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Xanthosoma spp leaf extract as green corrosion inhibitor for Al – Cu – Mg Alloy in simulated seawater environment

Adams SM[1]✉, Suleiman IY[2], Musa AA[3], Momoh IM[4]

[1]Department of Metallurgical and Materials Engineering, University of Nigeria, Nsukka E-mail: sani.adam@unn.edu.ng
[2]Department of Metallurgical and Materials Engineering, University of Nigeria, Nsukka Email: idawu.suleiman@unn.edu.ng
[3]Department of Metallurgical and Materials Engineering, Ahmadu Bello University, Zaria Nigeria Email: abdulrahman@abu.edu.ng
[4]Department of Metallurgical and Materials Engineering, Kogi State Polytechnic, Lokoja, Nigeria Email: rhodave2011@gmail.com

✉**Corresponding author**
Department of Metallurgical and Materials Engineering, University of Nigeria, Nsukka,
Nigeria
E-mail: sani.adam@unn.edu.ng

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ABSTRACT

Corrosion inhibition effect of *Xanthosoma spp* leaf extract on Al-Cu-Mg alloy in simulated seawater has been studied using gravimetric method at 303k, 313k and 323k temperatures with various concentrations (0.1, 0.2, 0.3, 0.4, and 0.5) g/L of the extract. The inhibition efficiency was found to increase with increasing inhibitor concentration. The effect of temperature on the corrosion inhibition of alloy indicated an increase in the corrosion rate as temperature increased and subsequent decrease in the inhibition efficiency. Thermodynamic data calculated are suggestive of adsorption of inhibitor molecules on metal surface. Experimental data fitted into Langmuir's adsorption isotherm. Hence, the corrosion inhibition effect of the extract was rationalized via adsorption mechanism

Keywords: Simulated seawater; Al-Cu-Mg alloy, *Xanthosoma spp leaf,* Weight loss method; Corrosion rate, Adsorption isotherm

1. INTRODUCTION

Aluminium can be alloyed with different elements like copper, zinc, magnesium, manganese, silicon, as well as lithium. Its applications include foil covering, food packaging industry, food and chemical industry, vehicle paneling, marine cages, air frames, chemical plants, pressure vessels, road tankers, transportation of ammonium nitrate, irrigation pipes and window frames.

Al-Cu-Mg alloy is an alloy in which copper is the major alloying element and magnesium as minor. The alloy has moderately high strength with medium or poor impact resistance, poorest corrosion resistance. The marine and pipeline industries have continued to face the problem of corrosion and subsequent deterioration of infrastructure exposed to actual hostile marine environments [1].

Protective oxide films formed on the aluminium surface have a dual nature. These films consist of an adherent comact, and stable inner oxide film covered with a porous, less stable outer layer, which is more susceptible to corrosion [2]. The use of inhibitors is one of the most practical methods for protecting metallic corrosion, especially in hostile environment like seawater. It is well established that inhibitors function in one or more ways to control corrosion; by adsorption of a thin corrosion product, or by changing the characteristics of the environment resulting in reduced aggressiveness [3]. Although many synthetic compounds show good corrosion inhibition ability, the search for most non toxic environmentally friendly inhibitors are the focus now in metallic corrosion prevention. *Xanthosoma spp* (Cocoyam) leaf is an aquatic weed that grows in swampy environment of Bonny Island. The plant is a native of Tropical America but widely cultivated and naturalized in other tropical regions. From the photochemical investigation of the leaf, it is worthy to note that the leaves of this aquatic weed contains hetero atoms (N and O) and the availability of π electrons in the aromatic system which are inherent in its complex mixture of glycosides, saponins, alkaloids, terpenes, tannins, phenolic substances and flavonoids [4]. Not much use of it is made by the locals both for domestic or other purposes.

Throughout the ages, plants have been used by human beings for their basic needs such as shelters, production of food stuffs, fertilizers, flavors and fragrance, clothing, medicines and last but not the least, as corrosion inhibitors as noted by [5]. The use of corrosion inhibitors is the most economical and practical method in reducing corrosive attack on metals. Corrosion inhibitors are chemicals either synthetic or natural which when added in small quantity to an environment decrease the rate of attack by the environment on metals [6].

Generally the mechanism of the inhibitor is one or more of three that are cited below:

- the inhibitor is chemically adsorbed (chemisorption) on the surface of the metal and forms a protective thin film with inhibitor effect or by combination between inhibitor ions and metallic surface;
- the inhibitor leads a formation of a film by oxide protection of the base metal;
- the inhibitor reacts with a potential corrosive component present in aqueous media and the product is a complex.[7]

2. EXPERIMENTAL

Preparation of Plant Extracts

Xanthosma spp (Cocoyam) leaves were plucked from a waterlogged area in Nsukka Local Government area of Enugu State and identified at the Biological Science Department, University of Nigeria, Nsukka. The *Xanthosma spp* leaves were dried under shade and ground to powder, and then dissolved in 500 ml of distilled water and heated in a water bath at 60 ^{O}C. Thereafter the solution was filtered and the filtrate concentrated to 200 ml in a water bath at 100 ^{O}C. The stock solution of the extract so obtained was used in preparing different concentrations of the extract 0.1, 0.2, 0.3, 0.4, and 0.5 g respectively [8].

Materials

The Al-Cu-Mg alloy with chemical composition (wt. %) as follows: Cu = 4.0; Mg = 0.35; Zn = 0.10 and balance Al was produced according to the method described elsewhere [9]. Coupons were cut into 10 X 15 mm size were used for weight loss measurements, and were mechanically abraded with 400, 600, 800 and 1000 grade of emery papers and thereafter degreased with acetone, washed with distilled water and dried in air before immersing in the medium.

Phytochemical screening

The phytochemical screening of the plant was carried out at Chemistry Department of the University of Nigeria, Nsukka; using a standard procedure [10 - 11].

Weight Loss Measurement

Al-Cu-Mg alloy coupons were immersed in five beakers containing various concentrations of the corrosion inhibitor (0.1, 0.2, 0.3, 0.4, and 0.5) g/l and a sixth beaker without the inhibitor which was used as the control. For the experiment at 303K, the coupons were retrieved after 24 hours. They were thoroughly cleaned and washed with distilled water, degreased with acetone and weighed with an electronic balance. The same experiments were repeated at 313k, and 323k respectively and the same process of weighing was applied. The difference between the present and previous weights were computed and recorded as the weight loss. From the weight loss, the corrosion rates (CR) were calculated using the equation

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

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

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

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:

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

3. RESULTS AND DISCUSSION

Phytochemical screening

Table 1 shows the phytochemical screening of methanol extract of *Xanthosoma spp* Leaf. The results obtained indicate that Tannins, Saponins, Flavonoids, Glycosides, Phytosterols and Alkaloids are present in the methanol extract of *Xanthosoma spp* Leaf extracts; hence the inhibition efficiency of methanol extract of plant may be attributed to the phytochemical constituent of the extract.

Table 1 Phytochemical Screening of Xanthosoma leaf extract

Substances	Presence
Phenol	++
Flavanoids	++
Tannins	++
Saponins	++
Alkaloids	+
Glycosides	++
Phytosterols	+

++ = highly present; + = moderately present

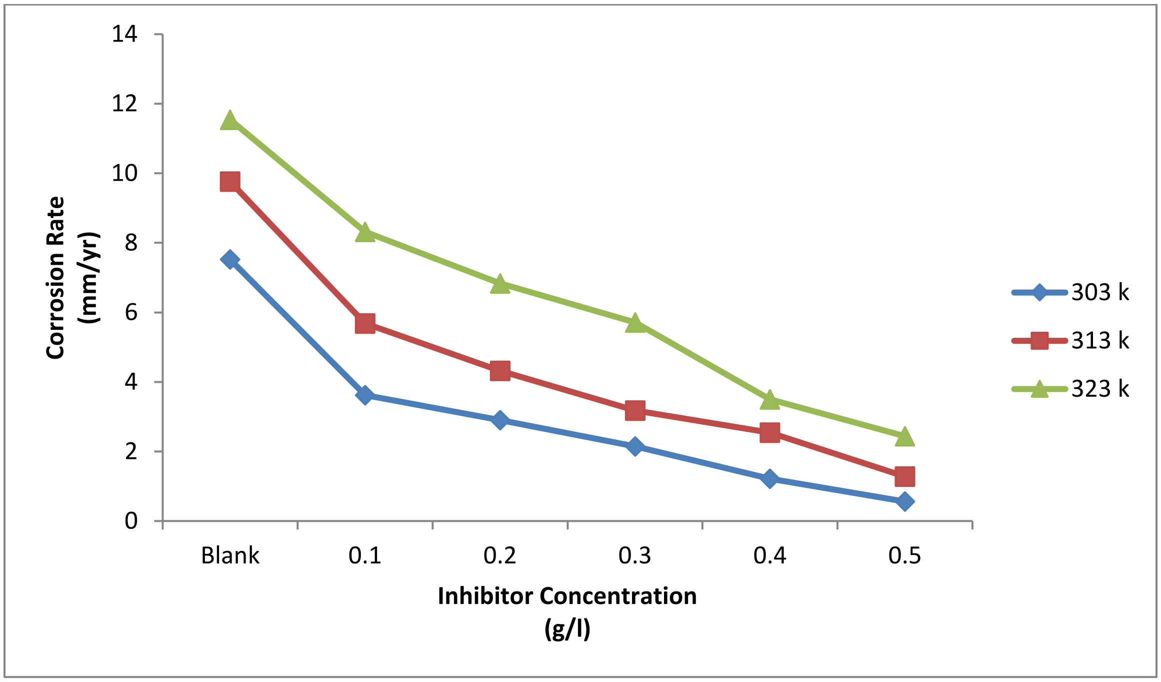

Figure 1 Variation of Corrosion Rate against Inhibitor Concentration of Al-Cu-Mg Alloy in the Presence and Absence of Xanthosoma leaf extract

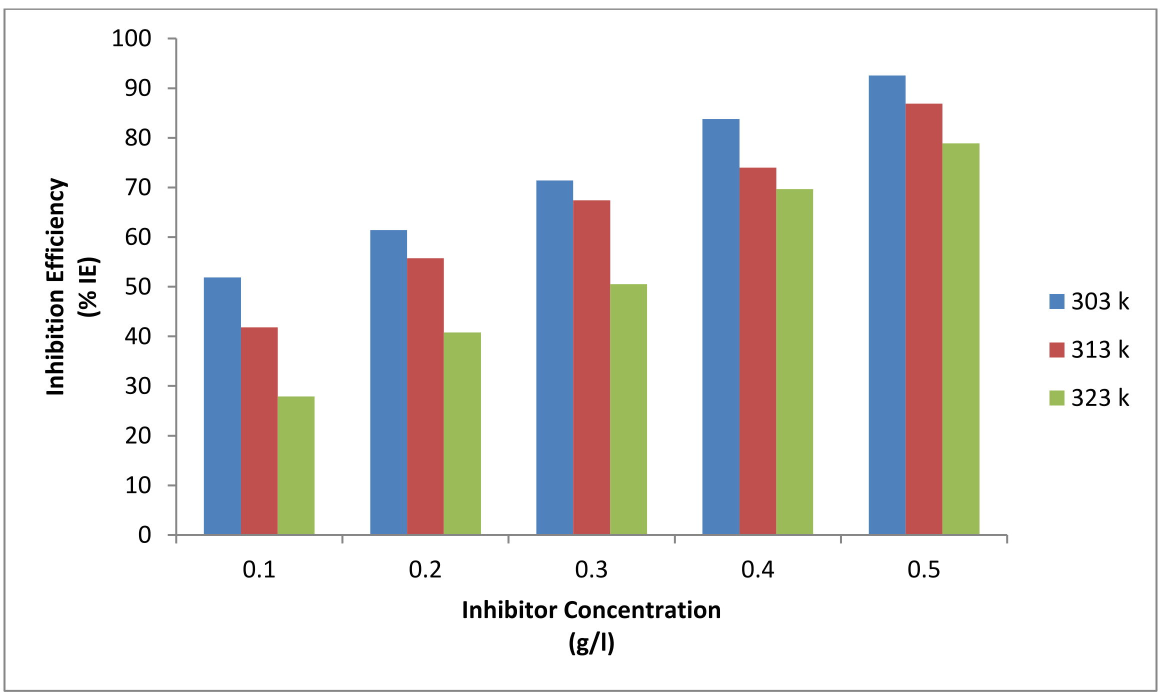

Figure 2 Variation of Inhibitor Efficiency against Inhibitor Concentration of Al-Cu-Mg Alloy in the Presence and Absence of *Xanthosoma* leaf extract

Effect of inhibitor concentration on corrosion rate

The variation of corrosion rate with immersion time at different temperatures are shown in Figure 1 and it was observed that the corrosion rate of the alloy in simulated seawater environment decreased with addition of inhibitor. At 303k, the corrosion rate for the control is 7.52 mm/yr but this value was reduced to 0.56 mm/yr in the presence of inhibitor. Similar trend was observed with increase in temperature. 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 alloy compared with the uninhibited samples [12]. The least corrosion rate was obtained at 303 k, in 0.5 g/l concentration. However, as the temperature increased, the corrosion rate increase with 313 k having the highest values of corrosion rates. This could be that there is desorption of inhibitor from the alloy surface or break down of protective film formed earlier due to increase in temperature thereby exposing it to the aggressive environment.

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 *Xanthosoma* leaf extract. At a temperature of 313 k, maximum inhibition efficiency of 92.55 % was obtained at 0.5 g/l inhibitor concentration. The reduction in inhibition efficiency at 313 k and 323 k can be attributed to the acceleration of the breakdown of the passive film at higher temperature.

Effect of Temperature

The effect of temperature on the corrosion of Al-Cu-Mg alloy in the absence and presence of XLE 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 Figures 4, 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 Figures 5 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 enthyalpy and entropy of activation for the corrosion process can be calculated. Values of Ea, ΔSa, and ΔHa are presented in Table 1-5. 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 XLE 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 2 Corrosion rates (mm/yr) against inhibitor concentration of Al-Cu-Mg alloy at 303 k, 313 k, and 323 k in the presence and absence of *Xanthosoma* leaf extract

Inhibitor Concentration (g/l)	Exposure Time (24 HOURS) 303 K	313 K	323 K
Control	7.52	9.76	11.54
0.1	3.62	5.68	8.32
0.2	2.90	4.32	6.88
0.3	2.15	3.18	5.71
0.4	1.22	2.54	3.50
0.5	0.56	1.28	2.44

Table 3 Inhibitor Efficiency against Inhibitor Concentration of Al-Cu-Mg alloy at 303 k, 313 k, and 323 k in the presence and absence of *Xanthosoma* leaf extract

Inhibitor Concentration (g/l)	Inhibition Efficiency (% IE)		
	303 K	313 K	323 K
Control	_	_	_
0.1	51.86	41.80	27.90
0.2	61.44	55.74	40.81
0.3	71.41	67.42	50.52
0.4	83.78	73.98	69.67
0.5	92.55	86.89	78.86

Table 4 Langmuir adsorption isotherm for the calculated ΔG^o_{ads} of Al-Cu-Mg Alloy

Temperature (K)	R^2	ΔG^o_{ads}
303	0.990	- 7.09
313	0.987	-7.976
323	0.937	-9.282

Table 5 Activation energy parameters for for Al-Cu-Mg alloy in the absence and presence of Xanthosoma leaf extract

Inhibitor Conc. (g/l)	Ea (kJ/mol)	ΔHa (kJ/mol)	ΔSa (kJ/mol)	Q_{ads} (kJ/mol)
Blank	17.5	14.8	- 179.31	_
0.1	33.9	31.5	- 130.48	- 41.65
0.2	35.1	32.4	- 129.56	- 93.69
0.3	39.6	37.1	-116.74	- 36.40
0.4	43.0	40.6	- 109.14	- 32.97
0.5	59.9	58.7	- 56.32	- 48.94

Adsorption isotherm

The adsorption behavior of *xanthosoma* leaf extract (XLE) was investigated. The test revealed that adsorption of XLE on the surface of the Al-Cu-Mg alloy is constant with Langmuir adsorption isotherm. 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 $log\frac{c}{\theta} = c + 1/k$ (5)

Logarithm of equation 4, equation 5 is obtained. The plot of log c / Ɵ versus log c as shown in Figure 3 gave linear plots indicating that Langmuir adsorption isotherm is applicable to the adsorption of XLE on the surface of the aluminium alloy.

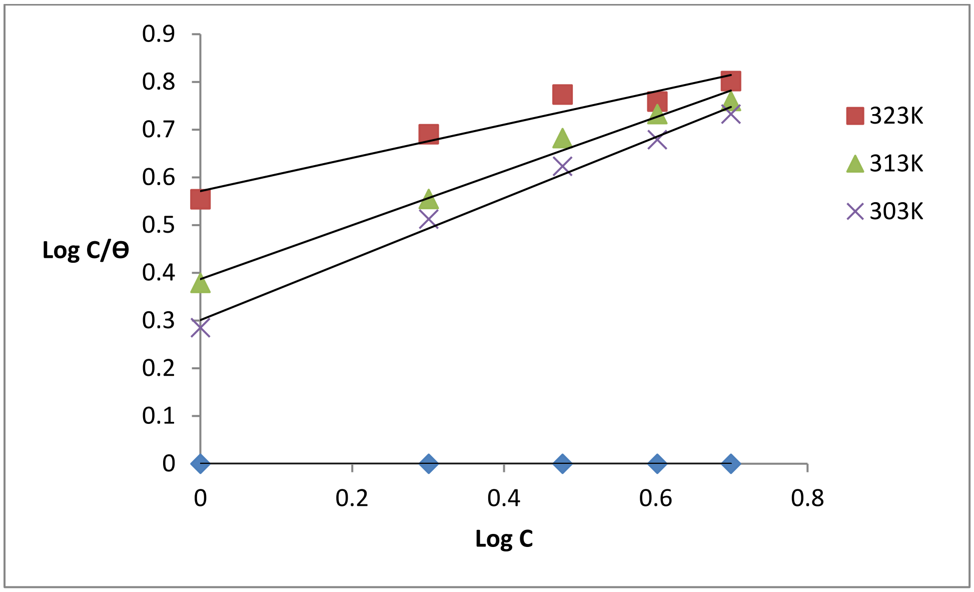

Figure 3 Langmuir adsorption plot for Al-Cu-Mg alloy of *Xanthosoma* Leaf Extract at different temperatures in simulated seawater

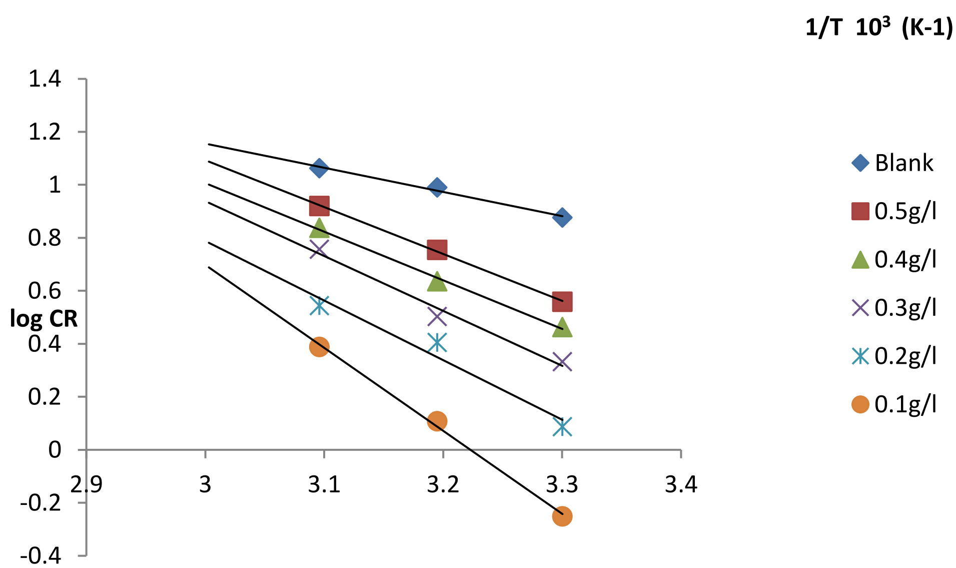

Figure 4 Arrhenius plots of log CR versus 1/T for Al-Cu-Mg alloy in the absence and presence of *Xanthosoma* leaf extract

Thermodynamic parameters play an important role in studying the inhibitive mechanism. The standard adsorption free energy (ΔG^o_{ads}) was obtained according to [15].

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

Where R is the molar gas constant, T is the temperature in Kelvin, 55.5 is the molar concentration of water and $K_{ads} = \Theta/(1 - \Theta)\ C$.

Calculated values of the free energies are presented in Table 5. 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) [16]. From the result obtained, the values were found to be negative, physisorption, and a suggestion that the adsorption of XLE onto the Al-Cu-Mg surface is a spontaneous process and adsorbed layer is stable [17].

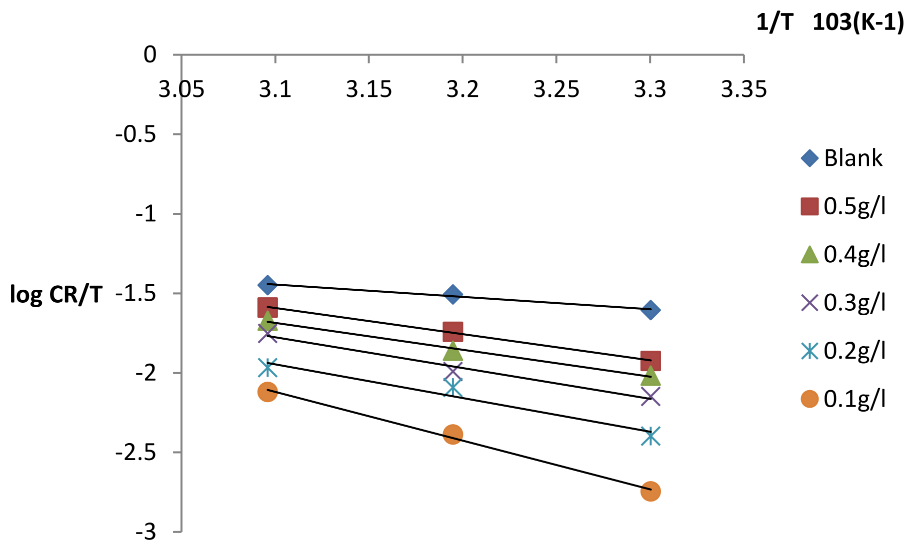

Figure 5 Arrhenius plots of log (CR/T) versus 1/T for Al-Cu-Mg alloy in the absence and presence of *Xanthosoma* leaf extract

4. CONCLUSION

From the results of weight loss of corrosion rate of Al-Cu-Mg alloy in simulated seawater using *Xanthosoma* leaf extract as corrosion inhibitor, the following conclusions were drawn:

1. The corrosion rate in the presence of XLE (inhibitor) decreases with increase in the concentration of the inhibitor
2. The extract (XLE) can be used as inhibitor for Al-Cu-Mg alloy in simulated seawater environment
3. The percentage inhibition efficiency (% IE) increased with increase in concentration of the inhibitor. However, it decreases with increase in temperature.
4. It has been established that the adsorption process followed a physisorption.

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Conflicts of Interest: The authors declare no conflict of interest.

REFERENCE

1. Aisha H. Al-Moubaraki1, Awatif Al-Judaibi, Maryam Asiri1 (2015): Corrosion of C-Steel in the Red Sea: Effect of Immersion Time and Inhibitor Concentration. *Int. J. Electrochem. Sci.,* 10 **,**4252 – 4278
2. El-Sayed M. Sherif (2011). Corrosion and Corrosion Inhibition of Aluminium in Arabian Gulf Seawater and Sodium Chloride Solutions by 3-Amino-5-Mercapto-1, 2, 4- Triazole. Int. J. Electrochem. Sci., 6, 1479-1492
3. Hackerman.N. (1990). Corrosion Science. Mater Perform, 29(2) 44
4. Khaled K.F.,(2008). Molecular simulation, quantum chemical calculations and electrochemical studies for the inhibition of mild steel by triazoles. *Electrochim.Acta* 53,3484-3492
5. Benali O, Benmehdi A, Hasnaui O, Selles C. and Salghi R. (2013) Green corrosion inhibitor: inhibitive action of tannin extract of *Chamaerop shumilis* plant for the corrosion of

mild steel in 0.5 M H2SO4. *J. Mater. Environ. Sci*. 4(*1*): 127 - 138

6. Lebrini, M., Robert, F. & Bros C. (2011). Alkaloids extract from Policoureaguinesis as corrosive inhibitor for C38 steel in 1 M hydrochloric acid medium. International Journal of Electrochemical Science, 6: 847-859.
7. Hong Ju, Zhen-Peng Kai, Yan Li, (2008). "Aminic nitrogen-bearing polydentate Schiff base compounds as corrosion inhibitors for iron in acidic media: A quantum chemical calculation," Corrosion Science, vol. 50, Issue 3, pp. 865-871, 2008.
8. Ambrish, S.V,Singh.K and Quaraishi.M.A (2010). Aqueous Extracts of Kalmegh (Andrographis paniculata) leaves as green inhibitors for mild steel in Hydrochloric acid solution. *Department of Chemistry,Udai Pratap Autonomous College. Varansi 221002, India.* Article ID: 275983, 10.
9. Abdulwahab, M., Kasim, A., Fayomi, O.S.I., Asuke, F. and Popoola, A.P.I. (2012). Journal of Materials and Environmental Science, 3. (6), PP.1177
10. Varghase, J., Tumkur, V.K.., Ballal, V. and Bhat, G.S. (2013). Anti-Microbial Effect of *Anacardium Occidentale* Leaf Extract against Pathogens Causing Periodontal Disease. Advanced Bioscience Biotechnology, 4, PP. 15-18
11. Harborne, J.B. (1973) Phytochemical Methods a Guide to Modern Techniques of Plant Analysis, Chapman and Hall, New York, PP.279
12. Adams S.M, Yaro S.A, Abdulwahab.M, Umaru.O.B (2015). Corrosion inhibition study of Al-Cu-Ni alloy in simulated seawater environment, Nigerian journal of technological development, 12, (1), p.p 6-11.
13. Lebrini, M., Robert, F., Roos C. (2010). Experimental and theoretical study for corrosion inhibition of mild steel in normal hydrochloric acid solution by some new macrocyclic polyether compounds. Int. J. Electrochem. Sci. 5: 1698.
14. Singh, A; Singh, VR, and Quraishi, M.A (2010): Inhibition Effect of environmentally Benign Kuchla (Strychnos Nuxvomica) Seed Extract on corrosion of mild steel in HCl Acid solution. Int. J. Corr, 2010, 1, 01 – 10.
15. Obot, I. B, Umoren, S. A, and Obi-Egbedi, N. O. (2011): Corrosion inhibition and adsorption behavior for aluminium by extract of Aningeria Robusta in HCl solution: Synergistic effect of iodide ions. *J. Mater. Environ. Sci.* 2(1) (2011) 60 – 71.
16. Hui Cang, Zhenghao Fei, Jinling Shao, Wenyan Shi, Qi Xu (2013). Corrosion Inhibition of Mild Steel by Aloes Extract in HCl Solution Medium. Int. J. Electrochem. Sci., 8, 720 – 734
17. Stephen G. Yiase, Sylvester O. Adejo, Tersoo G. Tyohemba, Ungwanen J. Ahile, and Joseph A. Gbertyo (2014). 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.