International Journal of
Chemical and Pharmaceutical Sciences
2011, April., Vol.2 (1)

ISSN: 0976-9390
IJCPS

Inhibitive efficacy of *vinca rosea* extract on stainless steel in natural sea water environment

***Deepa Rani P, Manimehalai S, Sathya S, Thanga meena D and Selvaraj S.**

Post graduate and Research Department of chemistry,

Sri Paramakalyani College, Alwarkurichi, Tamil Nadu, India.

***Corresponding author:** E-Mail: rani.Deeps@yahoo.in

ABSTRACT

The inhibition efficacy of *Vinca rosea* extract on stainless steel in Natural sea water environment has been studied by mass loss measurement at various time and temperature. The inhibition efficiency is markedly higher in natural sea water environment with addition of *Vinca rosea* extract compared with those in the inhibitor free solution. The inhibition efficiency increased with increase of inhibitor concentration but decreased with rise in temperature and exposure time. Based on the values of activation energy and variation of inhibition efficiency with temperature, a physical adsorption mechanism is proposed for the adsorption of *Vinca rosea* on the surface of stainless steel. It is found to follows Langmuir adsorption isotherm. The corrosion product on the stainless steel surface in the presence and absence of alcoholic extract of the inhibitor is analysed by UV and IR studies.

Key words: Corrosion inhibition, stainless steel, *Vinca rosea,* isotherm, Natural sea water.

1. INTRODUCTION

Iron and its alloys find utility in a spread spectrum of many industrial units because of its low-cost and excellent mechanical properties. For this reason, the corrosion behaviour of these metals has attracted more attention of several investigators. Iron and steel is the most corrosion vulnerable metal. Thus, much attention is given for its protection from the hostile environments. The heavy loss of metal is a result of its contact with the pollution environment can be minimized to a great extent by the use of corrosion inhibitors[1]. Inorganic compounds like chromates, phosphates, molybdates etc. and a varity of organic compounds containing heteroatom like nitrogen, sulphur and oxygen are being investigated as corrosion iinhibitors[2-5]. Pure synthetic chemicals are costly, but most of them risk being highly toxic to human beings and their disposal creates pollution problems. Plant extracts are environmentally friendly, bio-degradable, non-toxic, easily available and of potentially low cost. Most of the naturally occurring substances are safe and can be extracted by simple procedures. Recent literature is aware of researchers to investigate different extracts for corrosion inhibition applications. The examples are numerous such as fenugreek[6], heena[7], olive[8], jojoba[9], black pepper[10], onion and garlic[11] etc. Many of these naturally occurring substances proved their ability to act as corrosion inhibitors for the different metals and its alloy in various aggressive media. The aim of our present study is to investigate the corrosion inhibition effect of Vinca rosea (Nithyakalyani) leaves as a cheap and environment friendly corrosion inhibitor on stainless steel in sea water environment by mass loss method. The characterization of the corrosion product on the metal surface in the presence and absence of alcoholic extract of inhibitor is analysed by UV and IR studies.

2. MARERIALS AND METHODS

2.1. Stock solution of *Vinca rosea* extract

Vinca rosea leaves were collected in and around courtallam hills area, shade dried and ground well to powder form. Exactly 150g of dried powder with required quantity of ethyl alcohol was added to cover the powder completely in a RB flask and left it for 48 hrs. The resulting paste was refluxed for 48hrs and boiled with activated charcoal (about 1g) to remove hung and the pure plant extract was collected.

2.2. Chemical properties of *Vinca rosea*

The species has long been cultivated for herbal medicine and as an ornamental plant. Main chemical components are ajmaline, catharanthaine, leurosidine, vincristine, vinblastine, vinorelbine, vindesine, vincamine and vinorelbine[12]. The substances vinblastine and vincristine extracted from the plant are used in the treatment of leukemia[13]. Vinca has more than four hundred known alkaloids. Some are used by the pharmaceutical industry for the treatment of childhood leukemia, Hodgkin’s disease, testicular cancer and cancerous tumors[14]. There are two classes of active compounds in Vinca: alkaloids and tannins. The major alkaloid is known as vincamine. A closely related semi-synthetic derivative of vincamine widely used as medicine is known as ethyl-apovincaminate or vinpocetine. It has vasodilating, blood thinning, and memory-enhancing actions. Over 130 constituents with an indole or dihydroindole structure; including the principal component vindoline; vincaleukoblastine (vinblastine), 22 - oxovincaleukoblastine (vineristine), reserpine, vincamine, alstonine, leurocristine, ajmalicine, vinine, vinomine, vinoxine, vintsine, leurosine. These alkaloids are cytotoxic and target sites in cell division thus preventing mitosis to proceed. Although for a normal person, this action of the vinca alkaloids can be toxic but they are helpful agents in stopping the division of cancerous cells. Vinca alkaloids are used in the prevention and treatment of cancer.

2.3. Specimen preparation

Rectangular specimen of Stainless steel were mechanically pressed cut to form different coupons, each of dimension exactly 5.0x2x2 Cm. The specimens were mechanically polished; a hole drilled at one end for free suspension and numbered by punching. The specimens were decreased with acetone, washed with distilled water and well polished with emery paper, cleaned, rinsed and dried then stored in desiccators for present study.

2.4. Mass Loss method

In the mass loss measurements on Stainless steel in triplicate were completely immersed in 50ml of the test solution in the presence and absence of the inhibitor. The metal specimens were withdrawn from the test solutions after an hour at 303K to 333K and also measured 24 to168 hrs at room temperature. The Mass loss was taken as the difference in weight of the specimens before and after immersion using LP 120 digital balance with sensitivity of ±1 mg. The tests were performed in triplicate to guarantee the reliability of the results and the mean value of the mass loss is reported.

From the mass loss measurements, the corrosion rate was calculated using the following relationship.

$$\text{Corrosion Rate}\left(\text{mmpy}\right) = \frac{87.6 \times W}{DAT} \rightarrow \quad (1)$$

Where, mmpy = millimeter per year, W = Mass loss (mg), D = Density (gm/cm^3),
A = Area of specimen (cm^2), T = time in hours.

The inhibition efficiency (%IE) and degree of surface coverage (θ) were calculated using equation (2) and equation (3), respectively.

$$\%\ IE = \frac{W_1 - W_2}{W_1} \times 100 \rightarrow \quad (2)$$

$$\theta = \frac{W_1 - W_2}{W_1} \rightarrow \quad (3)$$

Where W_1 and W_2 are the corrosion rates in the absence and presence of the inhibitor respectively.

4. RESULTS AND DISCUSSION

4.1. Weight loss measurements

The corrosion and inhibition behavior of stainless steel in Natural sea water environment containing various concentration of ethanolic *vinca rosea* leaves (VRL) extract are studied at different time (24hrs to168hrs) and temperature (303K to 333K) respectively. The degree of surface coverage versus various concentration of VRL extract on stainless steel at different time in natural sea water is represented in Fig.1.

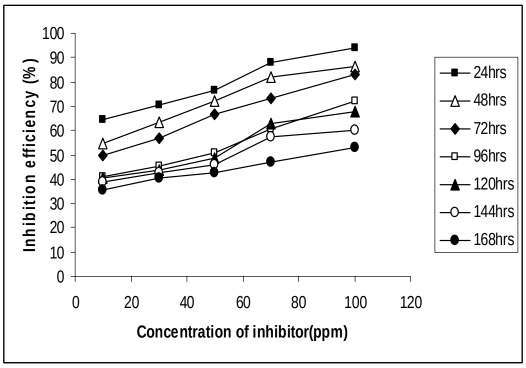

Figure: 1 **Corrosion parameters of stainless steel containing various concentrations of VRL extract at different time in Natural sea water.**

It is clearly indicates that the degree of surface coverage and percentage of inhibition efficiency increased with increase of VRL concentration and gradually decreased with increase of exposure time. The maximum 94.12% of inhibition efficiency is achieved and it is almost maintained above 60% even after 120hrs exposure time. The maximum inhibition efficiency may be the adsorption of the plant constituents (mainly ajmaline, catharanthaine, leurosidine, vincristine, vinblastine, vinorelbine, vindesine, vincamine and vinorelbine) on the stainless steel surface by the interaction of π-electrons or lone pair electron of hetero atoms with the metal surface. The rich of nitrogen atom is present in almost all the chemical compound in VRL extract. Because of the big molecules present in the phytoconstituent of VRL extract can able to cover a large surface area on adsorption. In the case of stainless steel the maximum inhibition efficiency is achieved due to the surface area completely covered with the thin film formation preferentially co-ordinate with inhibitor[15].

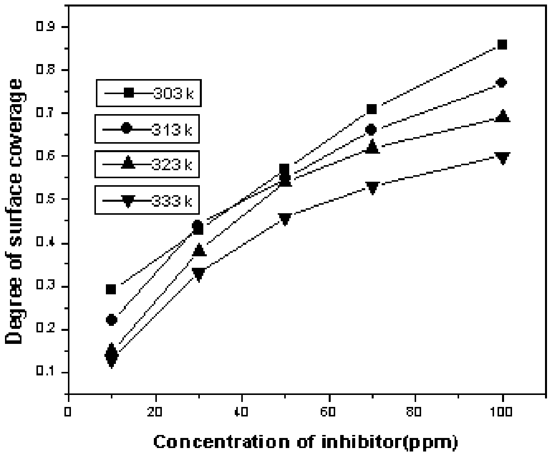

Figure: 2 **Corrosion parameters of stainless steel containing various concentration of VRL extract in Natural sea water at 303-333K.**

The figure-2 shows that the various concentration of VRL extract versus degree of surface coverage on stainless steel at 303-333K respectively. It can be seen from the figure that the percentage of inhibition efficiency of VRL extract on stainless steel was significantly reduced with raise in temperature form 303-333 K. This is may be due to some kind of competition between forces of adsorption and desorption the surface of the metals by certain specific molecules in the extract, deactivate the corrosion inhibition reactions in the different layers and cathodic sites on the steel surface . The maximum of 85.72 and 60.00% of inhibition efficiency is achieved at 303-333K respectively. The decrease of inhibition efficiency with rise in temperature is suggestive of physical adsorption mechanism.

4.2. Activation energy

The activation energy (Ea) for the corrosion of stainless steel in the presence and absence of VRL extract in natural sea water environment is calculated using Arrhenius theory. Assumptions of Arrhenius theory is expressed by equation (4)[16].

$$CR = A\exp(-E_a/RT) \quad \rightarrow \quad (4)$$

$$\log(CR_2/CR_1) = E_a/2.303R(1/T_1 - 1/T_2) \rightarrow \quad (5)$$

Where CR_1 and CR_2 are the corrosion rate at the temperature T_1 (303K) and T_2 (333K) respectively. The values of Corrosion rate obtained from the mass loss measurements are substituted in equation (4) and the calculated values of activation energy are presented in Tables 1 and 2. The activation energy increased with increase of inhibitor concentration i.e, 21.31 to 50.11 for VRL extract. The activation energy were found to be lower than the threshold value of 80 KJ/mol required for chemical adsorption indicating that a physical adsorption mechanism is applicable to the adsorption of VRL[17].

4.3. Adsorption consideration

The heat of adsorption on Brass in the presence of inhibitor is calculated by the following Equation -6.

$$Q_{ads} = 2.303\ R\ [\log(\theta_2/1-\theta_2) - \log(\theta_1/1-\theta_1)] \times (T_2T_1/T_2-T_1)$$

Where R is the gas constant, θ_1 and θ_2 is the degree of surface coverage at temperatures T_1 and T_2 respectively. The calculated values of Q_{ads} are reported in Table-1. These values are ranged from -28.12 to -39.43 KJ/mol. The negative values are indicated that the adsorption of inhibitor on stainless steel surface is exothermic[18].

Table: 1 **Calculated values of Activation energy (E_a) Q_{ads} and of VRL extract on Stainless steel in sea water environment.**

Concentration of inhibitor (ppm)	% of I.E		E_a ($KJmol^{-1}$)	Q_{ads} ($KJmol^{-1}$)
	30°	60°		
Blank	--	--	21.31	---
10	0.29	0.13	26.72	-28.12
30	0.43	0.33	25.62	-11.92
50	0.57	0.46	27.43	-12.36
70	0.71	0.53	35.03	-21.68
100	0.86	0.60	50.11	-39.43

Adsorption studies are very important to determine the mechanism of corrosion reaction. The most frequently used isotherms are Langmuir, Temkin, Frumkin and Flory- Huggins and Bockris-Sinkles[19-21].

Langmuir adsorption isotherm is the ideal adsorption isotherm for physical and chemical adsorption on a smooth surface. Langmuir adsorption isotherm of VRL extract on Stainless steel surface proceeded according to the Equation- 7.

$$\log(C/\theta) = \log C - \log K \rightarrow (7)$$

From Equation-6, by plotting the values of $\log(C/\theta)$ versus log C, linear plots are generated (fig-4). Inspection of this figure reveals that the experimental data fitted the Langmuir adsorption isotherm of VRL extract on stainless steel surface, meaning that there is no interaction between the adsorbed species

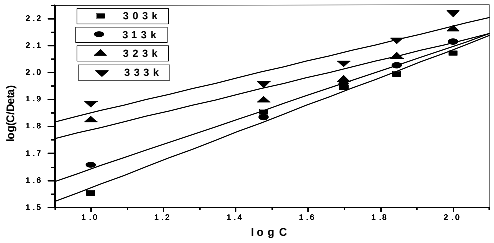

Figure: 3 **Langmuir isotherm for adsorption of VRL extract on stainless steel in Natural sea water environment.**

4.4. Morphology examination of stainless steel

4.4.1. UV Analysis

Figures 4 and 5 show that the UV visible spectrum of the corrosion product on the surface of stainless steel in the absence and presence of VRL extract in Natural sea water environment.

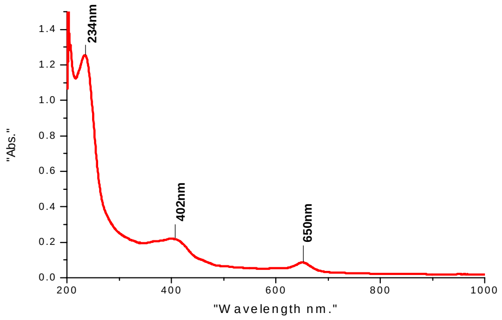

Figure: 4 **UV absorption spectrum of the corrosion product on stainless steel in the absence of inhibitor in Natural sea water environment.**

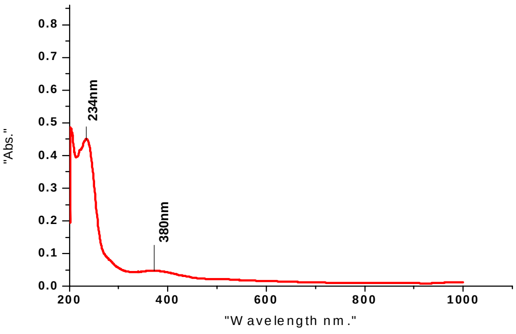

Figure: 5 **UV absorption spectrum of the corrosion product on stainless steel in the presence of VRL extract in Natural sea water environment.**

In the UV spectrum, three absorption bands around 234nm, 402nm, 650 nm and two bands around 234nm, 380nm are noticed in figures 4 and 5 respectively. In the presence of inhibitor one band (650nm) is lost and the another one band (402nm) is shifted to shorter wavelength region (380nm) i.e.; Hypsochromic shift (or) Blue shift. This results reveals that the binding between the active group present in the inhibitor and the surface of the metal.

4.4.2. IR analysis

Figures 6 and 7 reflect that the IR spectrum of the corrosion product on the stainless steel in the absence and presence of VRL extract in Natural sea water environment. On comparing both of the spectra, a few additional peaks are appeared (1061.03 Cm^{-1} assigned for strong –C-N stretch, 1429.81 Cm^{-1} for ⁻C-C stretch, 3343.13 Cm^{-1} and 2902.38 Cm^{-1} assigned for broad and sharp –O-H stretch) in the presence of inhibitor. From the fig .6 and 7 found that the -C-H bend was shifted from 709.91 Cm^{-1} to 614.27 Cm^{-1}, –C-N stretch was shifted from 1182.28 Cm^{-1} to 1162.06Cm^{-1}, the medium –C-H stretch was shifted from 1363.58Cm^{-1} to 1324.75Cm^{-1}, the bend -N-H was slightly shifted from 1639.81Cm^{-1} to 1638.78 Cm^{-1}. These results may also confirm that the FTIR spectra support the fact that corrosion inhibition of VRL extract on stainless steel in Natural sea water environment may be the adsorption of active molecule in the inhibitor and surface of the metal.

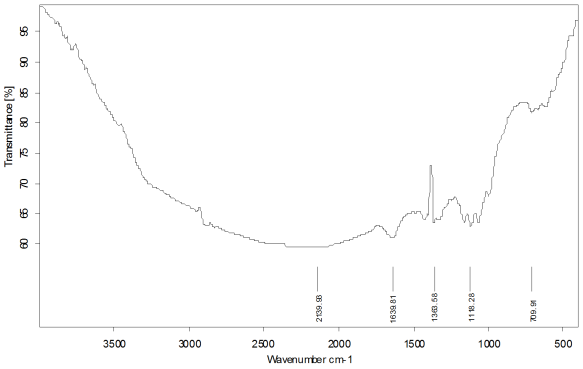

Figure. 6 **IR spectrum of corrosion product in the absence of inhibitor in Natural sea water environment**

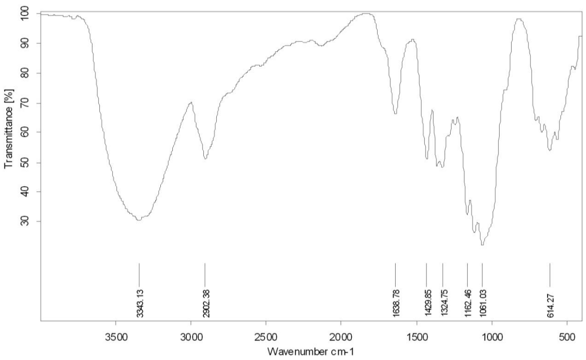

Figure: 7 **IR spectrum of corrosion product in the presence of VRL extract in Natural sea water environment**

4.3. Mechanism of inhibition

Vinca rosea is composed of numerous naturally occurring compounds. Over four hundred known alkaloids have been isolated and characterized from this plant. Among these are ajmaline, catharanthaine, leurosidine, vincristine, vinblastine, vinorelbine, vindesine, vincamine and vinorelbine are structurally related compounds. Most of these compounds have complicated molecular structures, higher molecular weights and significant number of Oxygen and Nitrogen atoms are incorporated in their structure. These compounds can adsorb on the metal surface via the lone pair of electrons present on their hetero atoms. The adsorption of such compounds on the metal surface creates a barrier for charge and mass transfer leading to a decrease in the interaction between the metal and the corrosive environment. As a result the reduction of corrosion rate on the metal surface. The inhibition properties of plant extracts may be due to the presence of hetero atoms and tannins in the VRL extract. Tannins are complex astringent aromatic glycosides found in various plants. They are made up of polyphenols and their heterocyclic derivatives. They may have been responsible for the formation of an oriented film layer which essentially discharges of H^{+} and dissolution of metal ions.

5. CONCLUSION

The following conclusions can be drawn from our present study:

The VRL inhibitor acts as an effective and efficient inhibitor for the dissolution process of stainless steel in Natural sea water environment.

The inhibition efficiency increased with increase of inhibitor concentration to reach maximum of 94.12% and it is gradually decreased with raise in temperature and period of contact.

The adsorption of the inhibitor on the stainless steel surface is spontaneous process and is consistent with the mechanism of physical adsorption. Langmuir adsorption isotherm is best described the adsorption characteristics of the inhibitor.

The corrosion product over the surface of stainless steel in the presence of inhibitor is characterized by UV and IR studies support that good performance of VRL extract on stainless steel in Natural sea water environment.

ACKNOWLEDGEMENT

The authors sincerely thanks to Dr, P.T.Perumal, Deputy Director, the Central Leather Research Institute, (CLRI), Adyar, Chennai, for giving the opportunity to take spectral studies. Also I would express our heartful thanks to the management of Sri Paramakalyani College, Alwarkurichi, for providing the lab facilities.

6. REFERENCES

1. Saratha R and Vasudha VG. e-**Journal of chemistry.,** 2009; 6(4): 1003-1008.
2. Refaey SAM. **Appl. Surf Sci.**, 2005; 240 (1-4): 396-406.
3. Quraishi MA and Sharma HK. **J.Appl. Electrochem.,** 2005; 35(1): 33-39.
4. Ali Sk A, Saeed MT and SU Rahman. **Corros Sci.,** 2003; 45(2): 253-266.
5. Ashassi-Sorkhabi A and Shaabani B. D Seifzadeh. **Appl.Surf.Sci.,** 2005; 239(2): 154- 164.
6. Kalpana M and Mehta GN. **Trans SAEST.** 2003; 38(10): 40-42.
7. EI-Etre AY, Addallah M and EI-Tantawy ZE. **Corros. Sci.,** 2005; 47(2): 385-395.
8. EI-Etre AY. J **Colloid Interface Sci., 2007**; 314(2); 578-583.
9. Chetouani V, Hammouti B and Benkaddour M. **Pigment and Resin Technology.,** 2004**;** 33: 26.
10. Pandian Bthi Raja and Mathur Gopalakrishnan Sethuraman. **Mater Lett.,** 2008; 62(17-18): 2977-2979.
11. Parikh KS and Joshi KJ. **Trans SAEST.,** 2004**:** 39(3-4); 29-35.
12. http/://www.motherherbs.com/vinca-rosea-extract.html
13. **a b c DrugDigest:** Catharanthus roseus**.**
14. **a b Flora of China:** Catharanthus roseus**.**
15. Deepa Rani P, Selvaraj S. **RASAYAN J. Chem,** 2010; 3: 473.
16. Emregul KC and Duzgun E. **O Atakiol. Corrosion Sci.,** 2006; 48: 3243.
17. Ebenso EE. **Bull. Electrochem.,** 2003; 19(5): 209.
18. Bhajiwala HM and Vashi RT. **Bull. Electrochem.,** 2001**;** 17: 441-448.
19. Bockris JOM and Swinkels DAJ. **J. Electrochem. Soc.,** 1964**;** 8 :736-743.
20. Ikeda O and Jimbo H and Tamura H. **J. Electroanal. Chem.,** 1982**;** 1: 127-141.
21. Parsons R. **J. Electroanal. Chem.**, **1964;** 2: 136-152.