EVALUATION OF INHIBITORY EFFECT OF PLANTS EXTRACT ON ZINC IMMERSED IN 0.1M HCl

[1]Ezeugo, J. N. O., [2]Onukwuli, O. D., [1]Nwanekezie, M. N, and [3]Umeonyiagu, I. E.
[1]Chemical Engineering Department, Chukwuemea Odumegwu Ojukwu University, Uli, Anambra State
[2]Chemical Engineering Department, Nnamdi Azikwe University Awka, Anambra State
[3]Civil Engineering Department, Chukwuemea Odumegwu Ojukwu University, Uli, Anambra State
Email: jn.ezeugo@coou.edu.ng

ABSTRACT
The inhibitive action of the ethanol extract of oil from Picralima nitida seeds, towards acid corrosion of zinc, is tested using weight loss, and thermometry methods. It was found that the extract acts as a good corrosion inhibitor for zinc corrosion in 0.1M HCl solution. The inhibitory action of the extract was discussed in view of Langmuir adsorption isotherm. It was revealed that the adsorption of the extract on zinc surface is governed by spontaneous process. The inhibition efficiency (IE) increases in line with corresponding increase in extract concentration. The temperature effect of the corrosion inhibition on the IE was studied. Revelation from the studies indicated that the presence of extract increases the activation energy of the corrosion reaction. Furthermore, from the calculated thermodynamic parameters, it was observed that Picralima nitida extract provides good protection to zinc against pitting corrosion in chloride ion containing solutions.

Keywords: Zinc, Corrosion, Picralima Nitida Seed, Inhibitor.

1.0 INTRODUCTION
Corrosion is an electrochemical process that gradually returns metals such as zinc to its natural state in the environment. In other words, corrosion can be said to be destruction of material resulting from exposure and interaction with the environment. It is a major problem that requires immediate confrontation for safety, environment, and economic reasons. This ugly menace was also identified by Thompson et al, 2007. Zinc consists of wide variety of alloys used since ancient times. Building industry frequently uses zinc alloys in roofing of house and other construction work because of its ductility and malleability. Therefore, zinc alloys are widely used in the production of many components and die-casting fittings in automobile and manufacturing and the mechanical industry, thanks to its super or super plasticity.

Zinc in spite of the so called super plasticity is not spared by corrosion, especially after prolonged period of exposure in corrosive environment, such as HCl. For this reasons a lot of efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors is one of them (Anuradha et al, 2007). The use of green inhibitors for the control of corrosion of zinc and alloys which are in contact with aggressive environment is an accepted and growing practice as confirmed by (Valdez et al, 2003; Taylor 2007; Khaled et al, 2008; Bothi et al, 2008). Large numbers of organic compounds are being studied to investigate their corrosion inhibition potential. Relation of these studies shows that organic compounds are not only expensive, but also toxic to living beings.

Plant extracts and organic species have therefore become important as an environmentally acceptable, readily available, and renewable source for a wide range of inhibitors (Rajendran et al 2004; Mesbah et al, 2007; Okafor et al, 2007). They are the rich sources of ingredients which have very high inhibition efficiency and hence termed "Green Inhibitors"(Lebrini et al, 2008; Radijcic et al, 2008; Refeay et al, 2008). Oguzie et al 2006, experimentally suggested that green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. The successful use of naturally occurring substances to inhibit the corrosion of the metals in acidic and alkaline environment have been reported by some research groups (Sharma et al 2009; Mabrouk et al, 2011; Eddy et al, 2012). Research efforts to find naturally organic substances or biodegradable organic materials to be used as effective corrosion inhibitors of a wide number of metals has been one of the key areas in this research work.

The aim of this study is to investigate the inhibitive properties of *Picralima nitida* seed extract onto zinc in hydrochloric acid media. Several studies have already been carried out and have remained focused on the *PNS* extract for their various pharmacological activities. Firstly, *Picralima nitida* plant is a tree that can reach a height of 35 meters, but is usually less. It is a commonly used herbal remedy in West Africa. All parts of the plant are bitter throughout its distribution area. The seeds, barks, roots and leaves have a reputation as a febrifuge and remedy for malaria as well as also being extensively used for pain relief and treatment of chest and stomach problems, pneumonia and intestinal worms (Nagam et al, 2012). A decoction of the seed is taken as a treatment for measles.The *Picralima nitida* seed contains many organic compounds, such as phenolics, terpenoids, and tannins as their major phytocompounds and also saponins, flavonoids and alkaloids in moderate amount to scavenge free radicals induce detoxification.

Presently, to the best of our knowledge no reported work in area of corrosion control has been carried out on the corrosion inhibitive properties of the *Picralima nitida* seeds extract. The study was carried out using weight loss (Gravimetric) method and FTIR analysis. The effect of temperature and concentration on the rate of corrosion were also studied, while isotherm parameters were calculated and listed on table.

2.0 EXPERIMENTAL METHODS

2.1Materials

Gravimetric tests were performed on 99.988% zn, other components (wt.%) are: Pb 0.003, Cd 0.003, Fe 0.002, Sn 0.001, Cu 0.00, Al 0.001. The sheet of zinc was cut into coupons (2.6 x 2.6 x 0.015cm), cleaned and polished with emery papers to expose shining polished surface. The coupons were degreased with acetone in order to remove any trace of oil and impurities and finally washed with double distilled water, dried in air and then stored in desiccators prior to use. The aggressive solution 1.0 M HCl was made from analytical grade hydrochloric acid (37%) and distilled water. *Picralima nitida* seeds collected from Uke in Anambra state, Nigeria, was sun-dried for three days. The dried seeds were ground to increase the surface area and stored in a closed container. For every of the extraction process, 30 grams of each of the ground *PNS* were measured and soaked in 100 ml of ethanol for 48 hours. At the end of the 48hrs, each plant mixture was filtered. The filtrate is the mixture of the plant extract and the ethanol. The extract

of *PNS* obtained in ethanol solvent was concentrated, distilled off the solvent and evaporated to dryness. The plant extract was weighed and stored for the corrosion inhibition study.

2.2 Fourier Transform Infrared (FTIR) Analysis of *Picralima nitida seeds* extract and Corrosion Products

The zinc was immersed in the HCl medium in the presence of the *PNS* extract. At the end of the corrosion study, the corrosion products in the beakers were collected with aid of sample bottles SHIMADZU FT-IR spectrophotometer, model: IR affinity – 1, 5/NA 2137470136 SI) was used for the determination of the functional groups of the seeds extract of PNS (pure) and corrosion products in the presence of the PNS extract (Octave,2003; Nwabunne et al, 2011; Nnanna et al, 2013; Rubite-Okorosaye 2004). Comparative analysis of various FTIR produced peaks were carried out in order to determine the exact functional groups for the corrosion inhibition processes.

2.3 Weight loss (gravimetric) Method using one factor at a time

The weight loss method was carried out applying one factor at a time. Considering the said method, the weight loss method was carried out at different temperatures and with various concentrations of the *PNS* extract. Weighed zinc coupons were separately immersed in 250 ml open beakers containing 200 ml of 1.0 M HCl. More so, zinc coupons were separately immersed in 150 ml open beakers containing 200ml of 1.0 M HCl with various concentrations of PNS extract.

The variation of weight loss was monitored periodically at various temperatures in the absence and presence of different concentrations of the extracts. At the appropriate time, the coupons were taken out, immersed in acetone, scrubbed with a bristle brush under running water, dried and reweighed. The weight loss was calculated as the difference between the initial weight and the weight after the removal of the corrosion product. The experimental readings were recorded. The weight loss (Δw), corrosion rate (CR) and inhibition efficiency (IE) were determined using the eqn (1), (2), and (3), respectively. The surface coverage was obtained using equation 4 (El-Etre, 2003).

$$\Delta w = w_i - w_f \qquad (1)$$

$$CR = \frac{w_i - w_f}{At} \qquad (2)$$

$$IE\% = \frac{w_o - w_i}{w_0} x\ 100 \qquad (3)$$

$$\theta = \frac{w_0 - w_1}{w_0} \qquad (4)$$

Where w_i and w_f are the initial and final weight of zinc samples respectively, W_1 ad W_0 are the weight loss values in presence and absence of inhibitor, respectively. A is the total area of the zinc sample and t is the immersion time while θ denotes surface coverage.

2.4 Effect of Temperature on the Corrosion Rate

Effect of temperature on the corrosion rate was described using Arrhenius equation

$$CR = A\, e^{-Ea/RT} \qquad (5)$$

Where CR is the corrosion rate of the zinc, A is the pre-exponential factor, Ea is the activation energy, R is the universal gas constant. Eqn. (5) can be linearized to form eqn. (6).

$$In\,(CR) = In\,A - \left({}^{Ea}/_{R}\right)\left(\frac{1}{T}\right) \qquad (6)$$

Considering the corrosion rate of the zinc at T_1 and T_2 as Cr_1 and CR_2, then eqn. (6) can be expressed by eq. (7) (Thompson et al, 2007; Patel et al, 2013)

$$In\left(\frac{CR_2}{CR_1}\right) = \left(\frac{Ea}{2.303R}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (7)$$

Thermodynamic parameter for the adsorption process

The heat of adsorption Q_{ads} ($KJmol^{-1}$) was calculated using eqn. (8) [21]

$$Qads = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - log\left(\frac{\theta_1}{1-\theta_1}\right) \times \frac{T_2\,T_1}{T_2 - T_1}\right] \qquad (8)$$

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

2.5 Consideration of the Adsorption isotherm

The data obtained for the degree of surface coverage were used to test for the applicability of different adsorption isotherms (Langmuir, Frumkin, Temkin and Flory-Huggins isotherms).

(a) Langmuir Isotherm

Langmuir isotherm can be expressed by eqn. (9) (Umoren and Ebenso, 2007).

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (9)$$

Where C is the concentration of the inhibitor, K is the adsorption equilibrium constant and θ is the degree of surface coverage. In logarithmic form, eqn. (11) can be expressed in eq. (10)

$$\log\frac{C}{\theta} = \log C - \log K \qquad (10)$$

(b) Frumkin Isotherm

Franklin adsorption isotherm can be expressed according to eqn. (11)

$$\log\left(Cc) * \left(\frac{\theta}{1-\theta}\right)\right) = 2.303logK + 2\,\alpha\theta \qquad (11)$$

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

(c) Temkin isotherm

Temkin isotherm can be expressed by eqn. (12) (Eddy, 2012)

$$\theta = \frac{2.303\log K}{2a} - \frac{2.303\log C}{2a} \qquad (12)$$

Where k is the adsorption equilibrium constant, a is the attractive parameter, θ is the degree of surface coverage, C is the concentration of the inhibitor

(d) Florry-Huggins Isotherm

The Flory-Huggins isotherm can be expressed by eqn. (13).

$$\log\left(\frac{\theta}{C}\right) = \log k + x\log(1 - \theta) \qquad (13)$$

Where x is the size parameter and is a measure of the number of adsorbed water molecules. The free energy of adsorption (ΔG_{ads}) was calculated according to eqn. (14) (Khadom et al, 2009; Cabot et al, 1991).

$$\Delta G_{ads} = -2.303RT \log (55.5K) \qquad (14)$$

Where R is thes gas constant. T is the temperature, K values obtain from the isotherms (Langmuir, Frumkin, Temkin and Flory-Huggins isotherm) were used to obtain the values of ΔG_{ads} according to eqn. (14).

3.0 RESULTS AND DISCUSSION

3.1 FTIR Analysis

FTIR Spectrophotometer is a strong instrument that can be used to identify the type of bonding, especially functional group (s) present in organic compounds. Figure 1 shows the IR spectrum of the ethanol extract of *PNS* extract. Initial absorption at 3952.4 to 3543.24cm^{-1} (associated hydroxyl) was overlapped by the strong stretching bond of O-H.The peak at 3477.62 to 3261.46cm^{-1} is attributed to medium and often broad stretch band of amines and amides, N-H. Wave band 3141.8 and 3053.02cm^{-1} are variable stretch of alkyl and aldehyde bond group, C-H. The absorption band at 2971.96cm^{-1} stands for strong and very broad stretch of carboxylic acid (free bond of alcohol). Wave band of 2751.94cm^{-1}, 2829.14cm^{-1} are two-peaked medium stretch bond of aldehyde, C ≡ C. The peak at 2404.54 to 2030.12 cm^{-1} represent variable and sharp stretch bond of alkyne and nitrite, C=N. Wave band 1837.48 cm^{-1}, 1658.65 cm^{-1} are strong representative of stretch bond of acids, esters anhydrides and aldehydes, C=O. The absorption bands 1597.8 cm^{-1}, 1439.54 cm^{-1} are multiple sharp, medium peaks stretch of aromatic bond, C=C. This shows that *Picralima nitida* leaves extract contains mixtures of compounds, that is, alkaloids, flavonoids, phenolics, phytates, terpenoids, tannins and steroids (Satapathy et al, 2009).

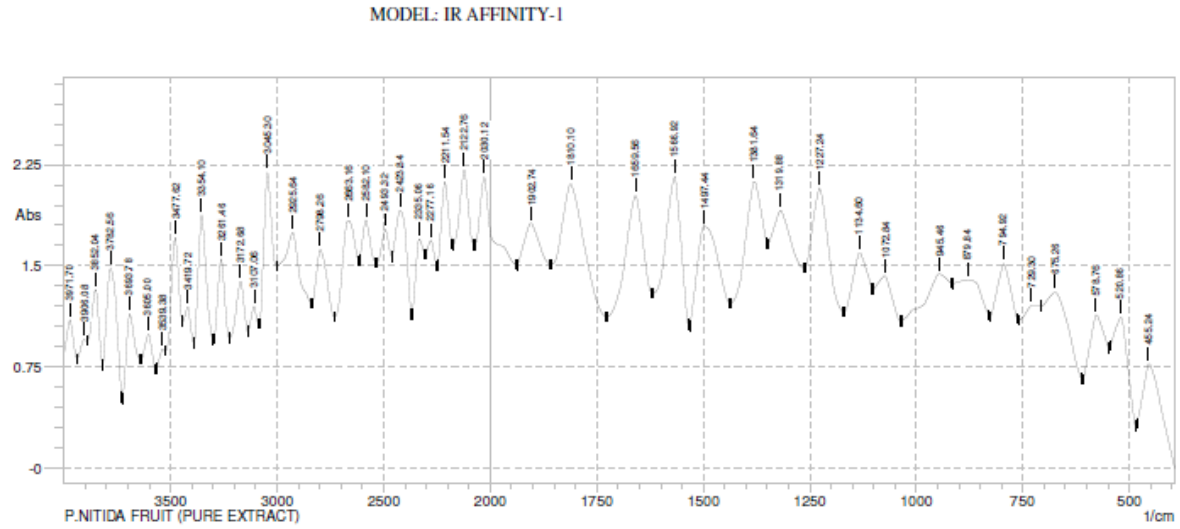

Figure 1(a): FTIR spectrum of picralima nitida fruit (pure extract)

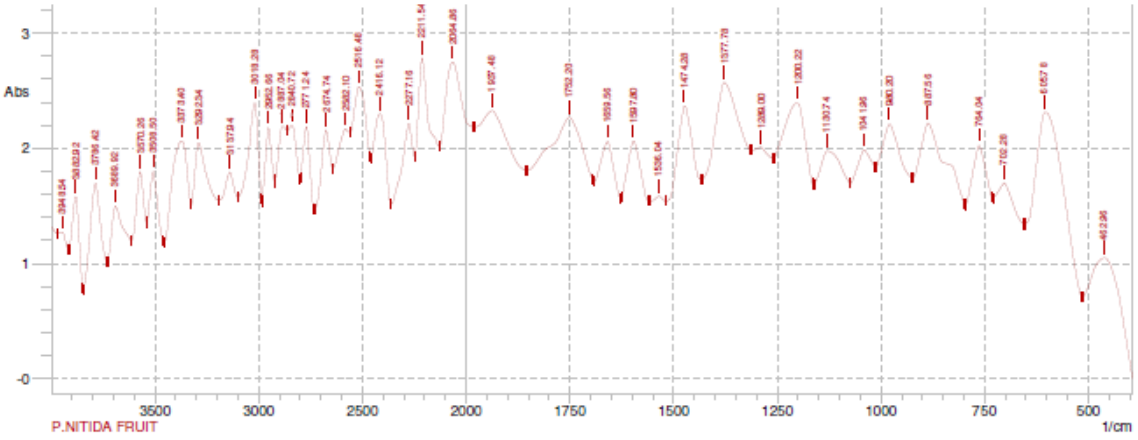

Figure 1(b): FTIR spectrum of *Picralima nitida* fruit extracts.

3.2 Weight Loss Measurement

Table 2 represent experimental results of weight loss and corrosion rate using one factor at a time. Inspection of the table reveals that the loss of weight increases proportionately with increasing time in all tested solutions. However, the rate of weight loss was affected by addition of *PNS* extract. The presence of the extract causes sharp decrease in the rate of weight loss. IEs at different concentrations of the extract were calculated using the equation:

$$IE(\%) = \frac{w_0 - w_1}{w_0} \times 100 \qquad (15)$$

Where W_1 and W_0 are the weight loss values in presence and absence of inhibitor, respectively.

Table 2. Corrosion inhibition of zinc in 0.1M HCl with *Picralima nitida* seeds extract

Time (hr)	Temperature (K)	Inhibitor conc. (gL^{-1})	Weight loss (g)	Corrosion rate (Mg/cm^2 hr)	Inhibition efficiency (%)	Degree of surf.cov.
12	303	0	0.521	4.824	-	-
		0.2	0.245	2.269	52.98	0.5298
		0.45	0.217	2.009	58.35	0.5835
		0.7	0.187	1.731	64.11	0.6411
		0.95	0.1	0.926	80.81	0.8081
		1.2	0.071	0.657	86.37	0.8637
12	313	0	0.545	5.046	-	-
		0.2	0.323	2.991	40.73	0.4073
		0.45	0.264	2.444	51.56	0.5156
		0.7	0.19	1.759	65.14	0.6514
		0.95	0.145	1.343	73.39	0.7339
		1.2	0.117	1.083	78.53	0.7853
12	323	0	0.61	5.648	-	-
		0.2	0.391	3.62	35.9	0.359
		0.45	0.31	2.87	49.18	0.4918
		0.7	0.23	2.13	62.3	0.623
		0.95	0.175	1.62	71.31	0.713
		1.2	0.172	1.593	71.8	0.718

The values of IEs and θs in different *PNS* extract concentrations are given in Table 2. The tabulated data revealed that, the *PNS* extract acts as a good corrosion inhibitor for the acid corrosion of zinc. The corrosion inhibition increases with increasing extract concentration. The analysis of the extract revealed that the ethanol extract contains toluene, formular;C_7H_8, molecular weight, 92, cyclohexane having formular C_8H_{16}, molecular weight 112, hexane, 1,3-cyclopenta deine, molecular weight, 156. It also contains at least ten non-volatile acids including eicosane and citric acids. The adsorption of the compounds on the electrode surface make a barrier for mass and charge transfers as confirmed by (El-Etre, 2003). The outcome of this situation leads to a protection of the metal surface from the attack of the aggressive anions of the acid. The extent of protection increases with increasing of the surface fraction occupied by the adsorbed molecules. As the extract concentration is increased, the number of the adsorbed molecules on the surface increases. Table 2 represents also the values of adsorption isotherm parameter. From the table, a parameter (θ), which was estimated from the IE values, could be used to represent the fraction of the surface occupied by the adsorbed molecules. In-depth examination of Table 2 revealed that the values of θ increases with increasing inhibitor concentrations. The dependence of the fraction of the surface occupied by the adsorbed molecules on the inhibitor concentration (c) is shown in fig. 3. A plot of C/θ versus C gives a straight line with unit slope. The results indicate that the adsorption of inhibitor molecules on the zinc surface follow Langmuir isotherm. In order words, the result suggests that there are no interactions or repulsion forces between the adsorbed molecules. It is of interest to note here that, the θ values obtained from the other used techniques also obey the Langmuir adsorption isotherm.

The standard adsorption free energy (ΔG_{ads}) was calculated using the following equation:

$$K = \frac{1}{999}\exp\left(-\frac{\Delta G_{ads}}{RT}\right) \quad (16)$$

Where 999 is the concentration of water in solution expressed in gL^{-1}. R is gas constant, and T absolute temperature. The mean value of standard adsorption free energy (ΔG_{ads}) was -46.4018 $kjmol^{-1}$. The negative values of ΔG_{ads} guarantee the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface. It is generally known that, values of ΔG_{ads} up to -20 $kjmol^{-1}$ is consistent with electrostatic interaction between the charged molecules and the charge metal (physisorption) while those around – 40$kjmol^{-1}$ or higher are associated with chemisorptions as a result of sharing or transfer of electrons from the molecules to the metal surface to form a coordinate type of bond. Other researchers, however suggested that the range of ΔG_{ads} of chemical adsorption processes for inhibitor in aqueous media lies between -21 and -42$kjmol^{-1}$.Similar results were gotten by (Umoren and Ebenso, 2007; Khadom et al, 2009).

Table 3. Adsorption parameters for the corrosion inhibition of Zinc in HCl by PNF extract

Adsorption isotherm	Temperature (k)	R^2	Log K	K	ΔGads (KJ/mol)	Isotherm property	
Langmuir	303	0.982	-0.209	0.6182	-8.907		
isotherm	323	0.984	-0.171	0.6745	-9.729		
Frumkin	303	0.961	-1.0938	0.0806	-3.774	α	2.083
isotherm	323	0.990	-0.9092	0.1233	-5.165		1.866
Temkin	303	0.877	-1.7884	0.0163	0.252	a	-3.046
isotherm	323	0.970	-1.2091	0.0618	-3.309		-2.271
Flory-Huggins	303	0.725	0.541	0.2877	-6.980	x	1.360
isotherm	323	0.904	0.251	1.98724	-12.339		1.095

From table 3, the values of ΔG_{ads} as recorded in the present work, has been considered within the range of physical adsorption. Limited increase in the absolute value of ΔG_{ads} at 303 K temperature, then, heat of adsorption decreases again at 313 k indicating that the adsorption was somewhat favorable at the experimental temperature, and *PNS* extract adsorbed according to physical mechanisms, i.e. desorption of inhibitor molecules when temperature increased.

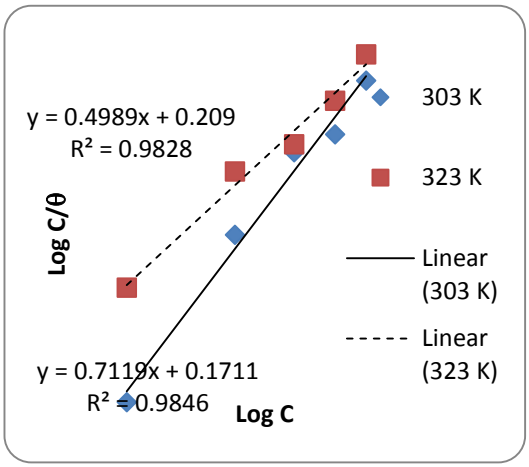

Figure 3: Plot of Langmuir isotherm for zinc in HCl with PNS extract.

Moreover, the major characteristic Langmuir isotherm can be expressed in terms of linear regression coefficient. The value of the linear regression coefficient is close to unity, hence adsorption of the *PNS* extract follows Langmuir isotherm and R^2 value is $0.984 \geq 0.982$. It is very important to note that the smaller values of R^2 indicate a highly favorable adsorption. $R^2 > 1$ unfavorable, $R^2 = 1$ linear, $0 < R^2 < 1$ favorable and if $R^2 = 0$ irreversible. The table 3 shows the various values of R^2 for the entire tested isotherms model. The values of k_{ads} are relatively small indicating that the interaction between the adsorbed extract molecules and metal surface is physically adsorbed.

A close look at Table 4 shows various inhibition concentration (gL^{-1}) and their respective activation energy (KJ mol^{-1}). From the table, calculated Ea value for the inhibited solution with *Picralima nitida* extract is 40.453 and 36.692 KJ mol^{-1} in the presence of the inhibitor of 0.95 and 1.2 gL^{-1} extract concentrations, while with 0.45 and 0.70 gL^{-1} concentration, the activation energies are 34.378 and 18.651 $kjmol^{-1}$, the higher values of Ea suggest that dissolution of zinc in the presence of inhibitor is slow, indicating a strong inhibitive action of phytocompounds of alkaloids, flavonoids and tannins presence in *Picralima nitida* seeds extracts, which leads to increasing the energy barrier for the corrosion process (Cobot et al,1991). Actually, toluene molecules (the main compound of *Picralima nitida* seeds extracts oil) are easily protonated and exist in 0.1M HCl medium in cationic form. Indeed, it is logical to assume that in this study, the electrostatic cation adsorption is responsible for the good protective properties of this compound.

Table. 4. Activation Energy and Heat of Adsorption for the Corrosion Inhibitor of Zinc in 0.1M HCl at various Inhibition sConcentrations

Inhibitor concentration (gL^{-1})	Ea (kj mol^{-1})	ΔG_{ads} (kj mol^{-1})
0.2	39.065	29.442
0.45	34.378	18.984
0.7	18.651	3.032
0.95	40.453	16.705
1.2	36.692	13.828

CONCLUSION

i. The *Picralima nitida* seeds extract acts as a good inhibitor for corrosion of zinc in 0.1M HCl solution. The IE increases with increasing extract concentration.
ii. The inhibitory action of the extract was carried out through adsorption of the extract compounds on zinc surface. The adsorption process is spontaneous, stable and obeys Langmuir adsorption isotherm.

iii. The adsorption process is physical as various studies technique points towards physisorption. More so, the increase in temperature decreases the IE of the extract.

iv. The presence of *PNS* extract increases the activation energy of the corrosion reaction.

v. The *Picralima nitida* seeds extract provide strong protection against corrosion of zinc in presence of chloride ions. The extent of inhibition increases with increasing extract concentration.

REFERENCES

Radijcic,A. Berkovic,K. Kova,S. Vorkapic,C.F.J. Corros. Sci 50 (2008) 1498 – 1504.

Khadom,A.A. Yaro, A.S. Altaie, A.A.H. Kadum, Portug. Electrochim. Acta 27 (6) (2009) 699 – 712.

A.K. Satapathy, G. Gunasekaran, S.C. Sahoo, K. Amit, P.V. Rodrigues, Corros. Sci. 51 (2009) 2848 – 2856.

A.Y. El-Etre, Corros. Sci. 45 (2003) 2485 – 2495.

B. Valdez, J. Cheng, F. Flores, M. Schorr, L. Veleva. Corrosion Rev. 21 (2003) 445 – 458.

E.E. Oguzie, Pigment. Resin. Tech. 35 (2006) 334 – 340.

E.M. Mabrouk, H. Shoky, K.M. Abu Al-Naja, Chem. Met. Alloys 4 (2011) 98 – 106.

I.J. Alinno, P.M. Ejikeme, America. Chem. Sci. J. 2 (2012) 122 – 135.

J. Anuradha, R. Vimala, B. Narayanasanly, S. Arochia, D.S. Rajendran, Lenn. Chem. Eng. Comm. 195 (2008). 352 – 366.

J.T. Nwabanne, V.N. Okafor, J. Emer. Trends. In Engin. And App. Sci. (JETEAS) 2 (2011) 619 – 625.

K.F. Khaled. Int. J. Electrochem. Sci. 3 (2008) 462 – 475.

K.O. Rubite-Okorosaye, N.C. Oforka, J. Appl. Sci. Environ. Mgt. 8 (2004) 57 – 61.

L. Octave, Chemical Reaction Engineering, 3rd eds. John Wily and sons, New York, 2003.

L.A. Nnanna, I.O. Owate, O.C. Nwadiuko, N.D., Ekekowe, W.J. Oji, Int. J. Mater. Chem. 3 (2013) 10 – 16.

M. Lebrini, M. Traisnel, M. Lagrenee, B. Mernari, F. Bentiss, Corros. Sci. 50 (2008) 473 – 479.

Mesbah, C. Juers, Lacouture, F. Mathieu, S. Rocca, E. Francois, J. Steinmetz, J. Solid State. Sci 9 (2007) 322 – 328.

N. Nagm, N.G. Kandile, E.A. Bad R, M.A. Mohammd, Corros. Sci 65 (2012) 94 – 103.

N.G. Thompson, M. Yunovich, D. Don mire, Corrosion Rev. **25**(2007) 247 – 262.

N.O. Eddy, B.I. Ita, S.N. Dodo, E.D. Paul, Green Chem. Lett. Rev. 5 (2012). 43 – 53.

N.S. Patel, S. Jauhariand, G.N. Melita, S.S. Al-Deyeb, I. Warad, B. Hammouti, Int. J. Electrochem. Sci. 8 (2013) 2635 – 2655.

P.C. Okafor, V.I. Osabor, E.E. Ebenso, Pig. Res. Technol. 36 (2007) 299 – 305.

P.L. Cabot, F.A. Centellas, J.A. Garrido, E. Perez, H. Vidal, Electrochem. Acta 36 (1991) 179.

P.R. Bothi, M.G. Sethuraman, Mater Lett. 62 (2008) 113 – 116

S. Rajendran, A.J. Amalraj, M.J. Joice, N. Anthony, D.C. Trevedi, M. Sundaravadivelu, Corrs. Rev. 22 (2004) 233 – 248.

S.A. Umoren, E.E. Ebenso, Mater Chem. Phys. 106 (2007) 393.

S.A.M. Refeay, A.E. Malak, A.M. Taha, F. Abdel-Fatah, H.T.M. Int. J. Electrochm. Sci. 3 (2008) 167 – 176.

S.K. Sharma, A. Mudhoo, G. Jain, E. Khamisa Green Chem. Lett. Rev. 2 (2009) 47 – 51.

S.R. Taylor, B.D. Chambers, Corros. Rev. 25 (2007). 571 – 590.

X. Li, S. Deng, Corros. Sci. 65 (2012) 299 – 308

E. Rodriquez-clemente, J.G. Gonzalez-Rodriguez and M.G. Valladares-Cisneros, *Int. J. Electrochem. Sci.*, 9 (2014) 5924-5936.

A. Espinoza-vazquez, G.E. Negron-Silva, D. Angeles-Beltran., H. Herrera-Hernandez, M. Romero-Romo, M. Palomar-Par dave[*2] Int. J. Electrochem. Sci., 9 (2014) 493-509.

S. Abd El-Aziz Fouda, Ahmed Abdel Nazeer, Y. Ayman El-Khateeb, and Mohamed Fakih. J. Korean Chemical Society. 58 (2014) 359-365.