Asian Journal of Chemistry; Vol. 29, No. 5 (2017), 1130-1134

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2017.20449

Extract of Different Plants of Nepalese Origin as Green Corrosion Inhibitor for Mild Steel in 0.5 M NaCl Solution

MANOJ RANA, SUSAN JOSHI* and JAGADEESH BHATTARAI*

Central Department of Chemistry, Tribhuvan University, GPO Box 2040, Kathmandu, Nepal

*Corresponding authors: Fax: +977 9841609766; Tel: +977 01 4333748; E-mail: susanjoshi68@gmail.com; bhattarai_05@yahoo.com

Received: 16 December 2016; *Accepted*: 18 February 2017; *Published online*: 10 March 2017; AJC-18313

Corrosion inhibition effect of *Areca catechu*, *Laurus nobilis* and *Catharanthus roseus* plant extracts on mild steel was investigated in 0.5 M NaCl solution in open air at 28 ± 1 °C using immersion tests, inhibition mechanism and corrosion potential measurements. The corrosion rate of the steel was decreased with increasing the concentration of the extracts up to 2000 ppm. *Catharanthus roseus* plant extract was found to be most efficient inhibitor among the three extracts used in this study. Adsorption of all three plant extracts on the surface of the mild steel obeyed both Langmuir and Temkin adsorption isotherms. *Areca catechu* and *Catharanthus roseus* plant extracts acted as an anodic type corrosion inhibitor, while *Laurus nobilis* extract acted as mixed type inhibitor based on the potential measurement. Consequently, all the three plant extracts can be used as an environmentally friendly inhibitor to control the corrosion of mild steel in aggressive environments.

Keywords: Green inhibitor, Plant extract, Corrosion, Mild steel, 0.5 M NaCl.

INTRODUCTION

Corrosion stand as one of the most serious problems in our modern societies and the resulting losses each year are in hundreds of billions of dollars [1,2]. Several ways to control the corrosion of the metallic materials are constantly reviewed and discussed by corrosion scientists and engineers. Nevertheless, the corrosion damage is not totally prevented but it can be minimized using different corrosion control methods [3,4]. The use of corrosion inhibitors (CIs) is one of the best known methods to control the corrosion and mostly used in the industries due to its low cost and easy practice method [5,6]. An efficient inhibitor is compatible with the environment and is economical for application [7]. Nowadays, the corrosion control method of metallic materials using various types of eco-friendly green corrosion inhibitors is becoming a fundamental research concern of corrosion scientists and engineers, because a corrosion inhibitor is a chemical substance that when added in small amounts to a corrosive environment, effectively decreases the corrosion rate of the materials exposed to corrosive environments [3-5].

A practical criterion for the selection of corrosion inhibitors is not only their inhibition efficiency but also safety of use, economic constraints and compatibility with other chemicals in the system. In the past, many inorganic salts and organic compounds employed as corrosion inhibitors were found to be quite toxic and do not fulfill completely the requirements imposed by the environmental protection standards, although they showed high corrosion inhibition efficiency even in aggressive solutions. The concern regarding toxicity and pollution free environment is recently increased, because of its direct impact on human health. Many inorganic salts and organic compounds employed as corrosion inhibitors are found to be quite toxic and do not fulfill all the requirements imposed by the environmental protection standards. Therefore, better alternatives for such toxic corrosion inhibitors are the green corrosion inhibitors.

In recent years, the reason for the search of less toxic corrosion inhibitors alternatives is becoming very interesting topics of research [8]. There is a trend of replacing harmful corrosion inhibitor by effective non-hazardous green corrosion inhibitors mostly of plant extracts, because the green inhibitors are generally biodegradable, do not contain heavy metals and impose zero or negligible toxicity to the environment and human beings. The green corrosion inhibitors extracted from plants presumably possess biocompatibility due to their biological origin. In addition, these plant extracts are easily available, because abundant of plant resources in nature.

On the other hand, in order to ensure the more durability of the new steel-structures exposed to aggressive environments, we need to understand what can be done to reduce the corrosion risk of the structural materials in different corrosive environments. In general, iron or steel passivated at a pH higher than

10, even though the passivity decreases in very strong alkaline solutions (*i.e.*, > 13.5 pH) where it has a tendency to dissolve to form highly soluble hypo-ferrite ($HFeO^{2-}$) in aqueous solution [3,4]. Therefore, a strong alkaline (not very strong) solution is generally employed in many chemical processing industries where iron or steel equipments are used [9]. In the past years, the corrosion behaviour of the mild steel was mainly investigated in acids [10-16] and alkalis [11,16-18]. The study of the corrosion behaviour of mild steel in NaCl solution is also becoming an important topic in the field of corrosion and several approaches for its control had been investigated previously [10,11,16,19,20].

The extensive researches have led to the discovery of new class of green corrosion inhibitors those are generally environmentally friendly. Few studies were reported about the corrosion behaviour of structural materials used in Nepal [10,11,15,16,21-23]. In this context, present work was focused to study the effect of plant extracts extracted from three different plants of *Areca catechu, Laurus nobilis* and *Catharanthus roseus*, on the corrosion behaviour of the mild steel in 0.5 M NaCl solution open to air at 28 ± 1 °C employing immersion tests, inhibition mechanism and corrosion potential measurements.

EXPERIMENTAL

Mild steel specimens for both immersion and electrochemical tests were prepared having dimension of 2 cm × 2 cm × 0.5 cm. The approximate chemical constituents of the mild steel specimen were reported as in wt. (%); C = 0.17, P = 0.05, Si = 0.04, Mn = 0.90, S = 0.05 and balance by iron. Prior to the immersion and electrochemical tests, the surface of each sample specimen was mechanically polished with different grades (200-1500 grit) SiC paper using ethanol, rinsed with acetone and dried by air blowing until the surface exhibited mirror like reflection in order to obtain reproducible results.

The corrosion test of the mild steel specimens was carried out in 0.5 M NaCl solution open to air at 28 ± 1 °C containing different concentrations (*i.e.*, 500, 1000, 1500 and 2000 ppm) of plant extracts (methanol fraction) extracted from *Areca catechu, Laurus nobilis* and *Catharanthus roseus* species of Nepalese origin. Prior to corrosion test, the surface of each mild steel specimen was mechanically polished with silicon carbide paper grit numbers 200-1500, rinsed with acetone and dried by air blowing in order to obtain reproducible results. The average corrosion rate (mm/y) of the individual steel specimen was estimated using weight loss method as given in eqn. 1 [4].

$$\text{Corrosion rate} = \frac{\Delta w \times 8760 \times 10}{d \times A \times t} \quad (1)$$

where, Δw is the weight loss of the steel specimen in gram (g), d is the density of the specimen in g/cm^3, A is area of the sample specimen in cm^2 and t is time of immersion in hour.

The corrosion inhibition efficiency ($IE_{CR\,\%}$) and the degree of surface coverage (θ) of the inhibitor molecule were estimated using following eqns. 2 and 3, respectively [24].

$$IE_{CR,\%} = \frac{CR_{(o)} - CR_{(inh.)}}{CR_{(o)}} \times 100 \quad (2)$$

$$\theta = \frac{CR_{(o)} - CR_{(inh.)}}{CR_{(o)}} \quad (3)$$

where, $CR_{(o)}$ and $CR_{(inh.)}$ are the corrosion rates in absence and presence of plant extract as a green corrosion inhibitor, respectively.

The corrosion inhibition mechanism was also studied using both Langmuir and Temkin adsorption isotherm models. The Langmuir adsorption isotherm equation is expressed by eqn. 4 [25], where the $C_{inh.}$ is the inhibitor concentration and K_{ads} is the adsorptive equilibrium constant. The K_{ads} value can be used to estimate the standard free energy of adsorption (ΔG°_{ads}) using eqns. 5 and 6 [26,27].

$$\frac{C_{inh.}}{\theta} = \left(\frac{1}{K_{ads}}\right) + C_{inh.} \quad (4)$$

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G^{o}_{ads}}{RT}\right) \quad (5)$$

$$\Delta G^{o}_{ads} = -RT \ln\left(55.5 \times K_{ads}\right) \quad (6)$$

where, R is gas constant, T is temperature and the value of 55.5 is the molar concentration of water in solution.

The Temkin adsorption isotherm model is linearly represented by eqn. 7 for a monolayer adsorption [28-30] and then we get a relation between degree of surface coverage (θ) and concentration of adsorbed inhibitor (C_{inh}) in g/L.

$$\theta = \frac{2.303B}{K} \log A_T + \frac{2.303B}{K} \log C_{inh.} \quad (7)$$

where, B (= RT/b_T) is constant related to heat of adsorption (J/mol), b_T is Temkin isotherm constant, R is gas constant and T is absolute temperature, A_T is Temkin isotherm equilibrium binding constant (L/g) and K is constant. The plot of θ *versus* log C_{inh} gives a straight line that would confirm Temkin adsorption isotherm.

For understanding the effects of three green inhibitors on the corrosion inhibition behaviour of the mild steel specimens, corrosion potential of the steel specimens was measured using a simple potentiometer (two electrode system; Osaw Digital Potentiometer) in 0.5 M NaCl solution open to air at 28 ± 1 °C containing different concentrations of three Nepalese plant extracts of *Areca catechu, Laurus nobilis* and *Catharanthus roseus*. A saturated calomel electrode (SCE) and the mild steel sheet were used as the reference and working electrodes, respectively.

RESULTS AND DISCUSSION

The effect of different concentrations (*i.e.*, 500, 1000, 1500 and 2000 ppm) of the extracts (methanol fraction) obtained from three Nepalese plants of *Areca catechu, Laurus nobilis* and *Catharanthus roseus* (called as Supari, Tejpatta and Baramashe, respectively, in Nepal), was studied after immersion for 240 h in 0.5 M NaCl solution in open air at 28 ± 1 °C and the estimated average corrosion rate is depicted in Fig. 1. The corrosion rate of the mild steel is generally decreased with increasing the concentrations of all three different plant extracts. The corrosion resistance property of the mild steel is signifi-

cantly improved in 0.5 M NaCl solution with additions of 1500-2000 ppm of methanol fraction of plant extract of *Catharanthus roseus* comparison with other two plant extracts of *Laurus nobilis* and *Areca catechu* as shown in Fig. 1. It is found that the order of the corrosion inhibition efficiency of these three plant extracts used in this study to the mild steel in NaCl environment is; *Catharanthus roseus* > *Laurus nobilis* > *Areca catechu* based on the results of the estimated corrosion rates. The results revealed that the *Catharanthus roseus* plant extract can be used as a good corrosion inhibitor to increase the corrosion resistance properties of different structural materials made by mild steel in aggressive chloride containing NaCl solution at ambient temperature.

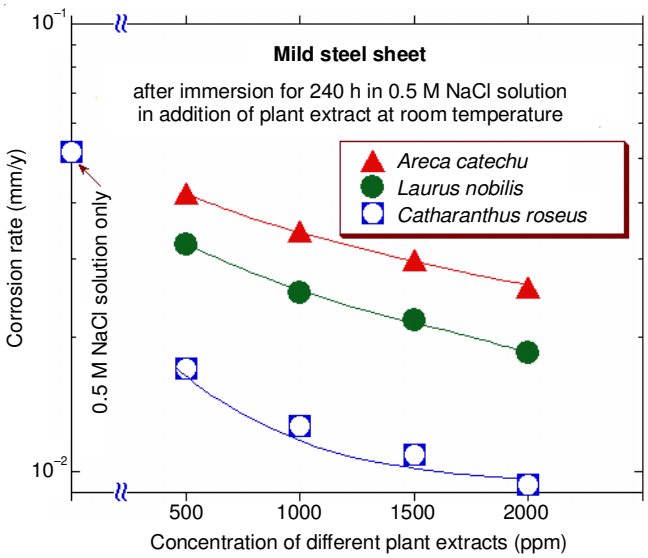

Fig. 1. Changes in the corrosion rates of mild steel sheet in 0.5 M NaCl solution in open air at 28 ± 1 °C, as a function of concentration of different plant extracts

The corrosion inhibition efficiency of different concentrations of extract of three plants (*i.e.*, *Areca catechu, Laurus nobilis* and *Catharanthus roseus*) in 0.5 M NaCl solution open to air at 28 ± 1 °C is shown in Fig. 2. Initially the inhibition efficiency is increased steeply with increasing the concentration of *Catharanthus roseus* plant extract up to 1000 ppm and the maximum inhibition efficiency of 82 % was obtained at 2000 ppm extract in 0.5 M NaCl solution.

On the other hand, the effects of the plant extracts of *Areca catechu* and *Laurus nobilis* on the corrosion inhibition efficiency of the mild steel specimens in 0.5 M NaCl solution is not effective even in 2000 ppm extract addition as comparison with the addition of the *Catharanthus roseus* plant extract. The maximum inhibition efficiencies of 65 % and 50 % was obtained at 2000 ppm extracts of *Laurus nobilis* and *Areca catechu*, respectively. The trend of the corrosion inhibition activity of these three plant extracts are in the order of extract *Catharanthus roseus* > *Laurus nobilis* > *Areca catechu*. Therefore, it is concluded from the corrosion inhibition efficiency study that the *Catharanthus roseus* plant extract can be used as a good green corrosion inhibitor to control significantly the corrosion behaviour of the mild steel in aggressive chloride containing environments and the result is in agreement with the results of immersion tests as shown above in Fig. 1.

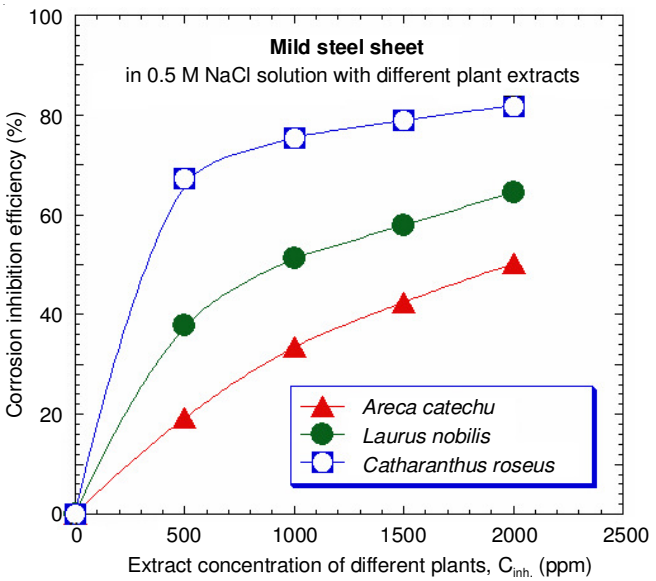

Fig. 2. Change in the corrosion inhibitor efficiency for the mild steel sheet in 0.5 M NaCl solution in open air at 28 ± 1 °C in presence of different concentrations of *Areca catechu*, *Laurus nobilis* and *Catharanthus roseus* plant extracts

The adsorption isotherms are of extreme importance in understanding the mechanism of the corrosion inhibition of metals and their alloys by plant extracts as green corrosion inhibitors in aggressive environments [26,27]. It describes the molecular interaction between the inhibitor molecules and the active sites on the surface of the metallic materials. The process of inhibitor adsorption on the surface of the mild steel grille sheet can be described by different isotherm models and Langmuir isotherm is the simplest one. Langmuir adsorption isotherm model is based on the assumption that all the adsorption sites are equivalent and the particle binding occurs independently from nearby sites being occupied or not [25,30].

Fig. 3 shows the relationship between the ratio of inhibitor concentration to surface coverage ($C_{inh.}/\theta$) and inhibitor concentration ($C_{inh.}$) for three different green corrosion inhibitors

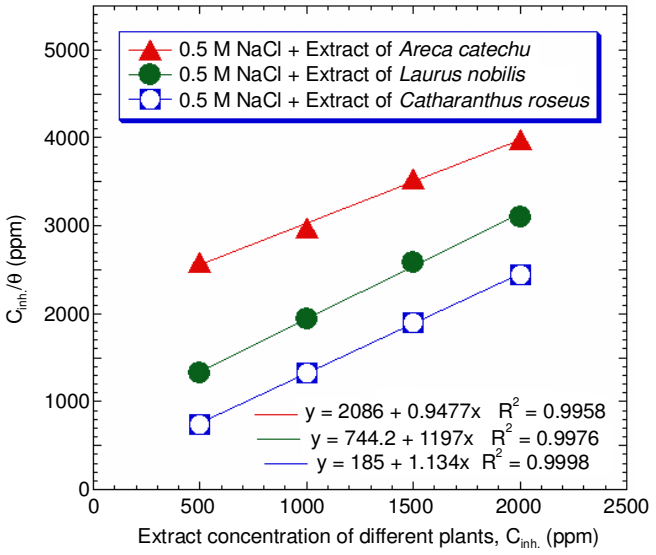

Fig. 3. Langmuir isotherm plot for the corrosion inhibition of mild steel in 0.5 M NaCl solution in open air at 28 ± 1 °C in presence of *Areca catechu*, *Laurus nobilis* and *Catharanthus roseus* plant extracts as green corrosion inhibitors

of *Areca catechu*, *Laurus nobilis* and *Catharanthus roseus* plant extracts in 0.5 M NaCl solution open to air at 28 ± 1 °C. The linear correlation coefficient (R^2) was used to choose the isotherm that best fit experimental data, because it was found almost equal to unity as shown in Fig. 3.

Similarly, plot of θ *versus* log C_{inh} gave straight lines that would confirm Temkin adsorption isotherm for the adsorption of the green corrosion inhibitors of *Areca catechu*, *Laurus nobilis* and *Catharanthus roseus* plant extracts in 0.5 M NaCl solution open to air at 28 ± 1 °C as shown in Fig. 4. This implies that the adsorption behaviour of all three plant extracts used in this study on the mild steel surface is best described by Temkin isotherm. In fact the applicability of Temkin adsorption isotherm verified a monolayer adsorption of the green inhibitors on a uniform mild steel sheet surface with interaction between the adsorbed species of the corrosion inhibitors [28-30]. These results indicated that the adsorption process obeyed both the Langmuir and Temkin adsorption isotherms to study the corrosion inhibition mechanism on the surface of the mild steel sheet by the green corrosion inhibitors of *Areca catechu*, *Laurus nobilis* and *Catharanthus roseus* plant extracts in 0.5 M NaCl solution open to air at 28 ± 1 °C.

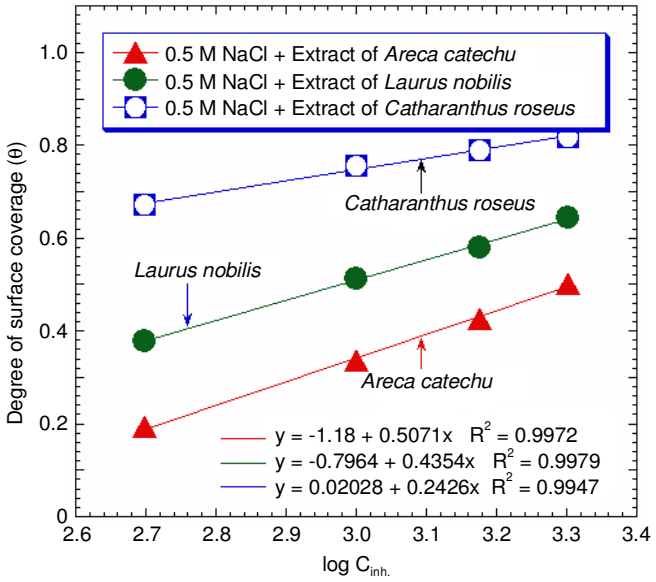

Fig. 4. Temkin isotherm for the corrosion inhibition of mild steel in 0.5 M NaCl solution in open air at 28 ± 1 °C in presence of *Areca catechu*, *Laurus nobilis* and *Catharanthus roseus* plant extracts as green corrosion inhibitor

The corrosion potential or open circuit potential (OCP) measurement was carried out for a better understanding of the corrosion behaviour of the mild steel in 0.5 M NaCl solutions open to air at 28 ± 1 °C in absence and presence of *Areca catechu*, *Laurus nobilis* and *Catharanthus roseus* plant extracts used as a green corrosion inhibitor. Fig. 5a-c show the effects of corrosion inhibitors of *Areca catechu*, *Laurus nobilis* and *Catharanthus roseus* plant extracts, respectively, in the changes of corrosion potential for the mild steel specimens after immersion for 24 h in 0.5 M NaCl solution, as a function of immersion time.

The figures clearly indicate that the corrosion potential of the mild steel specimens in presence of *Areca catechu* and

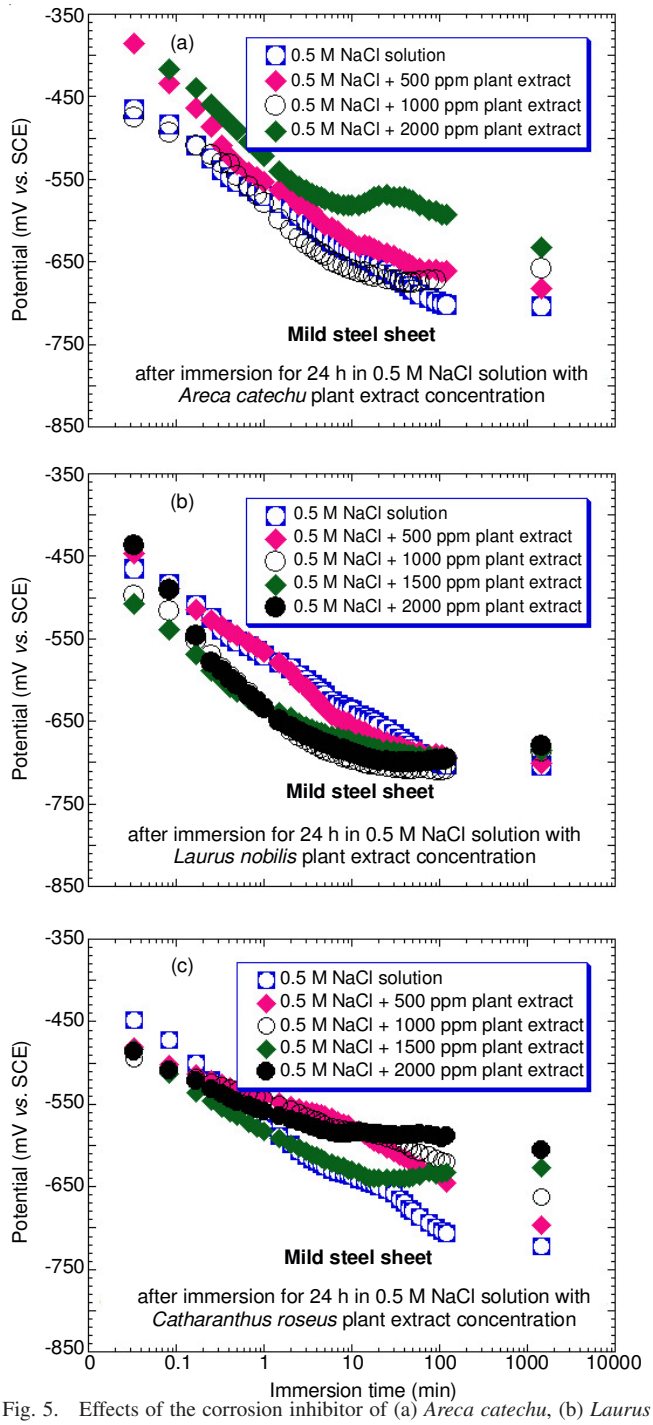

Fig. 5. Effects of the corrosion inhibitor of (a) *Areca catechu*, (b) *Laurus nobilis* and (c) *Catharanthus roseus* extracts in the corrosion potential for the mild steel in 0.5 M NaCl solution in open air at 28 ± 1 °C, as a function of immersion time

Catharanthus roseus plant extracts is shifted to more positive direction with increasing the concentration of the extracts as compared to the blank 0.5 M NaCl solution indicating these two extracts act as an anodic corrosion inhibitor. However, the corrosion potential for *Laurus nobilis* plant extract is negligibly shifted to positive direction indicating it to be mixed typed corrosion inhibitor.

Conclusions

The effect of three plant extracts extracted from *Areca catechu*, *Laurus nobilis* and *Catharanthus roseus* as green

inhibitors in the corrosion control of the mild steel sheet in 0.5 M NaCl and 1 M HCl solutions open to air at 28 ± 1 °C was studied using immersion tests, inhibition mechanism and corrosion potential measurements and the following conclusions are drawn.

• Three plant extracts used in this study can be used as environmentally friendly green corrosion inhibitor to increase the corrosion resistance properties of the mild steel in 0.5 M NaCl solution at ambient temperature.

• Corrosion inhibition efficiency of the plant extracts is found to be in the order of *Catharanthus roseus* > *Laurus nobilis* > *Areca catechu*.

• The corrosion inhibition mechanism of all three plant extracts on the mild steel surface was explained by the adsorption process, which is obeyed both the Langmuir and Temkin adsorption isotherms.

• Corrosion potential measurements showed the plant extracts of *Catharanthus roseus* and *Areca catechu* acted as anodic type of corrosion inhibitor, while the extract of *Laurus nobilis* acted as mixed type.

REFERENCES

1. G.H. Koch, M.P.H. Brongers, N.G. Thompson, Y.P. Virmani and J.H. Payer, FHWA-RD-01-156, Corrosion Costs and Preventive Strategies in the United States, NACE International, Washington, DC, USA, pp. 1-11 (2002); www.corrosioncost.com.
2. DNV GL, Assessment of Global Cost of Corrosion, Report No. OAPUS310GKOCH (PP110272)-1, Rev. 3, Appendix-A, pp. A1-A8 (2015); www.dnvgl.com.
3. R.W. Revie and H.H. Uhlig, Corrosion and Corrosion Control: An Introduction to Corrosion Science and Engineering, John Wiley & Sons Inc., New Jersey, USA, edn 4, p. 490 (2008).
4. J. Bhattarai, Frontiers of Corrosion Science, Kshitiz Publisher, Kirtipur, Kathmandu, p. edn 1 304 (2010).
5. S.A. Bardford, Corrosion Control, CASTI Publishing Inc., Alberta, Canada, p. 497, edn 2 (2001).
6. V. Cicek and B. Al-Numan, Corrosion Chemistry, Scrivener Publishing LLC, Salem, Massachusetts, USA, p. 173 (2011).
7. C.G. Dariva and A.F. Galio, in ed.: M. Aliofkhazraei, Corrosion Inhibitors –Principles, Mechanisms and Applications, In: Developments in Corrosion Protection, InTech Open Science, Chap. 16, pp. 365-379 (2014); https://doi.org/10.5772/57255.
8. S.R. Tayler and B.D. Chambers, Synergistic Combinations of Chromate Free Corrosion Inhibitors, US Patent No. US20090000958 A1 (2009).
9. S.L. Chawla and R.K. Gupta, Materials Selection for Corrosion Control, ASM International, Materials Park, Ohio, USA (1991).
10. J. Bhattarai, M. Rana, M.R. Bhattarai and S. Joshi, in Proceedings of *CORCON–2016,* NACE International; Gateway of India Section, New Delhi, India, Paper No. MI-17, pp. 1-8 (2016).
11. D. v.K and J. Bhattarai, *Int. J. Appl. Sci. Biotechnol.*, **4**, 183 (2016); https://doi.org/10.3126/ijasbt.v4i2.14885.
12. O.A. Paul, *Afr. J. Pure Appl. Chem.*, **8**, 37 (2014); https://doi.org/10.5897/AJPAC2014.0549.
13. A. Doner, E.A. Sahin, G. Kardas and O. Serindag, *Corros. Sci.*, **66**, 278 (2013); https://doi.org/10.1016/j.corsci.2012.09.030.
14. M.A. Amin, M.A. Ahmed, H.A. Arida, T. Arslan, M. Saracoglu and F. Kandemirli, *Corros. Sci.*, **53**, 540 (2011); https://doi.org/10.1016/j.corsci.2010.09.019.
15. J. Bhattarai, *Nepal J. Sci. Technol.*, **9**, 157 (2008); https://doi.org/10.3126/njst.v9i0.3181.
16. J. Bhattarai, *J. Nepal Chem. Soc.*, **24**, 31 (2009); https://doi.org/10.3126/jncs.v24i0.2388.
17. J.A. González, J.M. Miranda, E. Otero and S. Feliu, *Corros. Sci.*, **49**, 436 (2007); https://doi.org/10.1016/j.corsci.2006.04.014.
18. J.F. Newman, *Corros. Sci.*, **21**, 487 (1981); https://doi.org/10.1016/0010-938X(81)90078-0.
19. A.S. Hamdy, A.G. Saeh, M.A. Shoeib and Y. Barakat, *Electrochim. Acta*, **52**, 7068 (2007); https://doi.org/10.1016/j.electacta.2007.05.034.
20. Q. Jiang, Q. Miao, W. Liang, F. Ying, F. Tong, Y. Xu, B. Ren, Z. Yao and P. Zhang, *Electrochim. Acta*, **115**, 644 (2014); https://doi.org/10.1016/j.electacta.2013.09.156.
21. J. Bhattarai, D. Poudyal and K.P. Dahal, in Proceedings of 17th Asia Pacific Corrosion Control Conference (APCCC17), Mumbai, India, Paper No. 17039, pp. 1-12 (2016).
22. K.P. Dahal, D. Kc and J. Bhattarai, *BIBECHANA*, **11**, 94 (2014); https://doi.org/10.3126/bibechana.v11i0.10387.
23. J. Bhattarai, *Sci. World*, **11**, 43 (2013); https://doi.org/10.3126/sw.v11i11.8551.
24. M.A. Hegazy, A.S. El-Tabei, A.H. Bedair and M.A. Sadeq, *Corros. Sci.*, **54**, 219 (2012); https://doi.org/10.1016/j.corsci.2011.09.019.
25. I. Langmuir, *J. Am. Chem. Soc.*, **38**, 2221 (1916); https://doi.org/10.1021/ja02268a002.
26. A.K. Satapathy, G. Gunasekaran, S.C. Sahoo, K. Amit and P.V. Rodrigues, *Corros. Sci.*, **51**, 2848 (2009); https://doi.org/10.1016/j.corsci.2009.08.016.
27. C.R. Alentejano and I.V. Aoki, *Electrochim. Acta*, **49**, 2779 (2004); https://doi.org/10.1016/j.electacta.2004.01.039.
28. M.I. Tempkin and V. Pyzhev, *Acta Phys. Chim. USSR*, **12**, 327 (1940).
29. C. Aharoni and M. Ungarish, *J. Chem. Soc., Faraday Trans.*, **73**, 456 (1977); https://doi.org/10.1039/f19777300456.
30. K.Y. Foo and B.H. Hameed, *Chem. Eng. J.*, **156**, 2 (2010); https://doi.org/10.1016/j.cej.2009.09.013.