IARJSET

ISSN (Online) 2393-8021
ISSN (Print) 2394-1588

International Advanced Research Journal in Science, Engineering and Technology

Vol. 7, Issue 5, May 2020

Novel Extract of *Cyperus Esculentus* Leaves as Green Corrosion Inhibitor for Mild Steel in 0.5M NaCl Aqueous Solution

S.M. Adams[1], M. Abdulwahab[2], Ojiugo N.U[3], F.O. Anianwu[4], N.A. Urama[5], I.N. Okwudiba[6]

Department of Metallurgical and Materials Engineering, University of Nigeria, Nsukka[1,3,4,5,6]

Department of Metallurgical and Materials Engineering, Air Force Institute of Technology, Kaduna, Kaduna State, Nigeria[1, 2]

Abstract: In this paper, the effects of *cyperus esculentus* (tiger nut) leaves extract as corrosion inhibitor for mild steel in 0.5M NaCl solution was investigated. This is to replace the unfriendly, hazardous chromates, bromates, molybdates that have been used as corrosion inhibitors but harmful to lives. Weight loss method was used to study the corrosion behavior at the temperature range of 40 ºC and 60 ºC with inhibitor concentration from 0.1 – 0.5 g/l over an exposure period of 24 hours. The corrosion rates and inhibition efficiency were determined in the absence and presence of *cyperus esculentus* extract. The corrosion rates decreased with increase in inhibitor concentrations and the inhibition efficiency increased with increase in inhibitor concentration. But however, the inhibition efficiency decreased with increase in temperature. The trend of the result was used to propose the mechanism of inhibition. The inhibitor adsorption characteristic were approximated by Langmuir adsorption isotherm at all the temperatures and concentrations studied. The phenomenon of physical adsorption is proposed based on the thermodynamic parameters that govern the inhibition process.

Keywords: Cyperus esculentus, adsorption isotherm, chromates, molybdates, aqueous solution, NaCl

I.INTRODUCTION

The economic power of a country is determined by the output of steel, since developmental progress in the principal economic branches such as agriculture, transport, mining, manufacturing engineering, construction companies, etc. are unthinkable without steel. The role of ferrous metals in general and of steel in particular in the national economy is great [1].

In view of the above, industrial facilities exposed to corrosion are often protected against degradation by using several means such as coating, painting, oiling, anodic and cathodic protection, use of inhibitors, used of high purity metals, materials selection, etc. However, the use of inhibitors has been found to be one of the best methods for such protection against corrosion [2]. Inhibitors are chemical compounds that tend to retard the rate of corrosion of metals by adsorbing onto the surface of the metal either through the transfer of charge inhibitor molecule to charged metal surface or by electron transfer from inhibitor's molecule to the vacant mostly d-orbital of the metal [3].

Various studies have been carried out on the corrosion of metals in different environments and their inhibition performance via the use of plant of natural origin for the inhibition of the corrosion of metals in acidic, alkaline media were reported [4-6]. Researchers generally agree that most of these plants are green inhibitors because they are biodegradable, less toxic, and does not contain any heavy metal in them [7]. In the light of these, several plant extracts have been reported their corrosion inhibition properties are often attributed to their phytochemical constituents [8]. These include heteroatoms in their aromatic or long chain, possession of π - electrons or suitable groups may also facilitate the transfer of charge from the inhibitors molecule to charge metal surface.

Cyperus esculentus (popularly known as tiger nut in Nigeria) is an annual or perennial plant, growing to 90 cm tall, with solitary stems growing from a tuber. Leaves are yellowish green, shinny, grass like leaves are long and narrow, mostly basal and alternate, and they point outward from the stem in three directions. It has several names (chufa, sedge, nut grass, yellow nutsedge, tiger nutsedge, water grass and earth almond). The present study aimed at elucidating the potential of ethanolic extraction of *cyperus esculentus* as a corrosion inhibitor for mild steel in aqueous solution.

II.MATERIALS AND METHOD

2.1 *Materials*

The materials used in this work includes mild steel of known chemical composition as shown in Table 1 obtained from Universal Steel Company Limited, Lagos State, Nigeria. *Cyperus esculentus* leaves, corrosion bath, beakers, brush, grinding papers, emery papers, dessicator, digital weighing balance, ethanol, distilled water and hack saw.

TABLE 1: CHEMICAL COMPOSITION OF MILD STEEL USED FOR THE STUDY

Elements	Fe	C	Si	Mn	S	P	Cr	Ni	Cu	Al	Mo	V	Ti
Composition (% wt.)	97.75	0.21	0.25	0.77	0.03	0.02	0.13	0.13	0.33	0.29	0.02	0.003	0.009

2.2 *Collection of plant*

The leaves of *cyperus esculentus* (CE) was collected from a farm center in Kachia local government area of Kaduna State, Nigeria. The plant was confirmed by Herbarium in Biological Science Department at Ahmadu Bello University, Zaria. The leaves so confirmed were used for the study.

2.3 *Plant extraction*

The collected leaves were shade dried; powdered and about 500 g was mixed with the solvent (ethanol) in a round bottomed flask and kept air tight for 120 hours and was shaken frequently for uniform mixing and distribution of the powdered sample. The solution was filtered through a Whatmann no. 1 filter paper and the solvents present in the filtrate were evaporated to dryness. From the stock solution, various concentrations of the extract were prepared and were used for the corrosion study.

2.4 *Qualitative phytochemical test*

Phytochemical test was conducted on the extracts of cyperus esculentus using standard methods as reported elsewhere [9, 10].

2.5 *Weight loss method*

The samples were completely weighed before immersed in 250 ml of the test solution with and without the addition of different concentrations of *cyperus esculentus* extracts. The beaker was inserted into a water bath maintained at a temperature of 40 ^{0}C and 60 ^{0}C over an exposure time of 24 hours respectively. Each sample was withdrawn from the test solution, washed with brush under running water and rinsed with ethanol and air dried before re-weighing. This procedure was repeated for the varied temperatures. The difference in weight was recorded as the weight loss. From the weight loss, the corrosion rates (CR) were calculated using the equation

$$CR = \frac{87.6W}{DAT} \text{ mm/yr} \qquad (1)$$

Where W= weight loss in mg
D= density g/cm^3
A= area in cm^2
T= exposure time in hours

From the corrosion rate, the inhibition efficiency, (IE %) was calculated using the equation

$$IE\% = \frac{CRo - CR}{CRo} \times 100 \qquad (2)$$

Where CR_o is the corrosion rate without inhibitor and CR is the corrosion rate in the presence of inhibitor. The surface coverage, ϴ, was calculated from the corrosion rate as follows:

$$\Theta = \frac{CRo - CR}{CRo} \qquad (3)$$

III. RESULTS AND DISCUSSION

3.1 *Qualitative phytochemical test result*

The extract of *cyperus esculentus* leaves were screened for the presence of various secondary metabolites (phytochemical) such as alkaloids, tannins, steroids, flavonoids, saponins, phenols etc. The result of the finding is presented in Table 2 [11].

TABLE 2: QUALITATIVE PHYTOCHEMICAL SCREENING OF ETHANOL EXTRACT OF *CYPERUS ESCULENTUS*

Test	Result
Alkaloids	+++
Flavonoids	+++
Saponnins	—
Phenols	+++

IARJSET

ISSN (Online) 2393-8021
ISSN (Print) 2394-1588

International Advanced Research Journal in Science, Engineering and Technology

Vol. 7, Issue 5, May 2020

Steroids	++
Tannins	+++
Terpenoids	+++
Glycosides	+++

3.2 ***Effect of inhibitor concentration on corrosion rate***

The effect of corrosion rate versus exposure time at different temperatures is shown in Figure 1 and it was observed that the corrosion rate of the mild steel decreased with addition of inhibitor. At 40 ^{0}C, the corrosion rate for the control is 4.2 mm/yr and was reduced to 0.3 mm/yr in the presence of inhibitor been optimum. Similar trend was observed at 50 ^{0}C and 60 ^{0}C respectively. This may be due to the increased protection offered by the inhibitor as concentration increases, thereby preventing the breakdown of the passive films leading to an increase in the corrosion resistance of the mild steel compared with the uninhibited samples [12]. However, as the temperature increased, the corrosion rate was found to increase with temperature having the higher values of corrosion rates. This could be that there is desorption of inhibitor from the surface of the mild steel or break down of protective film formed earlier due to increase in temperature thereby exposing it to the aggressive environment.

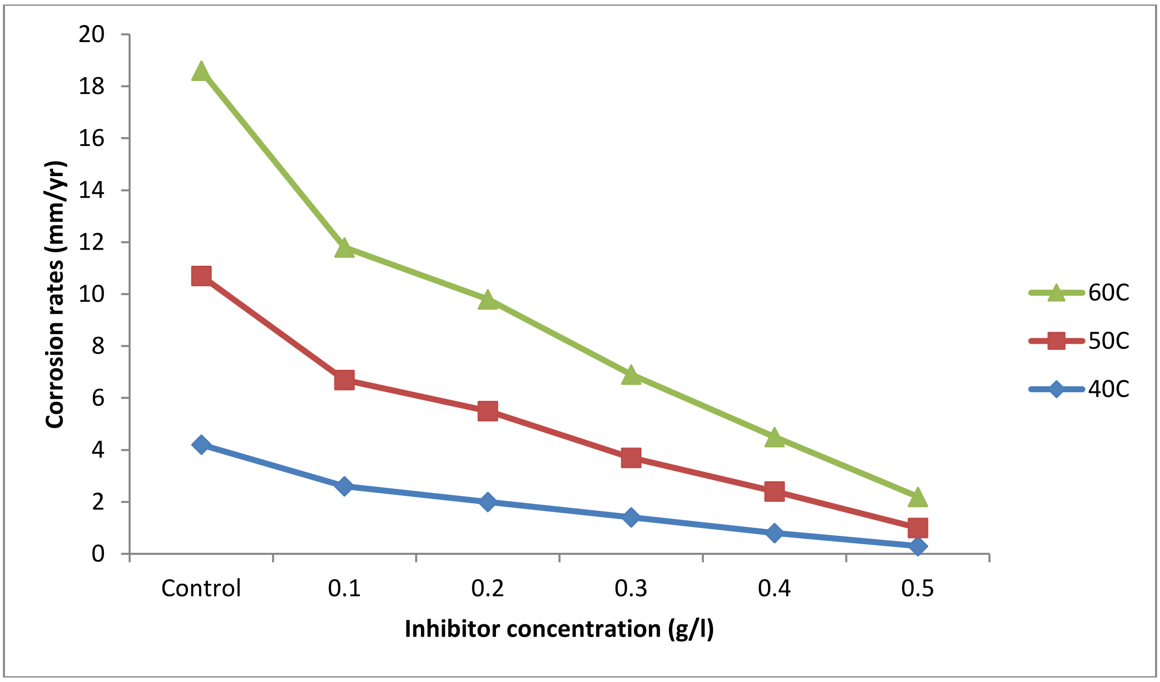

Figure 1: Corrosion rates against inhibitor concentration of mild steel in the absence and presence of *cyperus esculentus* leaves extract in NaCl aqueous solution

3.3 ***Effect of inhibitor concentration on inhibitor efficiency***

In Figure 2 the variation of inhibitor efficiency with inhibitor concentration is shown. The inhibition efficiency increased with increase in the concentration of *Cyperus esculentus* leaves extract. At a temperature of 40 ^{0}C, maximum inhibition efficiency of 92.86 % was obtained at 0.5 g/l inhibitor concentration. The reduction in inhibition efficiency at 50 ^{0}C and 60 ^{0}C can be attributed to the acceleration of the breakdown of the passive film at higher temperature.

DOI 10.17148/IARJSET.2020.7525

IARJSET
ISSN (Online) 2393-8021
ISSN (Print) 2394-1588
International Advanced Research Journal in Science, Engineering and Technology
Vol. 7, Issue 5, May 2020

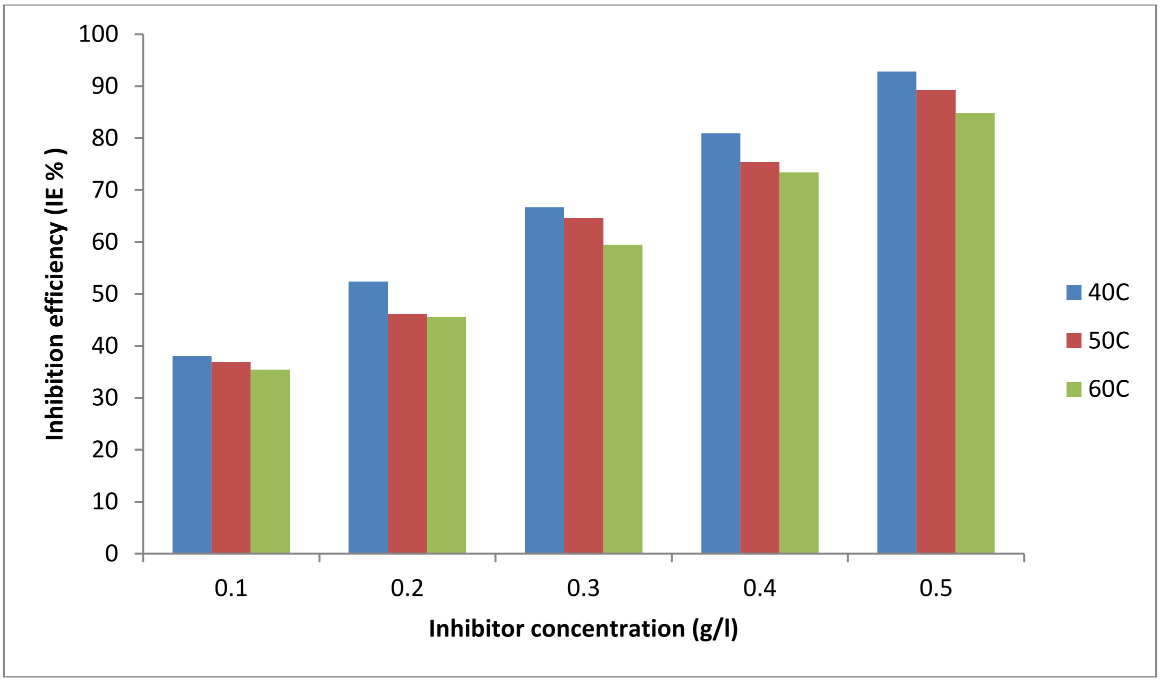

Figure 2: Inhibition efficiency against inhibitor concentration of mild steel in the absence and presence of *cyperus esculentus* leaves extract in NaCl aqueous solution

3.4 *Effect of Temperature*

The effect of temperature on the corrosion of mild steel in the absence and presence of *Cyperus esculentus* leaves was studied using the Arrhenius state equation as shown in Equations (4) and (5) [13].

$$\log CR = \log A - Ea/2.303RT \quad (4)$$

$$\log\left(\frac{CR}{T}\right) = \{\log (R/NA\,h) + \Delta Sa/2.303R\} - \Delta Ha/2.303RT \quad (5)$$

Where CR is the corrosion rate of the metal, A is the Arrhenius or pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the temperature of the system. N_A is the Avogadro's constant, ΔSa is the entropy of activation and ΔHa is the enthalpy of activation. From Equation 4, plot of log CR versus reciprocal of absolute temperature, 1/T is as presented in Figure 3, which gives a straight line with slope equal to $-\frac{Ea}{2.303R}$, from which the activation energy for the corrosion process can be calculated.

From Equation (5), plot of $Log\ CR/T$ versus reciprocal of absolute temperature, $1/T$, as shown in Figure 4 gives a straight line with slope equal to - $\frac{\Delta Ha}{2.303R}$ and intercept of $\left[Log\frac{R}{NAh} + \frac{\Delta Sa}{2.303R}\right]$, from which the enthalpy and entropy of activation for the corrosion process can be calculated. Values of Ea, ΔSa, and ΔHa are presented in Table 3. The values of the extrapolated activation energy, Ea were found to be greater where corrosion rate were inhibited than those obtained where there were no inhibition indicating that the extracts of *cyperus esculentus* leave extract retarded the corrosion of the alloy in the studied medium. It was also found that the activation energy was lowered than the value of 80 kJ/mol. required for chemical adsorption to take place, confirming that the adsorption occur through the mechanism of physical adsorption [14]. The increase in the activation energy is achieved presumably via formation of a thin coat or film on the metal surface that has become a barrier to both energy and mass transfer. However, increasing the solution temperature weakens the inhibition effect by enhancing the counter process of desorption. That is why the inhibition efficiency values decreased with increase in temperature.

TABLE 3: VALUES OF ACTIVATION ENERGY (EA), ENTHALPY (ΔHA) AND ENTROPY (ΔSA) CHANGE OF THE CORROSION.

Inhibitor concentration (g/l)	Ea (kJ/mol.)	ΔHa (kJ/mol.)	ΔSa (kJ/mol.)
Control	-27.61	24.81	215.11
0.1	-60.46	60.19	124.52
0.2	-42.21	40.22	179.65
0.3	-36.05	33.89	195.42
0.4	-33.49	31.19	200.86

0.5	-29.43	26.58	213.50

Temperature (^{0}C)	R^2	**ΔG* (kJ/mol.)**
40	0.899	-4.77
50	0.873	-8.06
60	0.873	-10.41

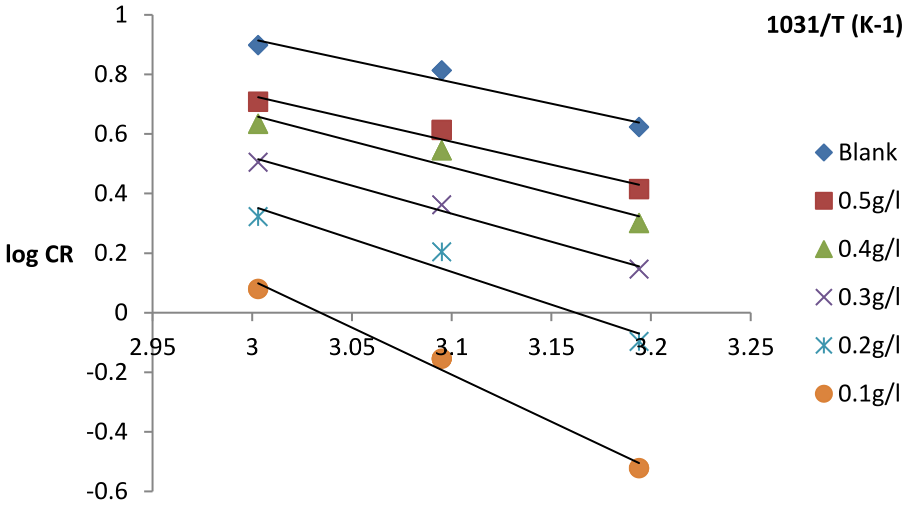

Figure 3: Log CR against 1/T

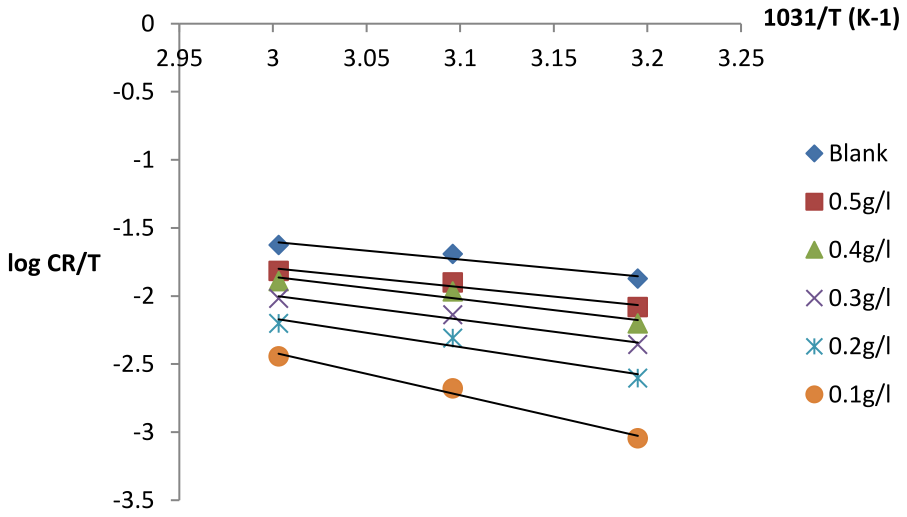

Figure 4: Log CR/T against 1/T

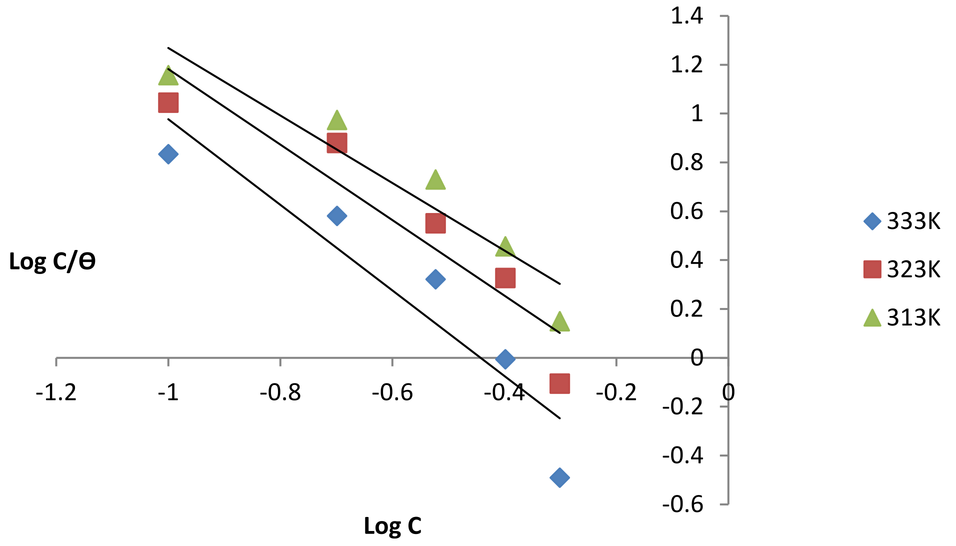

Figure 5: Log C/Ө against Log

3.5 ***Adsorption isotherm***

The adsorption behavior of *cyperus esculentus* leave extract was investigated. The test revealed that adsorption of bark extract on the surface of the mild steel is constant with Langmuir and adsorption isotherms. Langmuir adsorption model can be represented as follows

$$\frac{c}{\theta} = \frac{1}{K} + c \qquad (4)$$

where c is the inhibitor concentration and K is the adsorption equilibrium constant representing the degree of adsorption. θ is the degree of surface coverage [15]. Taking the

$$log\frac{c}{\theta} = c + 1/k \qquad (5)$$

Logarithm of equation 4, equation 5 is obtained. The plot of log c / Ө versus log c as shown in Figure 5 gave linear plots indicating that Langmuir adsorption isotherm is applicable to the adsorption of *cyperus esculentus* leave extract on the surface of the mild steel.

Thermodynamic parameters play an important role in studying the inhibitive mechanism. The standard adsorption free energy (ΔG^o_{ads}) was obtained according to [16].

$$\Delta Gads = -RT \ln (55.5\ K) \qquad (6)$$

Where R is the molar gas constant, T is the temperature in Kelvin, 55.5 is the molar concentration of water and K is the equilibrium adsorption constant.

$K_{ads} = Ө/(1 - Ө)\ C.$

Calculated values of the free energies are presented in Tables 4. Generally, values of ΔG^o_{ads} around -20 kJ / mol or lower are consistent with the electrostatic interaction between the charge molecules and the charged metal (physisorption); those around -40 kJ / mol or higher involve charge sharing or charge transfer from organic molecule to the metal surface to form a coordinate type of bond (chemisorptions) [17]. From the result obtained, the values were found to be negative, physisorption, and a suggestion that the adsorption of *cyperus esculentus* leave onto the mild steel surface is a spontaneous process and adsorbed layer is stable [18].

IV.CONCLUSION

After the study, and from the results of weight loss of corrosion rate of mild steel by *cyperus esculentus* extract as corrosion inhibitor, the following conclusions were drawn:

1. The corrosion rate of the mild steel in the presence of *cyperus esculentus* leaves extract decreases with increase in the concentration of the inhibitor
2. The extract *cyperus esculentus* leaves extract can be used as inhibitor for mild steel in the 0.5 M NaCl aqueous solution.
3. The inhibition efficiency (% IE) increased with increase in concentration of the inhibitor and also decreases with increase in temperature.
4. It has been established that the adsorption process followed a physisorption.

 DOI 10.17148/IARJSET.2020.7525

V.ACKNOWLEDGEMENT

The authors wish to acknowledge the assistance of the department of Metallurgical and Materials Engineering, University of Nigeria, Nsukka and the department of Metallurgical and Materials Engineering, Ahmadu Bello University Zaria for their equipment supports.

Conflict of interest
There is no conflict of interest associated with this work

REFERENCES

[1]. V. Kudrin. Steel making. Mir publishers Moscow, USSR, 129820, P11, 1985

[2]. E.E. Oguzie, G.N. Onuoha, and E.N. Ejike, Effect of Gongronema latifolium extracton aluminium corrosion in acidic and alkaline media. *Pigment Resin Technology, 36 (1):P.44_49, 2007*

[3]. N.O. Eddy, Y.H. Momoh, and E.E. Oguzie, Theoretical experimental studies on the corrosion inhibition potentials of some purines for aluminium in 0.1 M HCl. *Journal of advanced Research, 6: 203-217, 2015*

[4]. S.M. Adams, V.S. Aigbodion, I.Y. Suleiman, and I.M. Momoh, Thermodynamic, Kinetic and Adsorptive Parameters of Corrosion Inhibition of Mild Steel Using Polyalthialongifolia Bark Extract in 0.5 M H_2SO_4. *International Journal of Science and Engineering Invention, Vol.05, Issue 11, 2019. ISSN: 2455 – 4286, DOI: 10.23958/ijsei/vol05-i11/177*

[5]. C.A. Loto, R.T. Loto, A.P.I. Popoola, The Synergistic Effect of Tobacco and Kola tree Extracts on the Corrosion Inhibition of Mild Steel in Acid Chloride. *International Journal of Electrochemical Sciences, 6, 3830-3843, 2011*

[6]. P.C. Okafor, V.E. Ebiekpe, C.F. Azike, G.E. Egbung, E.A. Brisibe, and E.E. Ebenso, Inhibitory Action of Artemisia Annua Extracts and Artemisinin on the Corrosion of Mild Steel in H_2SO_4 Solution. *Bulletin of Electrochemistry, 22(9): 234-242, 2012.*

[7]. P.C. Okafor, V. Osabor, and E.E. Ebenso, Eco friendly corrosion inhibitors: Inhibitive action of ethanol extracts of Garcinia Kola for the corrosion of Aluminium in acidic medium. *Pigment and Resin Technology, 36(5):299-305, 2007.*

[8]. S.A. Umoren, E.E. Ebenso, Studies of anti-corrosive effect of Raphia hookeri exudate gum and halide ions on the corrosion inhibition of Al in HCl solutions. *Pigment Resin Technology, 37(3):173-182, 2008*.

[9]. N. Prakash and B. Ragavan, Phytochemical Observation and Antibacterial Activity of Cyperus Esculentus. *Ancient Science of Life, vol. 28. No. 4, 16-20, 2009.*

[10]. H.O. Edoga, D.E. Okwu, B.O. Mbaebie, Phytochemical Constituents of Some Nigerian Medicinal Plants. *African Journal of Biotechnology, 4: 685-688, 2005.*

[11]. R. Nandhini, T. Ananthi, Preliminary phytochemical analysis and antibacterial activity on bark extract of caesalpinia pulcherrima (L.). *Journal of Pharmaceutical Research. 5:83-86, 2016.*

[12]. R.B. Lakshman, Phytochemical Screening Quantitative Estimation Total Phenolic and Total Flavonoids.Anti Microbial Evaluation of Cyamopsis Tetragonoloba. *International Journal of Research in Pharmaceutical and Biomedical Sciences, Vol.3, 3, 2012.ISSN: 2229 – 3701*

13. M. Lebrini, F. Robert, C. Roos, Experimental and theoretical study for corrosion inhibition of mild steel in normal hydrochloric acid solution by some new macrocyclic polyether compounds. *International Journal of Electrochemical Science, 5, 1698, 2010.*

14. I.B. Obot, S.A. Umoren, and N.O. Obi-Egbedi, Corrosion inhibition and adsorption behavior for aluminium by extract of Aningeria Robusta in HCl solution: Synergistic effect of iodide ions. *Journal of Materials and Environmental Science, 2(1) (2011) 60 – 71, 2011.*

15. C. Hui, F. Zhenghao, S. Jinling, S. Wenyan, X. Qi, Corrosion Inhibition of Mild Steel by Aloes Extract in HCl Solution Medium. *International Journal of Electrochemical Science, 8, 720 – 734, 2013*.

16. G.Y. Stephen , O.A. Sylvester , G.T. Tersoo, J.A. Ungwanen, and A.G. Joseph , Thermodynamics, Kinetic and Adsorptive Parameters of Corrosion Inhibition of Aluminium using Sorghum bicolor Leaf Extract in H_2SO_4. *International Journal of Advanced Research in Chemical Science (IJARCS), VOLUME I, Issue 2, pp 38 – 46, 2014*.

17. A. Singh, V.R. Singh, and M.A. Quraishi, Inhibition Effect of environmentally Benign Kuchla (Strychnos Nuxvomica) Seed Extract on corrosion of mild steel in HCl Acid solution. *International Journal of Corrosion, 1, 1–10, 2010.*

18. V.K. Srinivasa , and R.S. Devaki, Production and Characterization of Al – 11% Si–3%Cu Alloy. *International Journal of Mechanical and Production Engineering.ISSN 2320-2090.*2(3):1-3, 2014.