Journal of Newviews in Engineering and Technology (JNET)
Vol 2, Issue 4, December 2020
Available online at http://www.rsujnet.org/index.php/publications/2020-edition

Thermodynamic and Adsorption Evaluation of Codiaeum Variegatum Brilliantissima - Zanzibar as Inhibitor of Mild Steel Corrosion in 1 M HCl

Izionworu, Vincent Onuegbu*[1]; Oguzie, Emmanuel Emeka [2] and Arukalam, Okechi Innocent[3]
1: Department of Chemical/Petrochemical Engineering
Rivers State University, Nkpolu-Oroworukwo, Port Harcourt, Nigeria
2: Center Leader of African Center of Excellence in Future Energies and Electrochemical Systems, Federal University of Technology, Owerri, Imo State, Nigeria.
3: Department of Polymer & Textile Engineering, Education & Training Coordinator, Africa Centre of Excellence in Future Energies and Electrochemical Systems, Federal University of Technology.
*Corresponding Author Email: vincent.izionworu@ust.edu.ng.

ABSTRACT:
This study evaluated the thermodynamic and adsorption properties of aqueous extract of Codiaeum Variegatum Brilliantissima - Zanzibar (Wire Croton) as an inhibitor of mild steel corrosion in 1 M HCl base stock solution using gravimetric measurement focused on the effect of immersion time, inhibitor concentration and temperature. The result showed that the adsorption of the cold aqueous extracts of Wire Croton on mild steel surface favored Langmuir adsorption isotherm as supported by an overall correlation coefficient (R^2) close to unity. The equilibrium constant of adsorption process (K_{ads}) for Wire Croton inhibitor evaluated mathematically is 0.0106, 0.0131, 0.1276, 0.1171 and 0.0269 (mg/L) with free energy of adsorption (ΔG^o_{ads}) values of 1.345, 0.821, -5.256, -5.182 and -1.445 kJ/mol for concentrations of 73.6, 147.2, 220.8, 294.4 and 368 mg/L exposed to 303, 313, 323, 333 and 343 K respectively. The small values of K_{ads} suggest weak adsorption which is corroborated by the low negative values of the free energy of adsorption, ΔG^o_{ads}, values obtained from thermodynamic measurements. The adsorption of Wire Croton inhibiting particles on the mild steel surface was favorable from thermodynamic point of view since values of ΔG^o_{ads} for more concentrations of the inhibitor were negative and provided proof that aqueous extract of the inhibitor is an efficient inhibitor.

KEYWORDS: Codiaeum Variegatum Brilliantissima – Zanzibar, Gravimetric, Adsorption, Adsorption Mechanism, HCl, Thermodynamic properties.

Cite This Article: Izionworu, V. O., Oguzie, E. E., & Arukalam, O. I. (2020). Thermodynamic and Adsorption Evaluation of Codiaeum Variegatum Brilliantissima - Zanzibar as Inhibitor of Mild Steel Corrosion in 1 M HCl. *Journal of Newviews in Engineering and Technology*. 2(4), 1 – 13.

1. INTRODUCTION:

Corrosion continuous to pose serious challenge to infrastructure causing loss in revenue (Izionworu *et al.*, 2021; NACE, 2016). The use of inorganic and organic inhibitors such as volatile inhibitors, Passivating inhibitors, Film inhibitors and Cathodic inhibitors has been welcomed in the past, particularly in the oil and gas field operations where they have yielded positive results in terms of reduced failure of installations and hence increased revenue. Although some level of successes has been recorded in the use of inorganic and organic inhibitors in corrosion control according to Chauhan *et al.* (2021), there are issues around their environmental suitability and health implications (Finsgar & Jackson, 2014; Umoren & Solomon, 2014).

These economic, health and environmental challenges gave rise to global search for cheap, convenient, safe and environmentally friendly corrosion inhibitors from natural organic substances that are usually biodegradable (Izionworu *et al.*, 2020a). Several research works have examined these alternative sources of corrosion inhibitor on carbon steel, mild steel and nickel sheets, while other studies have been performed on

Copyright © 2019 – 2020 JNET-RSU, All right reserved

aluminum sheets ((Jiyaul *et al.*, 2021; Amitha & Basu, 2011). Quite a few of these reported organic inhibitors have been developed by aqueous extraction with evaluation of their adsorption and thermodynamic properties. Researchers have proved that these properties are important in understanding the mechanism of inhibition of plant extracts (Izionworu *et al.*, 2020a; Izionworu *et al.*, 2020b; Manimegalai *et al.*, 2015; Alaneme *et al.*, 2015).

The investigation of Codiaeum variegatum Brilliantissima - Zanzibar (Wire Croton - WC), (CVB-WC) as a corrosion inhibitor with good efficiency is justified by the fact that CVB-WC like other plants contain phytochemical compounds that have similar molecular and electronic structures that look like the molecules of conventionally synthesized organic inhibitors (Izionworu *et al.*, 2021; Jiyaul *et al.*, 2021). This study therefore seeks to replace toxic inhibitors that cause harm to humans and the environment, provide low-cost bio-degradable, elucidate understanding in the use of CVB-WC as corrosion inhibitor with the required thermodynamic properties and demonstrate the possibility of production of inhibitors using minimal energy requirement.

2.0 MATERIALS AND METHODS

2.1 Plants

The leaves of the plant Codiaeum variegatum Brilliantissima - Zanzibar (Wire Croton - WC), (CVB-WC), were prepared and the extraction done as reported by Izionworu *et al.* (2021) following standard methods and as reported by Ambrish *et al.* (2010). The volume concentrations of the extract used were 73.6, 147.2, 220.8, 294.4 and 368 mg/L. All experiments were carried out at 27±1 ^{o}C and in aerated static solutions.
The concentration of the plant extract in the filtrate was determined following the method employed by Izionworu *et al.* (2020a).

2.2 Metal Steel Specimen and preparation

Mild steel specimen of density (7.86g/cm^3) with the percentage composition of C = 0.05%, Si = 0.03, Mn = 0.6, P = 0.35 and the remaining Fe was used. The mild steel metal for weight Loss analysis was mechanically press-cut to form coupons with dimension of 3cm x 3cm x 0.14cm. Each coupon was first scrubbed with emery paper (#200 to #1000), degreased with acetone and then dried with ethanol and stored in a desiccator before use (Izionworu *et al.*, 2020; Oguzie *et al.*, 2010; Arukalam *et al.*, 2016).

2.3 Reagents Used

33% Hydrochloric acid, 98% Ethanol and 98% Acetone, all of analytical grade, acquired from Sinopharm Chemical Reagent Co., Ltd were used without further purification and distilled water 1 M HCl base stock concentration used was prepared using standard acid dilution procedure.

2.4 Gravimetric Measurement

The gravimetric measurement was carried out using standard methods and as reported by Izionworu *et al.* (2020a) and Oguzie *et al.* (2010) to determine the corrosion rate (C_r), surface coverage (θ) and inhibition efficiency (IE%) at different temperatures of 303K, 313 K, 323 K, 333 K and 343 K using the equations (1), (2) and (3) respectively.

$$C_r(\mathrm{mmy^{-1}}) = \left({}^{87{,}600\Delta W}\!\big/_{\rho A t} \right) \qquad (1)$$

Where: ΔW is the average negative change in weight (g), ρ is the mild steel density (g/cm^3), A is the surface area of the coupon and t is the immersion time and 87,600 is the conversion constant from cm h^{-1} to mm y^{-1}.

$$\theta = \left(1 - \frac{C_r^{ihb}}{C_r^{blk}}\right) \qquad (2)$$

$$\text{IE\%} = \left(1 - \frac{C_r^{ihb}}{C_r^{blk}}\right) \text{ x } 100 \qquad (3)$$

Where Θ is the surface coverage, C_r^{blk} is the coupon corrosion rate in the blank corrodent solution, C_r^{ihb} is the rate of the coupon

Copyright © 2019 – 2020 JNET-RSU, All right reserved

corrosion in the presence of inhibitor in the corrodent solution. IE% is the inhibitor efficiency.

The temperature study was conducted in a thermostatic water bath that was maintained for temperature test at 313, 323, 333 and 343K. The weight loss measurement was done using Adam AAA 260LE analytical balance.

2.5 Determination of Adsorption Isotherm Model and Parameters for the Inhibitors

The weight loss data got from the temperature tests were fitted to Freundlich equation (4), Langmuir equation (5) and Temkin equation (6) by linear least-square methods using Origin 8.0 software to determine the model that gives the best description of the adsorption process of the plant extracts CVW-WC. This is in line with the reports of Izionworu *et al. (*2020a); Yadav *et al. (*2015); Amrita *et al.* (2015); and Wang *et al. (*2011).

$$\Theta = K_{ads} C_{inh} \qquad (4)$$

The Θ retains its meaning and is plotted against the concentration (C_{inh}) of the Plant extracts (inhibitor), where K_{ads} is the adsorption equilibrium constant showing the strength of adsorption – desorption process and got from the intercept of the plot.

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \qquad (5)$$

Where K_{ads}, Θ and C_{inh} retain their original meaning. C_{inh}/Θ is plotted against C_{inh} yielding straight line, and as the adsorption or desorption process equilibrium constant, a is the molecular interaction and C_{inh} represents the concentration of the crude extracts in this case volume percent of the corrodent (Yadav *et al.,* 2015). Following equation

$$\text{Exp}\ (-2a\Theta) = K_{ads} C_{inh} \qquad (6)$$

Where K_{ads} and C_{inh} retains their original meaning, and a is the molecular interaction. represents the concentration of the crude extracts in this case volume percent of the corrodent. Following equation (6), Θ was plotted against Log C_{inh}.

In all cases, a correlation coefficient (R^2) of unity or very close to unity is an indication that the Isotherm model best describes the nature of crude extract adsorption on the surface of the tested coupons.

K_{ads} values were equated to the standard free energy of adsorption, (ΔG^o_{ads}) (kJ.mol^{-1}) using expression of Equation (7) which gives the feasibility of the adsorption reaction following fundamental thermodynamic understanding (Izionworu *et al.*, 2020a; Solomon *et al.*, 2010; Wang *et al.*, 2011).

$$K_{ads} = {}^{1}/_{55} \exp\left({}^{-\Delta G^{o}{}_{ads}}/_{RT} \right) \qquad (7)$$

In the Equation (7), R is the gas constant (8.314 JK^{-1} mol^{-1}) and T retains its meaning as the absolute temperature, and the constant 55.5 is the concentration of water (mol.L^{-1}).

2.6 Determination of the Nature of the Adsorption – Physisorption and Chemisorption of CVB-WC

In order to determine the nature of the adsorption - physisorption, chemisorption or both, for the inhibitor CVB-WC the thermodynamic relationship of Equation (8) was used. This has been reported by Izionworu *et al. (*2020a), and Yadav *et al. (*2015):

$$\Delta G^0_{ads} = \Delta H^0_{ads} - T\Delta S^0_{ads} \qquad (8)$$

Where ΔG^0_{ads} is the standard representation of free energy of adsorption, ΔH^0_{ads} is the change in the adsorption standard enthalpy and ΔS^0_{ads} is the change in adsorption standard entropy, while T retains its usual meaning as temperature in K. ΔG^0_{ads} is plotted against T such that the intercept and slope of the resulting linear plot gives the values of ΔH^0_{ads} and ΔS^0_{ads} respectively.

2.7 Determination of Thermodynamic Activation Parameters of the Inhibitors

The thermodynamic properties of the activation adsorption parameters of corrosion processes of mild steel immersed in a corrodent solution of 1 M HCl in the presence and absence of CVB-WC was calculated using

Copyright © 2019 – 2020 JNET-RSU, All right reserved

weight loss data from experiments performed at an interval of 10 K from 303 – 343K after 3 hours of immersion. The apparent activation energies (E_a) (kcal.mol^{-1}) for the metal corrosion process in the corrodent system in the presence and absence of the inhibitor were evaluated from Arrhenius equation expressed as:

$$C_r = A \exp\left(-E_a/_{RT}\right) \qquad (9)$$

Equation (9) is further expressed as:

$$\log C_r = \frac{-E_a}{2.303RT} + \log A \qquad (10)$$

Where C_r , R and T retain their original meaning, A is the Arrhenius pre-exponential factor, Arrhenius plot of log C_r against 1/T for the corrosion of mild steel in 1 M HCl corrodent solution in the absence and presence of each inhibitor at different concentrations were plotted and the slope was identified while the activation energy (E_a) was got from the expression of Equation (11) also reported by Solomon *et al.* (2010); Amrita *et al.* (2015); and Yadav *et al.* (2015).

$$E_a = -\,(\text{slope}) \times 2.303R \qquad (11)$$

The standard enthalpy of activation (ΔH^o) and the standard entropy of activation (ΔS^o) were calculated from the transition state equation, Equation (12) was used. This expression has been used by Amrita *et al.* (2015); Yadav *et al.* (2015); and Solomon *et al.* (2010):

$$C_r = \frac{RT}{Nh} \exp\left(\frac{\Delta S^o}{R}\right) \exp\left(-\frac{\Delta H^o}{RT}\right) \qquad (12)$$

In equation (12), h is Plank's constant (6.62607004 x 10^{-34} m^{2}kgs^{-1}), N is the Avogadro number (6.022141 x 10^{23}) and all other terms retain their initial meaning.
The values of ΔH_a and ΔS_a were calculated respectively from the slope and intercept of the plot of $\log \mathrm{Cr}/T$ against $1/T$ such that:

$$\text{Slope} = -\Delta H^o/2.303\mathrm{R} \qquad (13)$$

$$\text{Intercept} = \log\left(\frac{\mathrm{R}}{\mathrm{Nh}}\right) + \Delta S^o/(2.303\mathrm{R}) \qquad (14)$$

3.0 RESULTS AND DISCUSSION

3.1 Effect of Temperature on the effectiveness of CVB-WC as an inhibitor

The result for C_r, *Ɵ* and IE% at diverse temperatures of 303K, 313K, 323K, 333K and 343K and different concentrations of CVB-WC calculated from the values of weight loss presented below graphically in Figures 1 and 2 represents the plots of the corrosion rate of the tested coupons in 1 M HCL corrodent with or without the inhibitor CVB-WC. The result obtained shows that the uninhibited (i.e., blank) corrodent had the highest corrosion rate as temperature increased from 303 to 343K, while there was an increase in corrosion rate for all inhibited corrodent solution containing different concentrations of the extract, the corrosion rates were minimal with a noticeable spike after 323 K and a lot more after 333 K.

The increase in the corrosion rate of the tested coupons in corrodent solutions with different concentrations of CVB-WC indicate a slight loss in inhibition at a high temperature of 343 K possibly due to changes like rapid etching, rupture desorption of the plant extract inhibitor, decomposition and possible rearrangement of the inhibitor taking place on the surface of the metal surface. These possibilities were corroborated as reported by Manimegalai and Manjula (2015). The possibility of decomposition of the extract particles at higher temperature suggests a physisorption, that is a physical adsorption of the particles to the metal surface (Olatunde *et al.*, 2020; Dauda *et al.*, 2013; Solomon *et al.*, 2010).

Copyright © 2019 – 2020 JNET-RSU, All right reserved

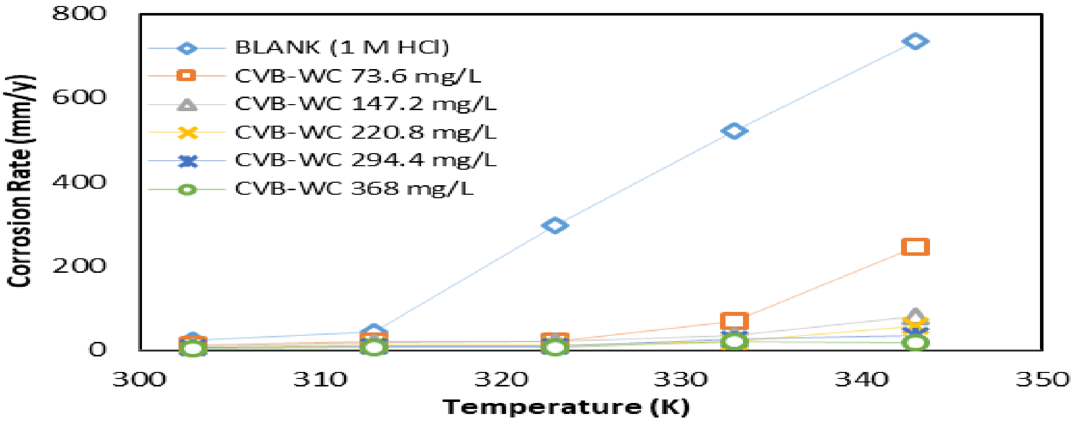

Figure 1: Plots of Corrosion Rate Against Temperature for Tested Coupons Corrosion in 1 M HCl solution With and without Different Concentrations of CVB-WC

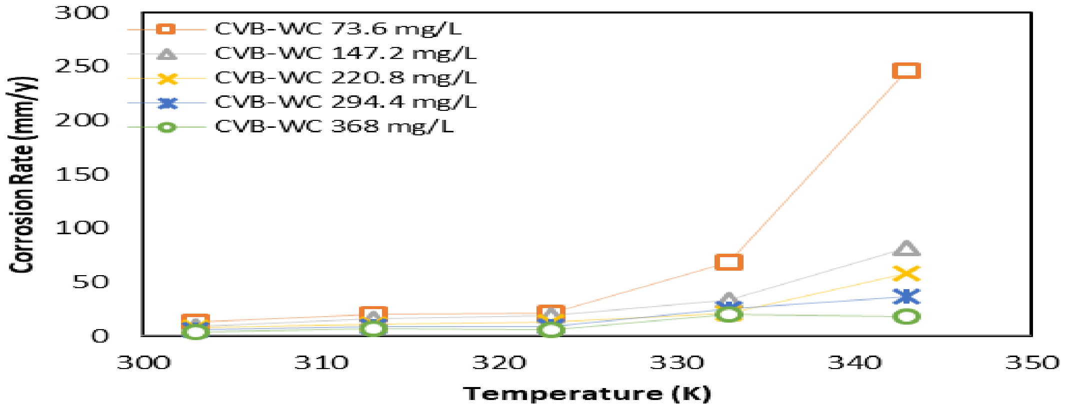

Figure 2: Plots of Corrosion Rate Against Temperature for Tested Coupons Corrosion in 1 M HCl solution With Different Concentrations of CVB-WC

The plots of Figure 3 present the values of IE% of the Tested Coupons in 1 M HCL corrodent with and without different concentrations of CVB-WC at 303, 313, 323, 333 and 343K from gravimetric measurement. From the table of results, it is seen that increase in concentration at 303 K resulted in increased inhibition efficiency by double the initial IE%. A similar trend is observed when the temperature was increased from 303 to 323K. However, at 333K the inhibition efficiency decreased slightly at 333K and more decrease at 343K for a corrodent with 73.60 mg/L of CVB-WC. A similar pattern is observed for other concentrations as the temperatures increased. It is likely that rise in temperature resulted in degradation of the active components of the CVB-WC inhibitor leading to reduced coverage of available active sites. The plots of Figure 3 show that as the concentration of CVB-WC increased the IE% also increased.

Copyright © 2019 – 2020 JNET-RSU, All right reserved

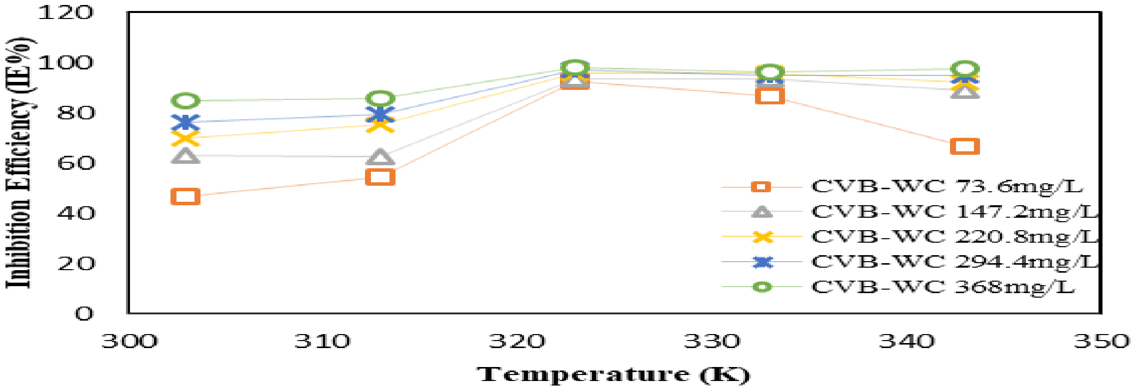

Figure 3: Plots of Inhibition Efficiency Against Temperature for the Tested Coupons Corrosion in 1 M HCl Solution in the presence of Varied Concentrations of CVB-WC

Also, it is obvious the IE% increased for all concentrations of CVB-WC as the temperature increased slightly above room temperature and they seem to converge at a temperature of 323 K and dropped in value as the temperature increased beyond 323 K and up to 333 and 343 K. The initial rise in IE% can be said to be due to the adsorption of the particles of the inhibitor at moderate temperature coupled with a larger number of surface area covered as the concentration improved. The nature of the adsorption of CVB-WC inhibitor is determined by the thermodynamic parameters analyzed in the next section. However, the IE% of the inhibitor reduced as the temperature increased because of the shift in the equilibrium constant towards the desorption of the particles on the Mild Steel surface (Singh *et al*., 2010; Yadav *et al*., 2015).

3.2 Adsorption Isotherm for CVB-WC

The experimental data fitted into different theoretical adsorption isotherms namely Langmuir, Temkin and Freundlich isotherms models and the result were most suitable for Langmuir isotherm given that the correlation coefficient (R^2) and slope value resulting from the Langmuir isotherm plots of are either unity or close to unity as seen in Table 1. This establishes that the inhibitor CVB-WC adsorbed on the mild steel surface following the Langmuir Isotherm model and fitted quite well at temperatures of 303 to 343 K and indicate that a particle of CVB-WC gets adsorbed on an active site of the mild steel surface forming a protective film on the surface of the metal thereby preventing the transfer of the mass and charge of the mild steel (Arukalam *et al.*, 2016; Felip *et al.*, 2013).

The equilibrium constant of adsorption process (K_{ads}) evaluated mathematically from the plot of Figure 4 and the resulting intercept values and ΔG^o_{ads} values calculated from the mathematical relationship of equation 8 are presented in Table 1. The slight decrease in negativity of ΔG^o_{ads} as temperature increased suggest that adsorption of the particles of CVB-WC on the metal surface is not sustained at high temperature suggesting that the adsorption process is physisorption in nature as described by Olatunde *et al.* (2020); Ashassi-Sorkhabi *et al.* (2008); and Farag *et al.* (2015). This is supported by Wang *et al.* (2011); and Yadav *et al.* (2015). It is known that when ΔG^o_{ads} value is up to – 20 kJmol^{-1}, then the inhibitor is adsorbed on the metal surface by means of physisorption while negative values more than – 40 kJmol^{-1} involve chemisorption process involving

Copyright © 2019 – 2020 JNET-RSU, All right reserved

coordinate bonding of the inhibitor molecules. In this case CVB-WC adsorption on the mild steel surface is a physisorption process.

The values of the enthalpy (ΔH^o_{ads}) and entropy (ΔS^o_{ads}) changes for adsorption of CVB-WC provides further insight into its nature of adsorption on the mild steel surface. Using the basic thermodynamic equation expressed in equation 9 and plotting ΔG^o_{ads} verses temperature (T) in kelvin (K) as seen in Figure 5. The calculated values of the standard enthalpy (ΔH^o_{ads}) and entropy (ΔS^o_{ads}) change calculated from the intercept and slope respectively for CVB-WC are as seen in Table 1. The positive ΔH^o_{ads} value implies that the adsorption of the inhibitor particles is an endothermic process. It has been reported that endothermic process where $\Delta H^o_{ads} > 0$, is partly due to chemisorption process while $\Delta H^o_{ads} < 0$, is exothermic adsorption process, which can either be Physisorption, chemisorption or a mixture of both Physisorption and chemisorption (Izionworu *et al.*, 2020a; Yadav *et al.*, 2015). As seen earlier the distinction between physisorption and chemisorption in an exothermic condition is the values of ΔH^o_{ads}. Absolute values of ΔH^o_{ads} lower than 40 kJ/mol indicates a physisorption process, whereas an absolute ΔH^o_{ads} value that approaches 100 kJ/mol is chemisorption. It can be deduced that the inhibitor CVB-WC gets adsorbed on the metal surface by physisorption. The negative value of ΔS^o_{ads} suggests that the particles CVB-WC before adsorption on the Tested Coupons surface moved freely in the bulk solution and then settled and got adsorbed on the metal coupons resulting into a negative entropy.

Table 1: Adsorption Parameters for CVB-WC Adsorption on Tested Coupons in 1 M HCL Solution at a Temperature range of 303-343 K.

(K)	Intercept	Slope	R^2	K_{ads}	ΔG^o_{ads} (kJ/mol)	ΔH^o_{ads} (kJ/mol)	ΔS^o_{ads} (J/mol/K)
303	94.6783	0.9539	0.98834	0.0106	1.345	35.474	-115.843
313	76.0868	0.9816	0.98771	0.0131	0.821		
323	7.8403	1.0023	0.99964	0.1276	-5.256		
333	8.5392	1.0156	0.99966	0.1171	-5.182		
343	37.1833	0.9209	0.99748	0.0269	-1.445		

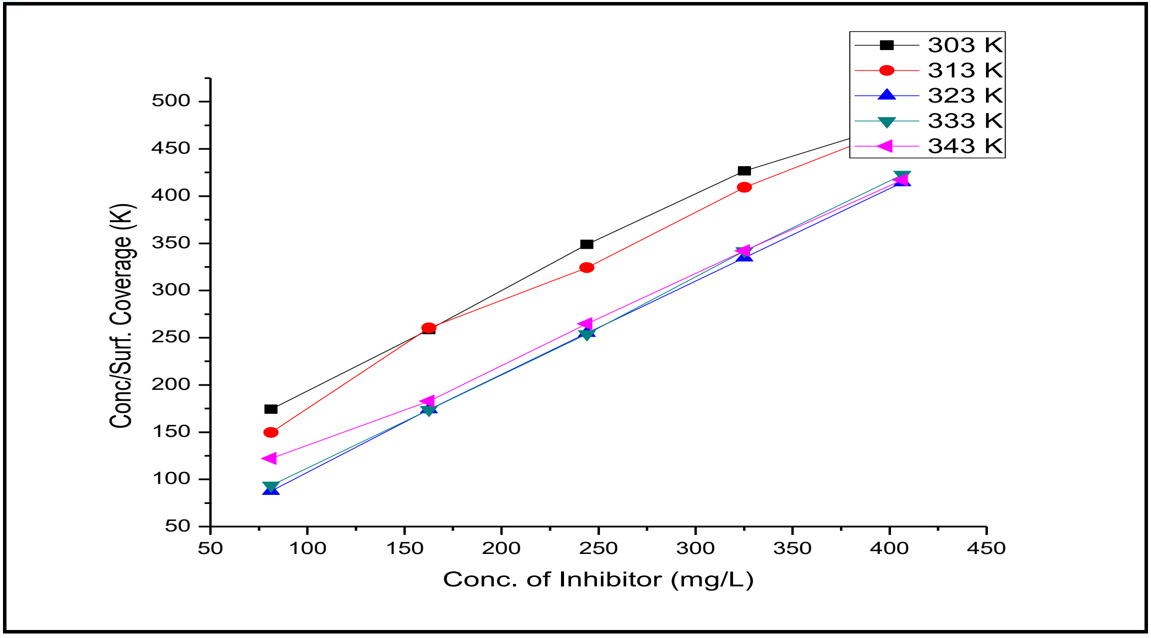

Figure 4: Langmuir Adsorption Isotherm of CVB-WC Extract on Tested Coupons Surface in 1 M HCL Solution at Different Temperature.

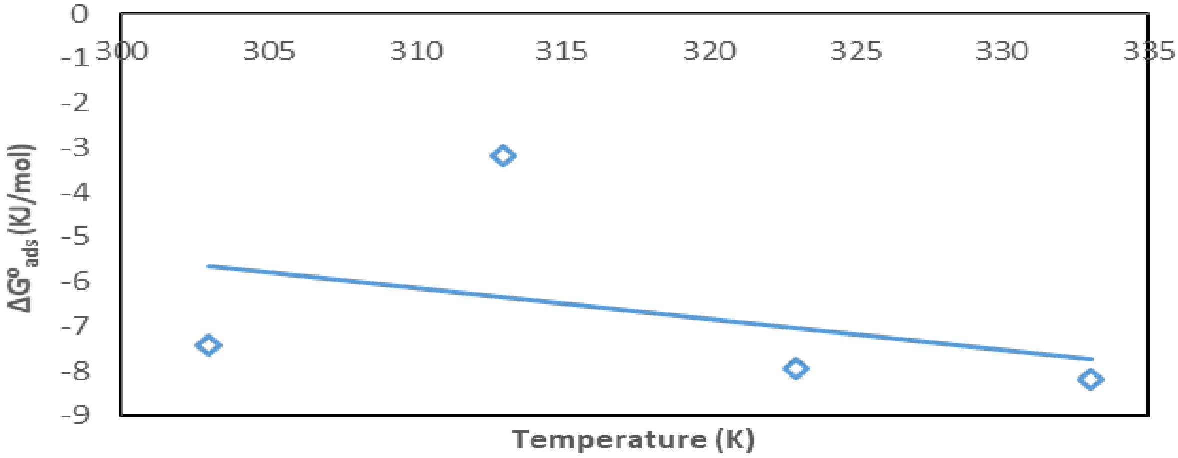

Figure 5: The Relationship Between Free Energy of Adsorbtion for CVB-WC and Temperature

3.3 Apparent Activation and Activation Thermodynamic Parameters of CVB-WC

While the result of apparent activation energy (E_a) calculated from Arrhenius equation of equations 9, 10 and 11 and the resulting Arrhenius plots of Figure 6 at a temperature range of 303 – 343 K in 1 M HCl corrodent solution with CVB-WC are reported in Table 2, the results show that the activation energy for the inhibited solution is lower than the blank's, uninhibited solution implying that a predominant chemisorption adsorption especially at higher temperature. The thermodynamic activation parameters namely – standard enthalpy of activation (ΔH^o) and standard entropy of activation (ΔS^o) of the corrosion process of the Tested Coupons in 1 M HCl solution using weight loss measurement in the absence and presence of CVB-WC at a temperature range of 393 to 343 K computed from the transition state equation, equation 12 and the slope and intercept got from equations 13 and 14 respectively from the transition state plots of Figure 7 for the Tested mild steel coupons in 1 M HCl

Solution with and without CVB—WC are presented in Table 2.

As expected from the concept of transition - state theory the values of ΔH° for concentration of CVB-WC and the corresponding values of E_a are close to each other. The positive value of ΔS° for the inhibitor suggest an activated complex that is a rate determining step and represents a dissociation step, this means that there is rise in disorder during the process of transition from transition state to activated complex state, this is understandable as the inhibitor was extracted using water and used in that state (Yadav *et al.*, 2015; Akalezi *et al.*, 2016). Also, the entropy reduced as the concentration of CVB-WC increased, this is likely because of the increase in "Partico-Molecule" interaction which increased their adsorption on the active sites of the mild steel.

Table 2: Thermodynamic Parameters for Tested Coupons in 1 M HCl Solution with and without CVB-WC Inhibitor Obtained from Weight Loss Measurement.

Inhibitor	Conc. (mg/L)	(Ea) ($kJmol^{-1}$)	ΔH° (kJ/mol)	ΔS° (J/mol/K)
Blank	-	81.1301	78.45	423.42
CVB-WC	73. 6	61.0941	58.42	349.33
	147.2	44.3048	41.63	293.13
	220.8	41.1708	38.49	280.32
	294.4	40.6691	37.99	276.93
	368	38.1244	35.45	265.46

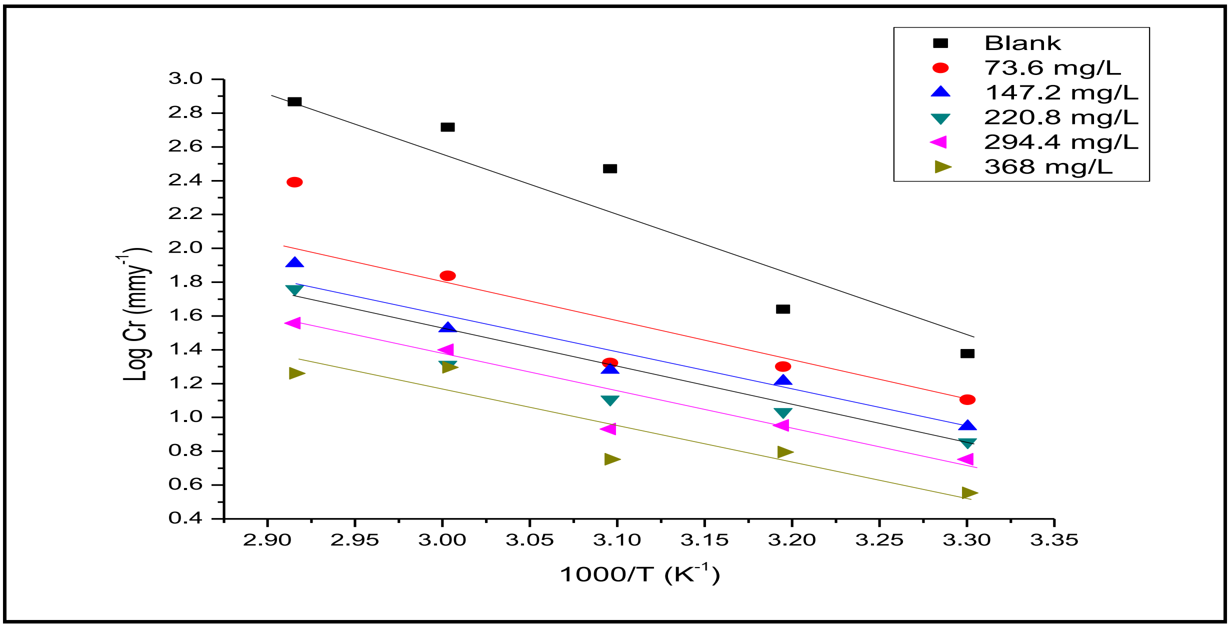

Figure 6: Arrhenius Plots of log Cr Verses 1000/T for Mild Steel Corrosion in 1 M HCl Solution with and without CVB-WC

Copyright © 2019 – 2020 JNET-RSU, All right reserved

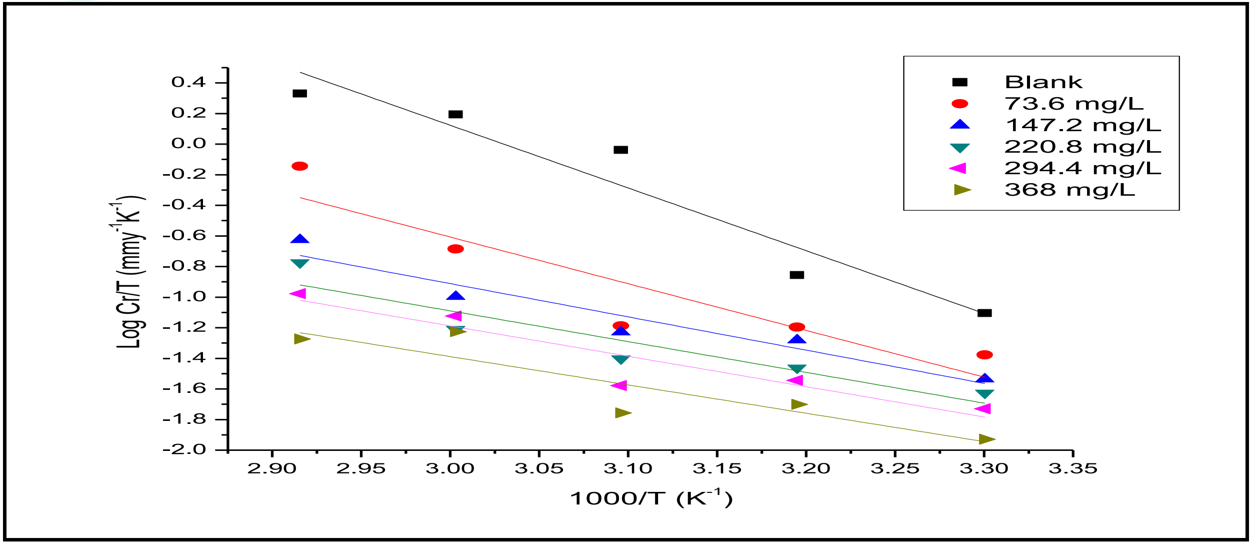

Figure 7: Transition State Plot of Log Cr/T Versus 1000/T for the Tested Coupons in 1 M HCl Solution with and without CVB—WC

3.4 Proposed Mechanism of Adsorption for CVB-WC,

The mechanism of inhibitor action on inhibition of mild steel corrosion in hydrochloric acid environment is basically what can be referred to as a "Partico-molecular" adsorption process since there are nano particles and molecules of the phytochemical compounds of the inhibitor. The negative values of the free energy of adsorption in the tested cold aqueous extract of CVB-WC indicate that the adsorption reaction is chemically feasible hence the inhibitor under evaluation inhibits the corrosion of mild steel in HCl environment by one or all of the following precepts: Mild steel in HCl environment results in a charged mild steel surface with empty d-orbitals.

Inhibitor particles containing– phytate, phenyl ring, aromatics such as alkaloid, tannin, flavonoid compounds reported in the FT-IR and GC-MS characterization with heteroatoms (N, O, P and possibly S), that have lone pair electrons get easily protonated in HCl media and ready to bond with the metal (Izionworu *et al.*, 2021). There are also delocalized π electrons on the double bonds of phenyl ring, phytate and aromatic compounds present in CVB-WC available for chemical bonding. The inhibitors also have neutral molecules.

The mechanism of adsorption of the tested inhibitors based on thermodynamic understanding follows one or more of the following paths which have been corroborated by Oguzie *et al.* (2007); Yadev *et al.* (2015); and Wang *et al.* (2011):

(i) Electrostatic (physical) attraction occurs between the charged inhibitor "portico-molecules" and charged d orbital of the mild steel surface. These particles lose their adsorption strength on the mild steel surface under elevated temperature as some are likely denatured losing their bonding energies. The increase in temperature also affects the interaction between the lone pair electrons of the heteroatoms (N, O), delocalized π electrons present in the inhibitor and already charged mild steel surface.

(ii) The inhibitor's lone pair electron resulting from heteroatoms N, O, P, and free delocalized π electrons in the double bonds of the phenyl ring and aromatics get adsorbed on the mild steel surface through chemical (chemisorption) reaction preventing corrosion. Again, increase in temperature and the aqueous nature of the extracts affect their consistent adsorption and partly affects the mechanism of the Anodic and cathodic reactions described in previous reports (Izionworu *et al.,* 2021).

Increase in temperature likely affects the compactly or loosely packed double layer of Chloride ion + CVB-WC formed by the charge density on the vacant d-orbitals of an iron atom that has chloride ions which attract protonated molecules of the inhibitors (Amitha-Rani & Basu, 2012).

There is also synergy of the nano "portico-molecules".

4.0 CONCLUSION

Codiaeum Variegatum Brilliantissima – Zanzibar (CVB-WC) was found to be an inhibitor for the corrosion of mild steel in base stock solution of 1 M HCl. The thermodynamic property evaluation shows that CVB-WC is concentration and temperature dependent. As a function of time of immersion, the inhibition efficiency did not show significant difference under the experimental condition implying that particles of aqueous extracts of CVB-WC formed a stable film on the metal surface at lower temperature of immersion with a possible degradation of the particles of the crude extracts as the temperature increased.

The study also revealed that the adsorption of the cold extracts of CVB-WC on mild steel surface obeyed Langmuir adsorption isotherm. With a correlation coefficient that is close to unity.

The values of inhibition efficiency of CVB-WC calculated from weight loss and potentiodynamic polarization curves reported by Izionworu *et al.* (2021) are in agreement that the inhibitors get adsorbed through physisorption and chemisorption processes. The report supports the findings in this study that cold water extract of CVB-WC act as both cathodic and anodic inhibitor hence they behave mostly as mixed-type inhibitor in hydrochloric acid. The activation energy, standard enthalpy and entropy of activation for the inhibition process indicate that the adsorption process in all cases were thermodynamically feasible.

REFERENCES

Alaneme, K. K., Olusegun, S. J., & Adelowo, O.T. (2015). Corrosion Inhibition and Adsorption Mechanism Studies of Hunteria Umbellata Seed Husk Extract on Mild Steel Immersed in Acidic Solutions. *Alexandria Engineering Journal.* 10, 45–51.

Amrita, B., Sagar, P., & Udayabhanu, G. (2015). Experimental and Theoretical Studies of Xanthan Gum and its Graft Co-Polymer as Corrosion Inhibitor for Mild Steel in 15% HCl. *Applied Surface Science* 353, 173-183.

Amitha-Rani, B. E., & Basu, J. B. B. (2011). Green Inhibitors for Corrosion Protection of Metals and Alloys: An Overview, *International Journal of Corrosion*, 2012, 1-15.

Arukalam, I. O., Ogbobe, O., Madufor, I. C., & Oguzie, E. (2016). Understanding the Influence of Molecular Weight on the Corrosion Inhibition Performance of Two Cellulosic Polymers. *American Chemical Science Journal*, 10(4), 1-14.

Ashassi-Sorkhabi, H., Seifzadeh, D., & Hosseini, M. G. (2008). EN EIS and Polarization Studies to Evaluate the Inhibition Effect of 3H-Phenothiazin-3-one, 7-Dimethylamin on Mild Steel Corrosion in 1 M HCl solution. *Corrosion Science*, 50, 3363-3370.

Chauhan, D. S., Quraishi, M.A., Wan-Nik, W.B., (2021). Vandana Srivastava, Triazines as a Potential Class of Corrosion Inhibitors: Present Scenario, Challenges and Future Perspectives. *Journal of Molecular Liquids*. 321, 1-19

Dauda, K.T., Atasie, V.N., Adetimilehin, A.A. (2013). Kinetics of the Inhibitory Effects of Ethanolic Extract of Vernonia Amydgalina on the Corrosion of Aluminium in 1.0 M HCl, *Chemother. Journal*. 3, 86–89.

Copyright © 2019 – 2020 JNET-RSU, All right reserved

Farag, A. A., Ismail, A. S., & Migahed, M. A. (2015). Inhibition of Carbon Steel Corrosion in Acidic Solution Using Some Newly Polyester Derivative. *Journal of Molecular Liquids* 211, 915-923

Felipe, M. B. M. C., Silva, D.R., Martinez-Huitle, C.A., Medeiros, S. R. B., & Maciel, M. A. M. (2013). Effectiveness of Croton Cajucara Benth on Corrosion Inhibition of Carbon Steel in Saline Medium. *Materials and Corrosion*, 64 (6), 530-534.

Finsgar, M., & Jackson, J. (2014) Application of Corrosion Inhibitors for Steels in Acidic Media for the Oil and Gas Industry: A Review. *Corrosion Science*, 86, 17-41.

Izionworu, V. O., Ukpaka, C. P., & Oguzie, E. E. (2020a). Inhibition of Mild Steel Corrosion in Acidic Medium Using Theobroma Cacao Pod. *International Journal of Scientific & Engineering Research*, 11(3), 255-265.

Izionworu, V. O., Oguzie, E. E., & Amadi, S. A. (2020b) Electrochemical, Sem, GC-MS and Ftir Study of Inhibitory Property of Cold Extract of Theobroma Cacao Pods for Mild Steel Corrosion in Hydrochloric Acid. *International Journal of Engineering Trends and Technology (IJETT),* 68 (2) 82-87.

Izionworu, V. O., Puyate, Y. T., & Wan-Nik, W. B. (2021). A Study of Wire Croton as An Inhibitor of Mild Steel in HCl Using Electrochemical – SEM – Gas Chromatography Mass Spectrometry and FTIR Measurements. (Unpublished report). *Journal of Newviews in Engineering and Technologies*. 3(1), 1-10.

Jiyaul, H., Chandrabhan, V., Vandana, S., & Wan-Nik, W. B. (2021). Corrosion Inhibition of Mild Steel in 1M HCl Using Environmentally Benign Thevetia Peruviana Flower Extracts. *Sustainable Chemistry and Pharmacy*.19, 1-13.

Manimegalai, S., & Manjula, P. (2015). Thermodynamic and Adsorption Studies for Corrosion Inhibition of Mild Steel in Aqueous Media by Sargasam Swartzii (Brown Algae). *Journal of Material and Environmental Science*. 6(6), 1629-1637.

National Association of Corrosion Engineers, (2016). International Measures of Prevention, Application and Economics of Corrosion Technology (IMPACT). http://impact.nace.org/documents/Nace-International-Report.pdf

Oguzie, E. E., Li, Y., & Wang, F. H. (2007). Corrosion Inhibition and Adsorption Behaviour of Methionine on Mild Steel in Sulphuric Acid and Synergistic Effect of Iodide Ion. *Journal of Colloid Interface Science,* 310, 90-98.

Oguzie, E. E., Enenebeaku, C. K., Akalezi, C. O., Okoro, S. C., Ayuk, A. A., & Ejike, E. N. (2010). Adsorption and Corrosion Inhibiting Effect of Dacryodis Edulis Extract on Low Carbon Steel Corrosion in Acidic Media. *Journal of Colloid Interface Science, 349*, 283-292.

Olatunde A. A., Oludare, J. O., Ebenezer, L. O. (2020). Thermodynamics and Adsorption Study of the Corrosion Inhibition of Mild Steel by Euphorbia Heterophylla L. Extract in 1.5 M HCl. *Results in Materials Elsevier*, 3, 1-7.

Pedroza-Perinan, D. E., Villalobos-Vasquez, M. A., Meza-Castellar, R. J., & Paz-Astudillo, I. C. (2016). Evaluation of Theobroma Cacao Pod Husk EXTRACTS as Corrosion Inhibitor for Carbon Steel. *CT&F – Ciecia, Tecnologia y Futuro*, 6(3), 147-156.

Saedah, R. A. (2013). Inhibition of Mild Steel Corrosion Using Juniperus Plants as Green Inhibitor. *African Journal of pure and applied Chemistry*. 8(1), 9-22.

Singh, A., Ahamad, I., Singh, V. K.,

Copyright © 2019 – 2020 JNET-RSU, All right reserved

Quraishi, M. A., & Quraishi (2010). Inhibition Effect of Environmentally Benign Karanj (Pongamia pinnata) Seed Extract on Corrosion of Mild Steel in Hydrochloric Acid Solution. *Journal of Solid-State Electrochemistry,* 15, 1087-1097.

Solomon, M. M., Umoren, S. A., Udosoro, I. I., & Udoh, A. P. (2010). Inhibitive and Adsorption Behavior of Carboxymethyl Cellulose on Mild Steel Corrosion in Sulphuric Acid Solution. *Corrosion Science Elsevier,* 52, 1317-1325.

Umoren, S. A., & Solomon, M. M. (2014). Recent Developments on Use of Polymers as Corrosion Inhibitors – A Review. *The open material science journal*, 8, 39-54.

Wang, X., Yang, H., & Wang, F. (2011). An Investigation of Benzimidazol Derivative as Corrosion Inhibitor for Mild Steel in Different Concentration HCl Solutions. *Corrosion Science Elsevier,* 53, 113-121.

Yadav, M., Sinha, R. R., Sarkar, T. K., Bahadur, I., & Ebenso, E. E. (2015). Application of New Isonicotinamides as a Corrosion Inhibitor on Mild Steel in Acidic Medium: Electrochemical, SEM, EDX, AFM and DFT Investigations. *Journal of Molecular Liquids,* 212, 686-698.

Copyright © 2019 – 2020 JNET-RSU, All right reserved