PHYTOCHEMICALS AS GREEN CORROSION INHIBITORS IN VARIOUS CORROSIVE MEDIA: A REVIEW

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ABSTRACT

There is an intensive effort underway to develop new plant origin corrosion inhibitors for metal subjected to various environmental conditions. These efforts have been motivated by the desire to replace toxic inhibitors used for mitigation of corrosion of various metals and alloys in aqueous solutions. Plants represent a class of interesting source of compounds currently being explored for use in metal corrosion protection in most systems, as possible replacement of toxic synthetic inhibitors. In this review article, research results on the use of eco-friendly phytochemicals as corrosion inhibitors have been summarized. A general introduction to the topic of corrosion mitigation by inhibitors is presented followed by extensive literature survey on the use of natural inhibitors for corrosion control of metals and alloys in different corrosive media.

INTRODUCTION

Metallic materials are still the most widely used group of materials particularly in both mechanical engineering and the transportation industry. In addition, metals are commonly used in electronics and increasingly also in the construction industry. However the usefulness of metals and alloys is constrained by one common problem known as corrosion. Corrosion is a naturally occurring phenomenon commonly defined as deterioration of metal surfaces caused by the reaction with the surrounding environmental conditions. Corrosion can cause disastrous damage to metal and alloy structures causing economic consequences in terms of repair, replacement, product losses, safety and environmental pollution. Due to these harmful effects, corrosion is an undesirable phenomenon that ought to be prevented.

There are several ways of preventing corrosion and the rates at which it can propagate with a view of improving the lifetime of metallic and alloy materials. The use of inhibitors for the control of corrosion of metals and alloys which are in contact with aggressive environment is one among the acceptable practices used to reduce and/or prevent corrosion. A corrosion inhibitor is a substance which when added in small concentration to an environment, effectively reduces the corrosion rate of a metal exposed to that environment. Corrosion inhibitors can be divided into two broad categories namely those that enhance the formation of a protective oxide film through an oxidizing effect and those that inhibit corrosion by selectively adsorbing on the metal surface and creating a barrier that prevents access of corrosive agents to the metal surface. Large numbers of organic compounds have been studied and analysed to investigate their potential as corrosion inhibitors (Riggs 1973, Raja and Sethuraman 2008). Most of these studies reveal that almost all organic molecules containing heteroatoms such as nitrogen, sulphur, phosphorous and oxygen show significant inhibition efficiency (Riggs 1973, Buchweishaija 1997, Raja and Sethuraman 2008). Despite of these promising findings about possible corrosion inhibitors, most of these substances are not only expensive but also toxic (Raja and Sethuraman 2008) non-biodegradable thus causing pollution problems. Hence, these deficiencies have prompted the search for their replacement.

Plants have been recognized as sources of naturally occurring compounds, some with rather complex molecular structures and having varying of physical, chemical and biological properties (Farooqi *et al*. 1997, Mukherjee *et al.* 1997, Philip 2001, Mutasingwa 2004, Magufuli 2009). Most of the compounds extracted from plants are enjoying the use in traditional applications such as pharmaceuticals and biofuels (Nkunya 2002). Furthermore, the use of naturally occurring compounds are of interest, because of their cost effectiveness, abundant availability and more importantly their environmentally acceptability. Due to these advantages, extracts of some common plants and plant products have been tried as corrosion inhibitors for metals and alloys under different environment (Abdel-Gaber *et al.* 2006, Ebenso and Ekpe 1996, Ebenso *et al*. 2004, Ekpe *et al.* 1994, Kliskic *et al.* 2000). The above attributes have made plants become an important source of a wide range of eco-friendly (green) corrosion inhibitors.

In this review paper, it is intended to highlight the work conducted in the search for alternative metal corrosion protection using plant resources. The paper therefore summarizes some work on the research and the use of green inhibitors reported in literature as part of contribution to the growing interest of exploring green corrosion inhibitors.

Metal Corrosion Inhibitors of Plant Origin

The use of phytochemicals as corrosion inhibitors can be traced back to 1960's when tannins and their derivatives were used to protect corrosion of steel, iron and other tools. In 1972, El Hosary *et al.* reported the use of common plant extracts as corrosion inhibitors. Plant extracts of tobacco from stems, twigs as well as leaves have been reported to show significant corrosion inhibition of aluminum and steel in both saline solutions and strong pickling acids (Davis *et al.* 2001). Extracts from leaves were investigated and found to be effective corrosion inhibitors for mild steel in 2 M HCl solutions. The authors reported maximum inhibition efficiency of 96% with only 0.01% tobacco concentration (100 ppm). Tobacco extracts are reported to contain high concentrations of chemical compounds including terpenes, alcohols, polyphenols, carboxylic acids, nitrogen containing compounds and alkaloids that may exhibit electrochemical activity such as corrosion inhibition (Davis *et al*. 2001). Some of their results are shown in Figure 1.

In 1981, Srivastava and Srivastava investigated the inhibition effect of tobacco, black pepper, castor seed, *Acacia* gum and lignin and found to be good corrosion inhibitors for steel in acidic media. Tobacco, lignin and black pepper were also found to be effective inhibitors for aluminium in acid medium. Further research on castor seed, black pepper and lignin on carbon steel corrosion in 5% HCl solution obtained 60 – 70% inhibition efficiency (Quraishi 2004).

Saleh and his co-workers (Saleh *et al.* 1982) carried out an intensive study on the inhibition effect of aqueous extract of *Opuntia ficus indica*, *Aloe eru* leaves and peels of orange, mango and pomegranate fruits on the corrosion of steel, aluminium, zinc and copper in both HCl and H_2SO_4 acid solutions using gravimetric and polarization measurement techniques. From their investigations, it was reported that the mango peel extract was the most effective corrosion inhibitor for Al and Zn whereas pomegranate fruit shells extract was most suitable for Cu. It was further reported that, all the extracts were more efficiently corrosion inhibitors in HCl solution as compared to H_2SO_4 solution.

Pravinar *et al.* (1993) reported the inhibitive effects of aqueous extract of *Eucalyptus* leaves on the corrosion of mild steel and copper in 1 M HCl solution. The inhibition efficiency has been investigated by galvanostatic polarization, mass loss measurements and surface characterization techniques. The inhibition efficiency was found to increase with increase in concentration of extract and decrease with increase in temperature. The extract was found to be a mixed type inhibitor (i.e. inhibits both cathodic and anodic reactions) predominantly of cathodic control.

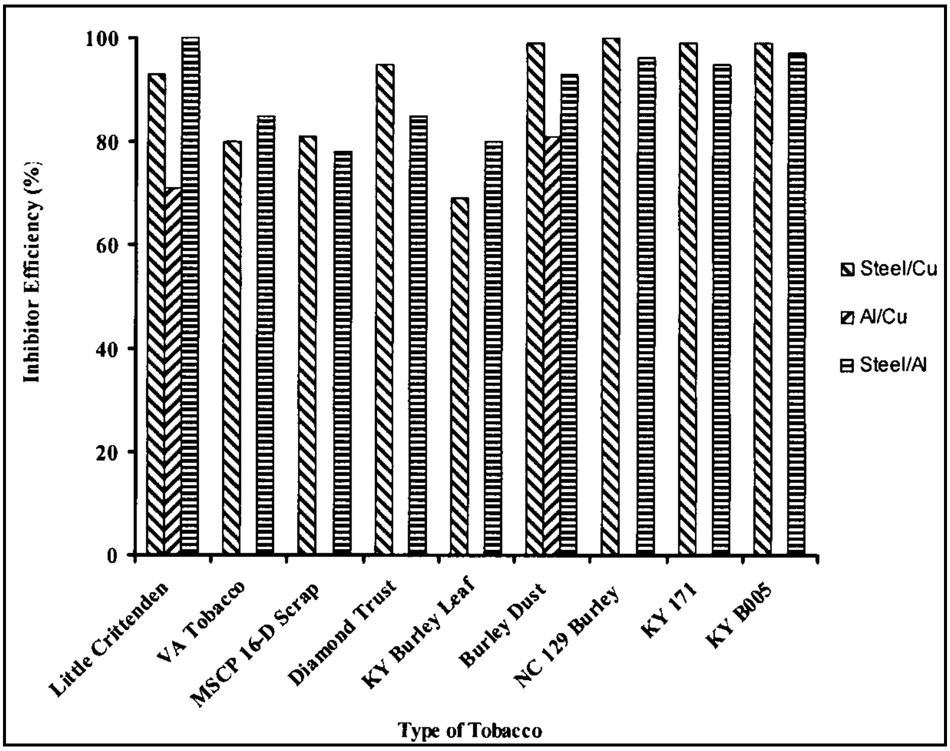

Figure 1: Inhibition efficiency of tobacco extracts for steel/Cu, Al/Cu, and steel/Al galvanic couples in 3.5% NaCl solution as measured by a zero resistance ammeter (ZRA) (Davis *et al.* 2001)

The inhibitive effects of pomegranate alkaloids on acid corrosion of mild steel in H_2SO_4 were also investigated by Aymen Hussein and Singh (1991) using galvanostatic polarization and mass loss measurements at different temperatures. It was found that pomegranate alkaloids have a good efficiency at low temperatures. They explained the observed efficiency to be due to the metal additive complex formation.

El-Etre (2003) has investigated inhibiting of aluminum corrosion using *Opuntia* extract. The inhibitive action of the extracts toward acid corrosion of aluminum was tested using mass loss, thermometry, hydrogen evolution and polarization techniques. It was found that the extract acts as a good corrosion inhibitor for aluminum corrosion in 2 M HCl solution. The inhibition efficiency was reported to increase as the extract concentration increases. The inhibition action of the extract was found to follow Langmuir adsorption isotherm. The author also reported that the *Opuntia* extract provides a good protection to aluminum against pitting corrosion in chloride ion containing solutions.

Leguminous seeds which are rich source of amino acids have also been studied for their corrosion inhibition potential. Subhashini

(2004) studied the inhibition effect of the seeds extracts of *Alfa alfa* (*Aa*), *Adenanthera pavonina* (*Ap*), *Phaseolus lunatus* (*Pl*), *Psophocarpus tetragonolobus* (*Pt*) and *Sesbania grandiflora* (*Sg*). The seed extracts were tested as corrosion inhibitors of mild steel in 1 M HCl and 0.5 M H_2SO_4 with various immersion time and concentrations. Inhibition performances were assessed using mass loss, polarization and electrochemical impedance spectroscopy. The surfaces of mild steel tested were analyzed using Fourier transform infrared spectroscopy and optical microscope. The results clearly indicated the decrease in corrosion rate with increase in concentration of the extract as well as with increase in immersion time. All the extracts investigated have shown maximum efficiency at 0.7% extract concentration. The corrosion inhibition performance of the extracts decreased in the following order: *Sg>Aa>Pt>Ap>Pl* in HCl and *Pt>Aa>Pl>Sg>Aa* in H_2SO_4. However, these extracts showed a better inhibition performance in HCl than in H_2SO_4. This was explained to be due to the adsorption of chloride ions on the metal surface than sulphate ions preferential.

The aqueous extract of the leaves of *Henna* (*Lawsonia*) has been tested as corrosion inhibitor of carbon steel, nickel, and zinc in acidic, neutral and alkaline solutions, using the polarization technique (El-Etre *et al.* 2005). *Lawsonia* is cultivated in Africa and Asia for medicinal and dyeing purposes (El-Etre *et al.* 2005). It was found that the extract acts as a good corrosion inhibitor for the three metals in all tested media. The authors (El-Etre *et al.* 2005) postulated that the degree of inhibition depended on the nature of metal and the type of the medium. For steel and nickel, the inhibition efficiency increased in the order: alkaline < neutral < acidic, while in case of zinc, it increased in the order: acid < alkaline < neutral, thereby reconciling with the observed concept of the *Lawsonia* extract being a mixed inhibitor. The inhibitive action of the extract was discussed in view of adsorption of the complex *Lawsonia* molecules onto the metal surface. El-Etre *et al.* 2005 found that this adsorption followed Langmuir adsorption isotherm in all tested systems. They also proposed that the formation of a complex between the metal cations and Lawsone (2-hydroxy-1,4-naphthoquinone) was an additional inhibition mechanism of steel and nickel corrosion.

In 2006, El-Etre and El-Tantawy reported the inhibitive action of *Ficus* extract towards general and pitting corrosion of carbon steel, nickel and zinc in different aqueous media. The study was performed using weight loss measurements, potentiostatic and potentiodynamic polarization techniques. It was found that the presence of *Ficus* extract in the corrosive media (acidic, neutral or alkaline) decreased the corrosion rates of the three tested metals significantly. The extract was reported to contain friedelin, epifriedelanol, nitidol (a triterpene, $C_{10}H_{50}O$) and a mixture of two sterols (Figure 2).

The extract of *Henna* leaves as environmentally friendly corrosion inhibitors of metals was also investigated by Al-Sehaibani 2000. The water extracts of *Henna*, *Lawsonia inermis* leaves powder were evaluated as corrosion inhibitor for steel and commercial aluminium in saline, acid and alkaline water. The maximum efficiency was attained by just 20 g/L of the extract. The inhibition efficiency of mild steel corrosion in HCl by the extract was 96% and that of aluminium in NaOH was up to 99.8% and observed no inhibition for steel and aluminium in NaCl solution. Some of the results are shown in Figure 3.

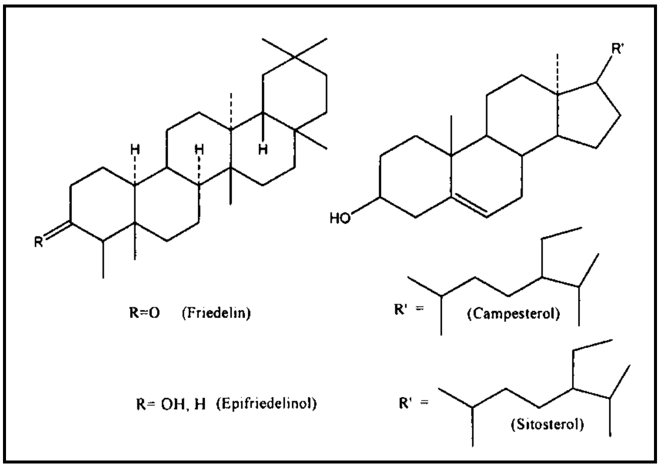

Figure 2: Chemical structures of some compounds contained in *Ficus* extract (El-Etre and El-Tantawy 2006).

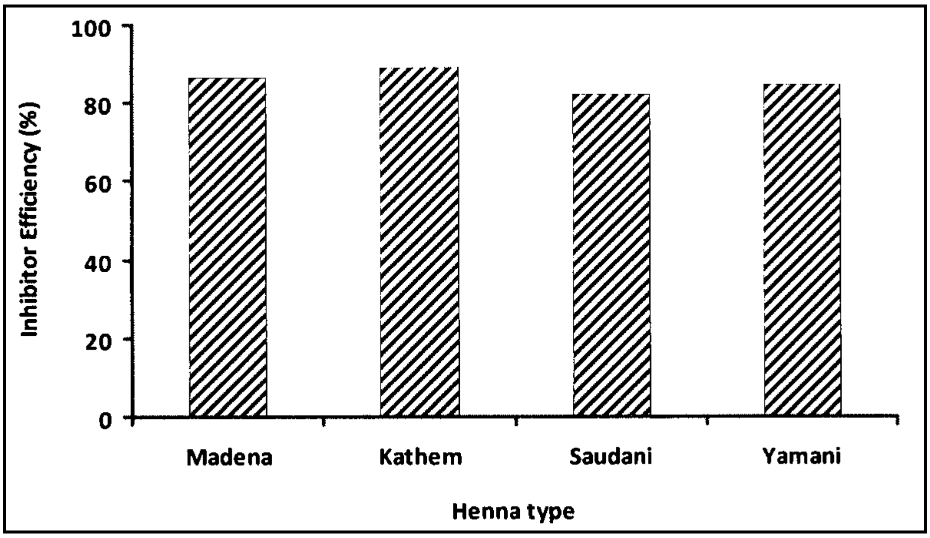

Figure 3:(a): Inhibition percentage of corrosion of steel 37 in 0.1 M HCl solutions in the presence of extracts of various brands of henna (Al-Sehaibani 2000).

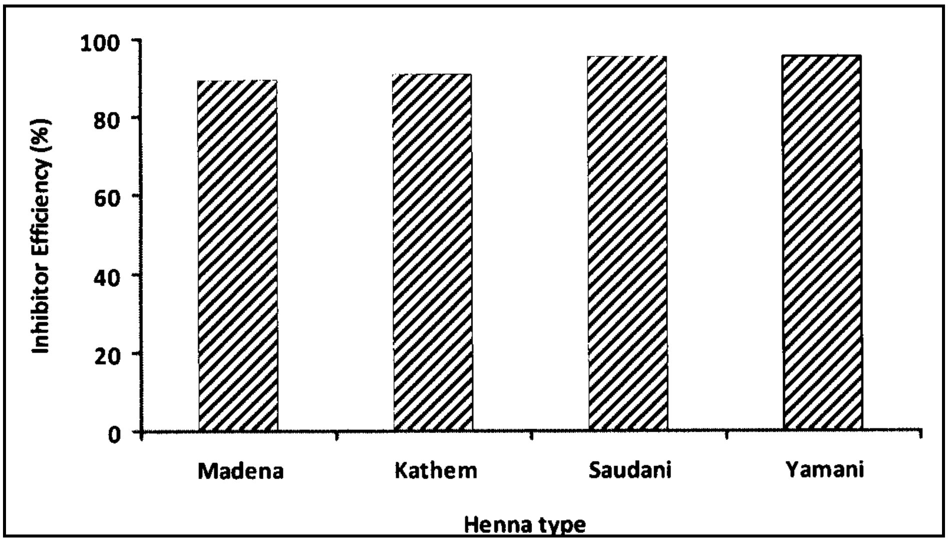

Figure 3:(b): Inhibition percentage of corrosion of aluminium in NaOH solutions in the presence of extracts of various brands of *Henna* (Al-Sehaibani 2000)

Chaieb *et al.* 2005, investigated the effect of eugenol and its derivative (acetyleugenol) extracted from the nail of giroflier (*Eugenia caryophyllata*) on the corrosion inhibition of steel in 1 M HCl solution. They used the weight loss measurements, electrochemical polarization and electrochemical impedance spectroscopy methods. Eugenol and acetyleugenol belong to a class of compounds called vanilloids and their chemical structures are shown in Figure 4.

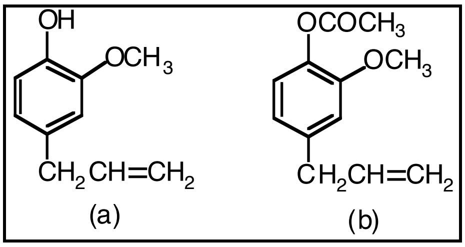

Figure 4: Molecular structures of chemicals extracted from *Eugenia caryophyllata*: (a) Eugenol and (b) Acetyleugenol (Chaieb *et al.* 2005).

These compounds are known to have some antioxidant properties and diets containing these antioxidants can reduce the risk of diseases such as cancer and possibly malaria, AIDS and ageing effects (Chaieb *et al.* 2005). It was observed that the extracts reduce the corrosion rate of steel in 1 M HCl significantly. Their inhibition efficiencies were found to increase with eugenol and acetyleugenol extract concentrations and attained 80 and 91% at concentration of 0.173 g/L, respectively. This implies that acetyleugenol is more active to the surface as compared to eugenol due to the presence of the carbonyl group.

Similarly, the effect of temperature was also investigated at the maximum concentration of both eugenol and acetyleugenol at 0.173 g/L. The results indicated that, as the temperature increases the inhibitor performance also increases. The percentage inhibitor performance changed from 64% at 298 K to 87% at 328 K. The adsorption of these extracts on the metal surface was reported to follow the Langmuir adsorption isotherm.

Some essentials oils have also been investigated as green corrosion inhibitors. Good examples are *Ginger*, *Henna*, *Jojoba* oil and *Artemisia* oil, reported to have very efficient corrosion inhibition for iron and steel in acidic media (Chetouani *et al.* 2004, Bouyanzer and Hommouti 2004).

The effect of natural occurring extract of *Artemisia* on the corrosion of steel in 0.5 M H_2SO_4 in the temperature range 298 – 353 K was studied using weight loss, electrochemical polarization and linear polarization methods (Bouklah and Hammouti 2006). The results obtained reveal that the extract reduces the corrosion rate quite significantly. The inhibition efficiency increases with the increase of *Artemisia* content at 10g/L to reach 95% and 99% at 298 and 353 K, respectively. The inhibition efficiency increased with temperature and it was found that the adsorption of *Artemisia* extract on the steel surface follows Langmuir adsorption isotherm. Similar results were reported on the *Artemisia* oil on the corrosion of steel in HCl (Bendahou *et al*, 2006, Bouklah and Hammouti 2006) and H_3PO_4 (Bouyanzer and Hammouti 2004). *Artemisia* has received a considerable attention as a promising and potent antimalarial drug and davanone (Figure 5) has been found to be its major constituent (Benjilali et al. 1982). Since davanone is a diketone compound, the inhibitory action may be interpreted by the formation of Fe(II)-davanone complex.

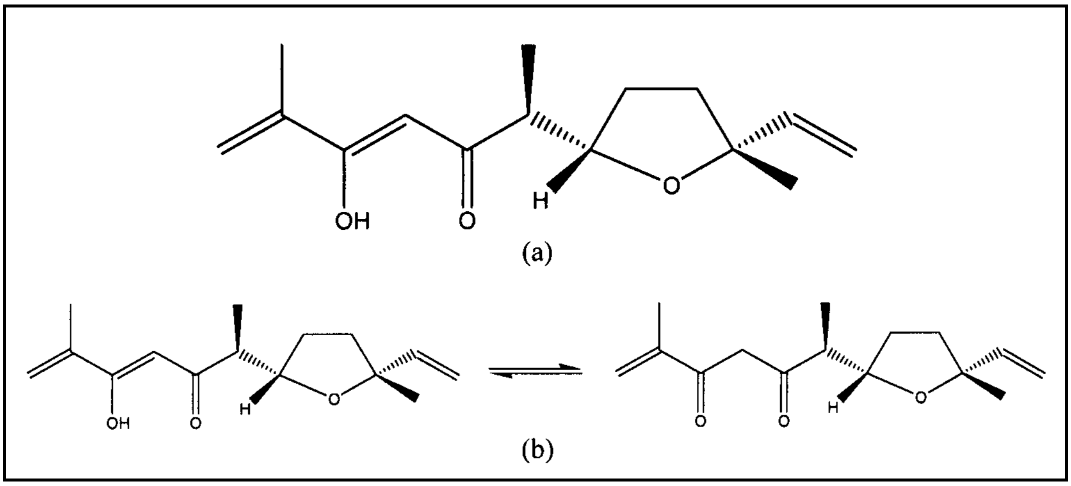

Figure 5: (a) Molecular structural of *Artemisia* extract – davonone, (b) Tautomeric equilibrium of davonone (Bouklah and Hammouti 2006).

Rehan (2003) conducted a research on the effect of water extracts from dry leaves of economic plants , date palm (*Phoenix dectylifera*), *Henna* (*Lawsonia inermis*) and corn (*Zea mays*) on the corrosion inhibition of commercial grade metals; steel, aluminum, and copper in acidic chloride and sodium hydroxide solution using weight loss, solution analysis and potential measurements. The inhibition action was found to critically depend on the metal type and solution composition. Only date palm and henna extract were found highly effective in reducing corrosion rate of steel in acidic chloride solution and aluminum in sodium hydroxide solutions. The inhibition efficiency increased with increasing the concentration of the extract. The inhibition was interpreted in terms of chemisorption of some active ingredients in the leaves according to Temkin isotherm. The results are summarized in Table 1.

The leaves of date palm and corn are generally by-products and used chiefly in Basketry and animal feeding, respectively. *Henna* leaves are used as hair dyestuff and used in shampoo industry due to the pleasant dermatological effect (Rehan 2003).

Table 1: **Weight loss, ΔW, together with calculated inhibition performance, I%, for different metals in the absence and presence of extracts from leaves of three economic plants at 25 ^oC (Rehan 2003).**

Metal	ΔW^o	Henna		Date Palm		Corn	
		ΔW	I%	ΔW	I%	ΔW	I%
0.2 M HCl							
Steel	5.40	0.75	86.1	1.65	78.7	4.88	9.6
	(5.51)	(0.81)	(85.3)	(1.21)	(78.0)	(4.99)	(10.2)
Aluminium	1.32	1.14	*	0.89	32.6	1.43	*
	(1.14)	(1.22)	(*)	(0.75)	(34.2)	(1.26)	(*)
Copper	1.29	0.88	31.8	1.01	21.7	1.07	17.2
	(1.31)	(0.92)	(29.8)	(1.07)	(18.3)	(1.10)	(16.1)
Brass	0.89	0.71	19.1	0.71	20.2	0.84	5.8
	(1.03)	(0.85)	(17.5)	(0.83)	(19.4)	(0.96)	(7.1)
0.2 M KOH							
Aluminium	31.70	1.27	96.0	9.32	70.6	30.50	3.8
	(32.30)	(1.31)	(95.9)	(10.1)	(68.7)	(31.21)	(3.4)

* No inhibition; The figures in the blackest represents results from solution metal ion analysis with atomic absorption

Over the years, our research group investigated Cashew Nut Shell Liquid (CNSL), an extract from the Cashew Nut Shells of the cashew tree (*Anacadium accidentale Linn*) for its inhibitive effects as green inhibitor for corrosion of carbon steel in carbon dioxide media using gravimetric, potentiodynamic polarization and electrochemical impedance techniques (Mutasingwa 2004, Philip 2001 and Philip *et al.* 2001). The molecular structures of the CNSL constituents are shown in Figure 6. The major constituent of this oil depends on the extraction method, whereby anacardic acid and cardanol are major constituents for cold extraction and thermo extraction, respectively. The tests were performed both under static and dynamic conditions. It was found that CNSL reduces the extent of electrochemical processes taking place on carbon steel undergoing corrosion. The inhibition efficiency increased with the increase of the extract concentration. Adsorption of CNSL was found to follow the Langmuir's adsorption isotherm. The oil was also found to function as an inhibitor of mixed type acting by blocking the active sites on both cathodic and anodic regions.

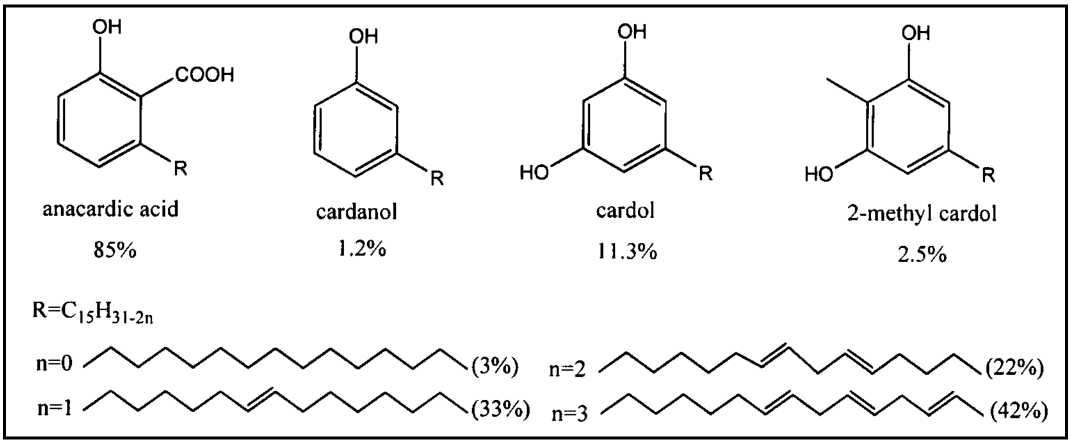

Figure 6: Chemical structures of the components of natural CNSL (cold extracted) (Philip *et al.* 2001).

Further investigation of CNSL green inhibitor on the effect of temperature on its corrosion protection performance was carried out by Mutasingwa 2004. Temperatures up to 80 ^{o}C were studied using an optimal concentration of the extract under dynamic condition. The results showed that the inhibition performance decreases as the temperature increases.

One among the crucial factors for the determination of the inhibition mechanism as well as the performance of the corrosion inhibitor is the solution pH. Most of the inhibitors are pH selective which depends on the molecular structure of the inhibitor, the metal corroding, the active species present in the solution and the composition of the inhibitor.

Philip et al. (Philip *et al.* 2002) investigated further on the solution pH effects of CO_2 saturated 3% NaCl solutions on the performance of CNSL using technical extracted CNSL at room temperature. The solution pHs investigated were 4.0, 5.5, and 6.0. It was found that as the solution pH changes from 4 to 6, a significant drop in current densities as well as anodic shifts of the open circuit potential was observed. This suggested a significant reduction of corrosion rate as the solution pH changes from 4 to 6.0. This observation made the author to demonstrate that CNSL performs more efficiently in solutions of higher pHs ≥ 6.0. Further, Philip *et al.* investigated the inhibition mechanism of this extract on carbon steel in CO_2 saturated 3% NaCl solutions using weight loss, UV/VIS and electrochemical techniques. It was found that the phenoxide ions from the CNSL were found to be responsible for the inhibition of corrosion of mild steel in CO_2 medium. It was also found that the surface charge of carbon steel is positive in solution containing CNSL. The authors suggested the mechanism of CNSL inhibitor adsorption to involve electrostatic attraction between the positively charged metal surface and negatively charged phenoxide ions as schematically shown in Figure 7.

Bendahou *et al.* (2006) evaluated the effect of natural *Rosemary* oil as green inhibitor on the corrosion of steel in H_3PO_4 media at various temperatures. Various techniques were used including gravimetric and electrochemical methods to characterize the corrosion mechanisms. Bendahou *et al.* (2006) demonstrated good agreement between the various methods explored for corrosion inhibition analysis. The polarization measurements showed that *Rosemary* oil acted essentially as a cathodic inhibitor. The efficiency of corrosion inhibition of the oil increased with the concentration of extract to attain 73% at 10g/L, but decreased with the rise of temperature from 25 to 75 °C range.

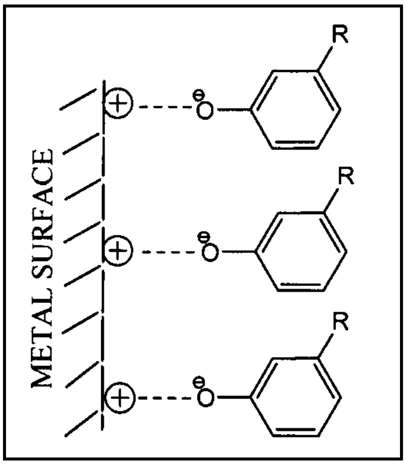

Figure 7: The schematic diagram for the cardanol adsorption mechanism on carbon steel surface (Philip *et al.* 2002).

The *Hibiscus sabdariffa* plant popularly known as "*Roselle*" which belongs to the *Malvaceae* family has basically been used in various foods and medicines. Its extract, the calyx of *Hibiscus sabdariffa* has been tested on the inhibition of mild steel corrosion in 2 M HCl and 1 M H_2SO_4 solution by gasometric technique (Oguzie, 2008). The results obtained showed that the corrosion inhibition efficiency of the extract calyx at concentration of 50% was 93% in 1 M H_2SO_4 and 90.4% in 2 M HCl. The author observed no effect on the inhibition performance as temperature changes in 1 M H_2SO_4.

Raja and Sethuraman (2008) studied the corrosion inhibitive effect of the extract of black paper on mild steel in 1M H_2SO_4 solutions. The rate of corrosion attack on the metal surface was assessed by conventional weight loss, Tafel polarization, impedance spectroscopy and Scanning Electron microscopy (SEM) techniques. Results of the weight loss study revealed that black pepper extract acts as a good inhibitor even at high temperatures. Polarization curves revealed the mixed mode of inhibition of black pepper extract. Analysis of impedance data has been made with equivalent circuit with constant phase angle element for calculation of the double layer capacitance value. SEM studies provided the confirmatory evidence for the protection of mild steel by the inhibitor.

Abdel-Gaber *et al.* 2008 studied the inhibition of aluminum corrosion in 2 M sodium hydroxide solution in the presence and absence of 0.5 M sodium chloride using *Damsissa* (*Ambrosia maritime, L*) extract employing different chemical and electrochemical techniques. Chemical gasometry technique showed that addition of chloride ions or *Damsissa* extract to sodium hydroxide solution decreases the volume of hydrogen gas evolved suggesting a decrease in the metal corrosion. Potentiodynamic results manifested that chloride ion retard the anodic dissolution of aluminum below the pitting potential in sodium hydroxide solution. *Damsissa* extract in the presence or absence of chlorine ion, influenced both the anodic dissolution of aluminium and the generated hydrogen gas at the cathode indicating that the extract behaves as a mixed type inhibitor. The decrease in the observed limiting current with increasing *Damsissa* extract concentration indicated that the anodic process is controlled by diffusion. The impedance results also showed that the *Damsissa* extract could serve as an effective inhibitor for the corrosion of aluminium in alkaline solutions. The impedance measurements verified the remarkable stability of the extracts during storage up to 35 days. *Damsissa* extract was found more effective in the presence of chloride ions than in the absence. Inhibition was found to increase with increasing concentration of the extract but decreases with increasing temperature.

Buchweishaija and Mhinzi (2008) investigated the inhibition effect of gum exudates from *Acacia seyal* var *seyal* on the corrosion of mild steel in drinking water using electrochemical techniques (i.e. potentiodynamic polarization and electrochemical impedance spectroscopy). These *Acacia* gum exudates are obtained from the stems and branches of sub-Saharan *Leguminosae* trees which grow extensively in central parts of Tanzania. These exudates particularly from *senegal* are permitted food additive (JECFA/FAO 1990, Glicksman 1983, Anderson and Stoddart 1966). It was found that *Acacia seyal* var *seyal* could serve as an effective green corrosion inhibitor for the mild steel in drinking water systems. The percentage inhibition efficiency was found to increase with increasing concentration of the gum. The inhibition efficiency was almost unaffected by the change of solution temperature.

The application of the acid extract of leaves of *Citrus aurantifolia* plant on the corrosion inhibition of mild steel in 1 M HCl solution was investigated using weight loss measurement and electrochemical studies (Saratha *et al.* 2009). The results obtained show that the extract served as an effective inhibitor for the corrosion protection of mild steel in 1 M HCl medium. The inhibitive action was discussed based on the adsorption isotherms and was found to fit all the models tested i.e. Langmuir, Temkin, Freundlich, Frumkin and Flory-Huggins. The polarization curves revealed that this extract acts as a mixed type inhibitor. The authors reported the inhibition efficiency of up to 97.5%. The inhibition mechanism was explained on the basis of adsorption of the phytochemical constituents (Figure 8) present in the extract through oxygen atoms.

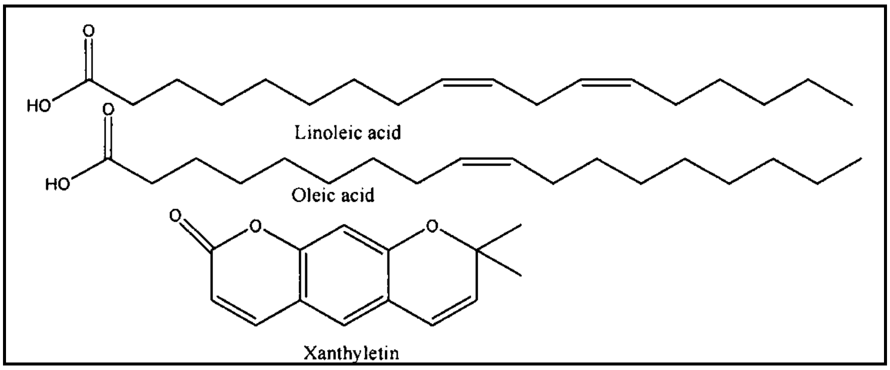

Figure 8: The phytochemical constituents present in acid extract of leaves of *Citrus aurantifolia* plant (Saratha *et al.* 2009)

Saratha and Vasudha (2009) investigated the acid extracts of *Nyctanthes arbortristis* leaves on the corrosion inhibition of mild steel in aerated 1 N H_2SO_4 solution. The results indicated the extract to be a good corrosion inhibitor. The phytoconstituents of leaf extracts were reported to contain alkaloidal principle named Nyctanthine. The leaves also contain mannitol, astringent principles, resinous tannic acid, flavanoids and iridoid glucosides (Saratha and Vasudha 2009). The presence of these heterocyclic compounds enhanced the adsorption of this acid extract on the metal surface leading to the effective inhibition of mild steel corrosion in sulfuric acid. The maximum inhibition efficiency of about 90% was recorded at the inhibitor concentration of 1% v/v.

James and Akaranta (2009) studied the inhibiting action of acetone extract of red onion skin on the corrosion of zinc in hydrochloric acid solution using weight loss method. The results of the study revealed that different concentrations of extract inhibit zinc corrosion. Inhibition efficiency is found to vary with concentration and temperature. The inhibition efficiency greater than 90% was attained at concentration of 0.08 g/L of red onion skin extract whose major constituent chemical structure is given in Figure 9.

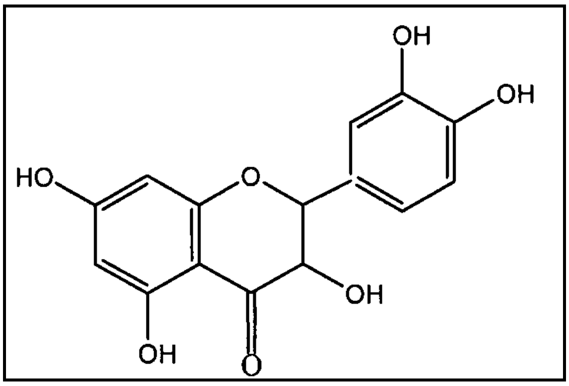

Figure 9: The molecular structure of quercetin extracted from red onion (James and Akaranta 2009)

Kumar *et al.* 2009, have studied the alcoholic extracts of leaves, latex and fruit from the *Calotropis procera* and *Calotropis gigantea* as corrosion inhibitors for mild steel in basic solution. The extracts were reported to reduce the corrosion rate of mild steel in basic solution and gave up to 81% efficiency. The corrosion inhibition potential of *Calotropis procera* on mild steel in sulphuric acid medium was also tested by weight loss, electrochemical, SEM and UV methods. *Calotropis procera* was found to show significant corrosion inhibitive effect on mild steel in sulphuric acid medium (Raja and Sethuraman 2009). Basically, *Calotropis* is used as a traditional medicinal plant with unique properties to treat common disease. The *Calotropis* extract contains uscharin (Figure 10) as a major constituent. The nitrogen, sulphur and oxygen of uscharin were reported to be responsible for its adsorption on the metal surface.

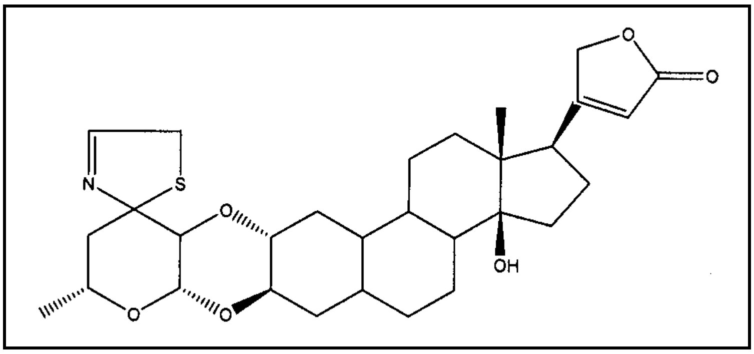

Figure10: The chemical molecular structure of major constituents of *Calotropis* extract–Uscharin (Raja and Sethuraman 2009).

The corrosion inhibition performance in almost all the sited plant extracts could be due to the presence of surface active constituents which normally enhance the film formation over the metal surface, thus mitigating corrosion. Inspection of the chemical structures of some of the constituents of the plants extracts reveal that all molecules are long chain hydrocarbons carrying a polar group(s) at one or either ends. The polar groups normally contain oxygen, nitrogen or sulphur atoms. These are in accordance to Riggs 1973, narration about molecular properties of organic inhibitors which include molecular size and its geometrical structure, bonding type, carbon chain length, type of atoms and characteristic molecular groups which are present in the molecule, molecular ability to form continuous layer on the metal surface or cross link, ability to react and form complex with metal atoms, metal ions or with corrosion products and the bonding strength to the metal surface.

CONCLUSION

The diverse set of research summarized and discussed indicates ongoing intensive research being carried out to tackle the problem of metal corrosion. Although it is realized that the preceding discussions are not infinitive the literature provided in this review reveal concerted efforts directed at the search for more green inhibitors as alternatives to the fossil origin toxic corrosion inhibitors. One main drawback is even with the growing interest in the search for green inhibitors the amount of research being undertaken is not significant compared to the effect of corrosion to the economy given the current consumption of mild steel. However, regardless of the drawback mentioned, this review has shown that the use of green corrosion inhibitors is the way forward in the search for safer and environmentally secure protection against metal corrosion. The use of green inhibitors also has the potential of being cost effective due to the renewability of its resources.

REFERENCES

Abdel-Gaber AM, Abd-El-Nabey BA, Sidahmed IM, El-Zayady AM, Saadawy M 2006 Inhibitive action of some plant extracts on the corrosion of steel in acidic media, *Corros. Sci.* **48**(9) 2765-2779.

Abdel-Gaber AM, Khamis E, Abo-Eldahab H and Adeel S 2008. Inhibition of aluminium corrosion in alkaline solutions using natural compound. *Materials Chem. Phys.* 109 (**2-3**) 297-305.

Al-Sehaibani H 2000 Evaluation of extracts of *Henna* leaves as environmentally friendly corrosion inhibitors for metals.

Meter. Wissen Werkst. Tech. **31**(12): 1060 – 1063.

Anderson DMW, Stoddart JF 1966. Studies of *Acacia senegal* (gum Arabic). *Carbohydr. Res.* **2**: 104 – 114.

Aymen HAM and Gurmeet S (1991) Pomergrate Alkaloids as corrosion inhibitor for mild steel in acidic medium. *J. Electrochem. Soc. India*, **40**(4): 153-157.

Bendahou M, Benabdellah M and Hammouti B 2006. A study of *Rosemary* oil as a green corrosion inhibitor for steel in 2M H_3PO_4. *Pigm. Resin Technol.* **35**(2): 95-100.

Benjilali B, Sarris J and Richard H 1982. Nouveaux che´motypes d'Artemisia herba-alba. *Sci. Aliment.* **2**: 515–527.

Bouklah M and Hammouti B 2006. Thermodynamic characterisation of steel corrosion for the corrosion inhibition of steel in sulphuric acid solutions by *Artemisia*. *Port. Electrochim. Acta* **24**: 457 – 468.

Bouyanzer A and Hommouti B 2004. A study of anti-corrosion effects of *Artemisia* oil on steel. *Pigm. Resin Technol.,* **33**: 287- 292.

Buchweishaija J 1997 Inhibiting Properties and Adsorption of an Amine Based Fatty Acid Corrosion Inhibitor on Carbon Steel in Aqueous Carbon Dioxide Solutions, Dr. Ing. Avhandling, NTNU.

Buchweishaija J, Mhinzi GS 2008. Natural products as a source of environmentally friendly corrosion inhibitors: The case of natural tree gum exudates from *Acacia seyal* var *seyal*, *Portugaliae Electrochimica Acta* **26**: 257-265.

Chaieb E, Bouyanzer A, Hammouti B and Benkaddour M 2005 Inhibition of corrosion of steel in 1 M HCl by eugenol derivatives. *J. Appl. Surf. Sci.* **246**: 199-206.

Chetouani A, Hammouti B, Benkaddour M 2004. Corrosion inhibition of iron in hydrochloric acid solution by jojoba oil. *Pigm. Resin Technol.* **33**: 26-31.

Davis GD, Anthony von Fraunhofer J, Krebs LA and Dacres CM 2001 The use of Tobacco extracts as corrosion inhibitors. *CORROSION* 2001 Paper 1558.

Ebenso EE and Ekpe UJ 1996 Kinetic study of corrosion and corrosion inhibition of mild steel in H_2SO_4 using *Carica papaya* leaves extract, *W. Afri. J. Biol. Appl. Chem.* **41**: 21-27.

Ebenso EE, Ibok UJ, Ekpe UJ, Umoren S, Jackson E, Abiola OK, Oforka NC and Martinez S 2004 Corrosion inhibition studies of some plant extracts on aluminium in acidic medium, *Trans of SAEST* **39**(4): 117-123.

Ekpe UJ, Ebenso EE and Ibok UJ 1994 Inhibitory action of *Azadirachta indica* leaves extract on the corrosion of mild steel in H_2SO_4, *J. W. Afri. Sci. Assoc.* **37**: 13-30.

El Hosary AA, Saleh RM and Shams El Din AM 1972 Corrosion inhibition by naturally occurring substances–1. The effect of *Hibiscus subdariffa* (karkade) extracts on the dissolution of Al and Zn. *Corros. Sci.* **12**(12): 897-904.

El-Etre AY 2003 Inhibition of aluminium corrosion using *Opuntia* extract. *Corros. Sci.*, 45 2485-2495.

El-Etre AY and El-Tantawy Z 2006 Inhibition of metallic corrosion using *Ficus* extract, *Portugaliae Electrochimica Acta* **24**: 347-356.

El-Etre AY, Abdallah M and El-Tantawy Z (2005) Corrosion inhibition of some metals using *Lawsonia* extract. *Corr. Sci.* **47**(2): 385-395.

El-Etre AY and El-Tantawy Z 2006 Inhibition of metallic corrosion using *Ficus* extract. *Port. Electrochim. Acta* **24**: 347-356.

Farooqi HI, Quraishi MA and Saini PA 1997 Natural compounds as corrosion inhibitors for mild steel in industrial cooling systems, Proceedings from European Federation of corrosion (EUROCORR.'97), Vol. I, Trondheim, Sept. 22-25, pp 186-194.

Glicksman M Ed. 1983. Food hydrocholloids, Vol. I & II CRC Press, Inc. Boca Raton Florida.

James AO and Akaranta O 2009. The inhibition of corrosion of zinc in 2 M hydrochloric acid solution with acetone extract of red onion skin, *Afr. J. Pure Appl. Chem.* **3**(11): 212-217.

JECFA/FAO 1990 Specifications for identity and purity of certain food additives. *Food and Nutrition* Paper No. 49, FAO, Rome.

Kliskic M, Radosevic J, Gudic S, Katalinic V 2000 Aqueous extract of *Rosmarinus officinalis L.* as inhibitor of Al-Mg alloy corrosion in chloride solution", *J. Appl. Electrochem.* **30**(7): 823-830.

Kumar S, Arora S, Sharma M, Arora P and Mathur SP 2009. Synergistic effect of *Calotropis* plant in controlling corrosion of mild steel in basic solution. *J. Chil. Chem. Soc.* **54**(1): 83-88.

Magufuli JPJ 2009 The potential of Anacardic acid Self-Assembled Monolayers from Cashew Nut Shell Liquid as Corrosion Protection Coatings, *PhD Thesis*, University of Dar es Salaam.

Mukherjee D, Berchman J, Rajsekkar A, Sundarsanan N, Mahalingam R, Maruthamuthu S, Thiruchelvam T and Karaikudi D 1997 Plant-based alkaloids inhibit corrosion of marine alloys, *Anti-Corros Method Material.* **44**(3): 186-194.

Mutasingwa J 2004 As assessment of Cashew Nut Shell Liquid as a corrosion inhibitor of mild steel alloys in flowing aqueous system, *MSc. Thesis*, University of Dar es Salaam.

Nkunya MHH 2002 Natural chemicals for disease and insect management, Professorial Inaugural Lecture, University of Dar es Salaam.

Oguzie EE 2008. Corrosion inhibitive effect and adsorption behaviour of *Hibiscus sabdariffa* extract on mild steel in acidic media. *Portugaliae Electrochimica Acta* 26, 303 – 314.

Philip JNY, Buchweishaija J and Mkayula LL 2001 Cashew Nut Shell Liquid as an alternative corrosion inhibitor for carbon steel. *Tanz. J. Sci.* **27**: 9-19.

Philip JYN, Buchweishaija J and Mkayula LL 2002 Mechanistic Studies of carbon steel corrosion inhibition by Cashew Nut shell Liquid, *Tanz. J. Sci*. **28**(2): 105-116.

Pravinar K, Hussein A, Varkey G and Singh G 1993 Inhibition effect of aqueous extracts of *Eucalyptus* leaves on the acid corrosion of mild steel and copper. *Transaction of the SAEST* **28**(1): 8-12.

Quraishi MA 2004 The naturally occurring products as corrosion inhibitors. *CORROSION 2004* Paper No. 04411.

Raja PB and Sethuraman MG 2008. Natural Products as Corrosion Inhibitors for Metals in Corrosive media – A Review, *Material Lett.* **62**: 113-116.

Raja PB and Sethuraman MG 2009 Inhibition of corrosion of mild steel in sulphuric acid medium by *Calotropis procera*. *J. Pigment Resin Technol.* **38**(1): 33-37.

Rehan HH 2003 Corrosion control by water-soluble extracts from leaves of economic plants. *Mat.-wiss. u. Werkstofftech.* **34**: 232-237.

Riggs OL 1973 Theoretical Aspects of Corrosion Inhibitors and Inhibition in Corrosion Inhibitors by C.C. Nathan (ed.) NACE.

Saleh RM, Ismail AA and El Hosary AA 1982 Corrosion inhibition by naturally occurring substances. VII. The effect of aqueous extracts of some leaves and fruit peels on the corrosion of steel, aluminum, zinc and copper in acids", *Br. Corros. J.* **17**(3): 131-135.

Saratha R and Vasudha VG 2009. Inhibition of Mild steel corrosion in 1N H_2SO_4 medium by acid extract of *Nyctanthes arbortristis* leaves, *E-J. Chem.* **6**(4): 1003-1008.

Saratha R, Priya SV and Thilagavathy P 2009. Investigation of *Citrus aurantifolia* leaves extract as corrosion

inhibitor for mild steel in 1 M HCl, *E-J. Chem.* **6**(3): 785 -795.
Srivastava K and Srivastava P 1981 Studies on plant materials as corrosion inhibitors. *Br. Corros. J.* **16**(4): 221-223.
Subhashini S 2004 Corrosion inhibition study of mild steel in acid media by extracts of some *Leguminous* seeds as eco-friendly inhibitors. *J. Camel Pract. Res.* **11**(1):27-34.