Comparative Account of *Jatropha curcas* on Brass (Cu-40Zn) in Acid and Sea Water Environment.

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ABSTRACT

The inhibition efficacy of alcoholic leaf extract of *Jatropha curcas* on Brass (Cu-40Zn) in 1N Hydrochloric Acid and natural sea water environment are carried out using mass loss measurements. Experiments are performed by varying immersion period, concentration of the inhibitor and temperature. The inhibition efficiency is markedly higher in addition of *Jatropha curcas* leaves extract in both media and compared with those in the inhibitor free solution. The inhibition efficiency increased with an increase of inhibitor concentration but decreased with rise in temperature and exposure time. Corrosion inhibition may be due to the spontaneous physical adsorption of the plant constituents on the surface of Brass. Experimental data fitted with the Langmuir and Frumkin adsorption isotherms. Comparing the corrosion product on the surface of Brass in the presence of inhibitor at both environments is studied by UV and IR spectra.

(Keywords: corrosion inhibition, brass, adsorption, isotherms, *Jatropha curcas*)

INTRODUCTION

Copper and its alloy are widely used in industry because of their good resistance to corrosion in cooling water systems, for shipboard condensers, power plant condensers, and petrochemical heat exchanger tubes, etc. Copper and its alloy are very interesting because of its great industrial importance.

The heavy loss of metal whenever in contact with acids can be minimized to a great extent by the use of corrosion inhibitors [1]. Most of the well known acid inhibitors are organic compounds containing hetero atoms such as nitrogen, sulphur, oxygen [2]. The organic compounds present in the inhibitor can adsorb on the metal surface, block the active sites and reduce the corrosion rate [3].

Many synthetic compounds offer good anti-corrosive action, but most of them risk being highly toxic to both humans and the environment. Presently, many researchers have reoriented their studies to the use of naturally occurring substances. Plant extracts and oils have become important as an environmentally acceptable, readily available, and renewable source of materials for a wide range of corrosion prevention studies. They are the rich sources of ingredients which have very high inhibition efficiency. Therefore the search for naturally occurring substances as corrosion inhibitor is a subject of great practical significance [4].

Many researchers have focused on natural products which are used as corrosion inhibitors for various metal and alloys in aggressive media [5]. Recently this kind of inhibitor has attracted more and more attention [6-13]. Despite the great availability and varieties of plant materials, only few herbal plants have been investigated. Our present attempt continues to focus on the broadening application of plant extracts for controlling metallic corrosion.

Jatropha curcas is a valuable multi-purpose crop to which can be used for bio-energy to replace fuels. It gives better results than gazoil because of its high oxygen content [14]. Bio-diesel produced from non crops like Jatropha is one of the most promising solutions for tackling the growing carbon emissions from Transport. The alcoholic leaf extract of *Jatropha curcas* used as a corrosion inhibitor on Brass in 1N Hydrochloric Acid and natural sea water environment is studied by mass loss method at various times and temperatures. The characterization of

corrosion product on Brass in the presence of inhibitor at both environments is also reported by UV and IR studies.

MATERIALS AND METHODS

Stock Solution of *Jatropha curcas* Extract

Jatropha curcas leaves were collected in and around the foothills of the Western Ghats area, shade dried, and ground well to powder form. Exactly 200g of dried powder with the required quantity of ethyl alcohol was added to cover the powder completely in a RB flask and left for 24 hrs. The resulting paste was refluxed for about 48 hrs and boiled with activated charcoal (about 1g) in order to remove hung and the pure plant extract was collected.

Specimen Preparation

Rectangular specimens of Brass were mechanically press cut to form different coupons, each of the exact dimensions 5.0x 2x 2.5 cm. The specimens were mechanically polished; a hole drilled at one end for free suspension, and numbered by punching. The specimens were degreased with acetone, washed with distilled water, well polished with emery paper, cleaned, rinsed, and dried then stored in desiccators for present study.

Mass Loss Method

In the mass loss measurements, Brass coupons, in triplicate, were completely immersed in 50 ml of the test solution of 1N HCl and natural sea water in the presence and absence of the inhibitor. The specimens were withdrawn from the test solutions after measured 24, 48, 72, 96, 120, 144, 168, and 288 hrs, at different temperatures such as 303 K and 333 K. The mass loss was taken as the difference in weight of the specimens before and after immersion determined 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.

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

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 3, respectively.

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

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

Where W_1 and W_2 are the corrosion rate in the absence and presence of the bio-inhibitor respectively.

RESULTS AND DISCUSSION

The Corrosion Behavior of Brass in Acid Environment

The corrosion parameters on Brass (Cu-40Zn) in 1N HCl containing various concentrations of *Jatropha Curcas* Leaves (JCL) extract at different times (24 to 288 hrs) and temperatures (303K and 333K) are shown in Figures 1 and 2, respectively. Figure 1 reflects that the surface coverage (θ) is increased with an increase of inhibitor concentration from 0 to 1000 ppm. The maximum of 94.73% inhibition efficiency is observed at higher concentrations of JCL extract and it is gradually decreased with increased exposure time. One fourth of the maximum inhibition efficiency is achieved even after 288 hrs exposure time.

Figure 2 represents that the surface coverage decreased with a rise in temperature. The maximum 83.33% and 66.66% of inhibition efficiency is attained at 30° and 60°, respectively. The reduction of inhibition efficiency with rise in temperature is suggested that the physical adsorption mechanism on the metal surfaces.
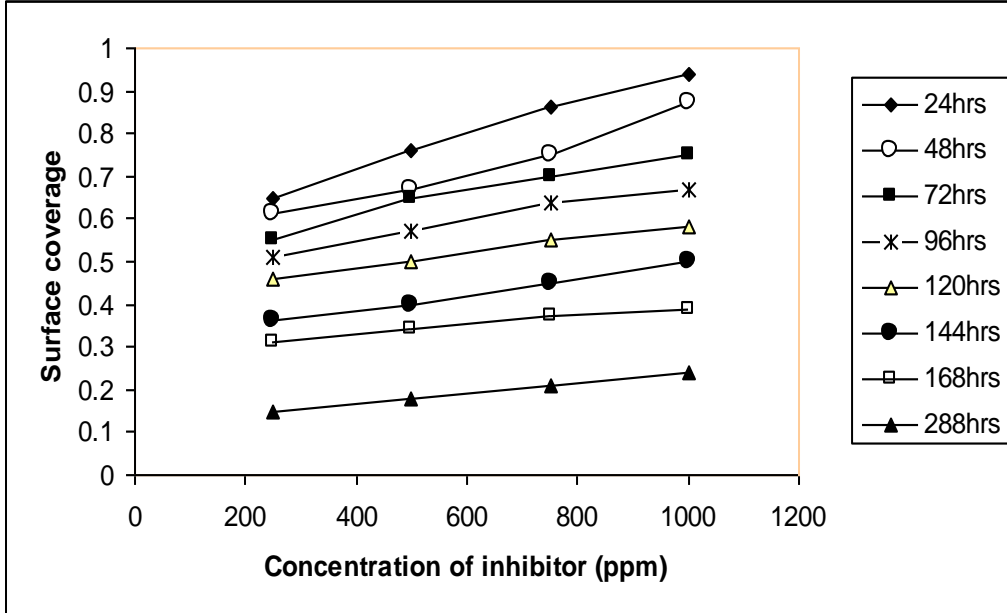
Figure 1: Corrosion Parameters of Brass Containing Various Concentrations of JCL extract at different Times in 1N HCl Environment.
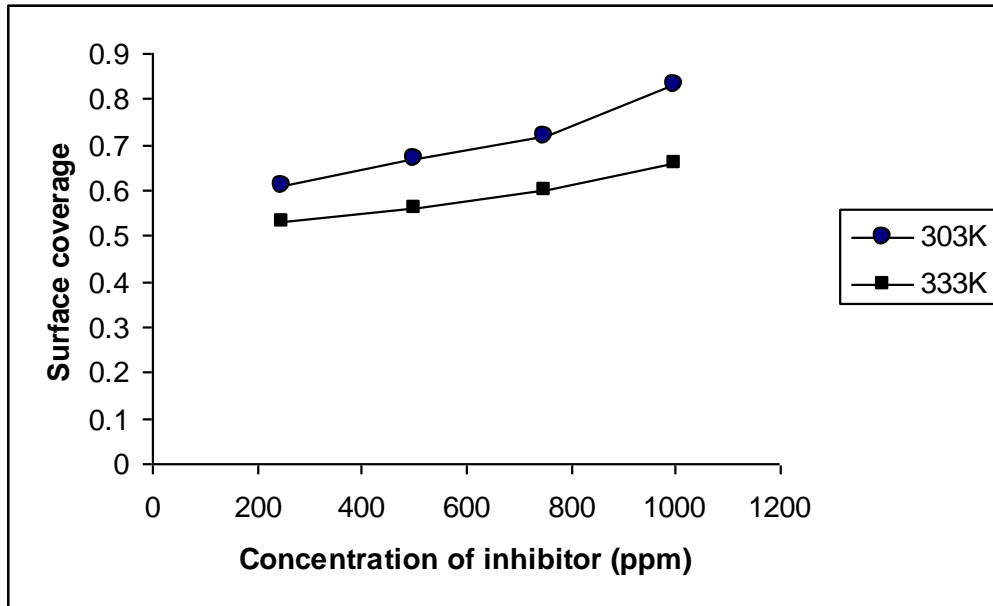

Figure 2: Corrosion Parameters of Brass Containing Various Concentrations of JCL extract at 303K and 333K in 1N HCl Environment.

The Dissolution Behavior of Brass in Natural Sea Water Environment

From Figures 3 and 4 we find the dissolution behavior on Brass (Cu-40Zn) in natural sea water containing various concentrations of JCL extract at different times and temperatures. The surface coverage is increased with increase of inhibitor concentrations and attained maximum of 96% of inhibition efficiency (Figure 3). The inhibition efficiency is decreased with a rise in temperature as in the case of acid environment.

In both environments the de-zincification of Brass in acid is comparatively higher than natural sea water. The maximum inhibition efficiency is attained due to the adsorption of phytochemical constituent (mainly diterpenoids Jatrophon, rare C-Glucosyl-flavonoids like isovitexin and vitexin [15], and HCN [16]) present in the JCL extract through hetero atom/ keto group/poly hydroxyl group in both acid and natural sea water environments.

The JCL extract is suitable inhibitor for Brass in both environments. However the higher inhibition efficiency is noticed in natural sea water than acid environment due to the presence of minerals and bio-living species in natural sea water. In both cases the percentage of inhibition efficiency is decreased with rise in temperature. This is indicate that at higher temperature there might be a desorption of active molecules present in the JCL extract from the Brass surface.

Effect of Temperature

The effect of temperature on the corrosion of Brass in the presence and absence of JCL extract was investigated using the Arrhenius equation [17].

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

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

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) to obtain the values of Activation energy (E_a). These values (Table 1) are ranged

from 19.383 to 33.671 KJ/mol, 19.385 to 45.011 KJ/mol for HCl and natural sea water environment indicating that JCL extract is adsorbed on the surface of Brass by physical adsorption. Also, the average value of E_a obtained from the blank was lower than values obtained for the systems containing various concentrations of JCL extract, suggesting that the extract retards the de-zincification of Brass in both sea water and hydrochloric acid environment.

Adsorption Considerations

The heat of adsorption on the surface of Brass in the presence of inhibitor in 1N HCl and Natural sea water environment is calculated by the following equation.

$$Q_{ads} = 2.303R\,[\log(\theta_2/1-\theta_2) - \log(\theta_1/1-\theta_1)]\;x\,(T_2T_1/T_2-T_1) \qquad \textbf{(6)}$$

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.

The calculated values of Q_{ads} are reported in Table 1. These values are ranged from -9.15 to -25.79 KJ/mol, - 4.93 to -34.48 for Brass in 1N HCl acid and natural sea water environment, respectively. The negative values are revealed that the adsorption of inhibitor on the surface of Brass is exothermic [18].

The observed data are tested graphically for fitting two isotherms like Langmuir and Frumkin on Brass surface in the presence of JCL inhibitor.

The Langmuir adsorption isotherm can be expressed by the following equation:

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

Here θ is the surface coverage, C is the concentration of the inhibitor and K is an adsorption coefficient. By plotting values of $\log C/\theta$ versus $\log C$, linear plots were generated (Figures 5 and 6) and conforming that the experimental data fitted with the Langmuir adsorption isotherm for the adsorption of JCL extract on Brass surface mean that there is no interaction between the adsorbed species (i.e; adsorbate and adsorbent) in both environment.
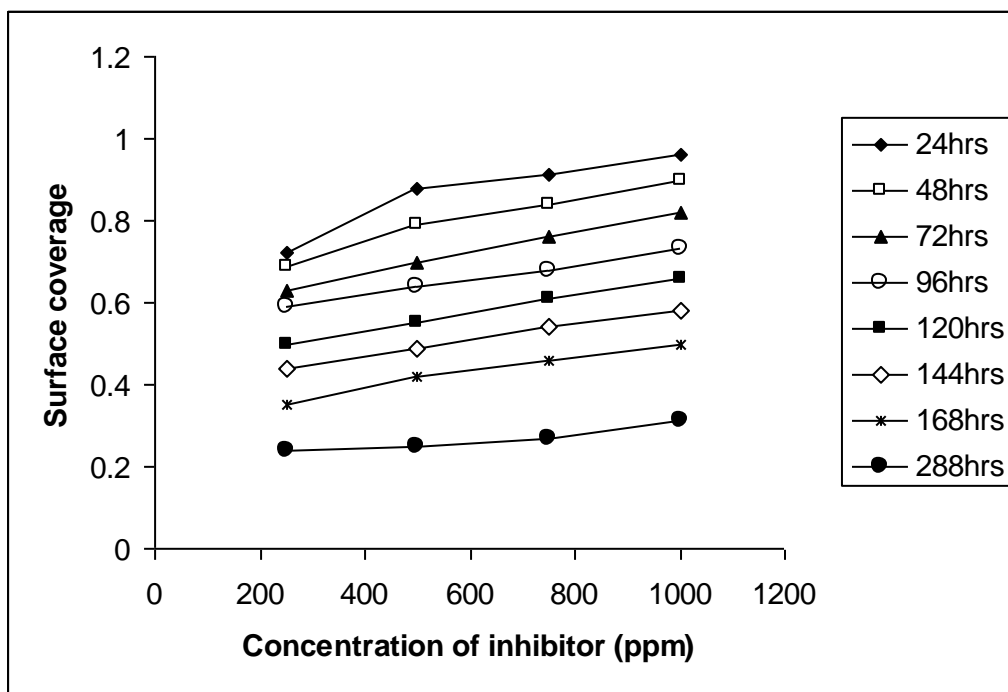
Figure 3: Corrosion Parameters of Brass Containing Various Concentrations of JCL Extract at Different Times in Natural Sea Water Environment.
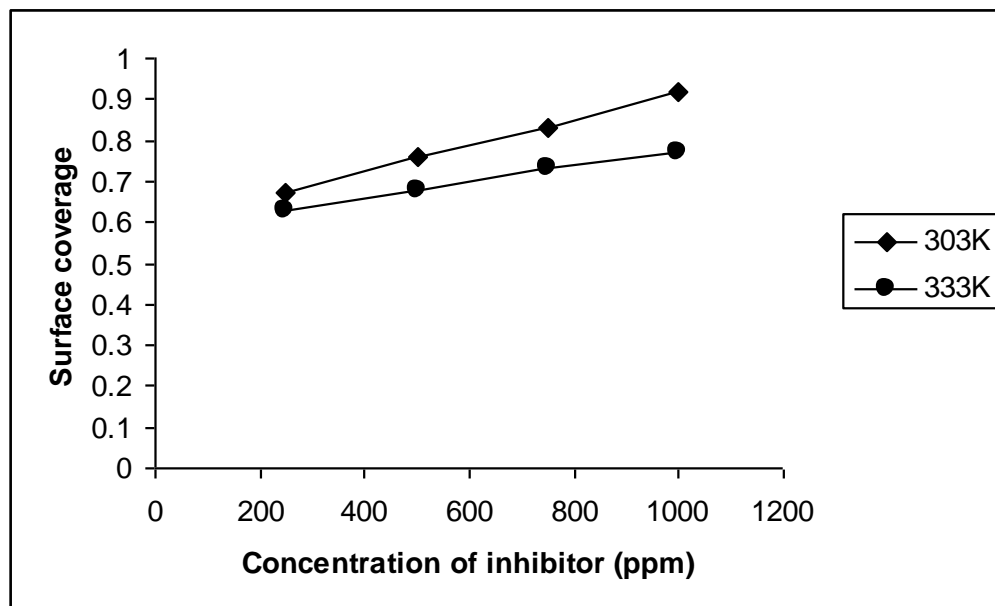

Figure 4: Corrosion Parameters of Brass Containing Various Concentrations of JCL Extract at 303K and 333K in Natural Sea Water.

Table 1: Calculated Values of Activation Energy (E_a) and Heat of Adsorption (Q_{ads}) of JCL Extract on Brass in 1N HCl and Natural Sea Water Environments.

S. No.	Concentration of inhibitor (ppm)	1N HCl		N. Sea Water	
		E_a (KJmol^{-1})	Q_{ads} (KJmol^{-1})	E_a (KJmol^{-1})	Q_{ads} (KJmol^{-1})
1.	Blank	14.283	---	16.954	---
2.	250	19.383	-09.15	19.385	-04.93
3.	500	21.623	-13.066	23.692	-11.15
4.	750	24.483	-15.074	30.725	-16.53
5.	1000	33.671	-25.795	45.011	-34.48
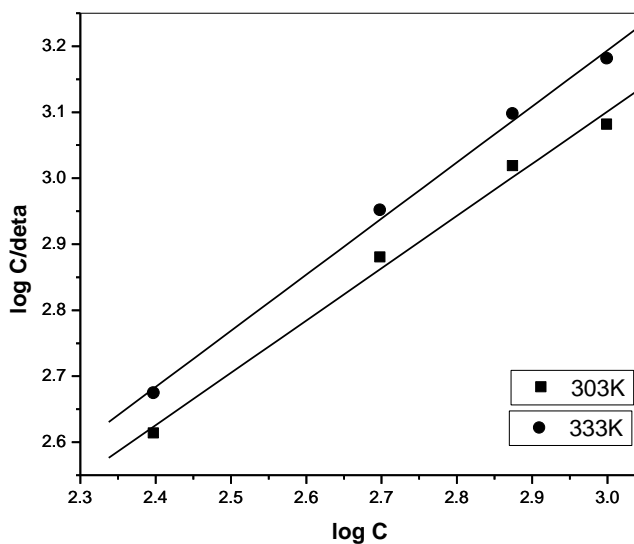
Figure 5: Langmuir Isotherm for Adsorption of JCL Extract on Brass in1N HCl Environment.
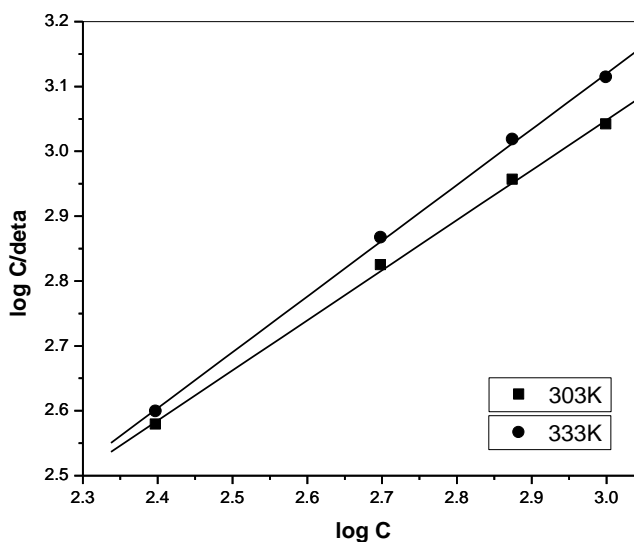

Figure 6: Langmuir Isotherm for Adsorption of JCL Extract on Brass in Natural Sea Water Environment.

The Frumkin adsorption isotherm can be expressed by using the equation:

$$\log\{[C](\theta/1-\theta)\}=2.303\log K+2\alpha\theta \qquad (8)$$

Where K is the adsorption-desorption equilibrium constant and α is the lateral interaction term describing the molecular interaction in adsorbed layer.

Figures 7 and 8 show the adsorption plots of JCL extract on Brass surface in IN HCl and natural sea water environments. From the observed results, the values of α are found to be positive indicating the attractive behavior of the inhibitor on the surface of the Brass [19].
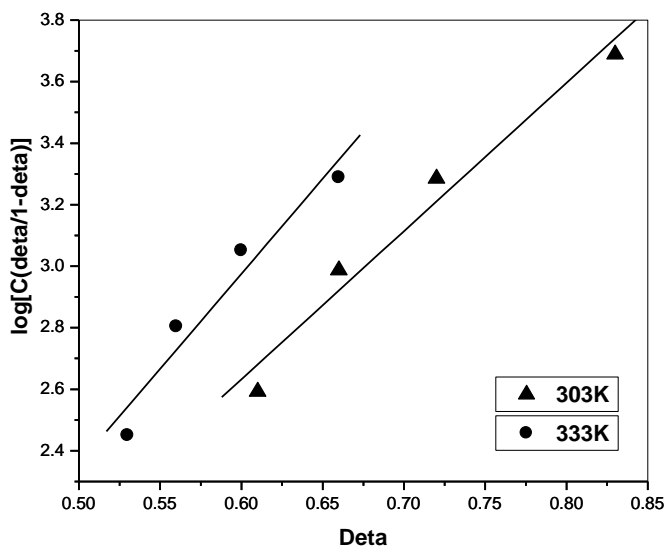

Figure 7: Frumkin Isotherm for Adsorption of JCL Extract on Brass in1N HCl Acid Environment.
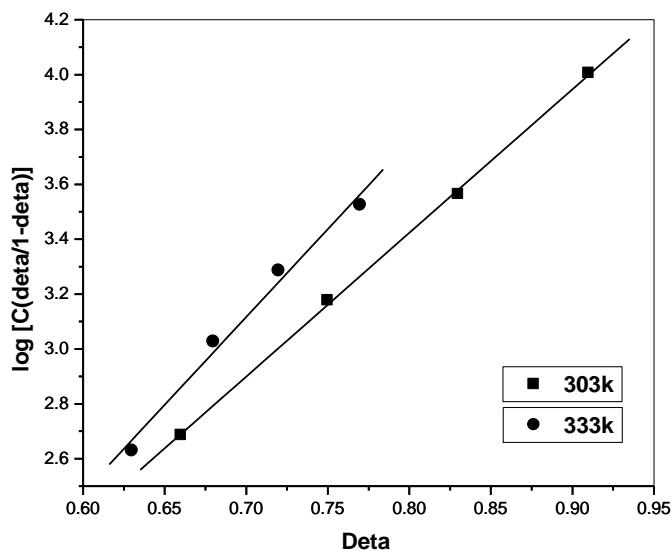

Figure 8: Frumkin Isotherm for Adsorption of JCL Extract on Brass in Natural Sea Water Environment.

The free energy of adsorption (ΔG_{ads}) of JCL extract on Brass in 1N HCl and natural sea water environment are calculated by using equation:

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

Where R is the gas constant, T is the temperature, K is the equilibrium constant of adsorption of JCL extract on the surface of Brass.

The values of K obtained from Langmuir and Frumkin adsorption isotherm are substituted into Equation 9 and the calculated values of ΔG_{ads} are recorded in Tables 2 and 3. The negative values indicate that the spontaneous adsorption of inhibitor on the surface of Brass [20].

UV Analysis

Figures 9 and 10 show that the UV visible spectrum of the corrosion product on the surface of Brass in the presence of JCL extract in acid and natural sea water environment. Comparing both spectra, two absorption bands around 270.50 nm and 360 nm have been noticed in acid and only one band, around 269 nm, is seen in natural sea water. These bands are assigned to π-π* transition and shifted to shorter wavelength region (i.e., Hypsochromic shift (or) Blue shift).

In the natural sea water environment, the second band is missing due to loss of their extended conjugation. These results reveal the coordination between the inhibitor and the metal ion in natural sea water and the acidic media. This may be conformed that the complex film formation between the Cu-Zn metal ions and the inhibitor.

Table 2: Langmuir and Femkin Adsorption Parameters for the Adsorption of JCL Extract on Brass in 1N HCl Environment.

Adsorption Isotherms	Temperature (Kelvin)	Slope	logK	R^2	ΔG_{ads} KJ/mol
Langmuir	303	0.7928	0.7231	0.9959	-23.05
	333	0.8506	0.6422	0.9983	-40.95
Temkin	303	4.8208	0.2604	0.9841	-08.30
	333	6.1786	0.7317	0.9691	-46.65

Table 3: Langmuir and Femkin Adsorption Parameters for the Adsorption of JCL Extract on Brass in Natural Sea Water Environment.

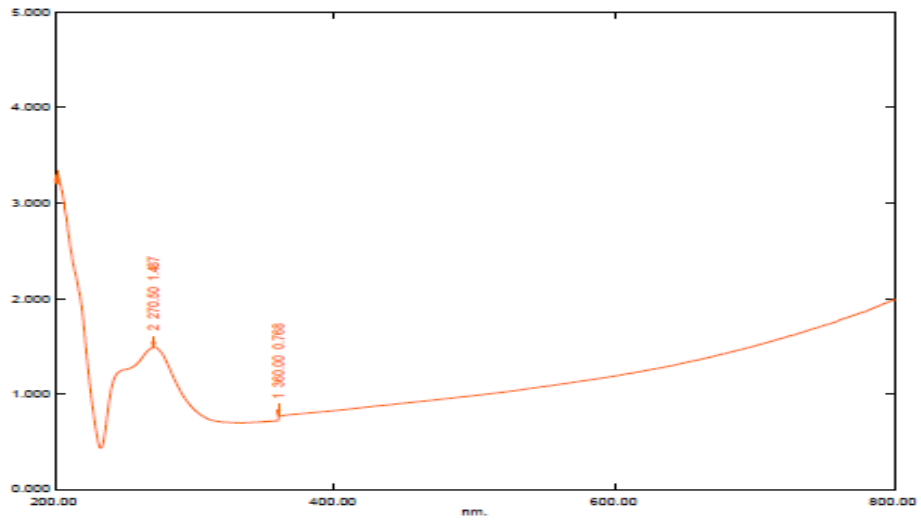| Adsorption Isotherms	Temperature (Kelvin)	Slope	logK	R^2	ΔG_{ads} KJ/mol
Langmuir	303	0.7724	0.7312	0.9993	-23.31
	333	0.8602	0.5396	0.9996	-34.41
Temkin	303	5.2350	0.7649	0.9997	-24.48
	333	6.4034	1.3660	0.9929	-87.10

Figure 9: UV Absorption Spectrum of the Corrosion Product on Brass in the Presence of JCL Extract in 1N HCl Acid Environment.
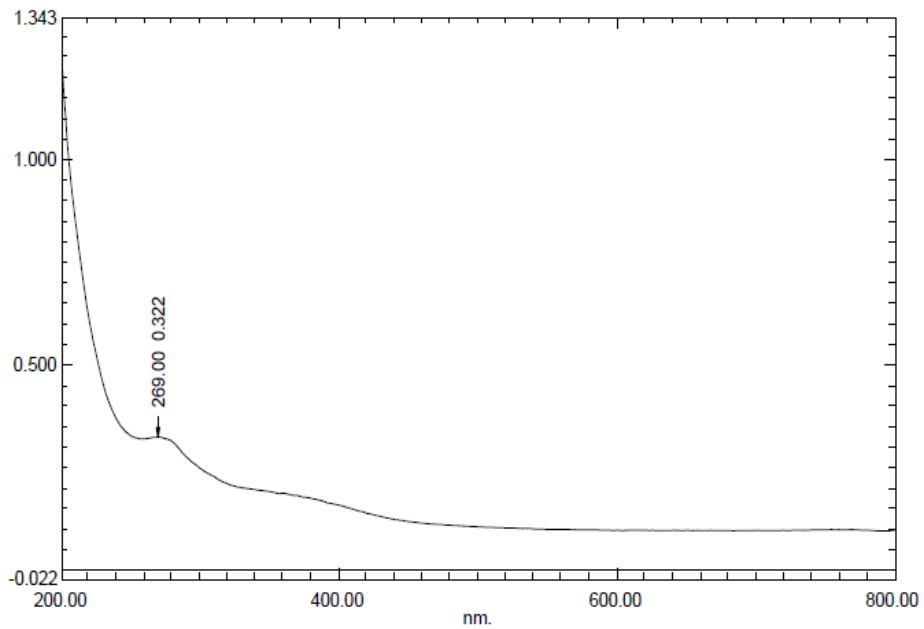

Figure 10: UV Absorption Spectrum of the Corrosion Product on Brass in the Presence of JCL Extract in Natural Sea Water Environment.

IR Analysis

Figures 11 and 12 reflect that the IR spectrum of the corrosion product on the Brass surface in the presence of JCL extract in acid and natural sea water environment. On comparing both spectra, a few peaks are missing in acid trace. We found that -OH stretching was shifted from 3300 to 3380 cm^{-1}, the –CH stretching frequency shifts from 2854.44 to 2923.87 cm^{-1}, and the –C = O stretching frequency shifts from 1658.62 to 1743.52 cm^{-1} in the acid environment.

In natural sea water, a broad –OH band occurs around 3410 cm^{-1}, a finger print region from 1882.39 to2036.68 cm^{-1}, the C=O band shifted from 1635 to 1720.38 cm^{-1}, and NH stretching occurs from 1018.34 to 1103.20 cm^{-1}, respectively. These results may also confirm the complex film formed on the anodic sites of the metal surface. The stretching frequency shifted from 1242.07 cm^{-1} to 1319 cm^{-1} is due to $Zn(OH)_2$ complex formed on the cathodic sites of the metal surface [21].
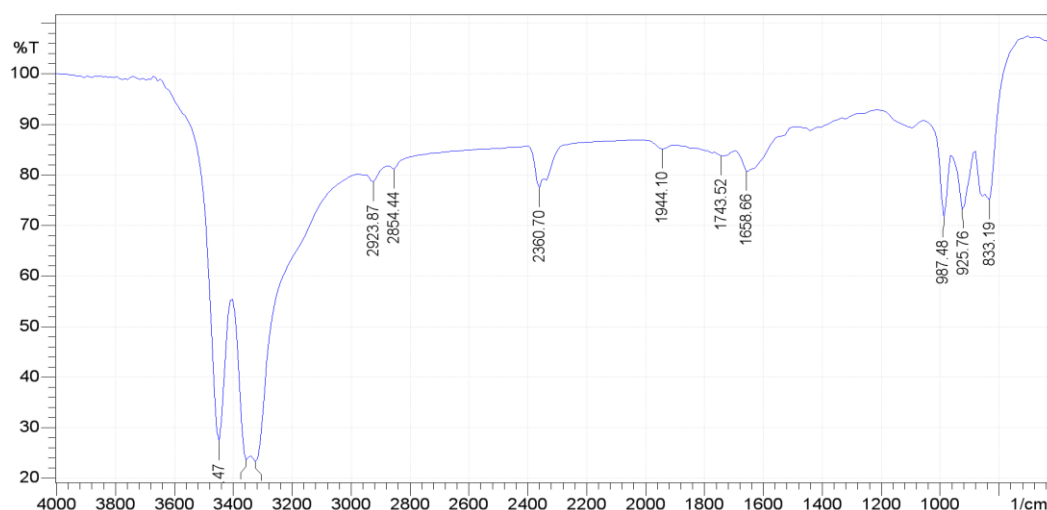

Figure 11: IR Spectrum of the Corrosion Product on Brass in the Presence of JCL Extract in 1N HCl Acid Environment.
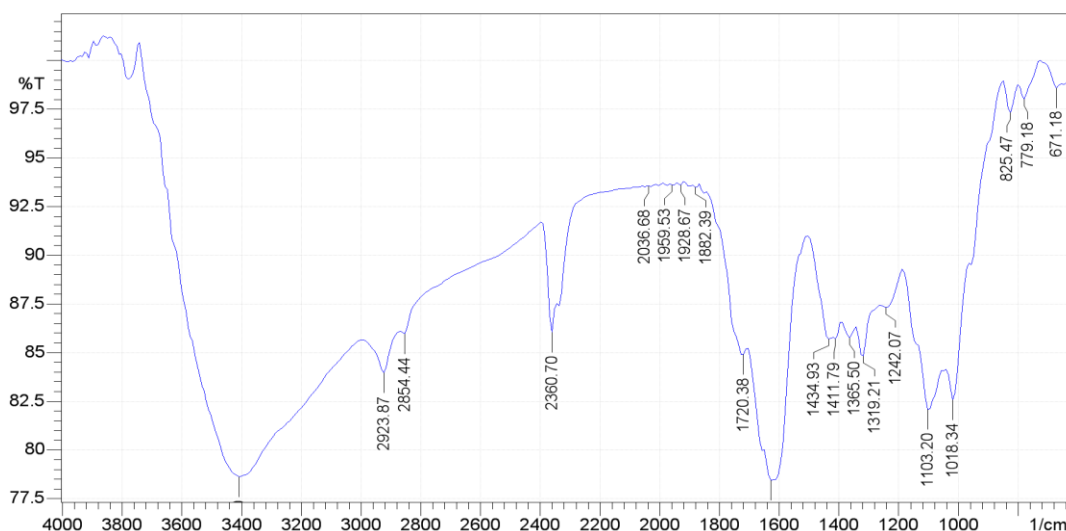

Figure 12: IR Spectrum of the Corrosion Product on Brass in the Presence of JCL Extract in Natural Sea Water Environment.

CONCLUSION

The following conclusions can be drawn from our present study:

- The JCL extract acts as an effective and efficient inhibitor for the dealloying process of Brass in both 1N HCl and natural sea water environments.

- The adsorption of the inhibitor is an exothermic and spontaneous process.

- The values of free energy suggested the physical adsorption of the inhibitor on the metal surface and it obeys Langmuir and Frumkin adsorption isotherms.

- The corrosion product over the surface of the Brass in the presence of JCL extract is characterized by UV and IR studies and may confirm that the complex film formed between the inhibitor and the metal ions.

- Inhibition efficiency of JCL extract in natural sea water is greater than in the acidic medium.

ACKNOWLEDGEMENT

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