ANTICORROSION AND KINETICS ASPECTS OF LEAVES EXTRACT AS A CORROSION INHIBITOR FOR MILD STEEL

#A. Satish and @A. Leema Rose

#Research Scholar, @Research supervisor

PG and Research Department of Chemistry, Holy Cross College (Autonomous)

(Affiliated to Bharathidasan University), Tiruchirappalli, Tamil Nadu, India

@Corresponding author

ABSTRACT

The combat against corrosion of metals is of technical, economic, ecological and aesthetic importance. The use of inhibitors is one of the best options for protecting metals and alloys from corrosion. The environmental toxicity of organic corrosion inhibitors has triggered the search for green corrosion inhibitors because they are biodegradable and do not contain heavy metals or other toxic compounds. Plant products are not only environmentally friendly and environmentally acceptable, but also inexpensive, readily available and renewable. Studies on the inhibition of corrosion of tannins, alkaloids, organic acids, amino acids and organic dyes of plant origin are interesting. This study focuses on the corrosion inhibition effects of *Phoenix Pusilla* leaf extract in 1M HCl solutions using weight loss techniques and followed by isotherms adsorption. The results obtained show that the extracts from 1M HCl solutions acted as good corrosion inhibitors. The inhibition efficiency was increased with the increase in the concentration of extract. Data from weight loss experiments and adsorption isotherms (Temkin and Freundlich) have shown that plant extract represents corrosion of steel in acidic media and confirms the adsorption mechanism. The result shows that extracts from *Phoenix pusilla* leaves act as corrosion inhibitors and can promote surface protection by blocking active areas on the metal.

Keywords: Anticorrosion, Mild steel, Hydrochloric acid, Phytochemicals, *Phoenix pusilla* leaves

INTRODUCTION

Corrosion is the deterioration of the metal due to a chemical attack or a reaction to its environment. This is a constant and continuous problem which is often difficult to completely eliminate (Bhuvaneswari *et al*., 2018). Prevention would be more practical and accessible than complete elimination. Corrosion processes develop rapidly after the protective barrier has been disturbed and are accompanied by a series of reactions which modify the composition and properties of the metal surface and the environment local, For example, the formation of oxides, the diffusion of metal cations in the coating matrix, local pH changes and the electrochemical potential (Torres *et al*., 2011). The investigation into the corrosion of mild steel and iron is of enormous theoretical and practical importance and, as such, has received considerable interest. Acid solutions, often used in industrial acid cleaning, decalcification acids, pickling acids and acidifying oil wells, require the use of corrosion inhibitors, to prevent their corrosion attack on metallic materials. Synthetic organic and inorganic corrosion inhibitors are effective but harmful to humans and the environment. Therefore, the investigation of corrosion protection, in particular for mild steel, using corrosion inhibitors on a plant basis, is of great interest, because plant extracts are found in abundance (Quuraishi *et al*., 2010).

Green corrosion inhibitors are inexpensive, less or nontoxic, biocompatible and do not contain heavy metals. Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment (Faustin *et al*., 2015). Recently, many eco-friendly corrosion inhibitors have been developed. For example, *Zygophyllum album* L Leave (Derfouf et al., 2017), *Anacyclus pyrethrum* L. stem (Selles et al., 2012) and *Mentha Pulegium* leaf extract (Khadraoui et al., 2015) were successfully reported for their anticorrosion properties. The observed results showed that all the above said plants have excellent anticorrosion effect and most importantly eco-friendly. In the present study, *Phoenix pusilla* leaves extract was investigated for antioxidant and its effectiveness as a natural inhibitor to prevent corrosion of mild steel in 1M HCl using the weight loss method and Adsorption Isotherm followed by Langmuir and Temkin model.

MATERIALS AND METHODS

Collection and Preparation of alcoholic extract

The leaves of *Phoenix pusilla* were collected from Sengipatti, Thanjavur, Tamil Nadu. The collected leaves were shade dried and make a fine powder using a mixer grinder. 10grams of *Phoenix pusilla* leaves powder was used for extraction. Extraction was completed with cold extraction using the maceration method in ethanol solvent for 24 hours using the "intermittent shaking" method to obtain an extract. The extract was filtered using Whatman filter No 1 paper and filtrate was used for phytochemical analysis and anticorrosive activity.

Qualitative Preliminary phytochemical analysis

Preliminary phytochemical test was carried out by using standard procedure (Sofowara 1993; Trease and Evans, 1989; Harborne 1973 and 1984).

ANTICORROSIVE STUDY

Effect of, *Phoenix pusilla* leaves extract in different concentrations on mild steel

The mass loss studies were carried out at temperature 37°C in 100 ml of blank 1M HCl and test solutions of various concentrations of *Phoenix pusilla* leaves extract (5, 10, 30, 50, 70 and 100 ppm) for 72 hours. At the end of the reaction the specimens were taken out, washed with water, dried with air drier and weighed. Blank has taken as without sample. Corrosion rates (decrease in weight in gram per cm^2 per hour) were calculated using the following expression.

$$\text{Corrosion Rate (CR) } (g.cm^{-2}\, h^{-1}) = \frac{W_1 - W_2}{A \times T}$$

Where, W_1 = initial weight of rod, W_2 = weight of rod after treatment, $W_1 - W_2$ = weight loss (g), A = surface area, T = time in hours

The surface coverage (ϴ) as a result of adsorption of inhibitor and inhibition efficiency (%) were calculated from corrosion rate values by using the following equation

$$\textbf{Surface coverage } (\Theta) = \frac{CR_B - CR_I}{CR_B}$$

$$\textbf{Inhibition efficiency \%} = \frac{CR_B - CR_I}{CR_B} \times 100$$

Where, CR_B = Corrosion Rate Blank and CR_I = Corrosion Rate Iinhibitor.

Adsorption Isotherm followed by Langmuir and Temkin model

The inhibition effect can be explained by adsorption of *Phoenix pusilla* leaves extract at the mild-steel surface. The *Phoenix pusilla* leaves extract replaces the water molecules at the metal interface according to the Langmuir and Temkin model (Hosseini et al., 2003; Rudresh and Mayanna, 1977).

Atomic Absorption Spectroscopy (AAS)

The effect of inhibitor on mild steel specimen was observed using atomic absorption spectroscopy. *Phoenix pusilla* leaves extract was tested for its efficiency against 1 M HCl by incubating mild steel in the absence and presence of inhibitor (5, 10, 30, 50, 70 and 100 ppm) for 3 h at 303 ± 1.00 K (Fadare et al., 2016). After immersion time, the corrodent solutions were observed for the concentration of dissolved ions in each solution to calculate the IE % using the following formula:

$$\textbf{IE \% = B-A/B} \times \textbf{100}$$

where, A and B represents the amount of dissolved ions in the uninhibited and inhibited (with different concentration of inhibitor) corrodent solutions

RESULTS AND DISCUSSION

Preliminary Phytochemical Screening of the plant Extract

In this study to investigate the phytochemical analysis of alcoholic extracts from the leaves of *Phoenix pusilla*. The qualitative phytochemical analysis of the alcoholic extracts of *Phoenix pusilla* leaves shown that the presence of tannin, saponin, flavonoids, steroids, terpenoids, triterpenoids, alkaloids, anthroquinone, polyphenol and glycoside.

Weight Loss Method

Among many experimental methods available to determine the percentage inhibition efficiency and corrosion rate, the weight loss method is the simplest and most frequently used. In this study, the experiments were carried out by varying the concentrations of the inhibitor. This study is also carried out at different temperatures and the immersion period is fixed at 72 h. The weight loss calculated, in grams, is the difference between the weight of metal coupon before and after immersion in a inhibitor solution. The corrosion rate of mild steel in 1M hydrochloric acid solution was studied by weight loss method in blank solution and with various concentration leaves of *Phoenix pusilla*.

Effect of Concentration of *Phoenix pusilla* leaves extract on corrosion inhibition

The inhibition efficiency and the corrosion rate values for all the studied inhibitors and the blank system are determined and given in Table 1 and figure 1. The corrosion rate decreases and the inhibition efficiency increases with the increase in the concentration of *Phoenix pusilla* leaves extract for all inhibitors and the concentration range is 5 to 100ppm for 72 h immersion of the metal in corrodent solution at room temperature. The inhibition efficiency increases because of the inhibitor molecules present in the *Phoenix pusilla* leaves extract getting adsorbed on the metal surface (Figure 1). The maximum inhibition efficiency and the lower corrosion rate are found at high concentration (100ppm) for inhibitors (85.96%) while minimum inhibition efficiency at low concentration (5ppm) for inhibitors (28.07%).

Table 1: Effect of *Phoenix pusilla* leaves extract in corrosion rates, inhibition efficiency and surface coverage at various concentrations

Concentrations (ppm)	Weight loss ($gm.cm^{-2}$)	Corrosion rate ($g.cm^{-2}/h$) × 10^{-4}	Surface coverage (Θ)	Inhibition efficiency (%)
Control	1.14	3.29	-	-
5	0.82	2.37	0.28	28.07
10	0.61	1.76	0.46	46.49
30	0.46	1.33	0.59	59.64
50	0.36	1.04	0.68	68.42
70	0.23	0.66	0.79	79.82
100	0.16	0.46	0.85	85.96

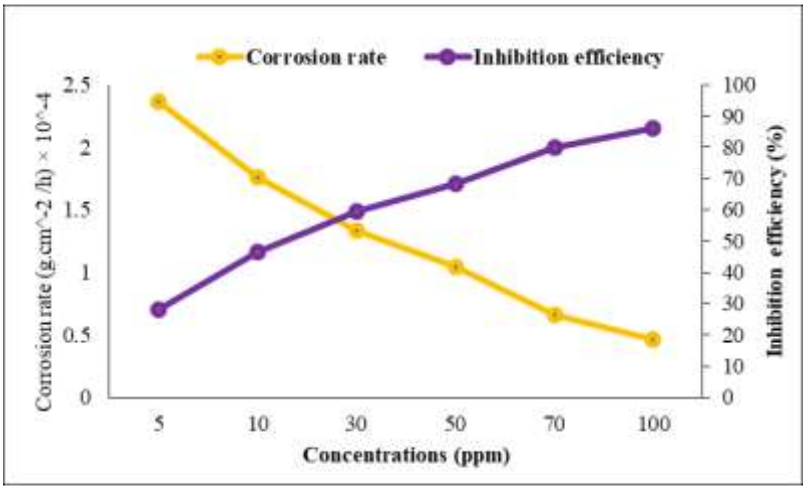

Figure 1: Effect of *Phoenix pusilla* leaves extract in anti-corrosion activity

Inhibition Adsorption Isotherm model

The inhibition effect can be explained by adsorption of *Phoenix pusilla* leaves extract at the mild-steel surface. The *Phoenix pusilla* leaves extract replaces the water molecules at the metal interface according to Langmuir and Temkin model figure 2 and 3.

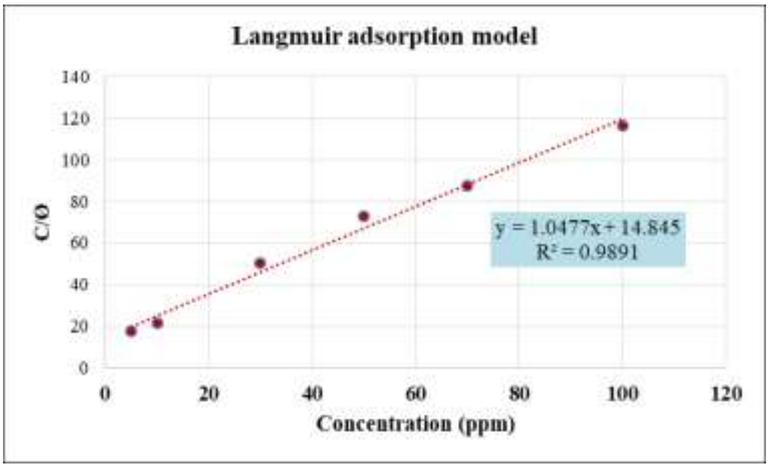

Figure 2: Langmuir Adsorption Isotherm plot for mild steel in 1M HCl with different inhibitory concentration of *Phoenix pusilla* leaves extract

The Langmuir adsorption model was applied. Plotting the experimental data C/θ versus C resulted in a fitted straight line as shown in Figure 8. Concentrations (ppm) is the inhibition concentration of *Phoenix pusilla* leaves extract and θ is the surface coverage. It is clear that the adsorption follows Langmuir adsorption isotherm, as indicated by the correlation coefficient (R) = 0.994 and the slope = 1.047 as expected from Langmuir model followed by Ali and Mahrousb (2017)

$$c/\theta = c + 1/K_{ads}$$

Thus, the adsorption of *Phoenix pusilla* leaves extract as corrosion inhibitor was harmonious with Langmuir adsorption isotherm. The strength and stability of the adsorbed layer formed by *Phoenix pusilla* leaves extract was evaluated from inverse of the plot intercept. The K_{ads} was found to be equal to 0.067 ppm^{-1}.

Temkin model was achieved by plotting log (θ/C) versus θ, Figure 9. The obtained straight line has adjustable correlation coefficient R = 0.974. Thus, Temkin model is less acceptable than Langmuir model because of less R value (Faiz et al., 2020).

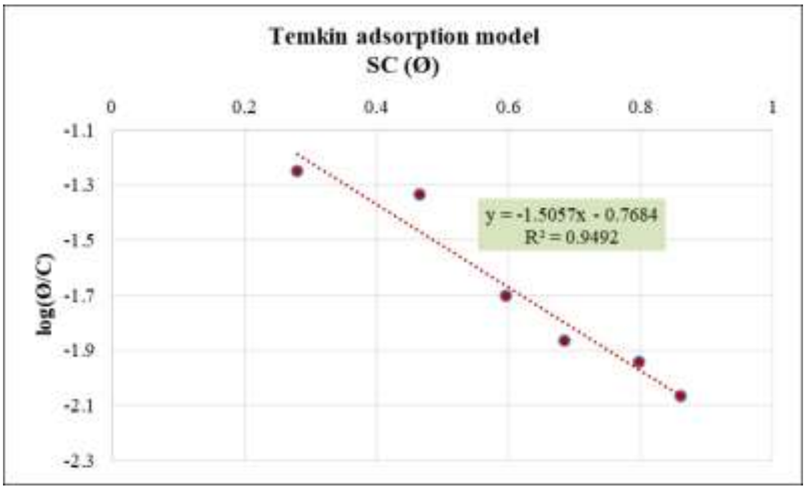

Figure 3: Temkin Adsorption Isotherm plot for mild steel in 1M HCl with different inhibitory concentration of *Phoenix pusilla leaves* extract

Atomic Absorption Spectroscopy

The analysis of dissolved ions in corrodent solution without inhibitor with that of corrodent solution with different concentrations of inhibitor (5, 10, 30, 50, 70, 70 and 100 ppm) were examined through AAS. The results (Table 2) were in correlation with mass loss measurement which exhibited corrosion inhibition in concentration dependent manner. Maximum level of inhibition against 1 M HCl corrosion was 80.46 % with 100 ppm at 303 ±1.00 K. A study on acid inhibitor preventing ferrous (iron) pigment corrosion. The inhibition efficiency of the plant extract based on concentration apparently happens by the adsorption of active constituents of *Phoenix pusilla* leaves onto the surface of metal forming protective film thereby prohibiting oxidation and reducing the ferrous (iron) ion diffusion in the corrodent solution.

Table 2: AAS study of dissolved ferrous (iron) ions in corrodent solution against 1 M HCl control and different concentrations of *Phoenix pusilla* leaves extract inhibitor

Concentrations (ppm)	Amount of ferrous (iron) corrodant (mg/l)	Inhibition efficiency (%)
Control	27.18	-
5	21.14	22.22
10	17.91	34.10
30	12.95	52.35
50	8.75	67.80
70	6.85	74.79
100	5.31	80.46

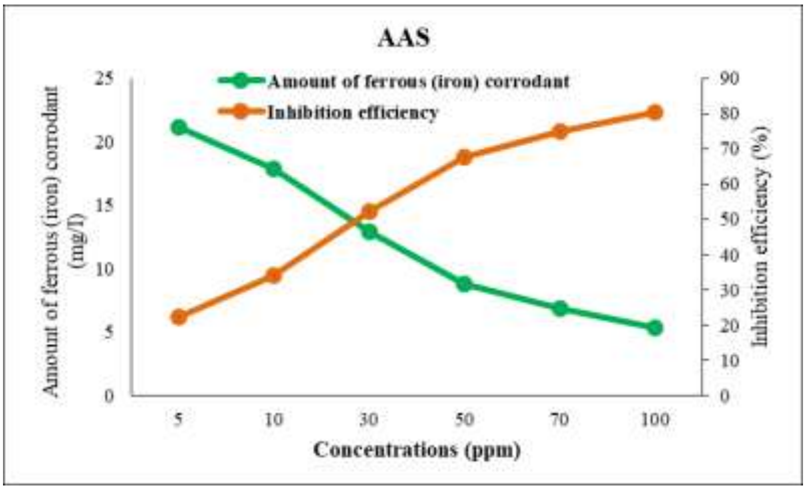

Figure 4: AAS study of dissolved ferrous (iron) ions in corrodent solution against 1 M HCl control and different concentrations of *Phoenix pusilla* leaves extract inhibitor

The present study, the efficacy of *Phoenix pusilla* leaves extract as an environmentally friendly inhibitor was demonstrated by investigating the mass loss behavior of mild steel in solutions of 1 M HCL. This indicates a high sensitivity of *Phoenix pusilla* leaves extract toward inhibition of mild steel in acidic medium. It was also observed that adsorption follows Langmuir and Temkin isotherm model.

Corrosion Inhibition Mechanism

The adsorption of the *Phoenix pusilla* leaves extract is caused by the adsorption of the phytochemical components contained in the extract on the metal surface, which prevent the surface of the metal from being attacked by acid and therefore do not allow the corrosion effect (Zakvi and Mehta, 1988) to occur. The delay in anodic dissolution in the presence of an inhibitory molecule has been described by the mechanism in which two absorbed intermediates are involved. Mild steel is known to have a coordinating affinity for sulfur, nitrogen and oxygen, which contain ligands (Abdel-Gaber et al., 2009). Corrosion of mild steel in extracts of vegetable HCl solutions can be inhibited due to the adsorption of plant substances present in plant extracts by their pair of electrons and p-solitary electrons with d-orbital on the surface of mild steel (De Souza and Spinelli, 2009; Oguzie, 2008; Flick, 1993).

Atoms such as N, O and S can form a covalent bond coordinated with the metal due to their pairs of free electrons and thus act as an inhibitor (Quraishi et al., 2010). The process can block active areas and thus reduce the corrosion rate. The aqueous leaf extract contains these atoms in their phyto constituents and could be adsorbed on the surface of the metal and reduce the area available for a cathodic and anodic corrosion reaction. In acid solution, the active components present in the inhibitor exist in the form of protonated species and adsorbing in the cathode-ray areas of mild steel, which reduces the development of hydrogen. Anode point adsorption is done via π electrons and a single pair of electrons in the heteratomy of the active components present in the inhibitor. For example, the leaf extract of Salvia officinalis has shown an activity of inhibiting decent corrosion on stainless steel 304 in a solution of 1M HCl due to the adsorption of phenolic components such as luteoline-7-glucoronide, carnosol (Soltani *et al*., 2012), through their heteratomas, including N and O, who acted as effective adsorption centers. *Osanthus* fragrance leaf extract has shown mixed corrosion inhibition activity against carbon steel in 1 M HCL (Li et al., 2012). In another study, the alkaloid extract of Geissospermum leaf also showed inhibitory activity of mixed typhoid on C38 steel in 1 M HCl, which was caused by the Langmuir adsorption isotherm (Faustin et al., 2015).

Conclusion

The *Phoenix Pusilla* leaf extract has shown promising corrosion inhibition properties for mild steel in a 1 M HCl medium. The inhibition effectiveness has been found to be directly related to the concentrations of extract. The adsorption of the inhibitor on the surface of the mild steel obeyed both the adsorption isotherms and Langmuir and Temkin. Other studies to assess the morphology of corrosion and to isolate and confirm the active phytochemicals which are responsible for the inhibition of corrosion of mild steel in acidic media are necessary.

References

Abd El-Maksoud, S. A. (2004). The effect of hexadecyl pyridinium bromide and hexadecyl trimethyl ammonium bromide on the behaviour of iron and copper in acidic solutions. *Journal of Electroanalytical Chemistry*, *565*(2), 321-328.

Abdel-Gaber, A.M., AbdEL-Nabey, B.A., Saa dawy, M., 2009.Corros. Sci. 51, 1038.

Ali, A.I.; Mahrousb, Y.S. Corrosion inhibition of C-steel in acidic media from fruiting bodies of *Melia azedarach* L extract and a synergistic Ni2+ additive. RSC Adv. *2017*, 7, 23687–23698.

Benabdellah, M., Benkaddour, M., Hammouti, B., Bendahhou, M., & Aouniti, A. (2006). Inhibition of steel corrosion in 2 M H3PO4 by artemisia oil. *Applied surface science*, *252*(18), 6212-6217.

Bentiss, F., Traisnel, M., Chaibi, N., Mernari, B., Vezin, H., & Lagrenée, M. (2002). 2, 5-Bis (n-methoxyphenyl)-1, 3, 4-oxadiazoles used as corrosion inhibitors in acidic media: correlation between inhibition efficiency and chemical structure. *Corrosion science*, *44*(10), 2271-2289.

Bhaskaran, R., Palaniswamy, N., Rengaswamy, N. S., & Jayachandran, M. (2005). A review of differing approaches used to estimate the cost of corrosion (and their relevance in the development of modern corrosion prevention and control strategies). *Anti-Corrosion Methods and Materials*, 52, 29.

Bhuvaneswari T.K.,, V.S. Vasantha, C. Jeyaprabha, Pongamia Pinnata as a green corrosion inhibitor for mild steel in 1N sulfuric acid medium, Silicon, 10 (2018) 1793–1807.

Buchweishaija, J., & Mhinzi, G. S. (2008). Natural products as a source of environmentally-friendly corrosion inhibitors: the case of gum exudate from Acacia seyal var, 26, 257.

De Souza, F. S., & Spinelli, A. (2009). Caffeic acid is a green corrosion inhibitor for mild steel. *Corrosion science*, *51*(3), 642-649.

Derfouf H., H. Rouabhi, Y. Harek, L. Larabi., Inhibitive Action of Aqueous Extract of Zygophyllum Album L Leaves on the Corrosion of Carbon Steel in Hydrochloric Acid Solution. Der Pharmacia Lettre. 9: 57-68 (2017).

Düdükcü, M., Yazici, B., & Erbil, M. (2004). The effect of indole on the corrosion behaviour of stainless steel. *Materials Chemistry and Physics*, *87*(1), 138-141.

Economic Effects of Metallic Corrosion in the United States, 1978a, NBS Special Publication 511-1, SD Stock No. SN-003-003-01926-7.

Economic Effects of Metallic Corrosion in the United States, 1978b, Appendix B, NBS Special Publication 511-2, SD Stock No. SN003-003-01927-5.

Fadare O.O.; Okoronkwo A.E; Olasehinde E.F. Assessment of Anti-Corrosion Potentials of Extract of *Ficus asperifolia* –Miq (Moraceae) on Mild Steel in Acidic Medium. *Afr. J. Pure and Appl. Chem*., 2016, 10, 8-22.

Faiz, M.; Zahari, A.A.; Awanga, K.; Hussin, H. Corrosion inhibition on mild steel in 1 M HCl solution by *Cryptocarya nigra* extracts and three of its constituents (alkaloids). RSC Adv. *2020*, 10, 6547–6562

Faustin, M.; Maciuk, A.; Salvin, P.; Roos, C.; Lebrini, M. Corrosion inhibition of C38 steel by alkaloids extract of Geissospermum laeve in 1 M hydrochloric acid: Electrochemical and phytochemical studies. Corros. Sci. 2015, 92, 287–300.

Flick, E.W. Corrosion Inhibitors: An Industrial Guide; Noyes Publications: Park Ridge, NJ, USA, 1993.

Galal, A., Atta, N. F., & Al-Hassan, M. H. S. (2005). Effect of some thiophene derivatives on the electrochemical behavior of AISI 316 austenitic stainless steel in acidic solutions containing chloride ions: I. Molecular structure and inhibition efficiency relationship. *Materials Chemistry and Physics*, *89*(1), 38-48.

Harborne JB. (1973) Phytochemical Methods; A guide to modern techniques of plant Analysis.2nd Edition, London New York. pp. 49-188.

Harborne JB. (1984) Phytochemical Methods.A Guide to Modern Technique of Plant analysis. London: Chapman and Hall, pp.78-210.

Hosseini, M.; Mertens, S.F.L.; Arshadi, M.R. Synergism and antagonism in mild steel corrosion inhibition by sodium dodecylbenzenesulphonate and hexamethylenetetramine. Corros. Sci. *2003*, 45, 1473–1489.

Khadraoui A., A. Khelifa, K. Hachama, H. Boutoumi, B. Hammouti., Synergistic effect of potassium iodide in controlling the corrosion of steel in acid medium by Mentha pulegium extract. Research on Chemical Intermediates. 41: 7973-7980 (2015).

Kilmartin, P. A., Trier, L., & Wright, G. A. (2002). Corrosion inhibition of polyaniline and poly (o-methoxyaniline) on stainless steels. *Synthetic metals*, *131*(1-3), 99-109.

Li, L.; Zhang, X.; Lei, J.; He, J.; Zhang, S.; Pan, F. Adsorption and corrosion inhibition of Osmanthus fragran leaves extract on carbon steel. Corros. Sci. 2012, 63, 82–90.

Nishimura, R., & Maeda, Y. (2004). SCC evaluation of type 304 and 316 austenitic stainless steels in acidic chloride solutions using the slow strain rate technique. *Corrosion Science*, *46*(3), 769-785.

Oguzie, E. E. (2007). Corrosion inhibition of aluminium in acidic and alkaline media by Sansevieria trifasciata extract. *Corrosion science*, *49*(3), 1527-1539.

Oguzie, E.E., 2008. Corros. Sci. 50, 2993.

Quraishi M.A., A. Singh, V. Singh, D.K. Yadav, K.S. Ashish, Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of Murraya koenigii leaves, Mater. Chem. Phys., 122 (2010) 114–122.

Raja, B. P., & Sethuraman, M. G. (2009). Strychnos nux- vomica an eco- friendly corrosion inhibitor for mild steel in 1 M sulfuric acid medium. *Materials and Corrosion*, *60*(1), 22-28.

Raja, P. B., & Sethuraman, M. G. (2008). Natural products as corrosion inhibitor for metals in corrosive media—a review. *Materials letters*, *62*(1), 113-116.

Rudresh, H.B.; Mayanna, S.M. Adsorption of n-Decylamine on Zinc from Acidic Chloride Solution. J. Electrochem. Soc. *1977*, 124, 340.

Sanyal, B. (1981). Organic compounds as corrosion inhibitors in different environments—a review. *Progress in Organic Coatings*, *9*(2), 165-236.

Selles C., B. Omar, T. Boufeldja, L. Larabi, Y. Harek., Green corrosion inhibitor: inhibitive action of aqueous extract of Anacyclus pyrethrum L. for the corrosion of mild steel in 0.5 M H2SO4. J. Mater. Environ. Sci. 3 : 206-219 (2012).

Sofowara A (1993). Medicinal plants and Traditional medicine in Africa. Spectrum Books Ltd, Ibadan, Nigeria. p. 289.

Soltani, N.; Tavakkoli, N.; Khayatkashani, M.; Jalali, M.R.; Mosavizade, A. Green approach to corrosion inhibition of 304 stainless steel in hydrochloric acid solution by the extract of Salvia officinalis leaves. Corros. Sci. 2012, 62, 122–135.

Torres V.V., R.S. Amado, C.F. De Sá, T.L. Fernandez, C.A. Riehl, A.G. Torres, E. D'Elia, Inhibitory action of aqueous coffee ground extracts on the corrosion of carbon steel in HCl solution, Corros. Sci., 53 (2011) 2385–2392.

Trease GE and Evans WC.(1989) Pharmacognsy.11th edn.Brailliar Tiridel Can. Macmillian publishers.

Zakvi, S.; Mehta, G. Acid corrosion of mild steel and its inhibition by *swertia aungustifolia*-study by electrochemical techniques. Trans. SAEST 1988, 23, 407–410.