# Effects of Kingiodendron *Pinnatum Leaves*(KPL) on Zinc in Natural sea water

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**Abstract  -**The inhibition efficiency of kingiodendron pinnatum leaves extract on Zinc in Natural Sea Water environment.  It has been investigated on various concentrations of inhibitor as well as temperature by mass loss measurement.  The observed results indicate that the percentage of inhibition efficiency is increased with increase of inhibitor concentration as well as temperature. Thermodynamic parameter viz ($E_a$, $Q_{ads}$, $\Delta G_{ads}$, $\Delta H$ and $\Delta S$) suggests that the adsorption of inhibitor is chemisorptions, exothermic and Spontaneous process.  The Corrosion product on the metal surface in the presence and absence of inhibitor is characterized by UV, FT-IR and SEM-EDX Spectral techniques.

**Keywords**: Zinc, KPL inhibitor, Natural Sea Water, Mass Loss, Adsorption

## 1. INTRODUCTION

Corrosion is defined as destruction or deterioration of a material (metal) because of its reaction with environment[1].  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 facts steel is almost used in all industries[2]. 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 dust[3]. Zinc is an industrially important metal and is corroded by many agents, of which aqueous acids are the most dangerous one[4]. 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 infrastructure[5]. The inhibitor must be eco-friendly to replace the older, which is more toxic and harmful to the environment. The recent years literature reveals that the study of corrosion inhibition of different metals with various green inhibitor have been reported. A few investigations are Red Peanut Skin[6], Musa species peels[7], *Vernonia Amygdalina[8] , Piper guinensis[9]***,** Henna extract[10], *Delonix regia* extracts[11], Rosemary leaves[12], natural honey[13], *opuntia* extract[14], khillah (*Ammi visnaga*) seeds[15], *Carica Papaya* and *Camellia Sinensis* Leaves[16], *Ricinuscommunis* Leaves[17], *Justicia gendarussa[18]*, *Vitis vinifera[19]*,*Punica granatum* peel[20]*,* Leaves of *Genus Musa*, *GenusSaccharum* and *Citrullus Lanatus[21]* have been studied onvarious metals and alloys. However only a limited number of literatures 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 onionskin[23], *Nypa fruticans Wurmb[24]*, *Aloe vera[25]*, henna (*lawsonia*) Leaves[26]. Thus, our present attention is to study the effect of adsorption and corrosion resistant behavior of Kinglodendron pinnatum leaves on zinc metal surface with natural sea water environment [27-36].

## 2  MATERIALS AND METHODS
### 2.1 Specimen preparation

Zinc specimen were mechanically pressed cut to form different coupons, each of dimension exactly $20cm^2$ (5x2x2cm),  polished with emery wheel of 80 and 120, and degreased with trichloroethylene, then washed with distilled water cleaned, dried  and then stored in desiccator for the use of our present study.

### 2.2 Preparation of *Kingiodendron Pinnatum Leaves (*KPL) Extract:

About 3 Kg of *Kinglodendron Pinnatum,* leaves was collected from in and around Western Ghats and then dried under shadow for 5 to 10 days. Then it is grained well and finely powdered, exactly 150g of this fine powder was taken in a 500ml round bottom flask and a required quantity of ethyl alcohol was added to cover the fine powder completely, and left it for 48 hrs. Then the resulting paste was refluxed for about 48 hrs, the extract was collected and the excess of alcohol was removed by the distillation process. The

obtained paste was boiled with little amount of activated charcoal to remove impurities, the pure plant extract was collected and stored.

2.3 Properties of Kingiodendron pinnatum leaves:

*Kingiodendron pinnatum leaves* belongs to *Euphorbiaceous* family and it is an annual herbaceous climbing plant with a long history of traditional medicinal uses in many countries, especially in tropical and subtropical regions. The common Name is Kolavu. The peel extract of this plant is used to regulate thyroid function and glucose metabolism. The phytochemicals present in this plant is flavonoids, alkaloids, saponins and triterpenes
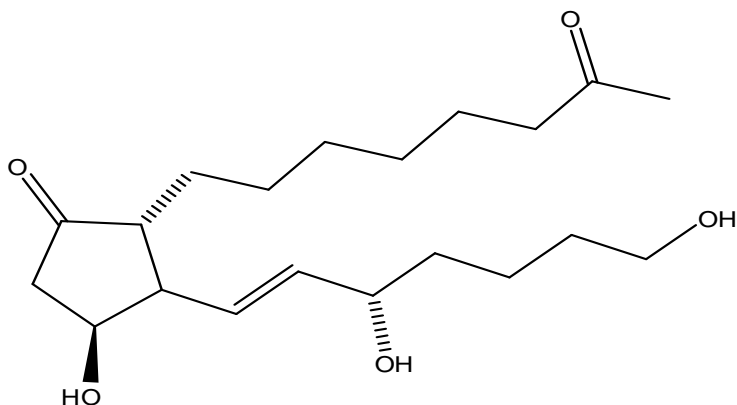


Figure 1: Chemical structure of the main active compounds present in *Kingiodendron pinnatum* leaves extract.

## 2.4 Mass loss measurement

In the mass loss measurements on Zinc in triplicate were completely immersed in 100ml 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 313K to 333K and also measured 24 to 360 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.

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

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 the following equations.

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

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

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

## 2.5 Adsorption studies

### 2.5.1 Activation energy

The activation energy ($E_a$) for the corrosion of Copper in the presence and absence of inhibitors in natural sea water environment was calculated using Arrhenius theory. Assumptions of Arrhenius theory is expressed by equation (4).

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

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

Where $CR_1$ and $CR_2$ are the corrosion rate at the temperature $T_1$ (313K) and $T_2$ (333K) respectively.

### 2.5.2 Heat of adsorption

The heat of adsorption on the surface of various metals in the presence of plant extract in natural sea water environment is calculated by the following equation.

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

Where R is the gas constant, $\theta_1$ and $\theta_2$ are the degree of surface coverage at temperatures $T_1$ and $T_2$ respectively.

### 2.5.3 Langmuir adsorption isotherm

The Langmuir adsorption isotherm can be expressed by the following Equation-4.10 is given below.

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

Where $\theta$ is the degree of surface coverage, C is the concentration of the inhibitor solution and K is the equilibrium constant of adsorption of inhibitor on the metal surface.

### 2.5.4 Free energy of adsorption

The equilibrium constant of adsorption of various plant extract on the surface of copper, mild steel and zinc is related to the free energy of adsorption $\Delta G_{ads}$ by equation (8).

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

Where R is the gas constant, T is the temperature, K is the equilibrium constant of adsorption.

## 3. RESULT AND DISCUSSION

### 3.1 Mass loss measurements

The dissolution behavior of Zinc in Natural sea water environment containing in the absence and presence of KPL extract with various exposure times (120 to 480 hrs) are shown in Table-1. The observed values are clearly indicates that in the presence of MEL inhibitor the corrosion rate significantly reduced from 0.2556 to 0.0408 mmpy (120 hrs) and 0.1380 to 0.0332 mmpy (480 hrs) with increase of inhibitor concentration from 0 to 1000 ppm. The maximum of 84 % of inhibition efficiency is achieved even after 120 hrs exposure time. This achievement is mainly due to the presence of active phytochemical constituents present in the KPL extract which is adsorbed on the metal surface and shield completely to prevent further dissolution from the aggressive media of chloride ion (Cl⁻).

**Table -1:** The corrosion parameters of Zinc in Natural Sea Water containing different concentration of KPL extract after 120 to 480 hours exposure time

| Con. of | 120 hrs | 240 hrs | 360 hrs | 480 hrs |
| --- | --- | --- | --- | --- |

| inhibitor (ppm) | C.R | % I.E | C.R | % I.E | C.R | % I.E | C.R | % I.E |
|---|---|---|---|---|---|---|---|---|
| 0 | 0.2556 | -- | 0.1840 | -- | 0.1397 | -- | 0.1380 | -- |
| 10 | 0.1942 | 24.00 | 0.1508 | 18.05 | 0.1022 | 26.82 | 0.1022 | 25.92 |
| 50 | 0.1635 | 36.00 | 0.1226 | 33.33 | 0.0954 | 31.70 | 0.0920 | 33.33 |
| 100 | 0.1431 | 44.00 | 0.0996 | 47.83 | 0.0886 | 36.53 | 0.0843 | 38.89 |
| 500 | 0.1022 | 60.00 | 0.0971 | 47.22 | 0.0783 | 43.90 | 0.0626 | 54.62 |
| 1000 | 0.0408 | 84.00 | 0.0511 | 72.22 | 0.0477 | 67.85 | 0.0332 | 75.93 |

## 3.2 Temperature Studies

The corrosion parameters of copper in Natural Sea Water containing various concentration of KPL extract with different temperature in range from 313 to 333K is shown in Table-2. In the absence of inhibitor, the corrosion rate increased from 23.3102 to 48.4621 mmpy at 313 to 333K, but in the presence of inhibitor, the value of corrosion rate decreased from 23.3102 to 4.9075mmpy and 48.4621 to 5.5210 mmpy with increase of inhibitor concentration at 313and 333K. The maximum of 88.60 % inhibition efficiency is achieved at 333K respectively. The value of inhibition efficiency is increased with rise in temperature (313-333K). This results clearly reflects that component present in the inhibitor on the metal surface is higher than the desorption process. It clearly shows that the inhibitor follows chemisorptions process

**Table -2:** The corrosion parameters of Zinc in Natural Sea Water containing different concentration of KPL extract at 313,323 and 333 K

| Con. of inhibitor (ppm) | 313 K | | 323 K | | 333 K | |
|---|---|---|---|---|---|---|
| | C.R | % I.E | C.R | % I.E | C.R | % I.E |
| 0 | 23.3102 | 68.42 | 25.7647 | -- | 48.4621 | -- |
| 10 | 7.3614 | 89.47 | 19.6305 | 23.80 | 16.5632 | 65.82 |
| 50 | 2.4537 | 92.10 | 7.9747 | 69.04 | 8.5882 | 82.27 |
| 100 | 1.8403 | 76.31 | 2.4537 | 90.47 | 5.5210 | 88.60 |
| 500 | 5.5210 | 78.94 | 11.0421 | 57.14 | 13.4957 | 72.15 |
| 1000 | 4.9075 | 68.42 | 9.8512 | 61.64 | 11.6554 | 75.94 |

## 3.3 Effect of Temperature

### 3.3.1 Activation energy:

The observed values of activation energy are ranged from 35.1417 – 54.2894 kJ/mol for Zinc in natural Sea Water containing various concentration of inhibitor. The average value of $E_a$ obtained from the blank (31.71581) is lower than that in the presence of inhibitor and clearly suggest that there is a strong chemical adsorption bond between the KPL inhibitor molecules and the Zinc surface.

**Table -3:** Calculated values of Activation energy ($E_a$) and heat of adsorption ($Q_{ads}$) of KPL extract on Zinc in Natural Sea Water environment**.**

| S. No | Conc. of inhibitor(ppm) | % of I.E | | $E_a$ (KJmol$^{-1}$) | $Q_{ads}$ (KJmol$^{-1}$) |
| --- | --- | --- | --- | --- | --- |
| | | $40^o$ | $60^o$ | | |
| 1. | 0 | -- | -- | 31.7158 | -- |
| 2. | 10 | 68.420 | 65.822 | 35.1417 | -1.0063 |
| 3. | 50 | 89.473 | 82.278 | 54.2894 | -0.0990 |
| 4. | 100 | 92.105 | 88.607 | 47.6093 | -0.3158 |
| 5. | 250 | 76.315 | 72.151 | 38.7343 | -1.1649 |
| 6. | 500 | 78.947 | 75.949 | 37.4853 | -0.7106 |

### 3.3.2 Heat of adsorption:

The value of heat of adsorption ($Q_{ads}$) on Zinc in Natural Sea Water containing various concentration of KPL extract is calculated and the values of $Q_{ads}$ are ranged from -0.0990 to -1.1649 kJ/mol (Table- 3). These negative values reveals that the adsorption of KPL extract on the surface of Zinc may follows exothermic process.

### 3.3.3 Adsorption studies:

The adsorption isotherm is a process, which are used to investigate the mode of adsorption and it characteristic of inhibitor on the metal surface. In our present study the Langmuir adsorption isotherm is investigated. The straight line (Fig-1) indicates that the inhibitor follows Langmuir adsorption isotherm.
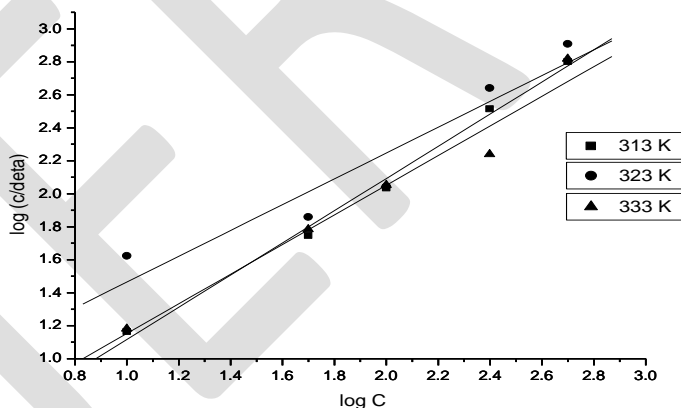


**Figure-2:**Langmuir isotherm for the adsorption of KPL inhibitor on Zinc in Natural Sea Water Environment

### 3.3.4 Free energy of adsorption:

The standard free energy of adsorption ($\Delta G_{ads}$) can be calculated using the Equation- (8) and the observed negative values are (Table-1) ensure that the spontaneity of the adsorption process and the stability of the adsorbed layer is enhanced.

**Table-4:** Langmuir adsorption parameters for the adsorption of KPL inhibitor on Zinc in Natural Sea Water

| Adsorption isotherms | Temperature (Kelvin) | Slope | K | R2 | Gads kJ/mol |
| --- | --- | --- | --- | --- | --- |
| Langmuir | 313 | 0.97585 | 0.14107 | 0.9966 | -5.356 |

| | 323 | 0.78254 | 0.68212 | 0.9061 | -9.760 |
|---|---|---|---|---|---|
| | 333 | 0.8987 | 0.25447 | 0.9662 | -7.331 |

### 3.3.5 Thermodynamics parameters

The another form of Transition State equation which is derived from Arrhenius equation as below (4)

$$CR = RT/Nh \ exp \ (\Delta S/R) \ exp \ (-\Delta H/RT) \ ----- \ (4)$$

Where h is the Planck's constant, N the Avogadro's number, $\Delta S$ the entropy of activation, and $\Delta H$ the enthalpy of activation. A plot of log (CR/T) vs. 1000/T gives a straight line (Fig. 4) with a slope of $(-\Delta H/R)$ and an intercept of $[\log(R/Nh)) + (\Delta S/R)]$, from which the values of $\Delta S$ and $\Delta H$ were calculated and listed in Table-5. The observed positive values of enthalpy of activation suggest that the endothermic nature of the metal dissolution process is very difficult. The increase of $\Delta S$ is generally interpreted with disorder may take place on going from reactants to the activated complex.

**Table -5:** Thermodynamic parameters of zinc in natural sea water obtained from weight loss measurements

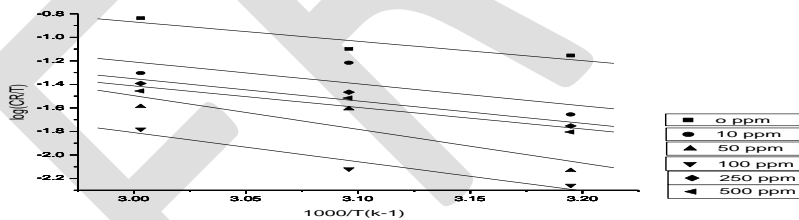| S.No | Concentration of KPL (ppm) | $\Delta H$ (kJ mol$^{-1}$) | $\Delta S$ (J k$^{-1}$ mol$^{-1}$) |
|---|---|---|---|
| 1 | 0 | 13.6787 | -51.9717 |
| 2 | 10 | 15.4953 | -49.3507 |
| 3 | 50 | 22.3972 | -26.8013 |
| 4 | 100 | 20.4333 | -39.0817 |
| 5 | 250 | 15.7525 | -49.7643 |
| 6 | 500 | 15.2221 | -51.8623 |



**Figure- 3:** The relation between log (CR/T) and 1/T for different concentrations of KPL extract.
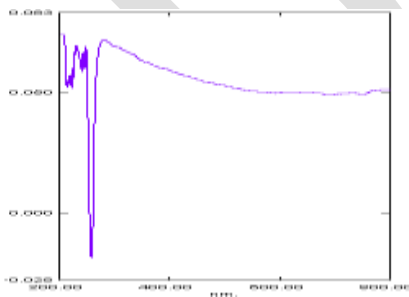
### 3.4 UV SPECTROSCOPY:



**Figure 4**          **Figure 5**

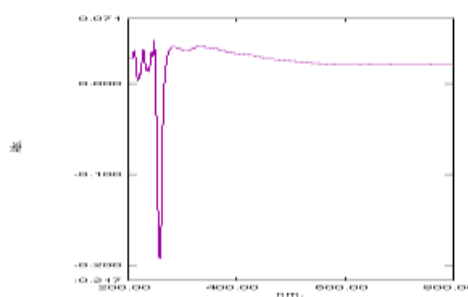**Figure- 4:** UV spectrum of ethanolic extract of KPL**, Figure -5:** Corrosion product on Zinc in Natural Sea Water in the presence of KPL extract

The Figures 4 and 5 shows that the UV visible spectrum of ethanolic extract of KPL and the corrosion product on the surface of mild steel in the presence of KPL extract in natural sea water respectively. In this spectrum, one peak is appeared around 300nm (Fig 3) and in the presence of inhibitor the band was disappeared. This change of absorption band may confirm that the strong co-ordination bond between the active group present in the inhibitor molecules and the metal surface.

## 3.5 FT-IR SPECTROSCOPY

### FT-IR studies of KPL extract on Zinc surface in Natural Sea Water:

The figures- 6 and 7 reflect that the FTIR spectrums of the ethanolic extract of inhibitor and the corrosion product on Zinc in the presence of KPL extract in Natural Sea Water. On comparing both of these spectra the prominent peak such as, the -O-H stretching frequency for alcohol is shifted from 2926.45 to 2927.41cm$^{-1}$, the C-O stretching in acid is shifted from 1117.55 cm$^{-1}$ to 1108.87cm$^{-1}$. and 1632.45 cm$^{-1}$ corresponds to C-O stretching frequency for carbonyl compounds is shifted to 1612 cm$^{-1}$. These results also confirm that the FTIR spectra support the fact that the corrosion inhibition of KPL extract on Zinc in Natural Sea Water may be the adsorption of active molecule in the inhibitor and the metal surface.
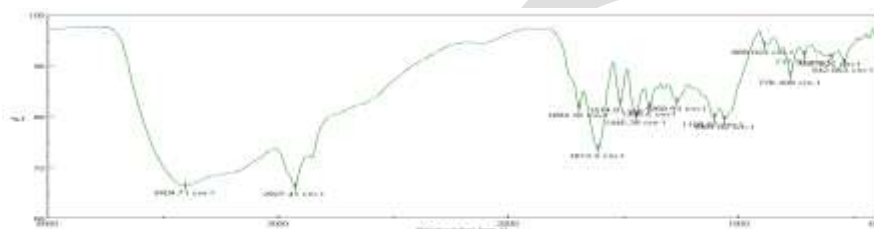


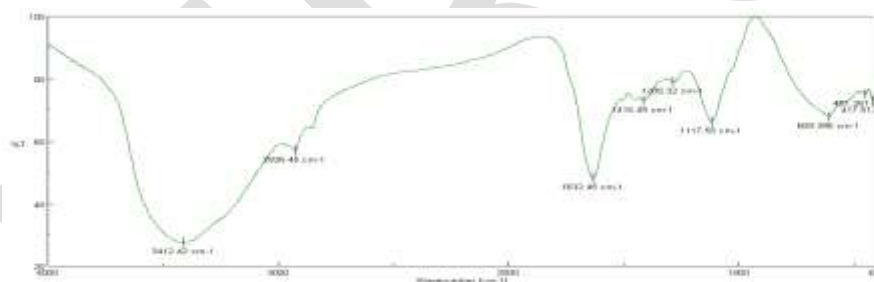**Figure-6:** FT-IR spectrum of ethanolic extract of *Kingiodendron pinnatum* leaves (KPL)



**Figure-7:** FT-IR spectrum for the corrosion product on Zinc in the presence of KPL extract with Natural Sea Water

## 3.6 EDX ANALYSIS

EDX spectroscopy was used to determine the elements present on the zinc surface before and after exposure to the inhibitor solution. Figures 8 & 9 represents the EDX spectra for the corrosion product on metal surface in the absence and presence of optimum concentrations of KPL extract with Natural sea water environment. In the absence of inhibitor molecules, the spectrum may confirms that the existence of zinc, iron, silicon, carbon, stannum. However, in the presence of the optimum concentrations of the inhibitors, oxygen atom is found to be present on the metal surface. It clearly indicates that the hetero atom such as oxygen present in the inhibitor molecules may involve the adsorption process with metal atom and hence it may protect the metal surface against the corrosion.
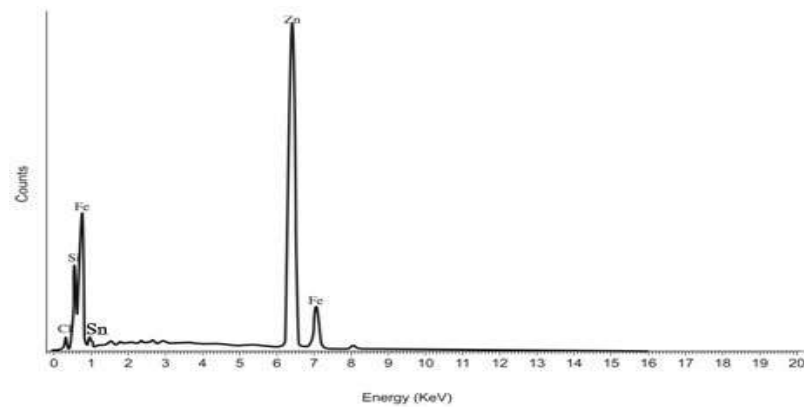
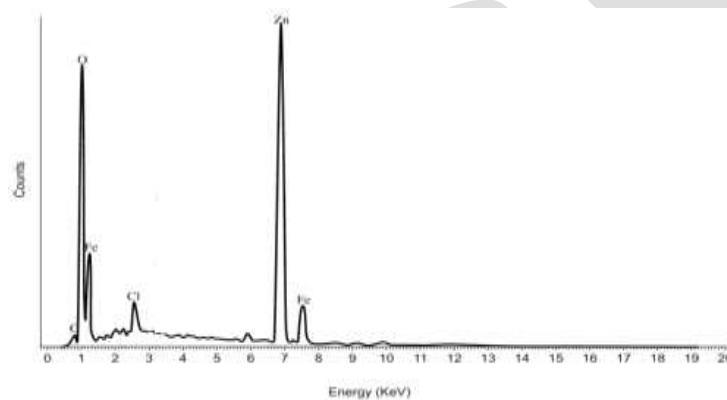**Figure -8:** EDX spectrum of the corrosion product on zinc surface in Natural seawater.



**Figure- 9:** EDX spectrum of the corrosion product on zinc surface with the presence of KPL extract in Natural seawater.

## 3.7 SEM ANALYSIS

The surface morphology of zinc surface was studied by scanning electron microscopy (SEM). The Figures-10 (a) and (b) shows the SEM micrographs of zinc surface before and after immersed in Natural seawater, respectively. The SEM photographs showed that the surface of metal has a number of pits with layer type, but in presence of inhibitor they are almost minimized by the formation of spongy mass covered on the entire surface of the metal.
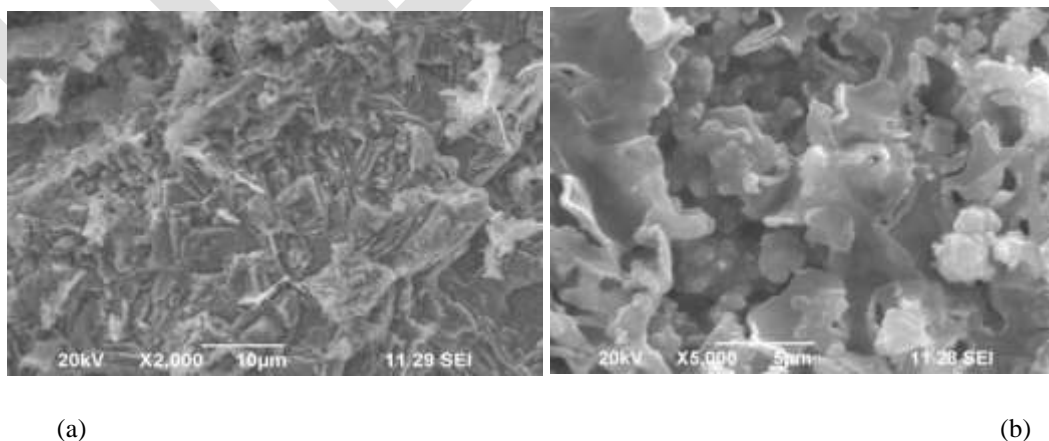


(a)                                                                                                          (b)

**Figure 10: SEM images of the zinc surfaces: (a) immersed in Natural sea water (b) immersed in natural sea water with KPL extract.**

## 4. CONCLUSION

Using *Kingiodendron pinnatum* leaves (KPL) extract on zinc in natural sea water

Using KPL extract on zinc, the corrosion rate markedly reduced with increase of concentrations from 0 to 500ppm.  Even though we attained the maximum 84% inhibition efficiency after 120 hours exposure time. This is due to strong bindings between the inhibitor molecule and ions from the metal surface.   In temperature studies, the percentage of  inhibition efficiency increased with rise of temperature ranges from 313 to 333K is due to the adsorption of active inhibitor molecules on the metal surface is higher than desorption process. The maximum 92% inhibition efficiency is attained and follows chemisorptions.  The thermodynamic parameters namely activation energy ($E_a$), heat of adsorption ($Q_{ads}$), Standard free energy adsorption ($\Delta G_{ads}$), enthalpy ($\Delta H$) and entropy ($\Delta S$), suggests that, strong chemical bond, exothermic, spontaneous process respectively.  The KPL inhibitor obeys Langmuir adsorption isotherm.  The film formation may also confirm UV, FTIR, SEM, EDX, spectral studies

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