

Preventive measures of zinc in natural sea water using *Cnidoscopus Chayamansa* leaves extract

¹ Bright A, ² Michlin Ruphina Maragatham S, ³ Malar vizhi I, ⁴ Kalirajan K, ⁵ Selvaraj S

^{1,2} Asst. Professor in chemistry, V V College of Engineering, Arasoor, Tisaiyanvilai, Tamilnadu, India

^{3,4,5} Postgraduate and Research Department of chemistry, Sri Paramakalyani College, Alwarkurichi, Tamilnadu, India

Abstract

Corrosion protection of zinc using *Cnidoscopus Chayamansa* leaves extract in natural sea water environment was studied by mass loss measurement with various period of contact and temperature. The observed result indicates that the corrosion inhibition efficiency was increased with increase of inhibitor concentration and temperature. The thermodynamic parameters viz; E_a , ΔH_{ads} , ΔG_{ads} , ΔS_{ads} were evaluated for corrosion process, which suggest that the adsorption is endothermic, spontaneous and chemisorptions. The inhibitor obeys both Langmuir and Temkin adsorption isotherm. The protective film formed on the metal surface was analyzed by using various spectroscopic studies viz; UV, FT-IR, XRD and SEM-EDX techniques.

Keywords: Inhibition, Zinc, *Cnidoscopus Chayamansa*, Natural Sea Water, Spectral Studies.

Introduction

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. Zinc is one of the most important non-ferrous metals, which finds extensive use in metallic coating, mainly used for the corrosion protection of steel [1]. Zinc is an industrially important metal and is corroded by many agents, of which aqueous acids are the most dangerous [2]. To avoid the zinc corrosion generally a coating of passive layer is given to its surface. The chromation is one such method wherein the surface of zinc is exposed to chromate solution for few seconds. The chromate solutions have been applied successfully to protect zinc surface from white rust [3]. But the strict regulation on the environment restricts the use of chromate solution since chromium element being toxic in nature. In an attempt to find corrosion inhibitors which are environmentally safe and easily available, there has been a growing trend in the use of natural products such as leaves or plant extracts as corrosion inhibitors for metals in various environment, because they are inexpensive, readily available, renewable sources of materials and ecologically acceptable. A few investigations are Red Peanut Skin [4], Musa species peels [5], *Vernonia Amygdalina* [6], *Piper guineensis* [7], Henna extract [8], *Delonix regia* extracts [9], Rosemary leaves [10], natural honey [11], *opuntia* extract [12], khillah (*Ammi visnaga*) seeds [13], *Carica Papaya* and *Camellia Sinensis* Leaves [14], *Ricinus communis* Leaves [15], *Justicia gendarussa* [16], *Vitis vinifera* [17], *Punica granatum* peel [18], Leaves of *Genus Musa*, *Genus Saccharum* and *Citrullus Lanatus* [19] have been studied on various metals and alloys. However only a limited number of literature is available for the corrosion inhibition by green inhibitor with zinc metal surface. Some investigators have been reported with zinc metal is *Ocimum tenuiflorum* [20], Red onion skin [21], *Nypa fruticans* Wurmb [22], *Aloe vera* [23], henna (*lawsonia*) Leaves [24] and *Cnidoscopus Chayamansa* [25]. Thus

our present attention is to study the effect of adsorption and corrosion inhibition of *Citrullus Vulgaris* peel on zinc metal surface with natural sea water environment.

2. Materials and Methods

2.1. Properties of *Cnidoscopus Chayamansa* Leaves

Cnidoscopus Chayamansa is commonly known as 'Chaya' plant. Chaya is a little known leafy green vegetable of dry regions of the tropics. The methanolic extract of *Cnidoscopus chayamansa* leaves was screened for antioxidant, hypoglycemic effect and antimutagenic properties. The Chaya leaves extract contain alkaloids, amino acids, tannins, flavanoids, terpenoids, glycosides, steroids, gallic acid, catechin, cystein, 2-amino-4(methylthio)butanoic acid, protocatechuic acid and rutine respectively. Chaya is a good source of protein, vitamins, carbohydrate, calcium, and iron. However, raw Chaya leaves are highly poisonous. They contain a high content of hydrocyanic acid. With Chaya, 1 minute of boiling destroys most of the acid. Chaya has also been used as a medicinal plant. Although many medicinal claims have been made for Chaya, it is mostly used for diabetes and kidney problems.

2.2. Stock Solution of *Cnidoscopus Chayamansa* Extract

Cnidoscopus Chayamansa (CCL) leaves were collected from the source and dried under shadow for about 48 hours, grinded well, then soaked in a solution of ethyl alcohol for about 48 hours. Then it is filtered followed by evaporation in order to remove the alcohol solvent completely and the pure plant leaves extract was collected. From this extract, different concentration of 10 to 1000 ppm stock solution was prepared using double distilled water and used throughout our present investigation.

2.3. Specimen Preparation

Rectangular specimen of zinc was mechanically pressed cut to form different coupons, each of dimension exactly 20 cm² (5x2x2cm) with emery wheel of 80, 120 and degreased with

trichloroethylene, washed with distilled water, cleaned and dried, then stored in desiccators for our present study.

2.4. Mass Loss Method

In the mass loss measurements, zinc specimens in triplicate were completely immersed in 100ml of the test solution in the presence and absence of the inhibitor. The specimens were withdrawn from the test solutions after immersion of 24 to 720 hours at room temperature and also different with temperature ranges from 303K to 333K after an hour. The mass loss of the specimens is taken as the difference in weight before and after immersion using 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.

$$\text{Corrosion Rate (mppy)} = \frac{87.6 \times W}{DAT} \quad \text{----- (1)}$$

(Where, mppy = millimetre per year, W = Mass loss (mg), D = Density (gm/cm³), A = Area of specimen (cm²), T = Time in hours)

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

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

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

(Where, W₁ and W₂ are the corrosion rates in the absence and presence of the inhibitor respectively)

3. Results and Discussion

Table 1: The corrosion parameters of zinc in natural sea water containing various concentration of CCL extract with different exposure time

Time (hrs)	Corrosion Rate (mppy)						Inhibition Efficiency (%)					
	0 ppm	10 ppm	50 ppm	100 ppm	500 ppm	1000 ppm	0 ppm	10 ppm	50 ppm	100 ppm	500 ppm	1000 ppm
24	0.751	0.647	0.596	0.492	0.388	0.285	-	13.79	20.68	34.48	48.27	62.07
120	0.249	0.212	0.186	0.150	0.114	0.093	-	14.57	24.99	39.56	54.16	62.49
240	0.272	0.236	0.189	0.139	0.106	0.078	-	13.32	30.46	48.57	60.92	71.41
480	0.377	0.298	0.221	0.172	0.124	0.076	-	20.97	41.23	54.29	67.03	79.72
720	0.348	0.268	0.218	0.171	0.099	0.055	-	22.83	37.23	50.86	71.48	84.13

The corrosion and inhibition behaviour of zinc in natural sea water containing various concentration of *Cnidoscopus Chayamansa* leaves (CCL) extract are studied at different period of contact (24 to 720hrs) and the observed results are listed in Table-1. It is clearly indicates that the percentage of

inhibition efficiency increased with increase of CCL concentration and also increased with increase of exposure time. The maximum of 84.13% of inhibition efficiency is attained at higher concentration.

Table 2: The corrosion parameters of zinc in natural sea water containing various concentration of CCL extract with different exposure temperature

Tem. (K)	Corrosion Rate (mppy)						Inhibition Efficiency (%)					
	0 ppm	10 ppm	50 ppm	100 ppm	500 ppm	1000 ppm	0 ppm	10 ppm	50 ppm	100 ppm	500 ppm	1000 ppm
303	109.9	72.07	61.51	39.76	29.82	24.23	-	34.46	44.07	63.84	72.88	77.96
313	79.53	44.11	24.85	22.36	19.26	15.53	-	44.53	68.75	71.88	75.78	80.47
323	162.2	113.1	50.33	39.14	26.09	22.37	-	30.28	68.99	75.86	83.91	86.21
333	202.6	174.6	140.4	59.65	32.93	24.85	-	13.80	30.67	70.55	83.74	87.73

The percentage of inhibition efficiency against various concentration of bio-inhibitor for zinc in natural sea water at different temperature (303K to 333K) was investigated and results are reflected in Table-2. It shows that the inhibition efficiency increased with increase of bio-inhibitor concentration and also increased with rise in temperature. The maximum of 87.73% and 77.96% inhibition efficiency is attained at 333K and 303K respectively. The gradual increase of inhibition efficiency with rise in temperature is suggestive of chemical adsorption mechanism.

Table 3: Calculated values of activation energy (E_a) and heat of adsorption (Q_{ads}) of CCL extract on zinc in natural sea water environment

Concentration of inhibitor (ppm)	E _a (KJ mol ⁻¹)	Q _{ads} (KJ mol ⁻¹)
0	72.606	-
10	74.885	-33.254
50	74.390	-16.144
100	70.900	8.539
500	68.352	18.912
1000	67.737	19.679

3.1. Effect of Temperature

The values of E_a for the corrosion of zinc in the presence and absence of CCL extract is calculated using the following Arrhenius equations (4) and its derived form equation (5).

$$CR = A_{exp} (-E_a/RT) \text{-----(4)}$$

$$\log (CR_2/CR_1) = E_a /2.303 R (1/T_1-1/T_2) \text{-----(5)}$$

Where, CR_1 and CR_2 are the corrosion rates of zinc at temperatures, T_1 and T_2 respectively, E_a is the activation energy and R is the universal gas constant. The value of activation energy for blank (72.606 kJ/mol) is higher than in the presence

of inhibitor on 1000ppm is given in Table-3. It is clearly indicates that the adsorption process is chemisorption.

3.2. Adsorption Consideration

The heat of adsorption on zinc in the presence of inhibitor is calculated by the following equation (6).

$$Q_{ads} = 2.303 R [\log (\theta_2/1- \theta_2)-\log (\theta_1 /1- \theta_1)] \times (T_2T_1/T_2-T_1) \text{---(6)}$$

Where, R is the gas constant, θ_1 and θ_2 is the degree of surface coverage at temperatures and T_1 and T_2 respectively. The Q_{ads} values are ranged from -33.254 to 19.679 kJ/mol (Table-3). This value clearly revealed that the adsorption of CCL extract on the surface of zinc metal is endothermic.

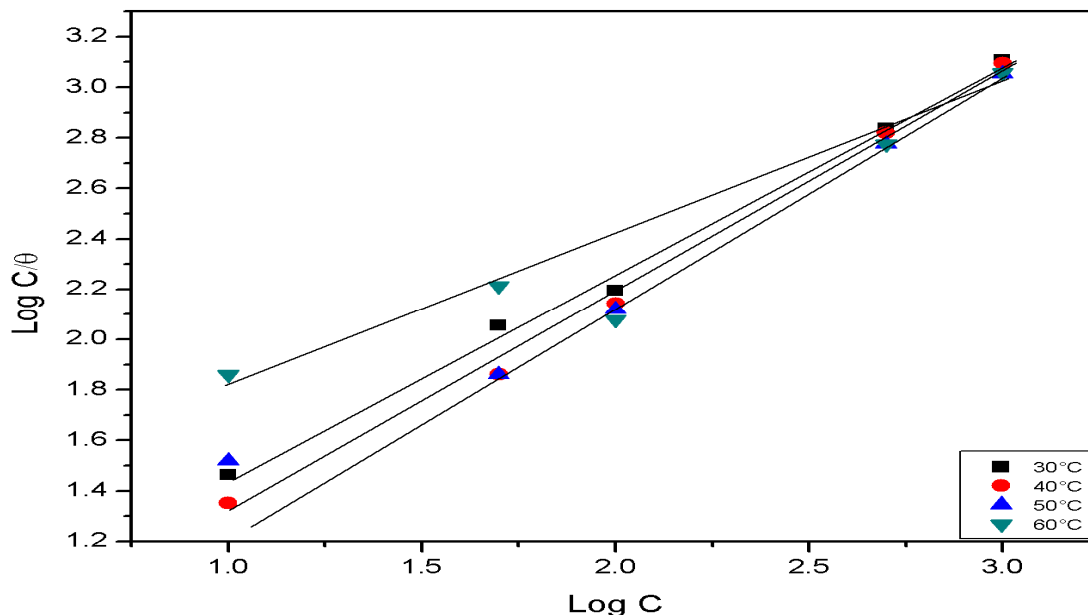


Fig 1: Langmuir adsorption parameters for the adsorption of CCL extract on zinc in natural sea water environment

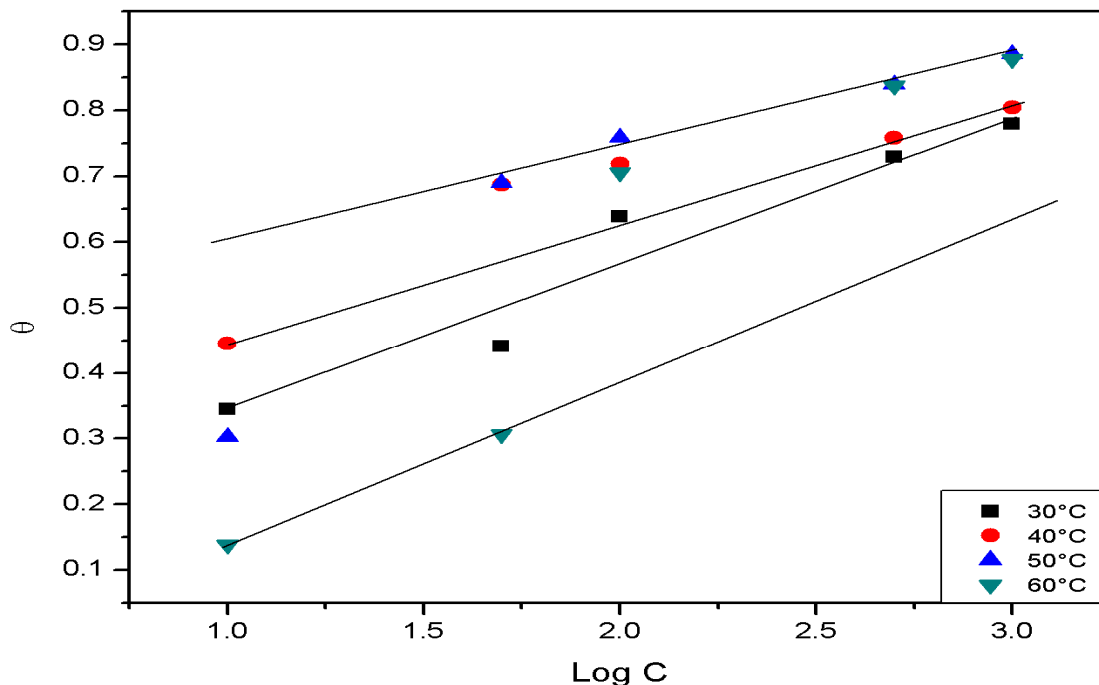


Fig 2: Temkin adsorption parameters for the adsorption of CCL extract on zinc in natural sea water environment

Table 4: Langmuir and Temkin parameters for the adsorption of CCL extract on zinc in natural sea water environment

Adsorption isotherm	Temperature	Slope	K	R ²	ΔG _{ads} (KJ mol ⁻¹)
Langmuir	303	0.8171	4.2864	0.9945	-13.787
	313	0.8857	2.5830	0.9944	-12.924
	323	0.7899	4.1942	0.9728	-14.638
	333	0.5957	14.378	0.8674	-18.503
Temkin	303	0.2270	1.3009	0.9173	-10.782
	313	0.1611	2.2275	0.7938	-12.538
	323	0.2687	1.3686	0.8085	-11.630
	333	0.3942	0.5664	0.8659	-9.4580

The adsorption isotherms are used to investigate the mode of adsorption and the characteristic of adsorption of inhibitor on the metal surface. In our present study the Langmuir, Temkin isotherms are investigated. The Langmuir and Temkin adsorption isotherm can be expressed by the equation (7) and equation (8) given below.

$$\log C/\theta = \log C - \log K \text{ ----- (7)}$$

$$\theta = K \ln C \text{ ----- (8)}$$

Where, θ is the surface coverage, C is the concentration of the inhibitor solution and K is an adsorption co-efficient. By plotting values of $\log C/\theta$ versus $\log C$, linear plots were generated (Fig-1) and confirming that the experimental data fitted with the Langmuir adsorption isotherm for the adsorption of CCL extract on metal surface. It means that there is no interaction between the adsorbed species (i.e.; adsorbate and

adsorbent). The Langmuir adsorption isotherm is better fit at 333K for zinc ($R^2=0.9945$).

A plot of θ versus $\log C$ gives a straight line for zinc in CCL extract in natural sea water environment (Fig-2). The straight line indicated that the inhibitor obeyed Temkin adsorption isotherm.

The adsorption of CCL extract on the metal surface is related to the free energy of adsorption (ΔG_{ads}) by the following equation (9)

$$\Delta G_{ads} = -2.303 RT \log (55.5 K) \text{ ----- (9)}$$

Where, R is the gas constant, T is the temperature and K is the equilibrium constant of adsorption. The values of intercept (K) obtained from Langmuir and Temkin adsorption isotherm is substituted in equation (9) and the calculated values of ΔG_{ads} are placed in Table-4. The negative values of ΔG_{ads} suggested that the adsorption of CCL extract onto metal surface is a spontaneous process and the adsorbed layer is more stable one.

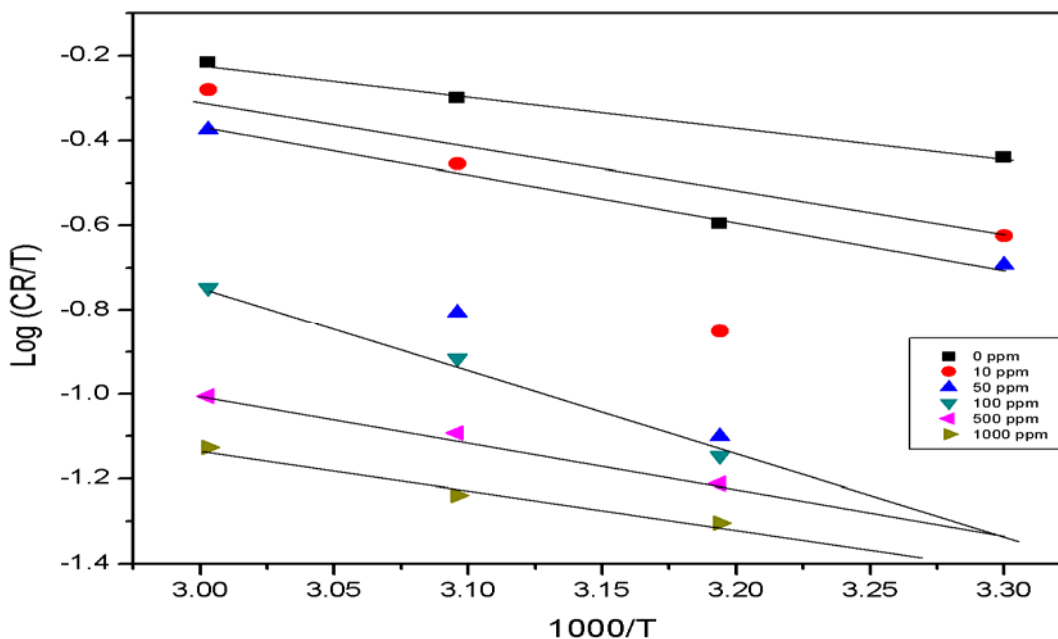


Fig 3: The relation between $\log (CR/T)$ and $1000/T$ for different concentration of CCL extract on zinc in sea water environment

3.3. Thermodynamics parameters

The another form of transition state equation which is derived from Arrhenius equation is shown below

$$CR=RT/Nh \exp (\Delta S/R) \exp (-\Delta H/RT) \text{ ----- (10)}$$

Where, h is the Planck's constant, N the Avogadro's number, ΔS the entropy of activation, and ΔH the enthalpy of activation.

A plot of $\log (CR/T)$ Vs $1000/T$ gives a straight line (Fig-3) with a slope of $(-\Delta H/R)$ and an intercept of $[\log(R/Nh)) + (\Delta S/R)]$, from which the values of ΔS and ΔH were calculated and listed in Table-5. The positive value of enthalpy of activation clear that the endothermic nature of dissolution process is very difficult.

Table 5: Thermodynamic parameters of zinc in natural sea water obtained from weight loss measurement

Concentration of CCL extract (ppm)	ΔH (KJ mol ⁻¹)	ΔS (KJ mol ⁻¹)
0	7.9853	10.241
10	11.7258	11.281
50	9.9814	10.573
100	5.0807	8.8813
500	0.8722	7.4266
1000	0.3825	6.9377

4. Morphology Studies

4.1. UV Analysis

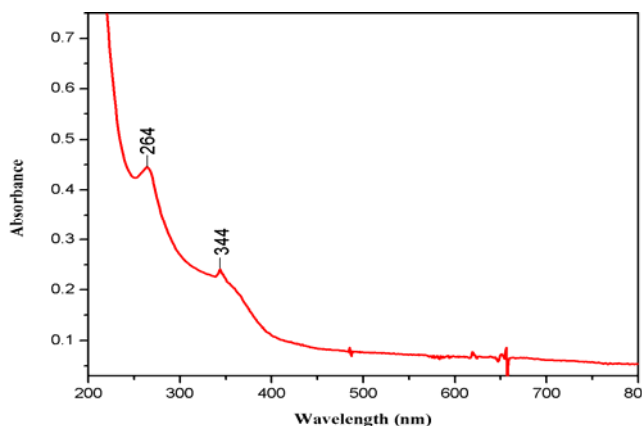


Fig 4

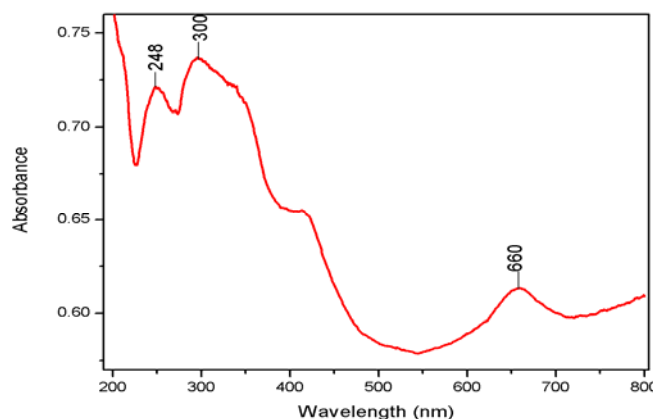


Fig 5

Fig 4 & 5: UV spectrum of ethanolic extract of CCL & the corrosion product on zinc in natural sea water in the presence of CCL extract.

Fig-4 & 5 shows that the UV visible spectrum of ethanolic extract of CCL and the corrosion product on the surface of zinc in the presence of CCL extract in natural sea water. In this spectrum, the two absorption bands around 264, 344 nm were noticed (Fig 4) but in the presence of inhibitor three bands was appeared around 248, 300 and 660nm. When compare both

these spectra, the changes of absorption band may confirmed the strong coordination bond between the active group present in the inhibitor molecules and the metal surface.

4.2. FT-IR Analysis

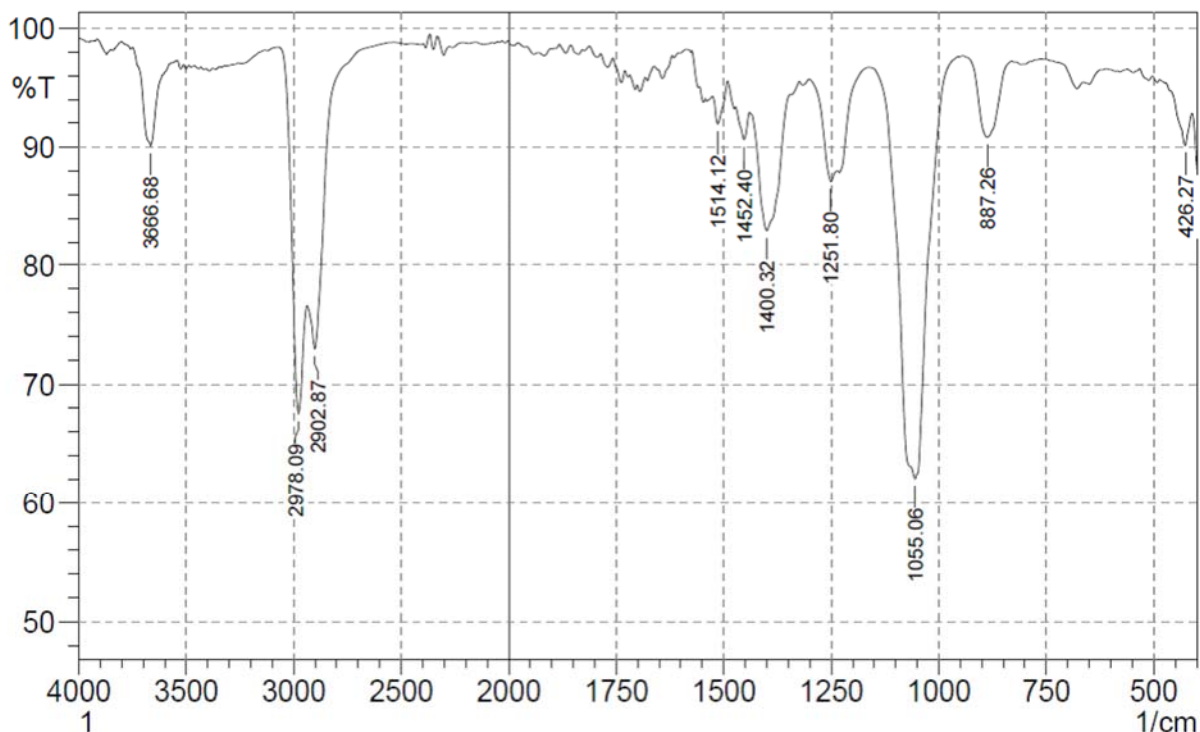


Fig 6: FT-IR spectrum of ethanolic extract of CCL extract

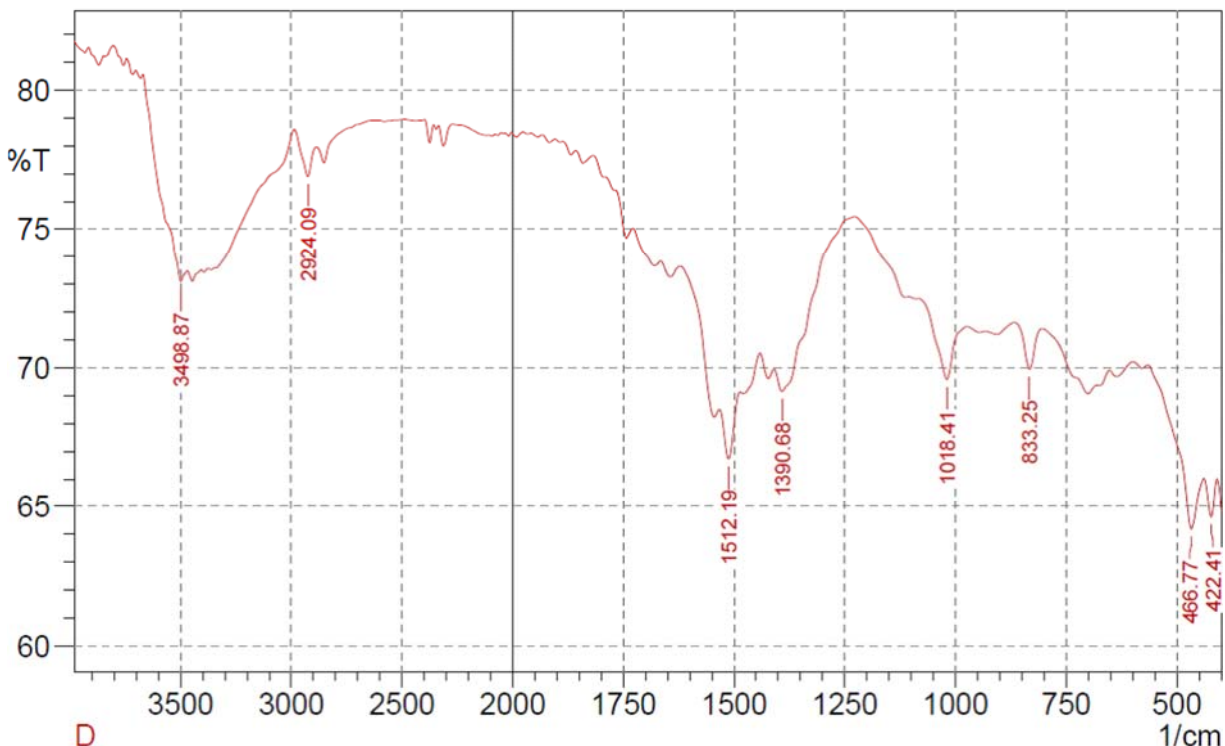


Fig 7: FT-IR spectrum for the corrosion product on zinc in the presence of CCL extract with natural sea water environment.

The Fig-6 and 7 reflect that the FTIR spectrum of the ethanolic extract of inhibitor and the corrosion product of zinc in the presence of CCL extract in natural sea water environment. On comparing both of the spectra the prominent peak such as, the C-N stretching frequency is shifted from 1055.06 to 1018.41 cm^{-1} , 881.26 cm^{-1} corresponds to S-OR stretching frequency is shifted to 833.25 cm^{-1} , the =N-H stretching in amine is shifted from 1514.12 to 1512.19 cm^{-1} . These results also confirm that the FT-IR spectra support the fact that the corrosion inhibition of CCL extract on zinc in natural sea water may be due to the adsorption of active molecule in the inhibitor on the surface of metal.

4.3. EDX Analysis

EDX spectroscopy was used to determine the elements present on the metal surface before and after exposure to the inhibitor solution. Fig-8 & 9 represents the EDX spectra for the corrosion product on metal surface in the absence and presence of optimum concentrations of CCL extract with natural sea water environment. In the absence of inhibitor molecules, the spectrum may confirm the existence of sodium and chlorine, which is present in natural sea water. However, in the presence of the optimum concentrations of the inhibitors, in addition to this sulphur and oxygen atom is found to be present on the metal surface. It is clearly indicates that the hetero atoms present in the inhibitor molecules may involve the adsorption process with metal atom and hence it may protect the metal surface against the corrosion.

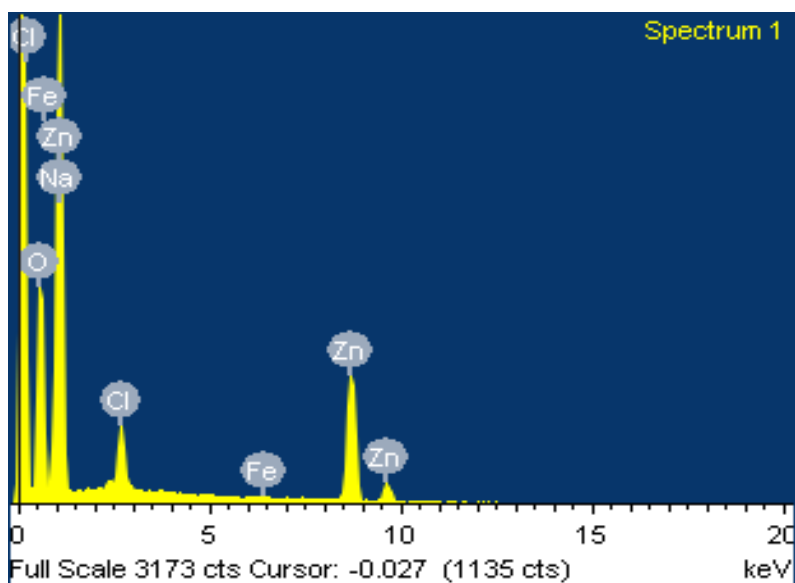


Fig 8: EDX spectrum of the corrosion product on zinc surface in natural sea water environment.

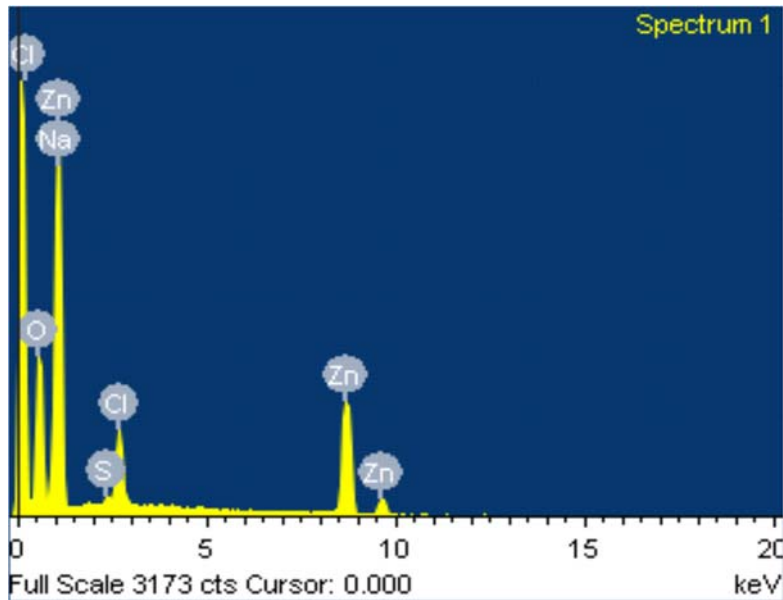


Fig 9: EDX spectrum of the corrosion product on zinc in the presence of CCL extract

4.4. XRD- Analysis

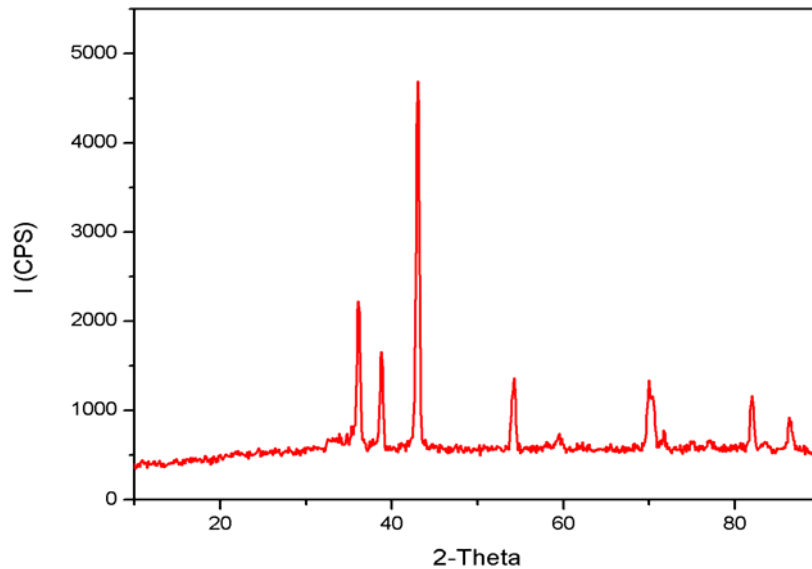


Fig 10: XRD- Analysis of Corrosion Product on zinc in the presence of CCL extract in natural sea water environment

The Corrosion product released from the zinc metal formed on their layer over the metal surface examined by XRD studies in the presence of inhibitor as shown in Fig-10. It reveals that the

film may be mainly combining with a rich amount of ZnS, ZnCl₂, ZnCO₃, ZnO etc with inhibitor.

4.5. SEM-Analysis

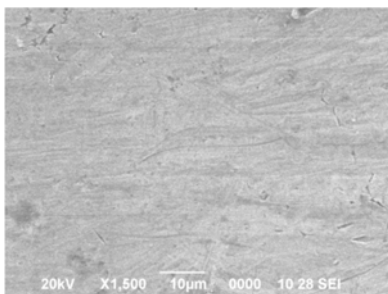
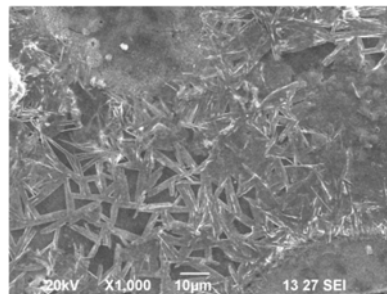
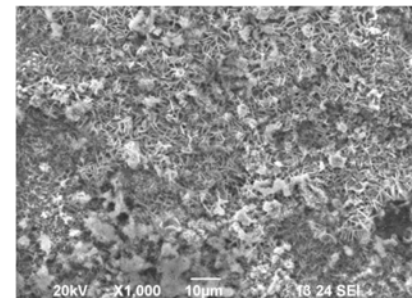


Fig 11(a)



11(b)

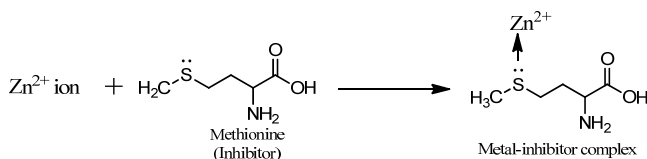
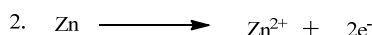
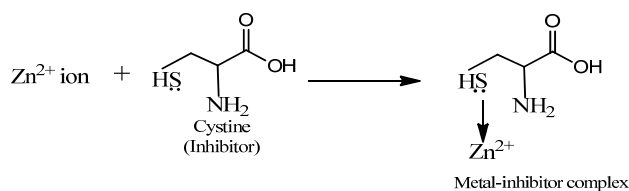
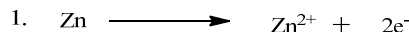


11(c)

Fig 11: SEM micrographs of (a) Polished Zinc surface, (b) without inhibitor, 0 ppm (c) with inhibitor, 500 ppm

A SEM micrograph of the polished zinc surface before immersion in natural sea water solution is shown in Fig-11(a). The micrograph shows the surface was smooth and without pits. The SEM micrograph of the corroded zinc surface in the presence of natural sea water are shown in Fig-11(b), showed that the surface of metal has number of cracks are visible in the surface. The influence of the inhibitor addition on the metal surface in natural sea water is shown in Fig-11(c). Here there is much less damage on the zinc surface, which confirms the inhibition action of CCL leaves extract. In accordance, it might be concluded that the adsorption film can efficiently inhibits the corrosion of metal surface.

5. Proposed Mechanism



6. Conclusion

From our present investigation the following conclusions can be drawn.

- The ethanolic extract of *Cnidioscolus Chayamansa* (CCL) leaves acts as good and efficient inhibitor for the corrosion of zinc in natural sea water environment.
- Inhibition efficiency increases with the increase of inhibitor concentration and also increases with rise in temperature.
- The adsorption of different concentrations of the CCL extract on the surface of the zinc in natural sea water followed both Langmuir and Temkin adsorption isotherm.
- The value of activation energy (E_a), enthalpy of adsorption (ΔH_{ads}) and free energy changes (ΔG_{ads}) indicates that the adsorption of inhibitor on metal surface follows chemical, endothermic and spontaneous process respectively.

References

1. Manov S, Noli F, Lamazouere AM, Aries L, Electrochemical and Surface Studies of Zinc in Alkaline Solutions Containing Organic Corrosion Inhibitors, J App Electrochem. 1999; 29(8):995-1003.
2. Gaur JN, Jain BL. J Electrochem Soc India. 1978; 27:117.
3. Hinton BRW, Wilson L. The corrosion inhibition of zinc with cerous chloride *Corros. Sci.*, 1989; 29:967.
4. James AO, Akaranta O, Awatefe KJ. Red Peanut Skin, An Excellent Green Inhibitor for Mild Steel Dissolution in Hydrochloric Acid Solution, An Int. J Of Chem. 2011; 2(2):133-139.
5. Eddy NO, Odoemelam SA, Odiongenyi AO. Ethanol extract of musa species peels as a green corrosion inhibitor for mild steel: kinetics, adsorption and thermodynamic considerations, *EJEAF Che.*, 2009; 8(4):243-253.
6. Nwabanne JT, Okafor VN. Inhibition of the Corrosion of Mild Steel in Acidic Medium by Vernonia Amygdalina, Adsorption and Thermodynamics Study, *JETEAS*, 2011; 2(4):619-625.
7. Ebenso EE, Eddy NO, Odiongenyi AO. Corrosion inhibitive properties and adsorption behaviour of ethanol extract of Piper guinensis as a green corrosion inhibitor for mild steel in H2SO4, *Afr. J Pure Appl Chem.* 2008; 2(11):107-115.
8. Ostovari A, Hoseinie SM, Peikari M, Shadizadeh SR, Hashemi SJ. Corrosion inhibition of mild steel in 1M HCl solution by henna extract, A comparative study of the inhibition by henna and its constituents (Lawsone, Gallic acid, α -d-Glucose and Tannic acid), *Corros. Sci.*, 2009; 51(9):1935.
9. Abiola OK, Oforka NC, Ebenso EE, Nwinuka NM. Eco-friendly corrosion inhibitor: The inhibitive action of *Delonix Regia* extract for the corrosion of aluminium in acidic media, *Anti-Corrosion Methods and Materials*, 2007; 54(4):219-224.
10. Kliskic M, Radoservic J, Gudic S, Katalinic V. Aqueous extract of Rosmarinus officinalis L. As inhibitor of Al- Mg alloy corrosion in chloride solution, *J Appl Electrochem.* 2000; 30(7):823-830.
11. El-Etre AY. Natural honey as corrosion inhibitor for metals and alloys. I. Copper in neutral aqueous solution, *Corros. Sci.* 1998; 40(11):1845-1850.
12. El-Etre AY. Inhibition of aluminum corrosion using *Opuntia* extract, *Corros. Sci.*, 2003; 45(11):2485-2495.
13. El-Etre AY. Khillah extract as inhibitor for acid corrosion of SX 316 steel, *Applied Surface Science.*, 2006; 252(24):8521-8525.
14. Loto CA, Loto RT, Popoola API. Inhibition Effect of Extracts of Carica Papaya and Camellia Sinensis Leaves on the Corrosion of Duplex (α β) Brass in 1M Nitric acid, *Int. J Electrochem Sci.* 2011; 6:4900-4914.
15. Saratha R, Kasthuri N, Thilagavathy P. Environment friendly acid corrosion inhibition of mild steel by Ricinus communis Leaves, *Der Pharma Chemica.*, 2009; 1(2):249-257.
16. Satapathy AK, Gunasekaran G, Sahoo SC, Kumar Amit Rodrigues PV. Corrosion inhibition by Justicia gendarussa plant extract in hydrochloric acid solution, *Corros. Sci.*, 2009; 51:2848-2856.
17. Deepa Rani P, Selvaraj S. Inhibitive action of vitis vinifera (grape) on copper and brass in natural sea water environment, *Rasayan J Chem.* 2010; 3(3):473-482.
18. Deepa Rani P, Selvaraj S. Inhibitive and adsorption properties of punica granatum extract on brass in acid media, *J Phytol.* 2010; 2(11):58-64.
19. Mohammad Ismail A, Abdulrahman S. Mohammad Sakhawat Hussain., Solid waste as environmental benign corrosion inhibitors in acid medium, *International Journal of Engineering Science and Technology.* 2011; 3(2):1742-1748.
20. Sharma Sanjay K, Ackmez Mudhoo, Jain Gargi, Sharma Jyoti. Inhibitory effects of *Ocimum tenuiflorum* (Tulsi) on

- the corrosion of Zinc in Sulphuric acid A Green approach, *Rasayan J Chem.* 2009; 2(2):332-339.
21. James AO, Akaranta O. The inhibition of corrosion of zinc in 2.0 M hydrochloric acid solution with acetone extract of red onion skin, *African Journal of Pure and Applied Chemistry.* 2009; 3(11):212-217.
 22. Orubite Okorosaye K, Oforka NC. Corrosion Inhibition of Zinc on HCl using *Nypa fruticans* Wurmb Extract and 1,5 Diphenyl Carbazone, *J Appl Sci Environ Mgt.* 2004; 8(1):57-61.
 23. Aboia OK, James AO. The effects Of Aloe vera extract on Corrosion and Kinetics of Corrosion process of zinc in HCl Solution, *Corrosion Science*, 2010; 52(2):661-664.
 24. El-Etre AY, Abdallah M, El-Tantawy ZE. Corrosion inhibition of some metals using lawsonia extract, *Corros. Sci.*, 2005; 47(2):385-395.
 25. Bright A, Michlin Ruphina Maragatham S, Malar vizhi I, Selvaraj S. Corrosion behavior of Zinc in 1.0 N hydrochloric acid with *Cnidocolus Chayamansa* – A Green Approach, *International Journal of Recent Scientific Research Research.* 2015; 6(4):3594-3601.