Evaluation of Inhibitive Performance of Acidic Extract of *Eichornia Crassipes* on Corrosion of Low Carbon Steel in 1M Sulphuric Acid Solution

*[1]Sidikat I. Kuye, [1]Emmanuel Amaechi,[1]Nurudeen O. Adekunle,[1]Olayide R. Adetunji,
[2]Alex F. Adisa and [3]Hezekiah O. Adeyemi
[1]Department of Mechanical Engineering, Federal University of Agriculture, Abeokuta, Ogun State, Nigeria
[2]Department of Agricultural Engineering, Federal University of Agriculture, Abeokuta, Ogun State, Nigeria
[3]Department of Mechanical Engineering, OlabisiOnabanjo University, Ago-Iwoye, Ogun State, Nigeria
ibiyemikuye01@gmail.com

Abstract- Corrosion inhibition potential of *Eichhornia crassipes* extract on low carbon steel in 1M sulphuric acid solution was investigated using gravimetric method and corrosion rate. The experiment was carried out for 3 hours at different concentration of *Eichhornia crassipes* extract and temperatures of 26.6°C, 40°C and 60°C. Arrhenius and improved Arrhenius equations were used to determine the thermodynamics properties of the reaction while the nature of the reaction was proposed by adsorption isotherms. The results showed that corrosion rate decreased in the presence of the extract except in 60oC. Inhibition efficiency also increased with extract concentration with the highest (82%) occurring at room temperature and 5% concentration. Inhibition efficiency decreased with increase in temperature with almost no inhibition at 60oC, this is associated with physisorption. Activation energy (E_a) and activation enthalpy (ΔH_{act}) both had positive values and they increased in the presence of *Eichhornia crassipes* extract, those for inhibited solution were higher than those for uninhibited solution, these can also be attributed to physisorption. Inhibition reaction obeyed Langmuir adsorption isotherm. Gibbs free energy (ΔG_{ads}) calculated for the reaction is -8.509 to -11.767 kJ mol^{-1}.

Keywords- Inhibitive performance, acidic extract, *Eichornia crassipes*, low carbon steel, sulphuric acid

1. Introduction

Degradation of metals is a common sight around us. This is known as corrosion and its effects are not desirable because qualities of engineering materials are jeopardized. Acids such as sulphuric and hydrochloric are often used for cleaning metals in the oil and chemical industries but they often leave behind corrosion of the metals. Continuous efforts are on-going towards reducing, if possible, completely eliminating corrosion. Inhibitors are employed for this purpose as they possess substances capable of reducing the reaction between a metal and its environment (Rani and Basu, 2012). Inhibitors can be organic or inorganic depending on their sources. The organic inhibitors can be synthetic or natural. Organic inhibitors have been established to be the best as they are biodegradable, nontoxic and environmentally friendly (Naik et al., 2016).

Organic compounds contain functional groups in their molecular structures that contain O, N, S, P atoms and multiple bonds that inhibit corrosion by displacing the water molecules on the metal and forming barrier against corrosion (Rani and Basu, 2012; Naik et al., 2016). Organic compounds can be expensive sometimes putting limitations to their applications. Attention is being given to natural plants as they are cheap, highly available, nontoxic, and environmentally friendly (Khadraoui et al., 2015). Plants possessing some of the atoms mentioned above have been and are still being investigated for their corrosion inhibition potentials. Plants are rich source of free radical scavenging molecules such as vitamins, terpenoids, phenolic acids, lignins, stilbenes, tannins, flavonoids, quinones, coumarins, alkaloids, amines, betalains and other metabolites which are rich in antioxidant activity (Lalitha and Jayanthi, 2012).

El-Etre (2006) carried out corrosion inhibition of natural honey on copper and reported that it was a good inhibitor. Opuntia extract, aloe vera leaves, orange and mango peels were evaluated by Saleh, Ismail and El Hosary (1982) to be good corrosion inhibitors to steel in 5 and 10% hydrochloric acid solution at temperatures of 25 and 40°C. Srivatsava and Srivatsava (1981) worked on tobacco, black pepper, castor oil seeds, acacia gum and lignin and concluded that they made very good inhibitors for steel in acid medium.

Ethanolic extract of *Ricinus communis* leaves was studied for the corrosion inhibition of mild steel in acid media by Anauda et al. (2005). *Telfaria occidentalis* extract inhibited corrosion in both sulphuric and hydrochloric acid media (Oguzie, 2004). *Stevia rebaudiana* leaves extract according to Cang, Shao and Xu (2012) inhibited mild steel corrosion in sulphuric acid solution. The inhibition which was said to occur via adsorption on the metal surface was reported to increase with extract concentration. Aquatic plants are incredibly rich in naturally occurring chemical compounds (organic acids, glucosinolates, alkaloids, flavonoids, terpenoids, polyphenols, and tannins) and most of them are known to have corrosion inhibition efficiency (Manimegalai and Manjula, 2015). Shanab and Shalaby (2012) investigated the corrosion inhibition potential of crude methanolic extract of Water hyacinth (*Eichhornia crassipes*) on magnesium alloy (AZ31E) in 0.15M NaCl and concluded that though initially the rate of inhibition was low but it later increased with extract concentration. Ulaeto et al. (2012) applied the acid extract of the roots and leaves of *Eichhornia crassipes* to inhibit mild steel corrosion in hydrochloric acid using gasometric technique and reported that inhibition took place through physisorption.

*Corresponding Author

Corrosion inhibition performance of plant extracts depends on the part of the plant and its location. One compound effective in a certain medium with a given metal may be ineffective for the same metal in another medium (Okafor et al., 2005). They investigated corrosion inhibition potential of acidic extract of *Eichhornia crassipes* on low carbon steel in 1M sulphuric acid. This may contribute to reduction of the cost of corrosion prevention in the industry as *Eichhornia crassipes* is highly available and posing environmental menace. *Eichhornia crassipes* can be found almost everywhere in the tropics and subtropics. It grows in ponds, pools, water tanks, lakes, even in irrigation channels. A plant that was initially prized for its beautiful flowers and was propagated as an ornamental plant by botanical gardens that later became one of the worst ecological problems in the world especially in Africa due to its aggression. Shorelines are literarily choking from the ecological effect of Water hyacinth which has led to the plant being infamous worldwide (Teygeler, 2000). *Eichhornia crassipes* is a free-floating perennial aquatic herb. However, phytochemical studies carried out revealed the presence of nutritionally important compounds like phenolics, flavonoids, glutathione and many other metabolites (Lalitha and Jayanthi, 2012). Some of these phytochemicals have been responsible for antioxidant activity in green inhibitors.

2. Experimental Methods

2.1 Specimen Preparation

Low carbon steel sheet was mechanically cut into dimensions 2 cm x 2 cm x 0.1 cm. A hole of 0.1 cm diameter was drilled in each of the specimens through which a string was passed for ease of suspension. The surfaces of the specimens were polished mechanically, cleansed in acetone and rinsed in distilled water prior to their use for the corrosion studies.

2.2 *Eichhornia crassipes* Extract Preparation

Fresh plants of *Eichhornia crassipes* used for this work were obtained from the lagoon side of University of Lagos, Akoka, Nigeria, though it is equally possible to collect them from ponds, channels and water tanks. They were cleaned and dried in a shade until there was no variation in weight. The dried leaves were pulverized and the extract was obtained by soaking 10g of the pulverized plant in 100 ml of 1M H2SO4 acid for 48 hours (Cang, Shao and Xu, 2012; Patel et al., 2013; Ibisi, Ngwamaghi and Okoroafor, 2015), after which it was filtered and the extract was mixed with 1M H_2SO_4 acid at concentration of 1%, 3% and 5% (v/v) for corrosion studies.

2.3 Gravimetric Studies

Gravimetric analysis was carried out by immersing the specimens into 50ml solution of 1 M H_2SO_4 acid in the absence and presence of the extract for the period of 3 hours. The experiment was carried out at 3 different temperatures (room temperature (26.6°C), 40°C and, 60°C and in triplicates. The weight of the specimens before and after immersion was determined using analytical weighing balance. The weight loss (ΔM) was calculated from the difference between initial (Mi) and final (Mf) weights. The average weight loss for three identical experiments was obtained and the Corrosion Rate (CR) is expressed according to Oguzie et al. (2008) and AbdEl Haleem et al. (2013) in Eq. 1

$$CR = \frac{\Delta W}{ST} \quad (1)$$

where, CR= corrosion rate
ΔM= weight loss
S = surface area of specimen
T= time in hours

Inhibition Efficiency (IE%) of the extract was determined according to Abd El Haleem et al. (2013) in Eq. (2)

$$IE\% = \left(1 - \frac{CR_{in}}{CR_{blank}}\right) \times 100 \quad (2)$$

where, CR_{in}= Corrosion rate with inhibitor
CR_{blank}=Corrosion rate without inhibitor

3. Results and Discussion

3.1 Chemical composition of steel sample

Results of the chemical analysis of the steel sheet revealed the chemical composition as: (wt%) Fe (98.4%), C (0.08%), Si (0.072%), Mn (0.498%), Ni (0.06%), Cr (0.0089%), Cu (0.53%), Co (0.183%), Al (0.015%), Mg (0.049%) S (0.062%), P (0.013%) with trace of other metals making up the balance.

3.2 Weight loss, corrosion rates and inhibition efficiency

Figures 1 and 2 show the weight loss and corrosion rate curves at all concentrations for the inhibition performance being investigated. It can be observed that weight loss and corrosion rate generally decreased in the presence of *Eichhornia crassipes* extract. This makes the plant a good corrosion inhibitor. The inhibition efficiency and surface coverage of the investigation are as shown in Table 1. Surface coverage is directly proportional to inhibition efficiency for any corrosion inhibition process. Inhibition generally increased in the presence of the extract (except in the case of 60°C) and more extract concentration led to more inhibition with the highest (82%) occurring at room temperature in 5% extract concentration. The protection barrier offered by the extract reduced at 60°C. This in addition to aggressive corrosion associated with low carbon steel in high temperature led to reduced inhibition efficiency.

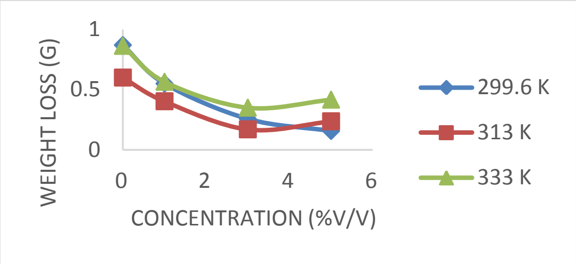

Fig. 1: Plot of Weight Loss against Concentration for all Absolute Temperatures

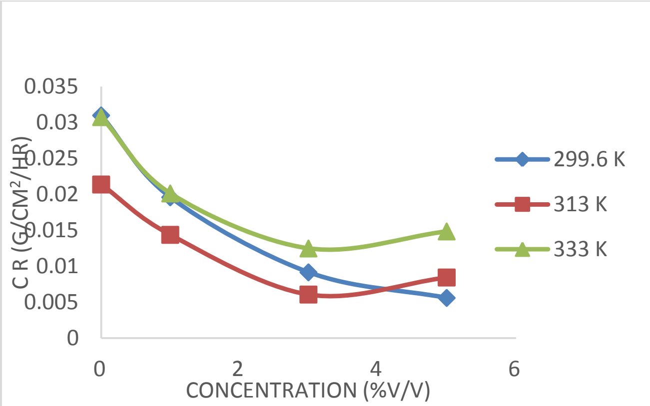

Fig. 2: Plot of Corrosion Rates against Concentration for all Absolute Temperatures

Table 1. Inhibition efficiency and surface coverage for the corrosion of low carbon steel in 1M sulphuric acid in the presence of *Eichhornia crassipes* extract

Concentration	Inhibition Efficiency (%)			Surface Coverage, θ (IE/100)		
	26.6°C	40°C	60°C	26.6°C	40°C	60°C
Blank	-	-	-	-	-	-
1% (v/v)	36.78	32.78	34.55	0.37	0.33	0.35
3%(v/v)	70.50	71.67	59.45	0.71	0.72	0.59
5%(v/v)	81.99	60.56	51.75	0.82	0.61	0.52

3.2 Effect of Temperature on Performance

Metals are sometimes subjected to operations at higher temperatures than the room temperature. This makes corrosion inhibition at high temperature very important, hence the reason for carrying out weight loss experiment at temperatures of 26.6°C (room temperature), 40°C and 60°C. The results obtained were used to calculate the thermodynamics parameters for the study. The relationship between the corrosion rate of a metal and temperature in corroding media can be obtained using Arrhenius Equation given by Eq. 3 according to Alaneme and Olusegun (2012).

$$\ln(CR) = \ln A - \frac{E_a}{2.303RT} \quad (3)$$

The activation entropy and activation enthalpy for the study were calculated using improved Arrhenius equation given by Eq. 4 according to Khadom et al. (2009).

$$CR = \frac{RT}{Nh}\exp\left(\frac{\Delta S_{act}}{R}\right)\exp\left(\frac{-\Delta H_{act}}{RT}\right) \quad (4)$$

where, E_a is the apparent activation energy, R is the molar gas constant, T is the absolute temperature and A is the frequency factor, ΔS_{act} is the activation entropy, ΔH_{act} is the activation enthalpy, N is Avogadro's number and h is Plank's constant.

The slopes of Arrhenius plot of ln(CR) against the reciprocal of absolute temperature (1/T) for the corrosion of low carbon steel in 1M sulphuric acid solution in the absence and presence of *Eichhornia crassipes* extract gave the E_a for the system under investigation. The thermodynamics parameters for this study are shown in Table 2. It can be seen from this table that the values of E_a which represent the total values of energy of activation including the energy required for the removal of corrosive media molecules (Lalitha and Jayanthi, 2012), increased in the presence of the extract compared with its absence and E_a increased with increase in extract concentration. This means that the activation energy for the system was increased by the extract. This agrees with the reports of Obi-Egbedi, Obot and Umoren (2012), Ulaeto et al. (2012), Al-Haj-Ali et al. (2014) and Naik et al. (2016) for physisorption inhibition where the E_a values for the inhibited were greater than the uninhibited. Labrabi et al. (2005) and Khadraoui et al. (2015) also attributed higher activation energy in the presence of inhibitor compared with its absence to physisorption inhibition, while the reverse was associated with chemisorption. Also, the slopes and the intercepts of improved Arrhenius plot of ln(CR/T) against 1/T gave the ΔH_{act} and ΔS_{act} respectively for the system. These values of ΔS_{act} and ΔH_{act} are also shown in Table 2 where it can be seen that ΔS_{act} has negative values depicting greater order during activation process. It can be observed from Table 2 that ΔH_{act} increased in the presence of the *Eichhornia crassipes* with its largest value occurring at 5% concentration.In a nut shell, E_a and ΔH_{act} increased with inhibitor concentration, this trend of ΔH_{act} agrees with what was reported for physisorption (Fouda, Al-Sarawy and El-Katori, 2006; Alaneme and Olusegun, 2012; Al-Mhyawi, 2014). The positive values of ΔH_{act} reflect endothermic nature of the reaction in the presence of the extract.

Table 2. Thermodynamic and activation parameters for corrosion of low carbon steel in 1 M sulphuric acid solution in the presence of *Eichhornia crassipes* extract

Concentration	Ea (kJ mol-1)	ΔHact (kJ mol-1)	ΔSact (J mol-1K-1)
Blank	1.6	-1.93	-281.445
1% (v/v)	3.33	-1.19	-282.61
3% (v/v)	20.77	6.40	-264.36
5% (v/v)	55.96	21.67	-215.76

3.3 Adsorption Parameters Considerations

The mechanism of inhibition can be understood by studying the adsorption isotherms which provide further information on the variation of adsorption with the concentration of extracts at constant temperature

(Alaneme and Olusegun, 2012). It is assumed that inhibitors prevent corrosion reaction through the blockage of active sites on the metal surface by adsorbed species of extract. It then means that corrosion will only occur in the area where there is no coverage. Inhibition efficiency is directly proportional to surface coverage (Khadom et al., 2009). The experimental data fitted into Langmuir isotherm model given according to Obi-Egbedi, Obot and Umoren (2012) by Eq.5.

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (5)$$

where,
θ = surface coverage (fraction, dimensionless),
C = extract concentration and
K_{ads} = adsorptive equilibrium constant
Plot of C/ θ against C showing the correlation coefficients (R2) is given by Figure 3.

The standard free energy of adsorption $\Delta G^o{}_{ads}$ was calculated using Eq. 6 in accordance to Zhang et al. (2010) and Al-Mhyawi (2014).

$$K_{ads} = \frac{1}{55.5}\exp\left(\frac{-\Delta G^o{}_{ads}}{RT}\right) \quad (6)$$

where, 55.5 is the concentration of water in the solution in 1 mol·dm-3, R the universal gas constant and T the thermodynamic temperature. Table 4 gives the adsorption parameters.

The negative values of $\Delta G°_{ads}$ depicts the spontaneity of the adsorption process and the stability of the adsorbed species on the low carbon steel surface (Khadom et al., 2009; Shukla and Ebenso, 2011).Generally, $\Delta G°_{ads}$ of -20 kJ mol-1 or lower are said to be consistent with the electrostatic interaction between charged organic molecules and the charged metal surface indicating physisorption (Abd El Haleem et al., 2013; Obi-Egbedi, Obot and Umoren, 2012).The $\Delta G°_{ads}$ for this system is from -8.509and -11.767 kJ mol-1 which indicates physisorption.

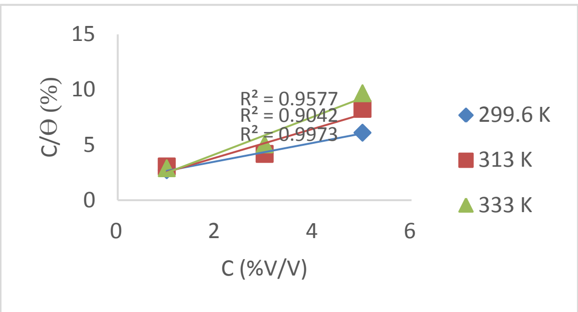

Fig. 3: Langmuir Isotherm for adsorption of *Eichhornia crassipes* extract

Table 3. Adsorption parameters for corrosion of low carbon steel in 1 M sulphuric in the presence of *Eichhornia crassipes* extract

Temperature	R2	K_{ads} (mol^{-1})	$\Delta G°_{ads}$ (kJ mol^{-1})
299.6 K	0.997	0.5486	-8.509
313 K	0.904	0.7936	-9.850
333 K	0.957	1.2639	-11.767

4. Conclusion

The inhibition potential of *Eichhornia crassipes* extract on low carbon steel in 1 M sulphuric acid at different temperatures using gravimetric method was investigated in this study. Results obtained showed that *Eichhornia crassipes* was a good corrosion inhibitor of low carbon steel in 1 M sulphuric acid environment and its performance increased with extract concentration but decreased with temperature. It can be concluded that *Eichhornia crassipes* can be put to industrial use in corrosion prevention due to its high availability thereby reducing its environmental stigma.

Reference

Abd El Haleem, S. M.,Abd El Wanees, S., AbdEl Aal, E. E., Farouk, A. (2013), Nitrogen and/or sulphur-containing organic compounds as corrosion inhibitors for Al in HCl solutions, Corrosion Science, vol. 68, pp. 1-3.

Alaneme, K. K., Olusegun, S. J. (2012),Corrosion inhibition performance of lignin extract of sun flower (Tithoniadiversifolia) on medium carbon low alloy steel immersed in H2SO4 solution, Leonardo Journal of Sciences, vol. 20, pp. 59-70.

Al-Haj-Ali, A. M., Jarrah, N. A., Muazu, N. D., Rihan, R. O. (2014), Thermodynamics and kinetics of inhibition of aluminum in hydrochloric acid by date palm leaf extract, Journal of Applied Sciences and Environmental Management, vol. 18, no. 3, pp. 543-551.

Al-Mhyawi, S. R. (2014), Inhibition of mild steel corrosion using Juniperus plants as green inhibitor, African Journal of Pure and Applied Chemistry, vol. 8, no. 1, pp. 9-22.

Anauda, L., Sathiyanathan, R. A., Maruthamuthu, S. B., Selvanayagam, M. C., Mohanan, S. B., Palaniswamy, N. B. (2005),Corrosion inhibition of mild steel by ethanolic extracts of *Ricinus communis* leaves, Indian J. Chem. Tech., vol. 12, no. 3, pp. 356-360.

Cang, H., Shi, W., Shao, J.,Xu, Q. (2012),Study of *Stevia rebaudiana* Leaves as green corrosion inhibitor for mild steel in sulphuric acid by electrochemical techniques, Int. J. Electrochem. Sci., vol. 7, pp. 3726 – 3736.

Fouda, A. S., Al-Sarawy, A. A., El-Katori, E. E. (2006), Pyrazolone derivatives as corrosion inhibitors for C-steel HCl solution, Desalination, vol. 201, pp. 1–13.

Ibisi, N. E.,Ngwamaghi, V. I., Okoroafor, D. O. (2015), Adsorption and inhibitive action of ethanol extracts of Mallotus Oppositifolius leaves for the corrosion of mild steel in 1 M hydrochloric acid solution, The International Journal of Engineering and Science, vol. 4, no. 7,pp. 31-37.

Khadom, A. A., Yaro, A. S., AlTaie, A. S., Kadum, A. A. H. (2009), Electrochemical, Activations and adsorption studies for the corrosion inhibition of low carbon steel in acidic Media, Portugaliae Electrochimica Acta, vol. 27, no. 6, pp. 699-712.

Khadraoui, A., Khelifa, A., Hachama, K., Mehdaoui, R. (2015), *Thymusal geriensis* extract as a new eco-friendly corrosion inhibitor for 2024 aluminum alloy in 1 M HCl medium, Journal of molecular Liquids.

Labrabi, L., Harek, Y., Benali, O., Ghalem, S. (2005), Hydrazide derivatives as corrosion inhibitors for mild steel in 1 M HCl, Prog. Org. Coatings, vol. 54, pp. 256 -262

Lalitha, T. P., Jayanthi, P. (2012), Study of antioxidant activity of ethanolic extract of fresh *Eichhornia crassipes*(Mart.) Solms, Der Pharmacia Sinica, vol.3, no. 2, pp. 271-277.

Manimegalai, S., Manjula, P. (2015),Thermodynamic and adsorption studies for corrosion inhibition of mild steel in aqueous media by Sargasamswartzii (Brown algae),J. Mater.Environ. Sci., vol. 6, no. 6, 1629-1637.

Naik, U. J., Jha, P. C., Lone, M. Y., Shah, R. R., Shah, N. K (2016), Electrochemical and theoretical investigation of the inhibitory effect of two Schiff bases of benzaldehyde for the corrosion of aluminium in hydrochloric acid, Journal of Molecular Structure, vol. 1125, pp. 63-72.

Obi-Egbedi, N. O., Obot, I. B., Umoren, S. A. (2012),Spondias mombin L. as a green corrosion inhibitor for aluminium in sulphuric acid: Correlation between inhibitive effect andelectronic properties of extracts major constituentsusing density functional theory,Arabian Journal of Chemistry, vol. 5, pp. 361-373.

Oguzie, E. E. (2004), Influence of halide ions on the inhibitive effect of Congo red dye on the corrosion of mild steel in sulphuric acid solute, Material Chemistry and Physics, vol. 87, no. 1, pp. 212- 217.

Oguzie, E. E. (2008), Evaluation of the inhibitive effect of some plant extracts on the acid corrosion of mild steel, Corrosion Science,vol. 50, no. 11, pp. 2993-2998.

Okafor, P. C., Ekpe, U. J., Ebenso, E. E., Umoren, E. M., Leizou, K. E. (2005), Inhibition of mild steel corrosion in acidic medium by Allium sativum. Bull. Electrochemica, vol. 21, pp. 347-352.

Patel, N. S.,Jauhariand, S., NMehta, G. N., Al-Deyab, S. S., Warad, I., Hammouti, B. (2013), Mild steel corrosion inhibition by various plant extracts in 0.5 M sulphuric acid, International Journal of Electrochemical Sciences, vol. 8, pp. 2635-2655.

Rani, B. E. A., Basu, B. B. J. (2012), Green inhibitors for corrosion protection of metals and alloys: an overview, International Journal of Corrosion (Hindawi Publishing Corporation) 2012, Article ID 380217, 15 pages.

Saleh, R. M., Ismail, A. A., El Hosary, A. A. (1982), Corrosion inhibition by naturally occurring substances VII. The effect of aqueous extracts of some leaves and fruit peels on the corrosion of steel, Al, Zn and Cu in acids, British Corrosion Journal, vol. 17, no. 3, pp. 131–135.

Shanab, S. M. M., Shalaby, E. A. (2012), Biological activities and anticorrosion efficiency of water hyacinth (*Eichhornia crassipes*), Journal of Medicinal Plants Research, vol. 6, no. 23,pp. 3950-3962.

Shukla, S. K., Ebenso, E. E. (2011), Corrosion inhibition, adsorption behavior and thermodynamic properties of streptomycin on mild steel in hydrochloric acid medium, Int. J. Electrochem. Sci., vol. 6, pp. 3277 – 3291.

Srivastava, K., Srivastava, P. (1981), Studies on plant materials as corrosion inhibitors. Br. Corros. J., vol. 16, no. 4, pp. 221-223

Teygeler, R. (2000), Water hyacinth papier. Contribution to a sustainable future [bi-lingual]. In (Torley and Gentenaar(eds.), Papieren Water/Paper and Water. Rijswijk,Gentenaar&Torley Publishers, pp. 168-188.

Ulaeto, S. B., Ekpe, U. J., Chidiebere, M. A., Oguzie, E. E. (2012), Corrosion inhibition of mild steel in hydrochloric acid by acid extracts of *Eichhornia crassipes*, International Journal of Materials and Chemistry, vol. 2, no. 4, pp158-164.