



Corrosion Protection of Zinc in Natural Sea Water using *Citrullus Vulgaris* peel as an Inhibitor

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Abstract

The effect of *Citrullus Vulgaris* peel on the corrosion of zinc in natural sea water has been studied by mass loss measurements at different time and temperature. The present investigation revealed that the percentage of inhibition efficiency is increased with increase of inhibitor concentration and decreased with rise in period of contact. The temperature studies reflect that the percentage of inhibition efficiency is decreased with increase of temperature and it indicates that the mechanism of physical adsorption. The calculated values of activation energy (E_a) also support the physisorption process. The thermodynamic parameters such as heat of adsorption (Q_{ads}) and free energy of adsorption (ΔG_{ads}) are suggested that the adsorption of inhibitor on the zinc metal surface is exothermic and followed by spontaneous process. Experimental data has fitted with the Langmuir and Temkin adsorption isotherm. The corrosion products on the metal surface in the presence and absence of inhibitor is analysed by FTIR and XRD studies. The rich of main compounds namely zinc oxide (ZnO) and Potassium diaquachlorozincate(II) ($K [ZnCl_3(H_2O)_2]$) are formed on the metal surface may be confirmed by XRD spectrum. The observed results concluded that the *Citrullus Vulgaris* peel could serve as an effective inhibitor on zinc in natural sea water environment.

Keywords: Mass loss, zinc, *citrullus vulgaris* peel, isotherm, inhibition.

Introduction

Corrosion is an economic problem in world wide. Since corrosion can damage the materials which are used to construct automobiles, pipeline systems (water,oil), bridges and buildings, petroleum refineries etc¹. Zinc metal has a numerous industrial applications and is mainly used for the corrosion protection of steel. Because steel exhibits a wide range of useful forms and mechanical properties. Due to these fact steel is almost used in all industries². The zinc-coated steel materials provide a greater resistance to corrosion, but they undergo rapid corrosion, when exposed to humid atmosphere leading to the formation of a corrosion product known as white dust³. Zinc is an industrially important metal and is corroded by many agents, of which aqueous acids are the most dangerous one⁴. Due to the increasing usage of zinc, the study of corrosion inhibition is most important one. Every year, billions of dollars are spent on capital replacement and control methods for corrosion infrastructure⁵. The inhibitor must be eco-friendly to replace the older, which is more toxic and harmful to the environment. The earlier literature reveals that the study of corrosion inhibition of different metals with various green inhibitor have been reported. A few investigations are Red Peanut Skin⁶, *Musa* species peels⁷, *Vernonia Amygdalina*⁸, *Piper guinensis*⁹, Henna extract¹⁰, *Delonix regia* extracts¹¹, Rosemary leaves¹², natural honey¹³, *opuntia* extract¹⁴, khillah (*Ammi visnaga*) seeds¹⁵, *Carica Papaya* and *Camellia Sinensis* Leaves¹⁶, *Ricinus communis* Leaves¹⁷, *Justicia gendarussa*¹⁸, *Vitis vinifera*¹⁹, *Punica granatum* peel²⁰, Leaves of Genus *Musa*, Genus

Saccharum and *Citrullus Lanatus*²¹ 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*²², Red onion skin²³, *Nypa fruticans Wurmb*²⁴, *Aloe vera*²⁵, henna (*lawsonia*) Leaves²⁶. 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.

Material and Methods

Preparation of *Citrullus Vulgaris* peel extract: Freshly available *Citrullus Vulgaris* peel were collected from the fruit stalls and dried under sun shade and then grinded in to fine powder. Approximately 100gm of this powder was soaked in 400ml alcohol in a beaker and kept it for 48hrs. It was filtered followed by evaporation in order to remove the alcohol and then the pure fruit peel extract was collected. The stock solution was prepared from this extract and used throughout the present investigations.

Specimen preparation: Rectangular specimen of Zinc were mechanically pressed cut to form different coupons, each of dimension exactly 5x2x2cm. The specimens were mechanically polished, a hole drilled at one end for free suspension and numbered by punching. After pickling the specimens were degreased with trichloroethylene, washed with distilled water

and well polished with emery wheel of 80 and 120, cleaned, dried and then stored in desiccators for present study.

Properties and Applications of *Citrullus vulgaris* peel: *Citrullus vulgaris* (CVP) belongs to Cucurbitaceae family and its originally from southern Africa. CVP has a phytochemical compound mainly Citrulline (Fig.1) an amino acid²⁷, flavanoids and polyphenols²⁸. These compounds have an antioxidant property that can protect the human from free radical damage²⁷. The CVP can medicinally used for cell division, healing of wounds, excretion of ammonia in urine, and create the amino acid namely arginine which may help to regulate blood sugar levels and improve the function of our arteries and other blood vessels²⁹. The peel can also used to cure the sickle-cell anemia-related afflictions³⁰ and plays an important role to protect hypothyroidism. It can also stimulate the thyroid activity in PTU-induced hypothyroid animals and lipid peroxidation inhibition³¹.

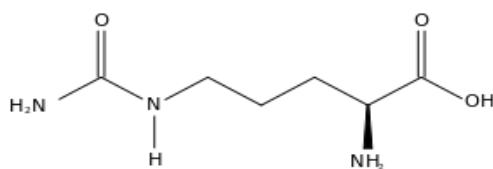


Figure 1
The structure of Citrulline

Mass Loss method: In Mass loss measurements, zinc specimen in triplicate were immersed in 50ml of the test solution in the presence and absence of the inhibitor. The Zinc specimens were withdrawn from the test solutions after an hour at the temperature range of 303K to 333K and after 24 to 480hrs at room temperature. The Mass loss was measured as the difference in weight of the specimens before and after immersion using LP 120 digital balance with sensitivity of ± 1 mg. The experiments 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 (mmpy) was calculated using the following relationship.

$$\text{Corrosion Rate (mmpy)} = \frac{87.6 \times W}{D \times A \times T} \quad (1)$$

where, mmpy = millimeter 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 the following equation (2) and equation (3), respectively.

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

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

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

Results and Discussion

The value of corrosion rate (mmpy) Vs various concentration of inhibitor (ppm) on Zinc electrode in Natural sea water environment is shown in figure 2. It reveals that the loss of mass gradually increased from 38mg to 70mg with increase of exposure time from 24 hrs to 480 hrs in the absence of inhibitor concentration. In the presence of CVP extract, the value of corrosion rate significantly reduced from 0.9725 to 0.2048 (mmpy) for 24hrs, and 0.0896 to 0.0154 (mmpy) for 480 hrs (figure 3) respectively. The maximum of 82.81% inhibition efficiency is achieved at 1000 ppm of inhibitor concentration even after 480 hrs exposure time. This is mainly due to the active phyto chemical constituent of CVP extract viz, π bonds, hetero atoms (O and N). The almost greater than 82% of surface coverage (θ) is due to the co-ordination between the Zinc metal and the hetero atom present in the inhibitor.

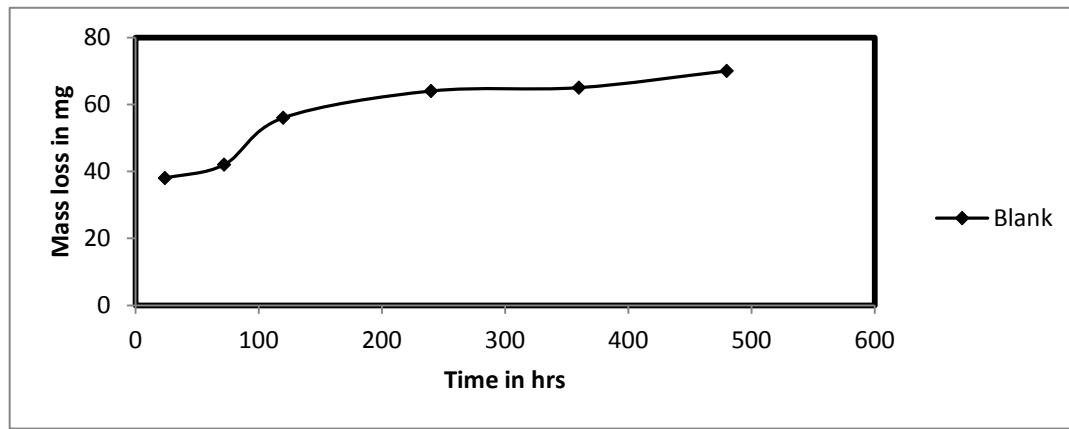


Figure-2
Variation of Mass loss of Zinc at different time in Natural Sea Water environment

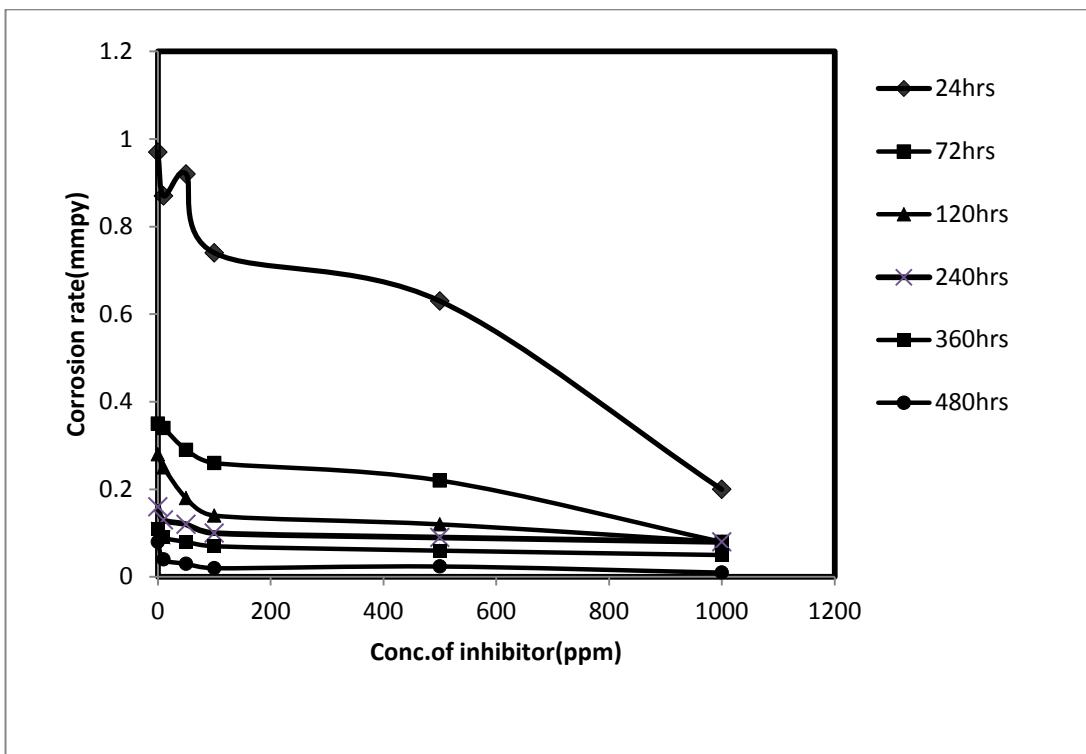


Figure-3
Variation of Corrosion rate with different Concentration of CVP extract on Zinc in Natural sea water environment

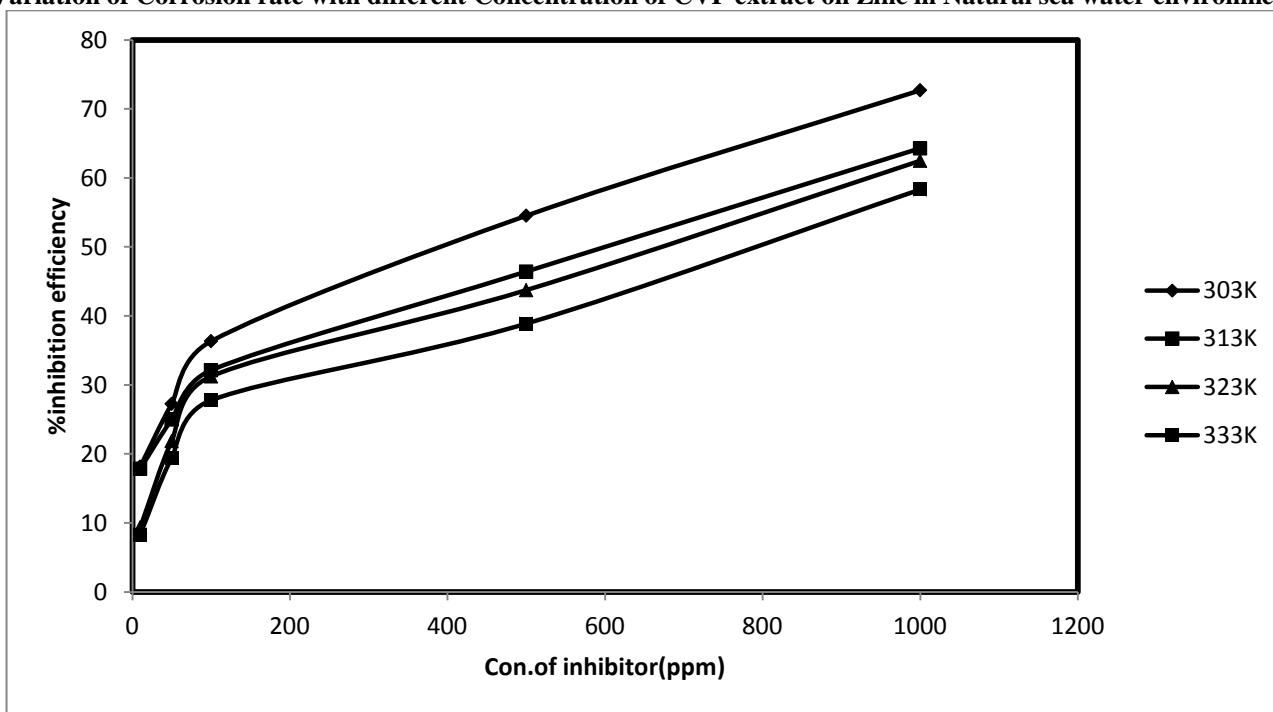


Figure-4
Variation of % Inhibition efficiency with Concentration of CVP extract on Zinc in Natural sea water environment

The figure 4 reflects that the concentration of inhibitor versus the percentage of inhibition efficiency (% IE) at various temperature from 303K to 333K. The maximum of 72.72% , 58.33 % inhibition efficiency is achieved at 303K, 333K respectively. The value of inhibition efficiency is decreased

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

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

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

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 (7.025 kJ/mol) is lower than in the presence of

with rise in temperature is suggested that physical adsorption mechanism. This results indicate that the adsorption of main active components present in the inhibitor shield the metal surface at room temperature. However it may be deshielded from the surface with rise in temperature.

inhibitors (table 1), which is clearly indicates that adsorption process is physisorption³²⁻³³.

Adsorption Studies: The values of Q_{ads} on zinc specimen in the presence of inhibitor is arrived by the following equation (6)

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

Where R is the gas constant, θ_1 and θ_2 are the degree of surface coverage at temperatures T_1 and T_2 respectively.

Table-1
Calculated values of Activation energy, % inhibition efficiency and Heat of adsorption of CVP extract in Natural sea water environment at 303K and 333

S. No	Concentration of Inhibitor(ppm)	Inhibition Efficiency (%)		E_a kJ/mol	Q_{ads} kJ/mol
		303K	333K		
1	0	7.025
2	10	18.18	8.33	36.337	-24.999
3	50	27.27	19.44	36.018	-12.397
4	100	36.36	27.78	36.698	-11.065
5	500	54.54	38.89	41.437	-17.733
6	1000	72.72	58.33	45.012	-18.014

The calculated Q_{ads} values (table 1) are ranged from -24.999 to -18.014 kJ/mol. This negative value indicates that the adsorption of CVP extract on the surface of Zinc metal is exothermic³⁴.

This adsorption isotherm of CVP extract on Zinc surface proceeded according to the following Equation (7)

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

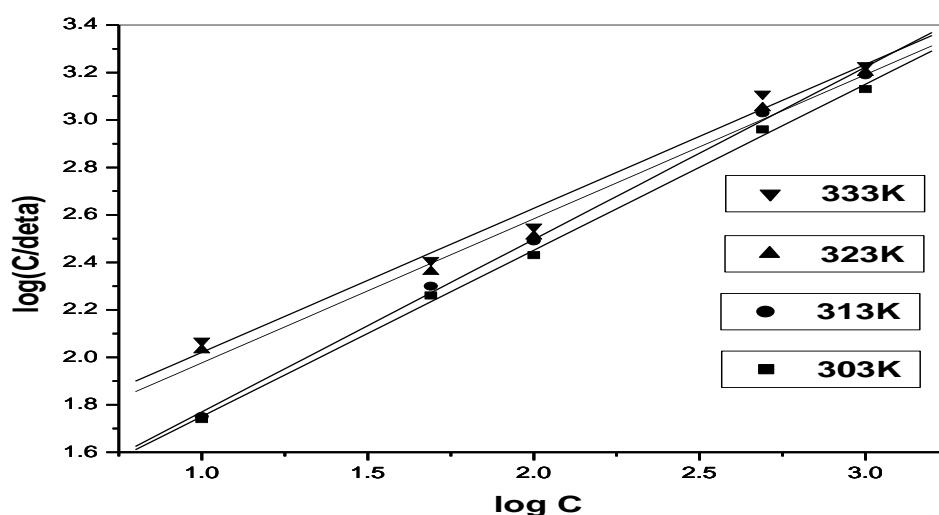


Figure 5
Langmuir isotherm for adsorption of CVP extract on Zinc in Natural sea water environment

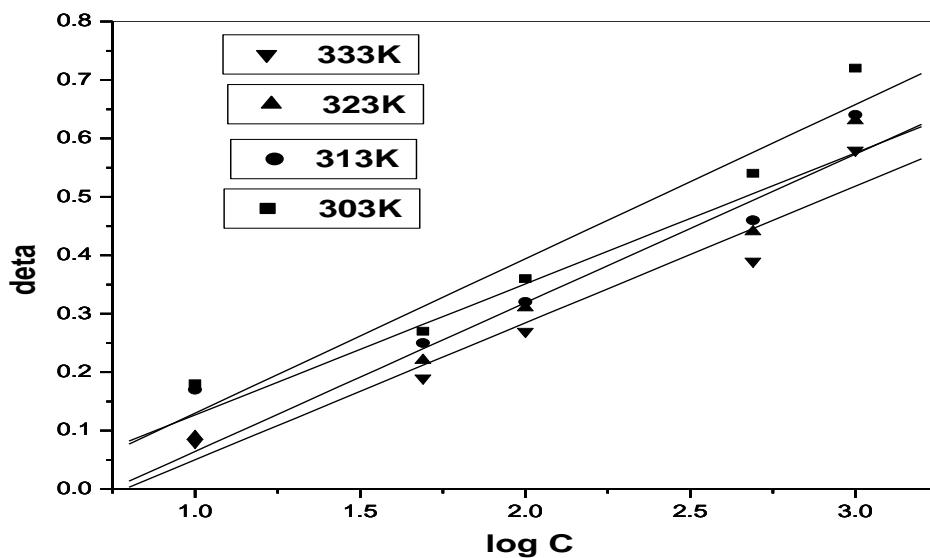


Figure 6
Temkin isotherm for the corrosion inhibition of CVP extract on Zinc in Natural sea water environment

By plotting the values of $\log(C/\theta)$ Vs $\log C$, linear plots are generated (figure 5). Inspection of this Fig. reveals that the experimental data fitted with the Langmuir adsorption isotherm, means that there is no interaction between the adsorbed species. The inhibitor also obeys Temkin adsorption isotherm which is represented in figure 6.

The equilibrium constant of adsorption of CVP extract on the surface of the metal is related to the free energy of adsorption (ΔG_{ads}) by the following equation (8)

$$\Delta G_{ads} = -2.303 RT \log (55.5 K) \quad (8)$$

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 (8) and the calculated values of ΔG_{ads} are placed in table 2. The negative values of ΔG_{ads} suggested that the adsorption of CVP extract onto metal surface is a spontaneous process and the adsorbed layer is more stable one.

Table-2

Langmuir and Temkin adsorption parameters for the adsorption of CVP extract on Zinc in Natural sea water environment

Isotherm	Temperature (K)	logK	R ²	ΔG _{ads} (kJ/mol)
Langmuir	303	-0.9034	0.9981	-0.1249
	313	-0.9543	0.9975	-0.1111
	323	-0.0727	0.9874	-0.8457
	333	-0.0174	0.9859	-0.9607
Temkin	303	-0.8723	0.9436	-5.058
	313	-1.0118	0.9266	-4.389
	323	-0.7211	0.9574	-6.328
	333	-0.7351	0.9436	-6.434

IR Analysis: Figures 7, 8 and 9 reflect that the IR spectrum of the alcoholic crystals of the inhibitor, the corrosion products on the zinc surface in the absence and presence of CVP extract in natural sea water environment and that of stretching frequency, the corresponding band assignment is shown in table 3. On comparing the above IR spectra, it found that the stretching frequency was shifted from 3359.77 to 3388.70 cm^{-1} for $-\text{OH}$,

1668.31 to 1633.59 cm^{-1} for amide $-\text{C}=\text{O}$ and 1448.44 to 1458.08 cm^{-1} for aromatic $-\text{C}=\text{C}$. In addition, the $-\text{CN}$ stretching frequency of amine, 1193.85 cm^{-1} (figure 7) is disappeared in figure 9 (corrosion product in the presence of inhibitor) may also confirm that the complex film is formed on the anodic sites of the metal surface.

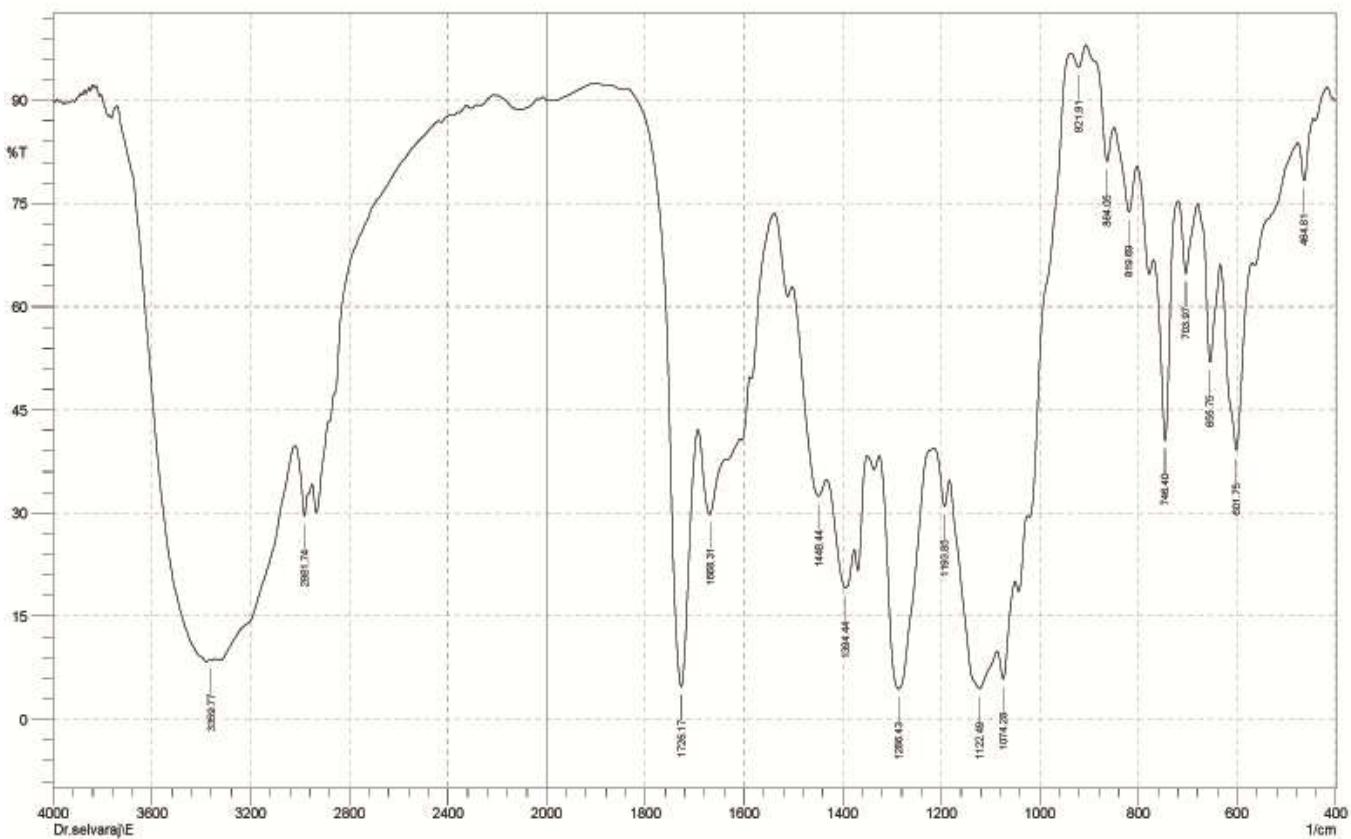


Figure-7
IR spectrum of the Alcoholic extract of CVP

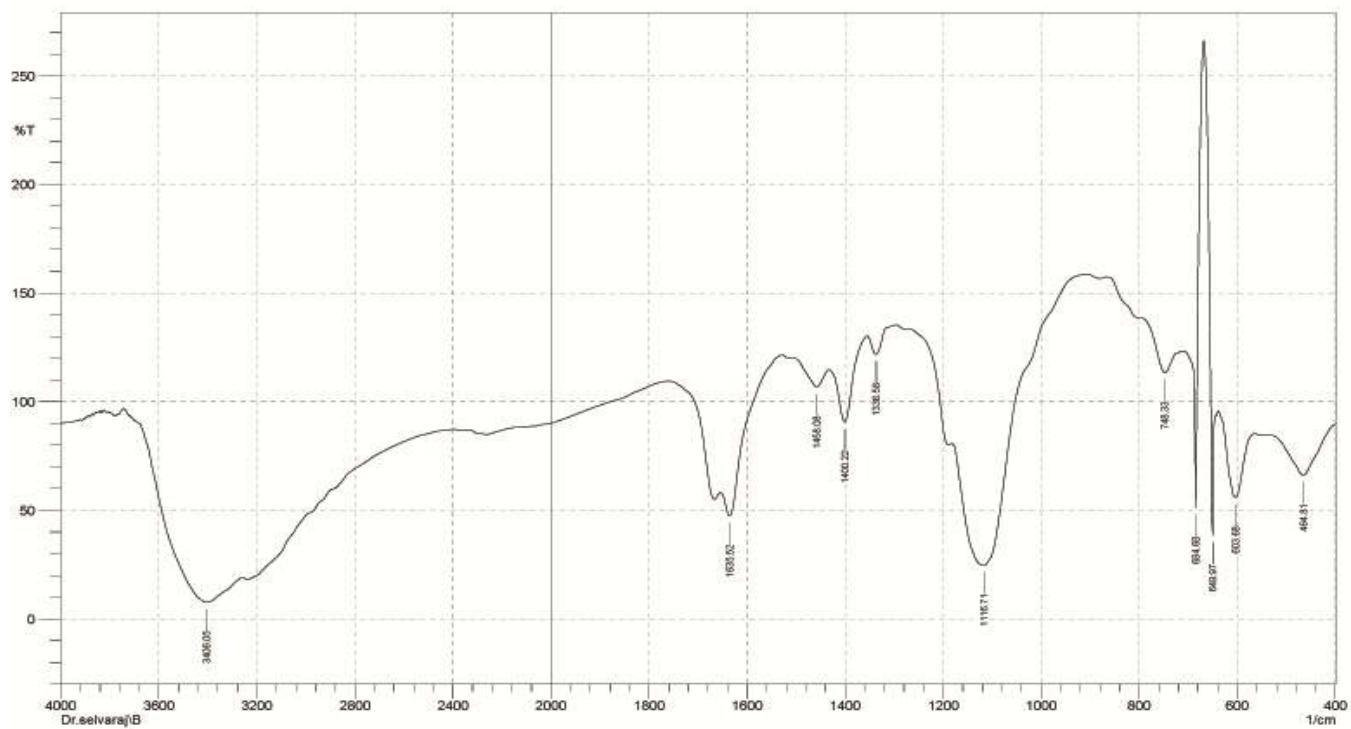


Figure-8
IR spectrum of the corrosion product on Zinc in the Natural Sea water environment

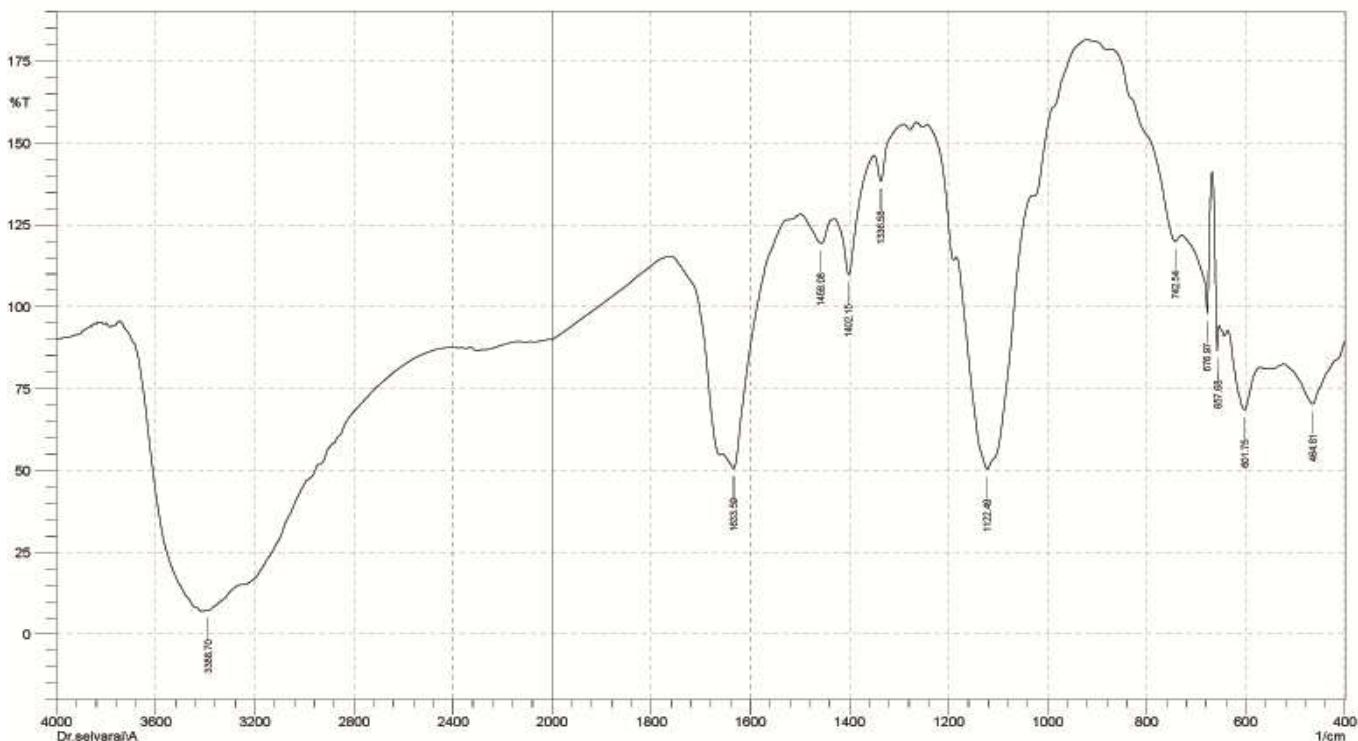


Figure-9

IR spectrum of the corrosion product on Zinc in the presence of CVP extract in Natural Sea water environment

Table-3
FTIR Stretching frequency and Band Assignment

Frequency (cm ⁻¹)	Band Assignment
Alcoholic crystals of inhibitor	3359.77 -OH Stretch (alcohol)
	2891.74 -C-H Stretch (Alkane)
	1726.17 -C=O Stretch
	1668.31 -C=O Stretch (Amide)
	1448.44 -C=C Stretch (Aromatic)
	1286.43 -C-O Stretch (Ether)
	1193.85 -CN Stretch (Amine)
Absence of inhibitor	3406.05 -O-H Stretch (alcohol).
	1458.08 and 1400.22-C=C-Stretch (Aromatic)
	1116.71 -CO Stretch
	684.68 and 649.97 -C-H deformation (Alkyne)
	603.68 -C-Cl (Chloro alkane)
Presence of Inhibitor	3388.70 -O-H Stretch (alcohol).
	1633.59 -C=O Stretch
	1458.08 and 1402.15 -C=C- Stretch(Aromatic)
	1336.58- CN stretch (Amine)
	742.54 and 676.97- C-H deformation (Alkyne)
	601.75- C-Cl (Chloro alkane)

XRD analysis: The corrosion products are scrapped from the Zinc surface in the presence and absence of CVP extract inhibitor is examined by XRD studies are shown in Fig. 10 and 11 respectively. The base peak (figure 10) is matched with the

standard peak of zinc chloride ($ZnCl_2$) which has a crystal structure of monoclinic with the lattice parameter values of $a=6.500, b=11.30, c=12.300\text{AU}$ which is taken from the JCPDS File no. PDF 740518. Another one peak is matched with the

standard peak of Zinc oxide (ZnO) has a hexagonal structure with the lattice parameter of $a = 3.253$, $c = 5.213$ AU which is taken from the JCPDS file no. PDF 891397 and the third one is matched with the standard peak of Potassium Zinc chloride hydrate ($K[ZnCl_3(H_2O)_2]$) which has a crystal structure of monoclinic in accordance with the JCPDS file no. PDF 760658 with lattice parameter values $a = 12.03$ $b = 10.09$ and $c = 6.260$ AU. The peak obtained from figure 11 is coincided with the

standard peaks for zinc nitride (Zn_3N_2) with the d value of 31.703. This compound has a crystal structure of simple cubic with the lattice parameter of $a=b=c=9.769$ AU which is taken from the JCPDS file no. PDF 880618. Hence the present XRD pattern is indeed a $K[ZnCl_3(H_2O)_2]$ and Zn_3N_2 compounds. It reflects that the thin film may be mainly combine with a rich amount of $K[ZnCl_3(H_2O)_2]$, ZnO and $ZnCl_2$ etc with the bio-inhibitor.

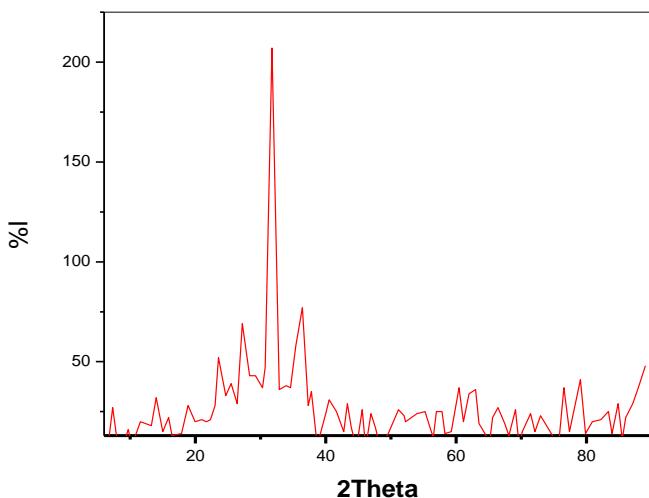


Figure-10
XRD spectrum of Zinc in the presence of CVP extract in Natural Sea water environment

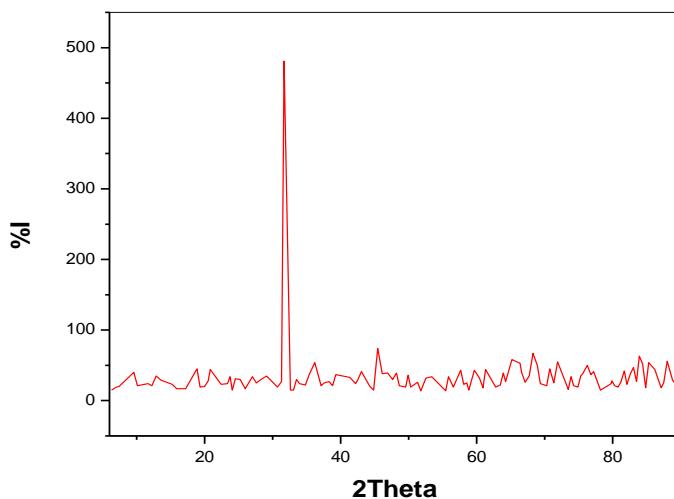


Figure-11
XRD spectrum of Zinc in Natural Sea water environment

Conclusion

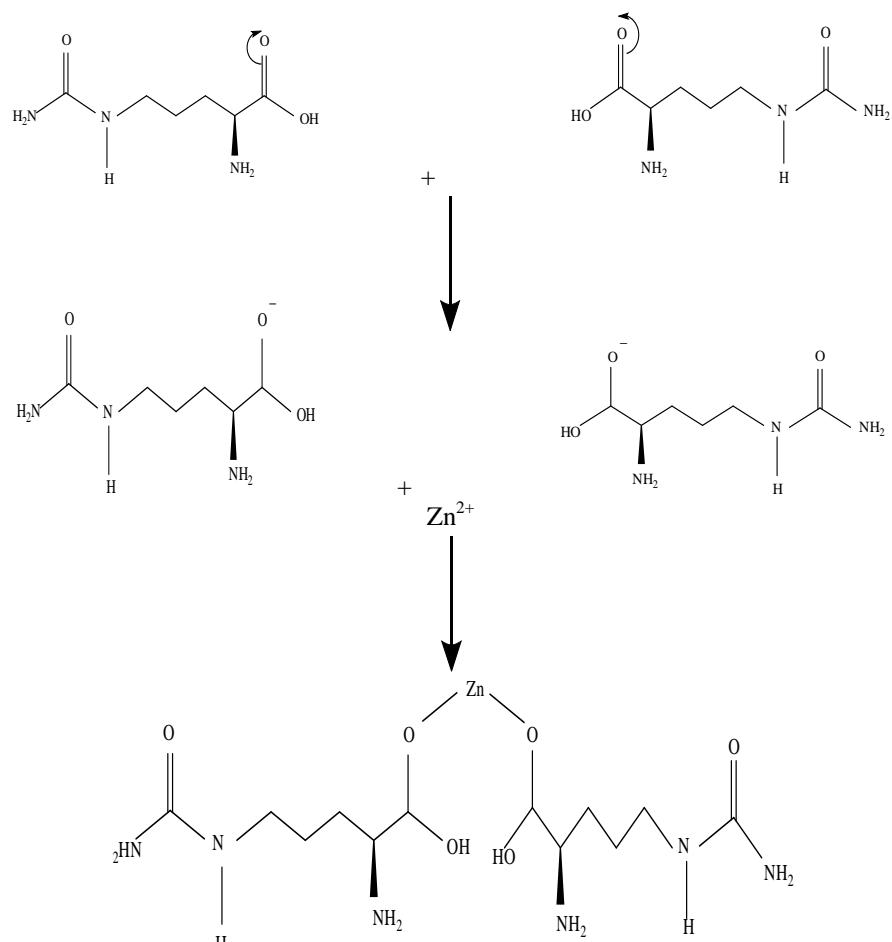
The alcoholic extract of CVP is used as a good corrosion inhibitor on zinc metal in natural sea water environment. The corrosion rate is gradually increased with increase of exposure

time in the absence of inhibitor. However in the presence of CVP the corrosion rate is significantly reduced and the maximum of 82% Inhibition efficiency is achieved even after 480hrs exposure time. In temperature studies, the inhibitive effect is slightly decreased with rise in temperature is suggestive

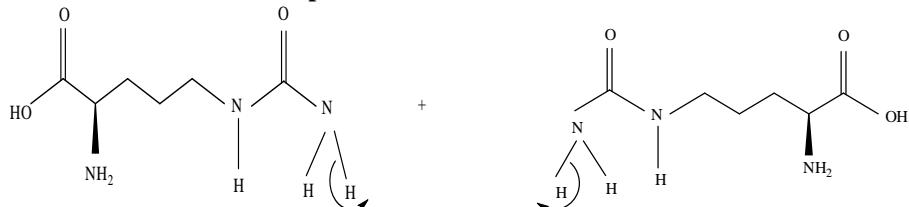
of physisorption process. The calculated values of E_a , Q_{ads} , ΔG_{ads} indicates that the adsorption of inhibitor on the metal surface is physisorption, exothermic and followed by spontaneous process. The inhibitor obeys Langmuir and Temkin adsorption isotherm. The corrosion products over the surface of metal is characterized FTIR and XRD. The shifting frequency of FTIR spectra confirms that the formation of protective film on Zinc metal surface. The formation of complexes such as $K [ZnCl_3(H_2O)_2]$, ZnO , $ZnCl_2$ is also confirmed by XRD studies.

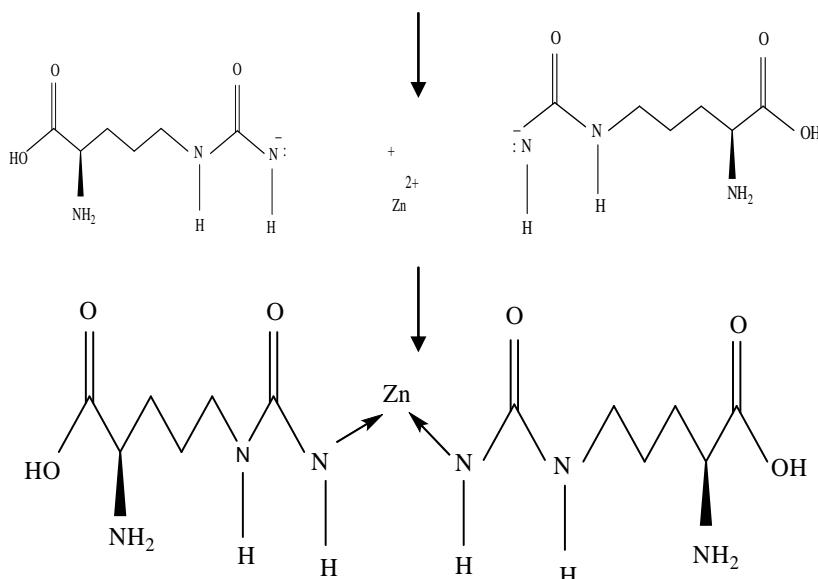
Mechanism: The main active phyto constituents in the CVP extract is a Citrulline. From the chemical structure of Citrulline (figure 1), the molecules contains heteroatoms such as oxygen, nitrogen. The presence of the electronegative oxygen, nitrogen

in citrulline might have enhanced the electron donating ability of this compound and hence its inhibition efficiency. Also, the functional groups ($-C=O$, $-NH_2$ and $-COOH$) presence in citrulline might have provided sites for the adsorption of the inhibitor on the surface of Zinc. Therefore the following mechanism have been proposed for the adsorption of citrulline on the surface of zinc. i. In aqueous medium, the oxygen atom present in each citrulline molecule can donate electron to vacant d-orbital of the zinc and formed a coordinate covalent bond (scheme 1). ii. Another mechanism is shown by scheme 2. In this scheme, the electron donated for the formation of Zn-citrulline complex is provided by the amide functional group instead of the carbonyl group as shown in Scheme 1



Scheme-1
Mechanism of adsorption of Citrulline on the surface of Zinc metal





Scheme-2
Mechanism of adsorption of Citrulline on the surface of Zinc metal

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