International Journal of Advanced Research in Chemical Science (IJARCS)
Volume 3, Issue 12, December 2016, PP 34-40
ISSN 2349-039X (Print) & ISSN 2349-0403 (Online)
http://dx.doi.org/10.20431/2349-0403.0312005
www.arcjournals.org

Corrosion Inhibition of Copper in Seawater by Xanthosoma Spp Leaf Extract (XLE)

[1]Hart Kalada.G*, [2]Orubite- Okorosaye.K, [3]James. Abosede .O

[123]Department of Pure and Industrial Chemistry, P.M.B 5323, University of Port Harcourt, Rivers State, Nigeria

Abstract: *The inhibitive action of Xanthosoma spp Leaf extracts (XLE) on the corrosion of copper in seawater has been studied using the weight loss technique. Various concentrations (1%,2%,3%,4% and 5% v/v) of XLE were used at temperatures 303, 313, 323 and 333K.The inhibition efficiency was found to increase with increasing inhibitor concentration. The effect of temperature on the corrosion inhibition of copper indicated an increase in the corrosion rate as temperature increased and subsequent decrease in the inhibition efficiency. Highest inhibition efficiency of 85% was obtained at 300K with inhibitor concentration 5%v/v and the least inhibition efficiency of 18.11% at 333K with inhibitor concentration 1%v/v. Thermodynamic data calculated are suggestive of adsorption of inhibitor molecules on metal surface. Experimental data fitted into Langmuir's adsorption isotherm. Once again a common weed shows potential as corrosion inhibitor for copper in an aggressive corrosive environment.*

Keywords: *Sea water; Copper; Xanthosoma spp; Weight loss method; Corrosion rate*

1. INTRODUCTION

The marine and pipeline industries have continued to face the problem of corrosion and subsequent deterioration of infrastructure exposed to actual hostile marine environments (Aisha H.et al 2015). The loss of material even for short-term exposures is important in part because protective measures are not always wholly effective (Wan Nik et al 2015). Corrosion is a major problem in desalination plants. In parts of the world with short supply of fresh water, there is an increasing use of sea water for fresh water production (Bardal.E, 2004).Most metal structures used in sea water (ships, oil platforms, piers, pipelines, etc.) are traditionally made of mild low-carbon and low alloy steels as well as copper based alloys. These are subject to corrosion, especially if unprotected. Seawater containing chloride is very corrosive to metals. More so if metals are dipped in seawater, a loss in the metals quality and its failure is imminent (Rahmanto, et al, 2002).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 (Hackerrman .N, 1990).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. Literature records many plant extracts as effective corrosion inhibitors for iron or steel as well as copper and its alloys in aggressive corrosion media (Hamdy and El-Gendy, 2013, Orubite O.K and Oforka,N.C, 2004 Bammou.L.2014, Kalada G.H and James.AO. 2011, D.T et., al 2013,Nnabuk O.E,2009,Abiola et., al 2007 Rajendran, A. and Karthikeyan, C. 2012).Some of these plants are common aquatic weeds that have found use as corrosion inhibitors.

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 XLE it is worthy to note that the leaves of this aquatic weed contains hetro 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 (Khaled, 2008) .Not much use of it is made by the locals both for domestic or other purposes.

Table1. *Phytochemical components of Xanthosoma spp leaf extract*

Substances	Presence
Phenolic Substances	+ +
Flavonoids	+ +
Arthocyanidins	+ ++
Phytosterols	+
Tannins	+ +
Saponins	+ +
Alkaloids	+
Glycosides	+ +
Cyanogenic glycosides	+ +
Cardiac glycosides	+ +

+++ = highly present, ++ = moderately present, - = absent or presence in negligible quantity.

Source: *Mohan et-al. (2012).*

In this present work, corrosion inhibition of copper in seawater by Xanthosoma spp (cocoyam leaf) extract using weight loss method was investigated.

2. EXPERIMENTAL

2.1. Material Preparation

For this experiment 99% pure copper sheets where obtained from the Science/Engineering Workshop, University of Port Harcourt. Each sheet was 1mm in thickness and was mechanically press-cut into rectangular coupon size of 4mm by 3mm..The coupons were polished with emery paper (600 grade), washed with deionized water, degreased with acetone, dried and weighed before experiments.

2.2. Preparation of Aggressive Medium (Seawater)

Artificial seawater was used for this research rather than natural seawater in order to minimize the biological effects as well as provide a reproducible solution of known composition. The formula of Axelrod Glen S. (2005) was employed in this preparation, (table 2).

Table2: *Formula for 35.00% artificial seawater*

SALT	Concentration (mg/l)
Sodium chloride (NaCl)	55
Sodium sulfate (Na_2SO_4)	10
Potassium chloride (KCl)	4
Sodium bicarbonate ($NaHCO_3$)	1
Boric acid (H_3BO_3)	0.010
Magnesium chloride ($MgCl_2.6H_2O$)	32
Calcium chloride ($CaCl_2.2H_20$)	4

Source: *Axelrod Glen S. (2005). Preparation of Artificial Seawater*

2.3. Preparation of Plant Extracts

Xanthosma spp (Cocoyam) leaves were plucked from a waterlogged area in Bonny Local Government area of Rivers State and identified at the University of Port Harcourt, Herbarium. The Xanthosma spp leaves were dried to constant weight and pulverized using an electric blender. The Xanthosma spp leaves were dissolved in 500ml of distilled water and heated in a water bath at $60^{O}C$ .Thereafter the solution was filtered and the filtrate concentrated to 200ml in a water bath at $100^{O}C$ (Ambrish et al, 2010). This was used as the corrosion inhibitor.

2.4. Weight Loss Measurement

Copper coupons were immersed in five beakers containing various concentrations of the corrosion inhibitor 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. At elevated temperatures, the coupons were retrieved after six hours. The same process of weighing was applied. The difference between the present and previous weights were computed and recorded as the weight loss.

The inhibition efficiency (I.E %) was calculated using the following equation:

$$IE\% = \frac{\mathbf{w - wi}}{w} \; \mathbf{x\,10\,0}$$

Where w and w_i are weight loss of steel coupons in the absence and presence of XLE respectively.

The corrosion rate (C.R) in millimeter per year (mmp y^{-1}) was computed using the relation:

$$C.R = \frac{\mathbf{KW}}{DAT}$$

Where W is the weight loss resulting from the difference in initial and final specimen weights (mg), A is the coupon surface area (mm^2), D represents the materials density (mg/cm3), K is the Rate Constant (87.6) and T is the time of exposure (hours).

3. Result and Discussion

3.1. Weight Loss Measurement

Table3. *Calculated values of corrosion rate (mmp y^{-1}) and inhibition efficiency (I.E %) for Copper corrosion in seawater in the absence and presence of various concentrations of Xanthosoma spp leaf extracts at different temperatures using weight loss method*

Inhibitor Concentration (v/v%)	Corrosion rate (mmp y^{-1})				Inhibition Efficiency (I.E %)			
	303K	313K	323K	333K	303K	313K	323K	333K
Blank (control)	0.29	0.34	0.37	0.43	-	-	-	-
1	0.26	0.27	0.30	0.35	24.5	22.13	20.15	18.11
2	0.18	0.21	0.24	0.29	40.0	38.00	36.24	31.95
3	0.13	0.16	0.19	0.22	55.00	52.00	50.03	48.04
4	0.09	0.11	0.13	0.15	70.00	68.42	66.11	61.99
5	0.04	0.064	0.07	0.09	85.00	82.17	79.68	77.01

The effect of addition of XLE on the weight loss of copper coupons in sea water as a corrosive medium was studied. The values of inhibition efficiency IE (%) and corrosion rate (CR) obtained from weight loss measurements at different concentrations of inhibitor at temperatures 303-333K are summarized in Table 3 above. It has been found that the extract inhibits the corrosion of copper, at all concentrations used (1%-5%v/v). An inspection of the results on table 3 indicates that copper coupons were protected to an extent in sea water. The values of corrosion rate obtained for the blank (no inhibitor) was more than when inhibitor was added to the corrosive media. Even at the lowest inhibitor concentration of 1% v/v corrosion rate (0.26 mmp y^{-1}) obtained was lower than the blank (0.29 mmp y^{-1}) at 303K.

This trend has been reported by several researchers confirming the effectiveness of plant extracts as corrosion inhibitors (Jame.A.O & Akaranta.O, 2009, Orubite.K.O, and Oforka N.C, 2004).

3.2. Effect of Inhibition on Corrosion Rate

Fig.1 below shows the effect of inhibitor concentration on the corrosion rate. As inhibitor concentration increased a corresponding decrease in the corrosion rate occurred. The rate was found to reduce progressively as the quantity of the extract increased. As evident in table 3, the lowest corrosion rate was at 0.044 mmp y^{-1} and highest at its lowest concentration of 0.26 mmp y^{-1}.The effect of concentration on chemical reaction is an established fact in chemistry. Increase in concentration means more reactant molecules available for a chemical reaction. From the photochemical investigation of XLE it is worthy to note that the leaves of this aquatic weed contains hetero atoms (N and O) and 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 (Khaled,2008) . Therefore increase in concentration means more of these heteroatoms adsorbed on the surface of the metal and subsequent decrease of corrosion rate. This is in agreement with findings from other works of Subir Paul and Ishita Koley, 2016 and Al-Otaibi et-al, 2012.

3.3. Effect of Inhibitor Concentration and Adsorption Mechanism

Inhibition efficiency plots are to access the effectiveness of an inhibitor in metal protection. This was done for XLE and presented in Figure 2. Inhibition efficiency as observed from the plot, increased with increased inhibitor concentration. The observed inhibition action of the XLE could be attributed to the adsorption of its components on the copper surface. The formed layer of adsorbed molecules isolates the metal surface from the aggressive medium leading to a decrease in the corrosion rate and hence a corresponding increase in its inhibition efficiency, as reported by James A.O et al, (2009). Plots of surface coverage (Θ) express the extent of coverage of inhibitor molecules on metal surface. Table 4 below shows surface coverage data obtained for XLE molecules on copper coupons immersed in sea water. As inhibitor concentration increased more XLE molecules are available to cover copper's surface thus forming a barrier between sea water and the copper coupons and subsequent protection of the copper coupons. Studies by Hamdy.A and Nour Sh. El-Gendy, (2013) and Aisha H. Al-Moubaraki et-al, 2015 are in agreement with these findings. It can also be deduced that from table 4 the activation energies (E_a) increases in the inhibited system as the concentration increases. The calculated values of E_a ranges from 11.02 - 3.13 $KJmol^{-1}$ is less than the threshold value (40 $KJmol^{-1}$). Such behavior coupled with the increased inhibition efficiency is evident of Physical adsorption mechanism.

Table4. *Calculated values of Average Surface Coverage (θ), Activation Energy and Heat of Adsorption for Copper corrosion in seawater in the absence and presence of various concentrations of Xanthosoma spp leaf extracts at different temperatures using weight loss method*

Inhibitor Concentration (v/v%)	Average Surface Coverage (θ)				Activation Energy (E_a) ($KJmol^{-1}$)	Heat of Adsorption ($KJmol^{-1}$)
	303K	313K	323K	333K		
Blank (control)	-	-	-	-	11.02	-
1	0.24	0.23	0.2	0.18	8.32	-3.01
2	0.2	0.38	0.36	0.32	13.35	5.25
3	0.55	0.52	0.5	0.48	14.72	-2.33
4	0.70	0.68	0.66	0.62	14.30	-2.97
5	0.85	0.81	0.79	0.77	22.13	-4.37

3.4. Effect of Temperature on Corrosion Rate

Temperature increases the rate of most chemical reactions. The corrosion reaction is not an exception. The effect of temperature on the corrosion rate was studied at temperatures 303-333K and presented in fig 1.This is also in line with other works of Oloruntoba, D.T., 2013 and Adams. S.M et-al, 2015 where the corrosion rate of copper in sea water increased as temperature increased. The lowest corrosion rate was observed at 303K (0.044mmp y^{-1}) and highest (0.26mmp y^{-1}) at 333K.Many metals are used in environments where temperatures differ from room temperature. This is the basis for studying the effect of temperature on the inhibitor efficiency.

The effect of temperature on the corrosion rate of copper in seawater with and without the XLE corrosion inhibitor was tested by the weight loss method over a temperature range from 303 to 333 k. The corresponding data are shown in table 4 above. Also from a close inspection of figure 3, it is clearly seen that the effect of increasing temperature leads to an increase in the corrosion rate with and without the corrosion inhibitor.

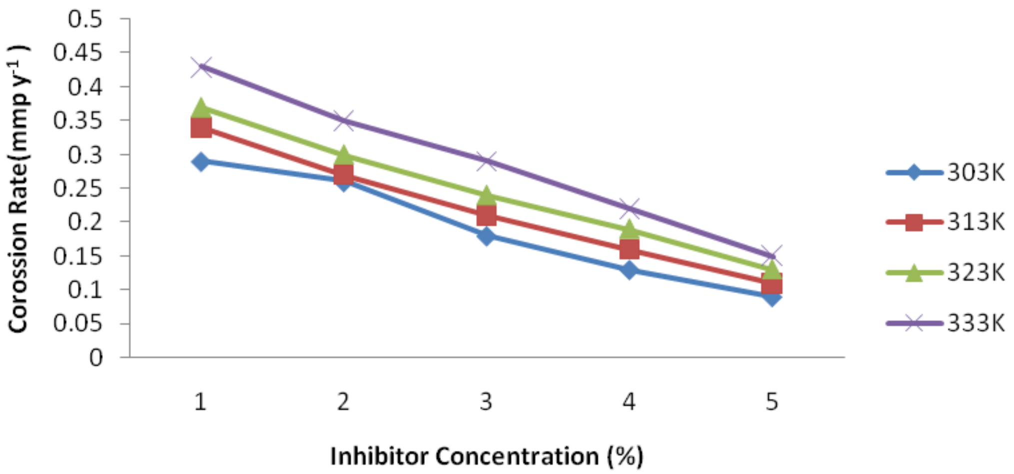

Fig1. *Average corrosion rate (mmp y-1) for Copper corrosion in seawater in the absence and presence of various concentrations of Xanthosoma spp leaf extracts at different temperatures*

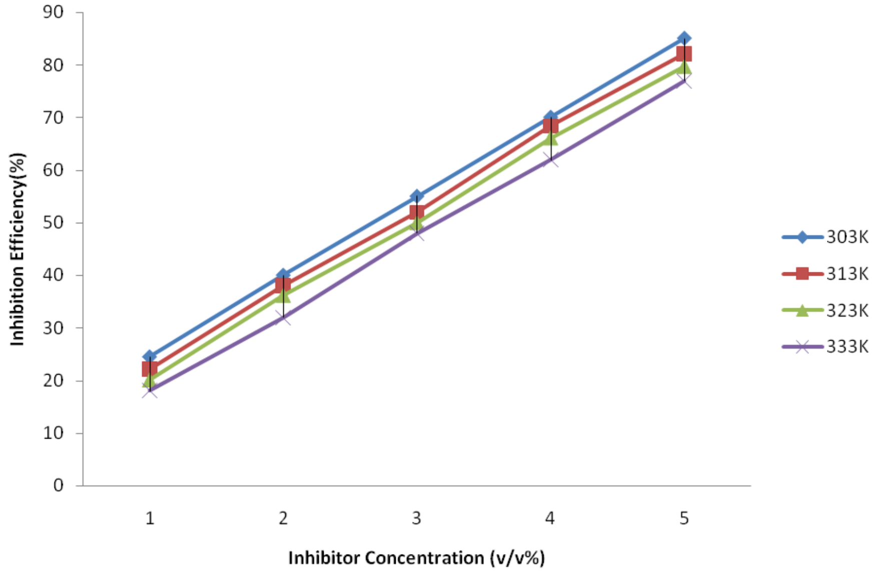

Fig2. *Average Inhibition efficiency (I.E %) for Copper corrosion in seawater in the presence of various concentrations of Xanthosoma spp leaf extracts at different temperatures using weight loss.*

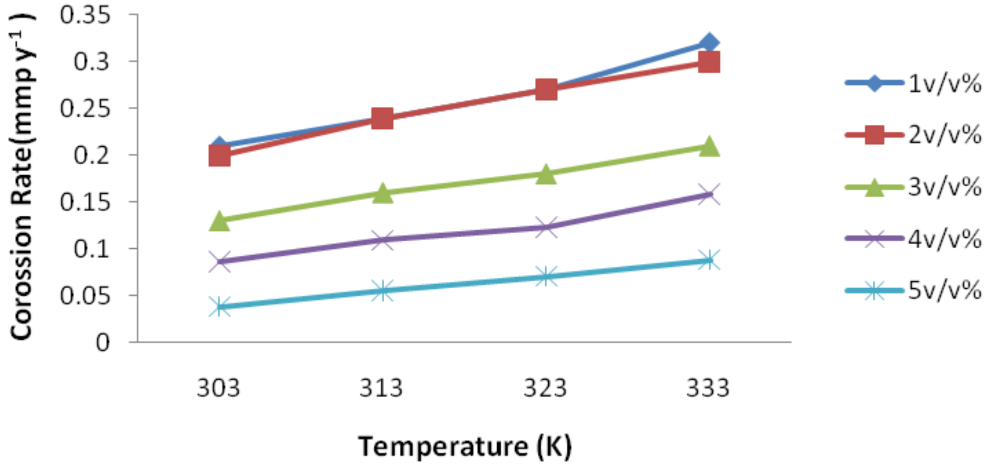

Fig3. *Effect of temperature on the corrosion rate of copper in seawater using XLE*

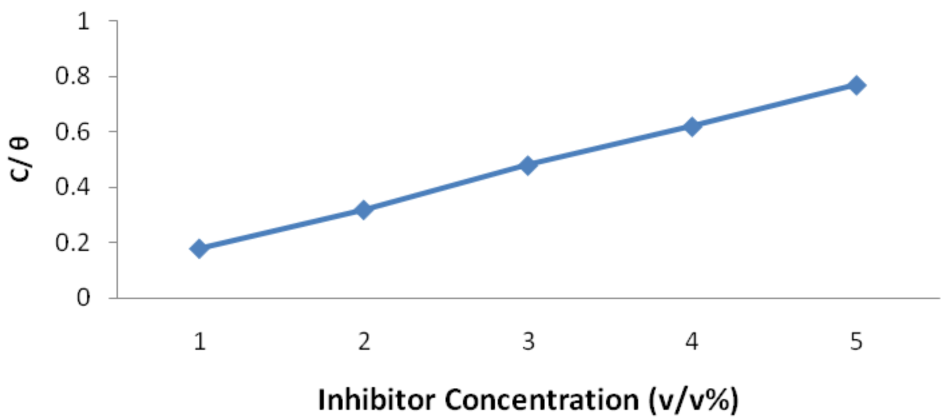

Fig4. *Langmuir Adsorption isotherm plot for corrosion of Cu in seawater at 333k containing different concentrations of XLE*

The effect of temperature on the inhibition efficiency is shown in Fig 2. The inhibition efficiency for the temperatures studied follow the trend 85 > 82.17 > 79.68 >77.01% (303,313,323 and 333K) respectively for the inhibitor concentration of 5%v/v. It was generally observed that inhibition efficiency increase with increasing inhibitor concentration but decrease with increasing temperature, indicating an increased rate of dissolution of copper coupons in sea water and a partial desorption of the temporary protective film as temperature increases. This further suggests a physisorption mechanism of the inhibitor molecules on the copper surface, which is in line with the works of Kalada Hart and A.O. James (2014). The extract showed some reasonable efficiency even at higher temperature. Although the inhibition efficiency decreased with corresponding temperature decrease, at the highest temperature (333K) studied, an inhibition efficiency of 77.01% was recorded when 5%v/v extract concentration was used. Most inhibition effiency record lower percentage at such high temperature (Nnanna A.L et-al., 2014).

4. Conclusion

Xanthosoma spp Leaf extracts (XLE) was found to inhibit corrosion of copper in seawater and the inhibition efficiency increased with increasing extract concentration. At the highest extract concentration of 5v/v%, the optimum inhibition efficiency of 85% was attained. The corrosion rate increased as temperature increased and a subsequent decrease in inhibition efficiency. The lowest and highest corrosion rate was 0.26 mmp y^{-1} (1v/v%) and 0.044 mmp y^{-1} (5v/v%) respectively at 303K and 0.35 mmp y^{-1} (1v/v%) and 0.097 mmp y^{-1} (5 v/v%) respectively at 333K. While the highest inhibition efficiency of 85% and the least inhibition efficiency of 18.11% were at 303K and 333K respectively. The adsorption of Xanthosoma spp Leaf extracts on the copper surface was found to obey the Langmuir adsorption isotherm and the average activation energy was 13.97 $KJmol^{-1}$ which aligns with a physical adsorption mechanism.

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