuss the potential of AZI extract as a corrosion inhibitor on metal surfaces, especially of mild steel, aluminum, and tin. The adsorption isotherm studies, chemical composition of AZI, effect of temperature on inhibition efficiency and computational analysis related with AZI adsorption on metals have also been discussed in detail. This work will further help in the understanding of the adsorption mechanism involved and hence inhibition effect of plant extract against metal corrosion.

**Keywords:** Green chemistry; *Azadirachta indica*; Corrosion; Green corrosion inhibitors; Computational calculations

## Review

### Introduction

"Green chemistry" provides an opportunity to design any research in non-polluting way with minimum production of waste and minimum consumption of energy. It is a philosophy which is equally applicable in all fields wherever chemistry involves (Sharma et al. 2010a; Sharma et al. 2011; Sharma et al. 2009a; Linthorst 2010). "Corrosion" is a phenomenon where chemistry helps to explain its mechanism and role of ions and energy behind it. It is simply a destruction of materials resulting from an exposure and the interaction with the environment. One of the latest and popular approaches is the use of substances called corrosion inhibitor. These inhibitor molecules consist ofheterocyclic compounds with polar functional groups (e.g. N, S, O, and P) and conjugated double bonds with different aromatic system. Basically, these substances adsorb on the metal surface to block the destruction reaction with aggressive media. They are both physically and chemically active adsorbate type substances (Thompson et al. 2007; Buchweishaija 2009). It is a major problem that must be confronted for safety, environmental, and economic reasons in various chemical, mechanical, metallurgical, biochemical, and medical engineering applications and more specifically, in the design of a much more varied number of mechanical parts which equally vary in size, functionality, and useful lifespan. Corrosion attack can be prevented by various methods such as materials improvement, combination of production fluids, process control, and chemical inhibition. Among these methods, the implementation of corrosion inhibition is the most excellent approach to avoid disastrous destruction of metals and alloys in corrosive media. The use of corrosion inhibitors is the most economical and convenient technique to control corrosive attack on metals. Corrosion inhibitors are chemicals either synthetic or natural which, when added in small amounts to an environment, decrease the rate of attack by the environment on metals. A number of synthetic compounds are known to be applicable as good corrosion inhibitors for metals (Quraishi et al. 2012; Kabanda et al. 2012a; Ebenso et al. 2012a). The

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importance of a corrosion study depend in the fact that corrosion causes great loses to our economy and is a major threat for human safety. Corrosion costs worldwide are therefore on the order of US$552 billion (Chauhan and Gunasekaran 2007; Schmitt et al. 2009a). Even countries like India is suffering badly due to this problem of corrosion (Sharma and Sharma 2011). Several efforts have been made using corrosion-preventive practices, and the use of green corrosion inhibitors is one of them (Anuradha et al. 2008; Mudhoo and Sharma 2010; Sharma et al. 2010b; Sharma et al. 2010c; Aboia and James 2010; Sharma et al. 2009b; Sharma et al. 2009c). On the other hand, the attractiveness and utilization of synthetic compounds as a corrosion inhibitor has come under severe criticism due to the harsh environmental regulations and toxic effects of synthetic compounds on human and animal life. Consequently, there exists the need to build up a new class of corrosion inhibitors with low toxicity, eco-friendliness, and good efficiency. Throughout the ages, plants have been used by human beings for their basic needs such as assembly of food stuffs, shelters, clothing, fertilizers, flavors and fragrances, medicines, and last but not least, as corrosion inhibitors (Ajmal et al. 1994; Bentiss et al. 2002). The use of natural products as corrosion inhibitors can be traced back to the 1930s when plant extracts of *Chelidonium majus* (Celandine) and other plants were used for the first time in $H_2SO_4$ pickling baths (Sanyal 1981). After then, interest in using natural products as corrosion inhibitors increased substantially and scientists around the world reported several plant extracts as promising green anticorrosive agents (Schmitt et al. 2009b). Most of the gums were also reported as good corrosion inhibitor due to their gum-metal complex forming capacity, availability of π-electrons and hetero atoms, and less toxic properties (Peter et al. 2015). The adsorption of organic molecules depends on the presence of π-electrons and hetero atoms (Jin et al. 2006; Raja and Sethuraman 2008a). Although synthetic organic inhibitors have shown effective corrosion inhibition, their cost, toxicity, and non-biodegradability lead us to look for green options. In this review, we are discussing about the various plant extract and especially *Azadirachta indica* as green corrosion inhibitor for mild steel, Al, and tin (Tables 1, 2, and 3).

### *Use of A. indica as a corrosion inhibitor against mild steel, aluminum, and tin corrosion*

*A. indica* (AZI, common name "Neem") is noteworthy for its biological and chemical uses (Fig. 1). It is known as "magical plant" for many diseases treatment (Kliˇski´c et al. 2000). It is very effective in the production of secondary metabolites (Kumar et al. 1996; Schaaf et al. 2000; Barton 1999). Neem is a member of the mahogany family, Meliaceae. Neem trees are attractive broad-leaved evergreens that can grow up to 30 m tall and 2.5 m in girth. Their scattering branches form rounded crowns as much as 20 m across. The fruit is a smooth, ellipsoidal drupe, up to almost 2 cm long (Jacobson 1986b).

The chemical compounds of neem belonged to a general class of natural products called "triterpenes" or "limonoids." These limonoids have an ability to block insects' growth who are responsible for harmful outcomes in agriculture and human health sector. New limonoids are still being discovered in neem, but azadirachtin, salannin, meliantriol, and nimbin are the best known and most significant ones (Qurasishi 2004). Nowadays, the use of neem as a corrosion inhibitorhas been widely investigated., so in Table 4, we summarize the corrosive properties of neem with respect to mild steel, aluminum, and tin metals.

Arab et al. (2008) found that AZI extract inhibits the corrosion of aluminum in 0.5 M HCl. Sharma et al. (2013) investigated the inhibitory efficacy of ethanolic extract of *A. indica* fruit for acid corrosion of aluminum.

The corrosion inhibition and adsorption properties of neem (AZI) mature leaves extract as a green inhibitor of mild steel (MS) corrosion in nitric acid ($HNO_3$) solutions have been studied and investigated by Sharma et al. (2009a; Sharma et al. 2010c; Sharma et al. 2010d) using a gravimetric technique for experiments conducted at 30 and 60 °C. According to Ayssar et al. (2010), the aqueous neem leaves extract was found to be an excellent potential corrosion inhibitor for carbon steel in 1.0 M HCl. Obiukwu et al. (2013) mentioned that the *A. indica* had a better effect with an inhibitive efficiency of 85 % for stainless steel. Investigation of Eddy and Mamza (2009) demonstrates that the rate of corrosion of mild steel in $H_2SO_4$ increases with the increase in the concentration of the acid and that ethanol extracts of the seeds and leaves of *A. indica* inhibit the corrosion of mild steel in $H_2SO_4$. According to Loto et al. (2011), the corrosion inhibition performance of neem leaf (*A. indica*) extract on the corrosion of mild steel was achieved in the dilute hydrochloric acid at 0.25 g/l extract concentration and also at 30 °C. In a recent study by Desai (2015a), it has been discussed that in HCl, AZI was an effective inhibitor against mild steel corrosion, the rate of corrosion increases with the increase in acid concentration and temperature. He also observed that a straight line in the plots of Langmuir adsorption isotherm suggests that the inhibitor's adsorption on steel followed Langmuir isotherm. Polarization study involved in this case indicates that the inhibitor functions as a mixed inhibitor (Desai 2015b). In an another study carried out by Ajanaku et al. (2015), authors highlighted that in the corrosion inhibition

**Table 1** Plants as corrosion inhibitors against mild steel corrosion

| Study Conducted | Plant product | Solution | Effect of temperature on percentage inhibition efficiency | Effect of concentration on percentage inhibition efficiency | Methods | Adsorption type and isotherm used | Reference |
|---|---|---|---|---|---|---|---|
| *Eichhornia crassipes* is noted as one of the most important and noxious freshwater weed; the extracts of its leaves and roots were reported as good corrosion inhibitor for mild steel corrosion in HCl solutions using gasometric technique, and its modeled structures provides additional insight into the mechanism of inhibitory action by DFT | *E. crassipes* (leaf and root) | HCl | Decrease with rise in temperature | Increase | Gasometric technique | (Physically adsorbed) | Ulaeto et al. 2012 |
| *Nauclea latifolia* commonly known as pin cushion tree is a straggling shrub or small spreading tree that belongs to the family Rubiaceae. The effects of ethanol (ENL), alkaloids (ANL), and non-alkaloids (NNL) extracts from the root of *N. latifolia* on the dissolution of carbon steel in $H_2SO_4$ solutions were shown their effective inhibition by followed trend ANL>ENL> NNL. Gasometric method was use to perform practical data and obtained results show that percentage inhibition efficiency increase with concentration but decrease with rise in temperature | *N. latifolia* (root) | $H_2SO_4$ | Decrease with rise in temperature | Increase | Gasometric technique | Temkin | Okafor et al. 2013 |
| Banana peel extract (constituent of this extract is bananadine (3Z,7Z,10Z)-1-oxa-6-azacyclododeca-3,7,10-triene) was reported as a good corrosion inhibitor with Zn in distilled water for carbon steel corrosion by the weight loss, thermometric , FTIR, and AFM analysis. Obtained results show that percentage inhibition efficiency first decrease with the addition of Zn but after increasing Zn concentration it increased | Banana peel extract + Zn | Distilled water | – | First decrease with Zn after increase with increasing concentration of Zn inhibition efficiency increases | Weight loss, thermometric , FTIR, and AFM analysis | – | Sangeetha et al. 2012 |
| By the use of quantum chemical calculations, the active compound were reported as follows: (Kalmegh) *Andrographis paniculata*—andrographolide, (Meethi Neem) *Murraya koenigii*— mahabinine and pyrayafoline, (Bael) *Aegle marmelos*—skimmianine, (Kuchla) *Strychnos nuxvomica*—brucine, (Shahjan) *Moringa oleifera*—arginine, (Orange) *Citrus aurantium*—threonine, and (Arjun) *Terminalia arjuna*—sitosterol, Due to these active molecules, they show their inhibition effect for corrosion | The extracts of (Kalmegh) *Andrographis paniculata*, (Meethi Neem) *Murraya koenigii*, (Bael) *Aegle marmelos*, (Kuchla) *Strychnos nuxvomica*, (Shahjan) *Moringa oleifera*, (Orange) *Citrus aurantium*, and (Arjun) *Terminalia arjuna* | HCl | – | – | DFT, molecule analysis, and quantum calculations | – | Singh et al. 2013 |

**Table 1** Plants as corrosion inhibitors against mild steel corrosion *(Continued)*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Aloe vera plant belongs to the family of Liliacea. The constituents of gel are polysaccharides, glycoproteins, vitamins, mineral, and enzymes. Obtained results show its synergistic type effect, and percentage inhibition efficiency was decrease with rise in temperature and increase with increasing extract concentration | Aloe vera | $HNO_3$ | Decrease with rise in temperature | Increase | Gravimetric technique | Chemisorption | Gupta and Jain 2014 |
| *C. sinensis* leaf extract reported as a corrosion inhibitor in aqueous medium by the use of weight loss, UV, and FT-IT methods. Obtained results show that inhibition efficiency increase with increasing inhibitor concentration but decrease with rise in temperature | *C. sinensis* leaf extract | Aqueose | Decrease with rise in temperature | Decrease | Weight loss method, pH, UV–vis, and FT-IR | Physical adsorption | Yamuna and Athony 2014 |
| *Hibiscus rosa-sinensis* leaves extract reported as a good corrosion inhibitor for mild steel in HCl medium by the use of weight loss and EIS techniques. Obtained results show that the percentage inhibition efficiency was increased with the increasing temperature and concentration and show mixed-type inhibitor effect, and adsorption process was spontaneous and followed the Langmuir, Flory-Huggins and Freundlich adsorption isotherms | *H. rosa-sinensis* (Jasud) | HCl | Increase | Increase | Gravimetric (weight loss) and electrochemical techniques | Langmuir, Flory-Huggins and Freundlich adsorption | Desai 2015a |
| *Ilex paraguariensis* extracts reported as a good corrosion inhibitor for carbon steel in HCl medium by the use of weight loss and EIS techniques. Its inhibition efficiency increased with the increase of concentration and time. Obtained results show that *I. paraguariensis* act as both type inhibitor and obeyed the Langmuir adsorption isotherm | *I. paraguariensis* | HCl | Increase | Increase | Weight loss and electrochemical measurements | Langmuir adsorption isotherm | Souza et al. 2015 |
| *Ruta graveolens* extract reported as a good corrosion inhibitor for mild steel corrosion in HCl medium by PDP and weight loss method. Obtained results show that percentage inhibition efficiency increase with increasing concentration of inhibitor but decrease with rise in temperature and obeyed the Langmuir adsorption isotherm | *R. graveolens* extract | HCl | Decrease with rise in temperature | Increase | Potentiodynamic polarization and weight loss techniques | Langmuir adsorption isotherm | Majeed et al. 2014 |
| *Musa sapientum* which is commonly called banana is a herbaceous plant, belonging to the family of Musaceae. It is reported as a good corrosion inhibitor | *M. sapientum* peels extract + concentrated tetraoxosulphate (vi) acid | $H_2SO_4$ | Decrease | Increase | Weight loss, E. chemical measurements | Physical adsorption | Salami et al. 2012 |

**Table 1** Plants as corrosion inhibitors against mild steel corrosion *(Continued)*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| for mild steel in $H_2SO_4$ medium with tetraoxosulphate (vi) acid by the use of E. chemical measurements. Obtained results show that corrosion rate decrease with increasing concentration rate of inhibitor but increase with rising temperature. Simply followed the physical adsorbtion | | | | | | | |
| Extract of fenugreek leaves reported as a good inhibitor for mild steel in HCl and $H_2SO_4$ solution but more efficient in HCl solution. Inhibition efficiency was decrease with rise in temperature but increase with increasing inhibitor concentration in HCl while both temperature and concentration increased the inhibition efficiency for mild steel in $H_2SO_4$ solution. Langmuir adsorption isotherm followed in HCl medium and Temkin followed in $H_2SO_4$ medium | Extract of fenugreek leaves | HCl and $H_2SO_4$ | Decrease in HCl solution but increase In $H_2SO_4$ solution | Increase in both solutions | Gravimetric technique | Langmuir in HCl solution, Temkin in $H_2SO_4$ solution | Noor 2007 |
| *Cotula cinerea, Retama retam, Artemisia herba* reported as good corrosion inhibitors for mild steel in $H_2SO_4$ medium by weight loss and EIS methods | *Cotula cinerea, Retama retam, Artemisia herba* | $H_2SO_4$ | – | – | Weight Loss and E. chemical measurements | – | Raja and Sethuraman 2008b |
| *Eclipta alba* reported as an effective corrosion inhibitor for mild steel in $H_2SO_4$ medium by the use of weight loss and potentiodynamic polarization methods. Obtained results show that inhibitor behave as mixed-type inhibitor; inhibition efficiency increase with concentration value but decrease with rise in temperature. Obeyed the Langmuir adsorption isotherm | *E. alba* | $H_2SO_4$ | Decrease with rise in temperature | Increase | Weight loss, potentiodynamic polarization, and impedance methods | Langmuir adsorption | Shyamala and Arulanantham 2009 |
| *Terminalia catappa* reported as a corrosion inhibitor in HCl medium by the use of weight loss and PDP methods. Obtained results show that inhibition efficiency increased with increasing concentration of inhibitor but decrease with rise in temperature and described as mixed-type inhibitor | *T. catappa* | HCl | Decrease | Increase | Weight loss, polarization, FTIR, and scanning electron microscope studies | Mixed-type inhibition | Vasudha and Saratha 2011 |
| *Theobroma cacao* peel polar extract reported as a corrosion inhibitor for mild steel in HCl medium by the use of weight loss method, potentiodynamic polarization, and EIS techniques. Obtained results show that inhibition efficiency increased with the inhibitor concentration level but decreased with the rise in temperature and obeyed the Langmuir adsorption isotherm | *T. cacao* peel polar extract (TCPE) | HCl | Decrease | Increase | Weight loss method, potentiodynamic polarization, and EIS techniques | Langmuir adsorption isotherm | Yetri et al. 2014 |
| | *C. bracteosum* | $H_2SO_4$ | | Increase | | | |

**Table 1** Plants as corrosion inhibitors against mild steel corrosion *(Continued)*

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| It's reported that the mature leaves of *Combretum bracteosum* extracts inhibited the corrosion of mild steel in $H_2SO_4$ medium by the use of gravimetric and hydrogen evolution methods. Obtained results show that the inhibition efficiency increases with the inhibitor concentration and decreases with temperature. Obtained result obeyed the Frumkin adsorption isotherm | | | Decrease with rise in temperature | | Gravimetric and hydrogen evolution | Frumkin adsorption isotherm | Okafor et al. 2009 |
| *Cyamopsis tetragonoloba* reported as an effective corrosion inhibitor for mild steel in HCl medium by use of weight loss, PDP, and EIS techniques. Obtained results show that inhibition efficiency increase with increasing inhibitor concentration but decrease with rise in temperature. Obeyed the Temkin and Langmuir adsorption isotherms | *C. tetragonoloba* | HCl | Decrease with rise in temperature | Increase | Potentiodynamic polarization | Temkin and Langmuir | Subhashini et al. 2010 |

**Table 2** Plants as corrosion inhibitors against aluminum corrosion

| Study Conducted | Plant product | Solution | Effect of temperature on percentage inhibition efficiency | Effect of concentration on percentage inhibition efficiency | Methods | Adsorption | Reference |
|---|---|---|---|---|---|---|---|
| *Phoenix dactylifera* reported as a good corrosion inhibitor for Al in NaOH solution by weight loss and PDP method. Obtained results show that inhibition efficiency increase with increasing temperature and concentration, followed the Temkin adsorption isotherm also | *P. dactylifera,* | NaOH | Increase | Increase | Weight loss, potentiodynamic polarization | Temkin adsorption isotherm | Rehan 2003 |
| The extracts of Damsissa, *Corchours oitorius* reported as a good inhibitor for the corrosion of aluminum in aqueous sodium carbonate by the use of gasometry, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) | Extracts of *Damsissa, Corchours oitorius* | Sodium carbonate | Decrease | Increase | Gasometry, potentiodynamic polarization | Langmuir and Flory-Huggins | Abd-El-Nabey et al. 2012 |
| *Rosmarinus officinalis* reported as a good corrosion inhibitor for aluminum in NaCl solution by the use of PDP method. Obtained result obeyed the Freundlich isotherm | *R. officinalis* | Chloride solution | Decrease with rise in temperature | Increase | Potentiodynamic polarization | Freundlich isotherm | Kliˇski´c et al. 2000 |
| The dissolution of Al and Zn in HCl and NaOH medium were inhibited by *H. subdariffa* (Karkade) extract. Obtained results show that corrosion rate increase with increasing temperature but decrease with increasing concentration. Physical adsorption phenomena were observed | *H. subhdariffa* extract | HCl and NaOH | Decrease with rise in temperature | Increase | Weight loss and the galvanostatic polarization | Physical adsorption | El-hosary et al. 1972 |
| *Vernonia amygdalina* reported as a fine corrosion inhibitor for aluminum in HCl and $HNO_3$ medium by the use of weight loss method. But its inhibition performance was much better in $HNO_3$ solution as compare to HCl medium | *V. amygdalina* | $HNO_3$ and HCl | – | Increase | Weight loss method | – | Avwiri and Igho 2003 |
| Saccharides (fructose and mannose) with the addition of ascorbic acid addition, reported as a good corrosion inhibitor for Al by the method of hydrogen evolution in alkaline medium | Saccharides (fructose and mannose) | Alkaline medium | – | – | Evolution of hydrogen | – | Muller 2002 |
| The inhibitive effect of leaf extracts of *Euphorbia hirta and Dialum guineense* on aluminum alloy (AA8011) was reported in HCl solution by the use of gravimetric technique. The results indicate that both extracts worked as good inhibitors and inhibition efficiency improved with concentration | Leaf extracts of *E. hirta* and *D. guineense* | HCl | Decrease | Increase | Gravimetric technique | Langmuir adsorption isotherm | Anozie et al. 2011 |
| The inhibition effect of *Newbouldia laevis* leaves extract reported as a good inhibitor on the corrosion of aluminum HCl and $H_2SO_4$ solutions by the use of gravimetric technique. Obtained results show that *N. laevis* inhibitor effect was more efficient in HCl than $H_2SO_4$. | *N. laevis leaves extract* | HCl and $H_2SO_4$ | Decrease | Increase | Gravimetric technique | Langmuir | Nnanna et al. 2012 |
| Coconut coir dust extract reported as a good inhibitor for aluminum corrosion in 1 M HCl medium by the use of weight loss and hydrogen evolution method. It was exhibited that percentage IE efficiency increased with increasing temperature and concentration. Obtained results show the Langmuir adsorption performance | Coconut coir dust extract | 1 M HCl | Increase | Increase | Weight loss and hydrogen evolution | Langmuir | Umoren et al. 2012 |

**Table 3** Plants as corrosion inhibitors against tin corrosion

| Study Conducted | Material | Solution | Effect of temperature on percentage inhibition efficiency | Effect of concentration on percentage inhibition efficiency | Methods | Adsorption | Reference |
|---|---|---|---|---|---|---|---|
| It is reported that lysine, arginine, methionine, cysteine were good corrosion inhibitors in citric acid solution by the potentiodynamic methods. Nitron-containing acids show 70 % inhibition as compared with sulfur-containing acids. All four acids act as a mixed-type inhibitor and show their inhibition effect on tin corrosion and obeyed Temkin adsorption isotherm. | Amino acids (lysine, arginine, methionine, and cysteine) | Citric acid | Decrease with rise in temperature | Increase but decrease after optimum concentration | Potentiodynamic polarization (PDP) | Temkin adsorption | Quraishi et al. 2004 |
| Alanine, glycine, glutamic acid, and histidine were used as environmentally safe inhibitors for the tin dissolution process | Amino acids (glycine) | Tartaric acid | Decrease | Increase | Weight loss, SEM, and EIS | Freundlich isotherm | El-Sherif Rabab and Badawy Waheed 2011 |
| Different varieties of holy basil, viz., *Ocimum basilicum* (EB), *Ocimum cannum* (EC), and *Ocimum sanctum* (ES) reported as corrosion inhibitors for tin in $HNO_3$ solution by the use of weight loss techniques. Obtained results show that inhibition efficiency increase with inhibitor concentration. Followed Langmuir adsorption isotherm | The leaves and stem extract of different varieties of holy basil, viz., *O. basilicum* (EB), *O. cannum* (EC), and *O. sanctum* (ES) | $HNO_3$ | – | Increase | Weight loss technique | Langmuir | Kumpawat et al. 2012 |

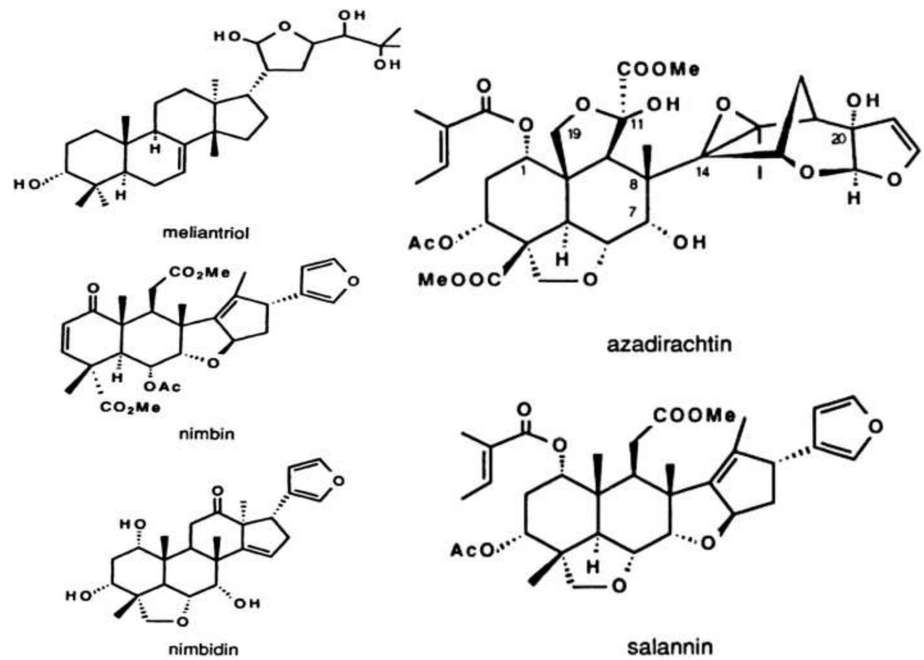


**Fig. 1** Main chemical compounds present in *Azadirachta indica*

study of AZI against aluminum metal in 1.85 M hydrochloric acid, the rate of the reaction has been studied by monitoring and measuring the volume of hydrogen gas evolved and the results were supported by various adsorption theories and the surface morphology studies using scanning electron microscopy (SEM). Authors suggested that the plant extract retards the acid-induced corrosion of aluminum and the volume of hydrogen gas evolved reduced with increasing extract concentration. Also, the Langmuir isotherm as the best model for the adsorption of *A. indica* indicates the suggested mechanism of adsorption—chemisorption (Ajanaku et al. 2015). A research conducted by Jain et al. (a research group at Tata Steel, Jamshedpur) published in *Tata Search* (2014) also highlighted the inhibition effect of AZI against mild steel in acid media (HCl and $HNO_3$), and the results of weight loss studies correlated well with polarization studies (Jain et al. 2014).

In a very interesting study by Bhola et al. (2014) published in *Engineering Failure Analysis*, authors investigated the inhibition effect of AZI extract on microbiologically influenced corrosion of API 5L X80 line pipe steel by a sulfate reducing bacterial (SRB) consortium. On the basis of the field emission scanning electron microscopy (FE-SEM) and energy dispersive spectroscopy (EDS) studies, electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR), and open circuit potential (OCP) were used to investigate the in situ corrosion behavior, and they concluded that neem extract has the capability to reduce the biocorrosion rate by approximately 50 % (Bhola et al. 2014), which is fairly high and very encouraging, clearly underlining the importance of AZI extract as a corrosion inhibitor.

### *Corrosion inhibition by AZI and computational modeling*

Computational methods are more and more appropriate in the study of corrosion inhibition capacity because they have the potential to support in the design of new compounds with good corrosion inhibition properties. These studies are assisting in reducing the experimental costs for testing many compounds with the objective of synthesizing the ones that have high promise for corrosion inhibition. Density functional theory (DFT) and molecular dynamics (MD) approaches are increasingly used for predicting the inhibition potential of compound for corrosion on geometrical, electronic, and binding property bases on metal surface (Kabanda et al. 2012b; Kabanda and Ebenso 2012; Ebenso et al. 2012b). Recently, more corrosion publications contained substantial quantum chemical calculations and molecular dynamics simulations (Obot et al. 2013; Kabanda et al. 2013; Obot and Gasem 2014). Such calculations are usually used to explore the relationship between the inhibitor molecular properties and their corrosion inhibition efficiencies. The use of quantum chemical methods in corrosion inhibitor studies of large number of small organic compounds has been highlighted by Gece (2008) and Obot (2014) in their detailed review. Attempt has

**Table 4** *Azadirachta indica* as corrosion inhibitor

| Concise manner | Metal | Plant product | Solution | Effect of temperature on percentage inhibition efficiency | Effect of concentration on percentage inhibition efficiency | Methods | Adsorption type and isotherm used | Reference |
|---|---|---|---|---|---|---|---|---|
| Mature leaves extract of neem reported as a green corrosion inhibitor for Zn in HCl medium by the use of gravimetric and thermometric methods | Zn | Mature leaves of neem | HCl | Decrease | Increase | Gravimetric and thermometric | Physical adsorption | Sharma et al. 2010c |
| Dry seed extract of AZI reported as a good inhibitor for mild copper corrosion in $HNO_3$ medium by weight loss and phytochemical analysis. Obtained results show that percentage inhibition efficiency increase with increasing concentration and show mixed type inhibition | Mild copper | Dry seeds extracts of AZI | $HNO_3$ | Decrease | Increase | Weight loss and phytochemical analysis | Mixed-type adsorption. | Sangeetha and Fredimoses 2011 |
| There were selected plants [*Occimum viridis* (OV), *Telferia occidentalis* (TO), *Azadirachta indica* (AZI), *Hibiscus sabdariffa* (HS), *Garcinia kola* (GK)] which extracts reported as good corrosion inhibitors for mild steel corrosion in HCl and $H_2SO_4$ by gasometric method. Obtained results indicate that all the extracts inhibited the corrosion process in both acid media and the presence of halide additive increase inhibition efficiency due to synergistic effect | Mild steel | AZI + halide additive | HCl and $H_2SO_4$ | No dependence | Increase | Kinetics activation parameters and gasometric technique | – | Oguzie 2008 |
| It is reported that AZI with iodide additive shows good inhibition for Al corrosion in HCl medium by PDP method. Due to synergistic effect, the adsorption was spontaneous and followed the Freundlich adsorption isotherm | Al | AZI and iodide ions as | HCl | Decrease | Increase | PDP techniques | Freundlich adsorption isotherm | Arab et al. 2008 |
| *Azadirachta indica* extract reported as an effective inhibitor for steel corrosion in the acid media by the gas volumetric techniques and obtained results show that consistence of Langmuir adsorption isotherm | Mild steel | AZI extracts | Different concentrations of HCl | Decrease | Increase | Gas volumetric technique | Langmuir isotherm adsorption (mixed inhibitor) | Oguzie 2006 |
| AZI reported as Al corrosion inhibitor in HCl medium by the use of weight loss and thermometric methods. Obtained results show that adsorption was exothermic, spontaneous, and obeyed the Freundlich, Temkin, and Flory-Huggins | Al | AZI | HCl | Decrease with rise in temperature | Increase | Weight loss and thermometric | Freundlich, Temkin, and Flory-Huggins | Ebenso et al. 2004 |
| AZI leaves reported as a corrosion inhibitor for mild steel in $H_2SO_4$ medium by the use of weight loss technique | Mild steel | AZI leaves | $H_2SO_4$ | – | – | Weight loss technique | Physical adsorption | Ebenso et al. 1998 |
| Ethanolic extract of AZI fruit reported as a good inhibitor for aluminum corrosion in HCl medium by the use of weight loss | Al | Ethanolic extract of AZI fruit | HCl | Decrease with rise in temperature | Increase | Weight loss thermometric | Langmuir adsorption isotherm | Sharma et al. 2013 |

**Table 4** *Azadirachta indica* as corrosion inhibitor *(Continued)*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| thermometric method. Obtained results show the presence of physical adsorption process like percentage inhibition efficiency increase with increasing concentration but decrease with rise in temperature and followed Langmuir adsorption isotherm | | | | | | | | |
| AZI mature leaf extract reported as good inhibitor for mild steel corrosion in $HNO_3$ medium by the use of gravimetric method. Obtained results show that percentage inhibition efficiency increased with increasing concentration but get down with the rise in temperature. Adsorption process was exothermic and consistent and best fitted into Frumkin adsorption isotherm | Mild steel | AZI mature leaf extract | $HNO_3$ | Decrease with rise in temperature | Increase | Gravimetric techniques | Frumkin adsorption isotherm | Sharma et al. 2010d |
| UAE neem extract reported as a good in hibitor for carbon steel corrosion in HCl medium by the use of weight loss method and obtained results show that percentage inhibition efficiency increase with increasing inhibitor concentration but decrease with rise in temperature and data was fit into Temkin adsorption isotherm | Carbon steel | UAE neem extract | HCl | Decrease with rise in temperature | Increase | Weight loss method | Temkin adsorption isotherm | Ayssar et al. 2010 |
| The inhibition effect of AZI extract reported as good inhibitor on stainless steel corrosion in HCl and $H_2SO_4$ medium by the weight loss method. Obtained results show that extract of AZI was better inhibitor as compare with other extract | Stainless steel | Plant extract | HCl + $H_2SO_4$ + tetraoxosulphate (IV) acid + trioxnitrate (V) acid solution | Decrease at high temperature | Increase | Weight loss method | Physical adsorption | Obiukwu et al. 2013 |
| It is reported that ethanol extract of leaves and seeds of *A. indica* shows its effective inhibition effect on mild steel corrosion in $H_2SO_4$ medium by the use of gasometric, gravimetric, and IR methods. Corrosion inhibition efficiency of the leaves is better than that of the seeds .According to findings, the reaction followed the physical adsorption and fit in Flory-Huggins adsorption isotherm | Mild steel | Ethanol extracts of seeds and leaves | $H_2SO_4$ | Decrease | Increase | Gravimetric, gasometric, and IR methods | Flory-Huggins adsorption isotherm | Eddy and Mamza 2009 |
| It is reported that the inhibition effect of AZI extract on mild steel corrosion in acidic medium was good but it's more clearly visible in HCl medium as comparison with $H_2SO_4$ solution. In HCl medium the percentage inhibition efficiency was increase with increasing concentration of inhibitor but it gets down on high temperature. Obtained results show the physical adsorption performance | Mild steel | Extract of AZI leaf | HCL and $H_2SO_4$ | Decrease with rise in temperature | Increase | Weight loss and PDP method | Physical adsorption | Loto et al. 2011 |
| | Mild steel | | | | | Gasometric | – | |

**Table 4** *Azadirachta indica* as corrosion inhibitor *(Continued)*

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Neem leaf extract reported as a good corrosion inhibitor for mild steel in chloride medium by the gravimetric method. It showed a comparison with or without neem leaf extract in salty water medium with heat treatment. IE increased with the increasing concentration of inhibitor in chloride- and heat-treated chloride medium but its decreased without inhibitor in chloride- and heat-treated chloride medium | | Extract of AZI leaf | Chloride (salty water medium) | Increase in neem + chloride medium but decrease in only-chloride medium | Increase in neem + chloride medium but decrease in only-chloride medium | | | Tuaweri et al. 2015 |
| Neem bark reported as efficient corrosion inhibitor for mild steel in HCl medium by the use of PDP method. Percentage IE efficiency increased with increased concentration but decreased with the rise in temperature and reported data fit into Langmuir adsorption isotherm | Mild steel | Neem ark | HCl | Decrease with rise in temperature | Increase | Potentiodynamic polarization | Langmuir (mixed-type inhibition ) | Desai 2015b |

**Table 5** Important molecular descriptors derived from DFT and molecular dynamics simulations (Obot et al. 2013)

| Descriptors | Explanation |
|---|---|
| Global quantum chemical descriptors | |
| $E_{HOMO}$ | Energy of the highest occupied molecular orbital |
| $E_{LUMO}$ | Energy of the lowest unoccupied molecular orbital |
| IP(≈- $E_{HOMO}$) | Ionization potential: removing an electron from a molecular system X ($X \rightarrow X^{+} + e^{-}$) |
| EA(≈- $E_{LUMO}$) | Electron affinity: attaching an additional electron to a molecular system X ($X + e^{-} \rightarrow X^{-}$) |
| $\mu = \left(\frac{\delta E}{\delta N}\right)_{v}$ | Chemical potential, defined as the change in electronic energy *E* upon change in total number of electrons *N* |
| $\chi = -\mu \approx -1/2(E_{HOMO} + E_{LUMO})$ | Absolute electronegativity |
| $\eta = -\left(\frac{\delta \mu}{\delta N}\right)_{v} \approx -(E_{HOMO} - E_{LUMO})$ | Molecular hardness, defined as the change in chemical potential *μ* upon change in total number of electrons *N* |
| $S = \frac{1}{2\eta}$ | Molecular softness |
| *A* | Molecular polarizability; note that molecules arrange themselves towards a state of minimum polarizability and maximum hardness |
| $\omega = \frac{\mu^2}{2\eta} = \frac{\chi^2}{2\eta}$. | Electrophilicity index |
| Charge distribution | |
| *QA(r)* | Net atomic charges (at atom *r*) |
| $E_{interaction} = E_{total} - (E_{surface} + E_{inhibitor})$ | Where $E_{total}$ is the total energy of the metal surface and inhibitor, $E_{surface}$ is the metal surface energy and $E_{inhibitor}$ is the energy of inhibitor molecule from plant extract |

also been made recently to extend the application of DFT-based quantum chemical and molecular dynamic simulations methods in order to understand the mechanism of adsorption of plant extract components on metal and alloys surfaces (Oguzie et al. 2013; Oguzie et al. 2010; Oguzie et al. 2012a; Umoren et al. 2014; Oguzie et al. 2012b; Obi-Egbedi et al. 2012). This is because the major criticism of the use of plant extract as corrosion inhibitor is often the inability to pinpoint which of the component(s) is/are actually responsible for the observed corrosion inhibition effect given that they are comprised of mixtures of organic compounds.

Although experimental studies on the application of AZI extract as a green corrosion inhibitors for different metals and alloys have been extensively reviewed in the work; the mechanism of interactions between the AZI extract component and the metal surfaces at the atomic level using molecular modeling studies is lacking and is still a matter of speculation. This difficulty can be tackled by the methodology of density functional theory and molecular dynamics simulations where selected DFT reactivity parameters of the individual major extracts components such as energy of the highest occupied molecular orbital ($E_{HOMO}$), energy of the lowest unoccupied molecular orbital ($E_{LUMO}$), energy band gap ($\Delta E$), and the interaction energy between the extract components and the metal surface can be correlated with the corrosion inhibitive effect of the plant extract. According to the description of frontier orbital theory (ObiEgbedi et al. 2011), HOMO is often associated with the electron-donating ability of an inhibitor molecule. High $E_{HOMO}$ values

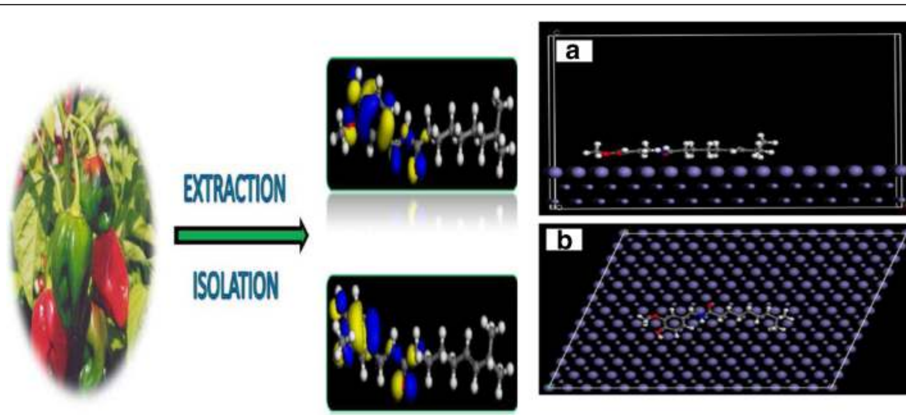


**Fig. 2** Computational modeling of capsaicin and dihydrocapsaicin (the two main extract components of *Capsicum frutescens*) (Oguzie et al. 2013)

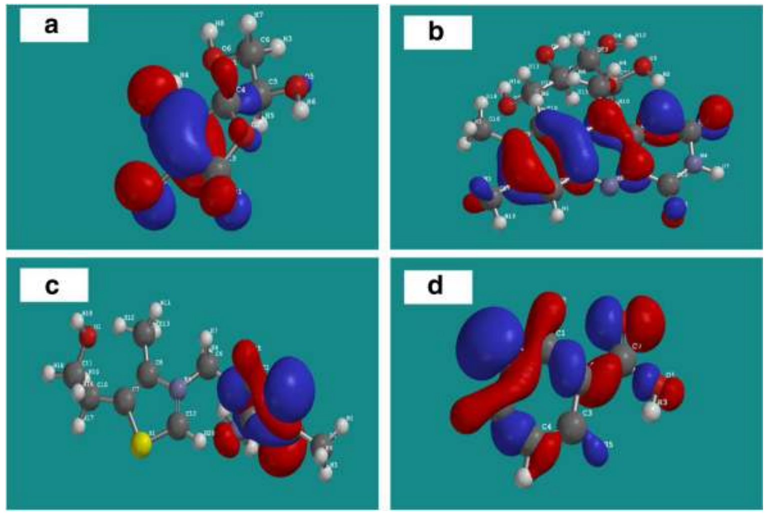


**Fig. 3** The highest occupied molecular (*HOMO*) orbital density of **a** ascorbic acid, **b** riboflavin (*RB*), **c** thiamine (*TH*), and **d** nicotinic acid (*NA*) which constitute the main constituents of *Spondias mombin* extract (Obi-Egbedi et al. 2012)

indicate that the molecule has a tendency to donate electrons to the metal with unoccupied d orbitals. $E_{LUMO}$ indicates the ability of the molecules to accept electrons (Obot and Obi-Egbedi 2010). The lower the value of $E_{LUMO}$ of inhibitor molecule is, the easier its acceptance of electrons from the metal surface (Obot et al. 2009). The gap between the LUMO and HOMO energy levels of the inhibitor molecules is another important index, low absolute values of the energy band gap ($\Delta E = E_{LUMO} - E_{HOMO}$) can indicate a good stability of the formed complex on the metal surface, therefore increasing the adsorption of a molecule on the metal surface (Xia et al. 2008). Some important reactivity parameters from DFT and molecular dynamics simulations (MDS) are summarized in Table 5. Also, Figs. 2 and 3 show examples of molecular modeling of major extract components from some plants used as corrosion inhibitors.

## Conclusions

From the above discussion, it is quite obvious that AZI is an effective green corrosion inhibitor against various metals, especially for mild steel, aluminum, and tin. A lot of potential is still untapped especially computational modeling of the major extract components of AZI on different metal surfaces, and many other plant materials and should be further explored by researchers working in the area of corrosion science and engineering. This will help in the understanding of the adsorption mechanism and hence inhibition effect of plant extracts against metal corrosion. Also of importance is the exploration of AZI and other plant materials in other corrosive environment such as CO2 corrosion, H2S corrosion, and in cooling water systems.

### Competing interests

The authors declare that they have no competing interests.

### Authors' contributions

SKS, KM and IBO all contributed equally in this manuscript. All authors read and approved the final manuscript.

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