The Effect of Temperature on Corrosion Inhibition of a Blend of African Star Apple Seed Extract on Mild Steel Immersed in HCl Solution

[1]C. C. Daniel-Mkpume, [1]A. C. Ani, [1*]G. E. Okonkwo, [1]P. O. Offor, [2]O.N. Iloanusi, [3]V. Egoigwe, [4]O. F. Abraham
{cynthia.daniel, ozoemena.ani, emenike.okonkwo, peter.offor, ogechukwu.iloanusi, sochima.egoigwe}@unn.edu.ng, abrahamojofriday.futa@gmail.com
[1]Department of Metallurgical and Materials Engineering University of Nigeria, Nsukka (UNN), [2]Department of Electronic Engineering UNN, [3]Department of Mechatronic Engineering UNN, [4]Federal University of Technology, Akure
*Corresponding author

ABSTRACT- This research focused on the temperature effect on the corrosion inhibition capabilities of african star apple seed extract (Chrysophyllum albidum) on mild steel immersed in hydrochloric acid of 0.1 M and 1.0 M. The corrosion rates of the metal substrates were studied using weight loss and electrochemical method at temperature differences of 30^oC, 50^oC and 70^oC with or without inhibitors for 3 hours. The chosen extract showed excellent inhibition efficiency from the weight loss results. It was discovered the corrosion barrier efficiencies of extract was dependent on the concentration of inhibitor and temperature of the prevailing service condition. Generally, the corrosion rate and current density of the mild steel substrates decreased with increase in inhibitor concentration at the varying working temperatures for both acid molarities. The results obtained at 50^oC revealed that the mild steel resulted in minimum corrosion rate value of 0.0038 mg/mm^2/yr with inhibitor efficiency of 95.00% for 0.1 M HCl At 50^oC and 0.0038 mg / mm^2 / yr with inhibitory integrity of 93.75% efficiency for 1.0 M HCl at 50 ^oC. Therefore, using the african star apple seed extract reduced the corrosion rate of mild steel in hydrochloric acid at temperatures above ambient value.

Keywords: *Mild steel, Corrosion rate, African Star Apple seed, Temperature, green inhibito*r

1.0 INTRODUCTION

The inhibitive properties of an inhibitor would be effective based on the prevailing service situation. One of several factors affecting inhibitors' capabilities is temperature (Oloruntoba et al., 2019). The need for safe industrial metals continues to arise with respect to our present technological temperature levels (Loto et al., 2011). But damage to these metals continues to pose threats and limitations in terms of use. Hence the need for barriers to control or rather slow down the deterioration rate of these materials (Popoola et al., 2013). Several inhibitors have been investigated and found effective which either could be organic or natural resources (Loto et al., 2011). Among the major problems of these restrictions are their poor cost-effectiveness, and accessibility (Popoola et al., 2013). This has resulted to researching on natural inhibitors (Ebadi et al., 2012). Damage to metals and alloys may be controlled by various methods like anodic protection, cathodic protection and chemical treatment. By all these means, corrosion control by chemical inhibition remains the easiest, cheapest and most efficient (Callister, 2007). This proposed corrosion inhibition as the best method to control the destruction of useful metallic properties in harsh environments (Oloruntoba et al., 2019). Corrosion inhibitors are substances which decrease or control the reaction of metals with severe working environment when added in calculated amount under the prevailing service condition (Zaki, 2006).

The corrosion of electropositive metals and alloys in the electrochemical series are thermodynamically favorable when they are in contact with corrosive environment such as chloride (Al-otaibi et al., 2012). This is one of the most difficult problems in the application of metals in the production and industrial sectors (Loto et al., 2011). The problem of corrosion continues to be a factor of paramount consideration in most industrial applications. Corrosion deteriorates and could possibly lead to the failure of machines and systems in diverse industries (Abimbola et al., 2013; Al-otaibi et al., 2012). Hence, the pertinent call for corrosion control research and development. Corrosion control is a costly process which industry invest enormously to achieve (Loto et al., 2011). Diverse reports show that the U.S. and the European Union spend about that 3-5% of their gross national product in corrosion control (Ebadi et al., 2012; Loto et al., 2011).

The strict environmental legislation and increasing ecological awareness among scientist have led to development of alternative sourcing of inhibitors known generally as green inhibitors to mitigate corrosion reactions (Oloruntoba et al., 2019). When choosing a barrier to control rust or corrosion, several factors such as the cost of the inhibitor, availability, and its eco-friendliness are considered (Loto et al., 2011; Oloruntoba et al., 2019). The environmental friendliness cannot be overemphasized because the byproduct of corrosion is released into the environment. These products thus released endanger the environment and living things (human beings, plants and animals). Hence the need for green inhibitors which are biodegradable and do not contain heavy metals or toxic compounds (Helen et al., 2014; Zaki Ahmad, 2006).

The aim of this research is to investigate the inhibitory effect of african star apple seed extract of various concentrations on the corrosion of mild steel in hydrochloric acid of 0.1 M and 1.0 M concentrations via weight loss method. African star apple seed (Chrysophyllum albidum) has been reported to be distributed in the low land rain forest zones and frequently in the villages (Olufunke & Adeola, 2017). This research is starting to become the first in its kind in the use of ASASE for corrosion inhibition especially for mild steel immersed in HCl.

2.0 EXPERIMENTAL SET-UP

The mild steel used for this research was procured from timber market in Nsukka local government area of_Enugu Nigeria. Its parts were cut into important cross-sections and ground successively with emery 240, 800, 1000 grit paper followed by stored in a humid environment desiccator to avoid degradation before their use in the corrosion studies (Oloruntoba et al., 2019).

Chrysophyllum albidum seeds were obtained from Ogige and Obolloafor markets in Nsukka, Nsukka local Enugu state, Nigeria between the months of January and March about the fruit carrying time (Ushie et al., 2014). The seeds were cleaned, which was then flushed out manually, and then sun dried for three weeks in order to minimize moisture with proper monitoring to avoid denaturing effects (Ebadi et al., 2012). Later the surface area of the models was increased by milling.

2.1 Weight Loss Measurements

Weighed mild steel substrate 0.35 cm x 0.85 cm x 0.85 cm were rinsed with distilled water and acetone first in order to remove any trace of grease. In preparing the solution, distilled water is used. For solutions of 0.1 M and 1.0 M, use Equation 1:

$$M_1V_1 = M_2V_2 \qquad (1)$$

The M_1 is the molar concentration of soluble acid, M_2 is the concentration of the reaction, V_1 is the volume of the soluble acid, and V_2 is the volume of the distilled water (Akalezi & Oguzie, 2016).

Four different concentrations (0.05, 0.1, 0.15, 0.2 mg/ml) of Chrysophyllum albidum seed extract were incorporated into 0.1 M and 1.0 M hydrochloric acid test solutions. The sample weight was taken before and after immersion in 100 ml of acidic solution which was heated to 30 ° C, 50 ° C and 70 ° C for 3 hours and the presence of inhibitors of varying concentrations (Oloruntoba et al., 2019). The weight loss was calculated by the weight difference. The percentage weight loss of inhibitor efficiency (IE) (Oloruntoba et al., 2019) and surface coverage (ϴ) (Ushie et al., 2014) were determined using equations 2 and 3 respectively.

$$IE = \frac{W - W_0}{W} \times 100 \qquad (2)$$

!

Where W_0 is the weight loss with the inhibitor at the said concentration and W is the weight loss without Inhibitor (Oloruntoba et al., 2019).

$$\Theta = \frac{W - W_0}{W} \qquad (3)$$

Where W and W_0 represent the weight loss of substrate without and with inhibitor respectively (Ushie et al., 2014)

Corrosion rate (CR) in mg / mm2 / year,was calculated using equation (4) (Oloruntoba et al., 2019).

$$CR = \frac{W}{A(\frac{T}{365})} \qquad (4)$$

When CR is the corrosion rate (mg / mm2 / year), w is weight loss, A is the substrate area (mm2) and T is the extended day from year (Oloruntoba et al., 2019).

2.2 Phytochemical Analysis

Chrysophyllum albidum seed extract has been screened (Akalezi & Oguzie, 2016) and found to contain phytochemical constituents such as alkaloids, balsamic saponins, cardiac glycosides, flavonoids, tannins, terpenoids, sterols, and oils notable for corrosion inhibition by physical adsorption.

RESULTS AND DISCUSSION

Temperature and Concentration Effect

The inhibitive effect of various concentrations of ASASE (African star apple seed extract) on mild steel at various temperatures was analyzed in both 0.1 M and 1.0 M HCl using a weight loss technique. Figure 1 shows the corrosion rate graph and the concentration of the inhibitor for mild steel at 0.1 M HCl at different temperatures (30, 50 and 70^{o}C) for both the blank (without inhibitors) and the substrate exposed to the inhibitor.

Figure 1 clearly depicts a reduction in the corrosion rate of the metal substrate in the presence of ASASE. The trend was minimal at 50 ^{o}C compared with 30 ^{o}C and 70 ^{o}C. The decrease in corrosion rate occurred with increasing inhibitor concentration (Parameswari et al., 2010). The effectiveness of the inhibitor was evident at the various temperatures. At 70^{o}C, 98.37%

efficiency was recorded as shown in Table 2 and Figures 1 and 2. Therefore, the efficiency of the inhibitor at higher temperatures can be achieved by mainly increasing the concentration to a calculated or proportionate inhibitor value (Loto et al., 2011).

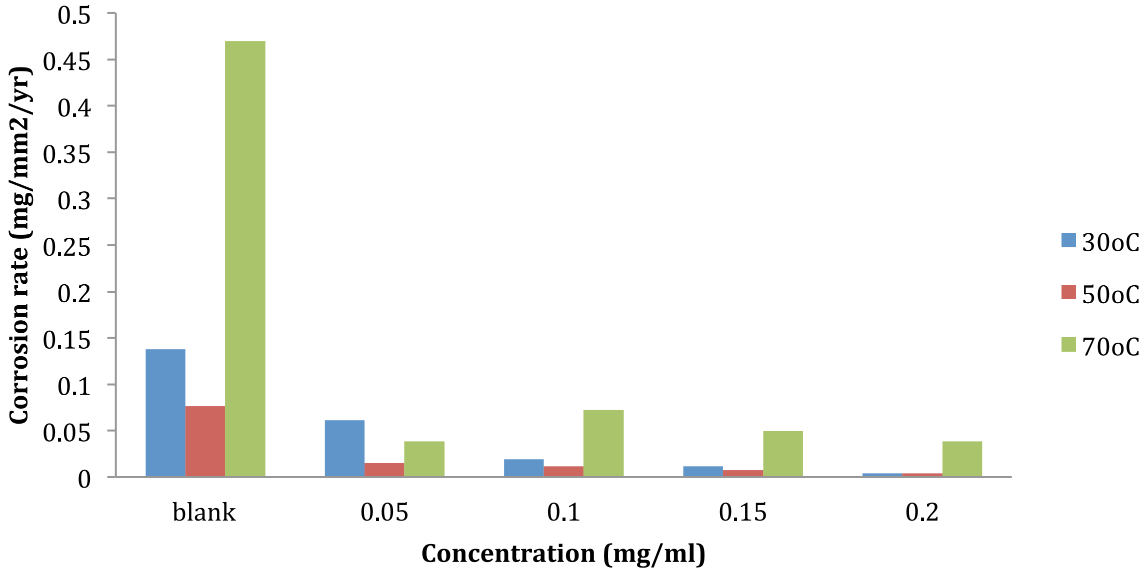

Figure 1: Plot of corrosion rate against inhibitor concentration for 0.1 M HCL at different temperatures of mild steel

The effect of temperature on corrosion rate of mild steel in free acid and in the presence of different concentration of ASASE was also studied for 30°C, 50 °C and 70°C. Increasing the acid concentration of from 0.1 M to 1.0 M showed a negative effect on the inhibitor efficiency (Mustafa & Ahmed, 2015). When increasing the acid concentration with respect to the varying temperatures, a decrease in the inhibition efficiency was noted as shown in Table 3 and Figures 3 and 4. The results obtained at 50°C revealed that the mild steel resulted in minimum corrosion rate value of 0.0038 $mg/mm^2/yr$ with inhibitor efficiency of 95.00% for 0.1 M HCl At 50°C and 0.0038 mg / mm^2 / yr with inhibitory integrity of 93.75% efficiency for 1.0 M HCl at 50 °C. Therefore, ASASE shows that it has inhibitory properties which are not only a function of the inhibitor concentration as claimed by some authors (Popoola & Fayomi, 2011) but also a function of the temperature of the prevailing condition of the service environment.

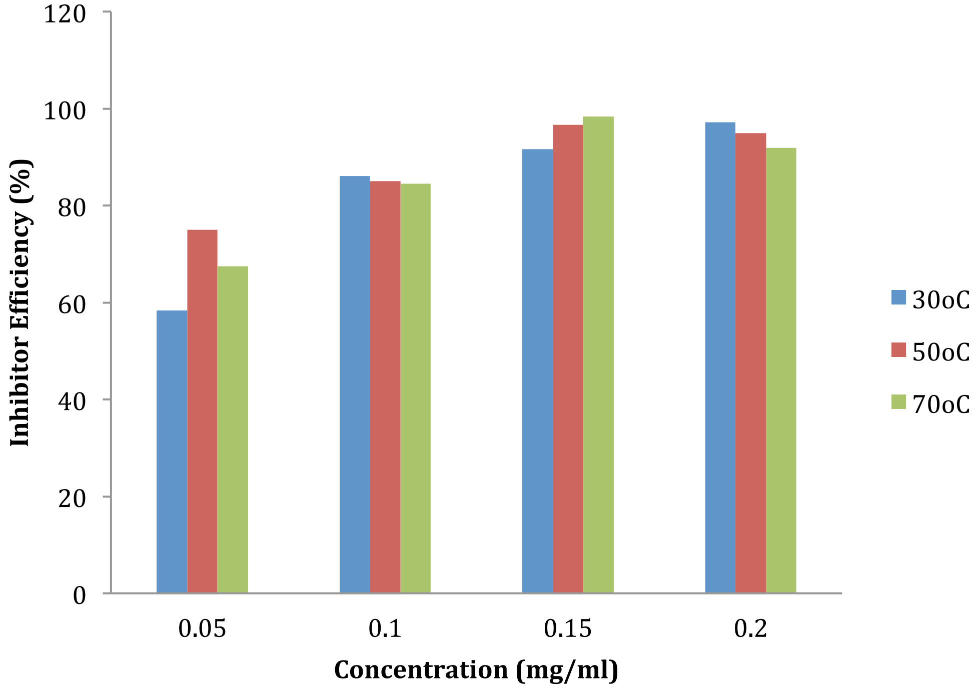

Figure 2: Plot of inhibitor efficiency against concentration for 0.1 M HCL at different temperatures of mild steel

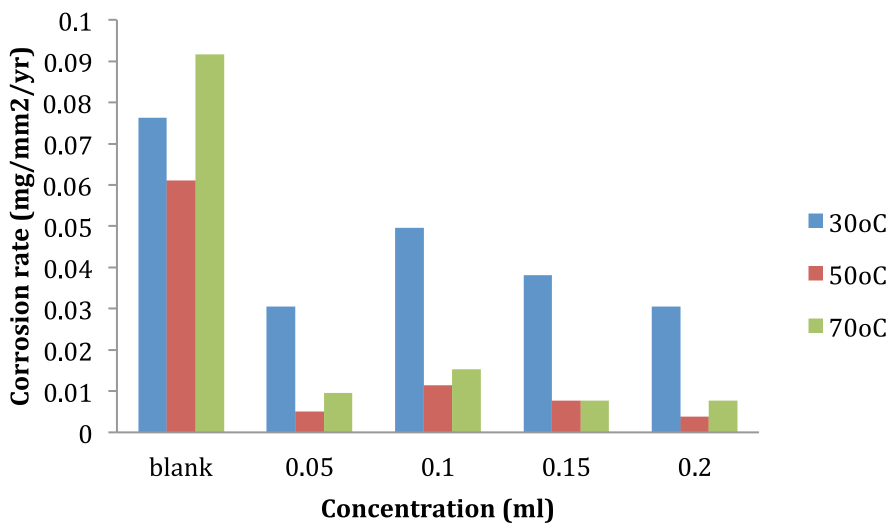

Figure 3: Plot of corrosion rate against inhibitor concentration for 1.0 M HCL at different temperatures of mild steel

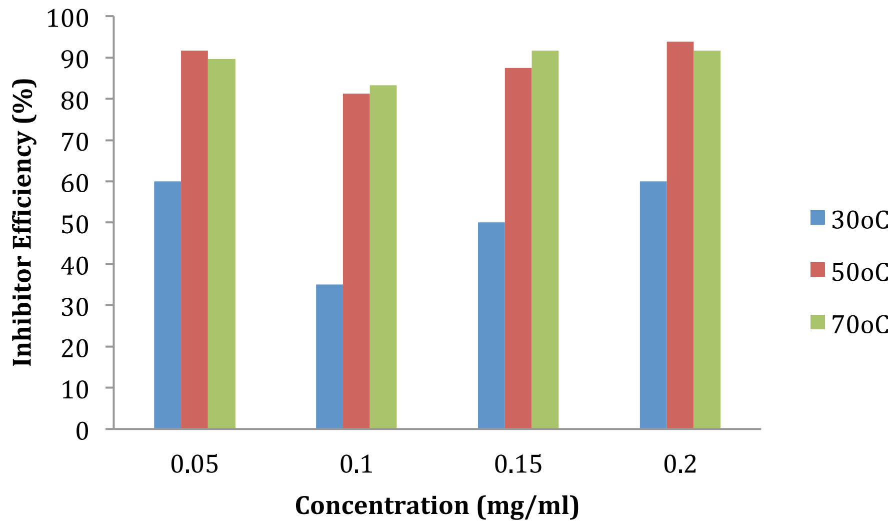

Figure 4: Plot of inhibitor efficiency against concentration for 1.0 M HCL at different temperatures of mild steel

Table 2: Calculated values of corrosion rate (mg / mm^2 / year), 0.1 M HCl weight loss inhibition efficiency for ASASE (%) and surface coverage level (Θ) relative to temperature change

Concentration of ASASE(mg/ml)	**Corrosion Rate (mg/mm²/yr)**			**Inhibition Efficiency (%)**			**Degree of Surface Coverage (Θ)**		
	30°C	50°C	70°C	30°C	50°C	70°C	30°C	50°C	70°C
Blank	0.1374	0.0763	0.4695						
0.05	0.0573	0.0191	0.1527	58.33	75.00	67.48	0.6154	0.0000	0.0790
0.1	0.0191	0.0115	0.0725	86.11	85.00	84.55	0.0769	0.1999	0.1772
0.15	0.0115	0.0076	0.0496	91.67	96.67	98.37	0.4615	0.4002	0.3948
0.2	0.0038	0.0038	0.0382	97.22	95.00	91.86	0.5385	0.1999	0.7429

Table 3: Calculated values of corrosion rate (mg / mm^2 / year), 1.0 M HCl weight loss inhibition efficiency for ASASE (%) and surface coverage level (Θ) relative to temperature change

Concentration of ASASE(mg/ml)	**Corrosion Rate (mg/mm²/yr)**			**Inhibition Efficiency (%)**			**Degree of Surface Coverage (Θ)**		
	30°C	50°C	70°C	30°C	50°C	70°C	30°C	50°C	70°C
Blank	0.0763	0.0611	0.0916						
0.05	0.0305	0.0051	0.0095	60.00	91.67	89.58	0.1999	0.5264	0.4285
0.1	0.0496	0.0115	0.0153	35.00	81.25	83.33	0.4002	0.3684	0.5715

0.15	0.0382	0.0076	0.0076	50.00	87.50	91.67	0.6001	0.4736	0.5715
0.2	0.0305	0.0038	0.0076	60.00	93.75	91.67	0.6001	0.4210	0.8772

It has been observed that the plant extract comprises of organic and resinous matter (Parameswari et al., 2010) some of which have good corrosion inhibition. This has been proven by the current research via the corrosion rate and inhibitor efficiency results. The extract employs adsorption of organic matter to produce a barrier to charge and mass transfer, hence, protects the mild steel surface from corrosion attack (Raja & Sethuraman, 2008). Oxygen-rich extracts contain aromatic compounds such as tannins, flavonoids, steroids and glycosides. Tannins are believed to form a passivating layer of tannates on the metal surfaces (Davis et al., 2001). The situation was created due to obstacles of micro anodes which are generated on the metal surface when it is in contact with electrolytes and thus inhibit further metal dissolution (Ochibo & Paiko, 2011).

CONCLUSIONS

These experimental results can be summarized as follows:

1. ASASE acts as an inhibitor for mild steel corrosion in 0.1 M and 1.0 M HCl environment.
2. The inhibition increased with increasing concentration of ASASE but decreased with temperature.
3. The inhibitory effect of the ASASE is not only a function of the inhibitor concentration but also a function of the temperature of the prevailing condition of the service environment.
4. This study provides new data on inhibition characteristics of ASASE with respect to concentration and temperature for 0.1 M and 1.0 M HCl service environment.

REFERENCES

Popoola, A.P.I and Fayomi, O.S.I (2011). Electrochemical Study of Zinc Plate in Acid Medium : Inhibitory Effect of Bitter Leaf (Vernonia Amygdalina). *International Journal of Electrochemical Science*, *6*, 4581–4592.

Popoola, A.P.I., Omotayo, S., Loto, C. A., & Popoola, O. M. (2013). Inhibitive Action of Ferrous Gluconate on Aluminum Alloy in Saline Environment. *Advances In Materials Science and Engineering*, *2013*, 8.

Akalezi, C. O., & Oguzie, E. E. (2016). Evaluation of anticorrosion properties of Chrysophyllum albidum leaves extract for mild steel protection in acidic media. *International Journal of Industrial Chemistry*, *7*(1), 81–92. https://doi.org/10.1007/s40090-015-0057-5

Al-otaibi, M. S., Al-mayouf, A. M., Khan, M., & Mousa, A. A. (2012). Corrosion inhibitory action of some plant extracts on the corrosion of mild steel in acidic media. *ARABIAN Journal of Chemistry*. https://doi.org/10.1016/j.arabjc.2012.01.015

Davis, G. D., Von Fraunhofer, J. A., Krebs, L. A., & Dacres, C. M. (2001). The use of tobacco extracts as corrosion inhibitors. *NACE - International Corrosion Conference Series*, *2001–March*(January 2001).

Ebadi, M., Basirun, W. J., Khaledi, H., & Ali, H. M. (2012). Corrosion inhibition properties of pyrazolylindolenine compounds on copper surface in acidic media. *Chemistry Central Journal 2012,* 1–10. https://doi.org/10.1186/1752-153X-6-163

Ghasemi, Z., & Seifzadeh, D. (2005). The inhibition effect of some amino acids towards the corrosion of aluminum in 1 M HCl + 1 M H 2 SO 4 solution. *Applied Surface Science*, *249*, 408–418. https://doi.org/10.1016/j.apsusc.2004.12.016

Helen, L. Y. S., Rahim, A. A., Saad, B., Saleh, M. I., & Raja, P. B. (2014). Aquilaria Crassna Leaves Extracts – a Green Corrosion Inhibitor for Mild Steel in 1 M HCl Medium. *International Journal of Electrochemical Science*, *9*, 830–846.

Loto, C. A., Loto, R. T., & Popoola, A. P. I. (2011). Corrosion and plants extracts inhibition of mild steel in HCl. *International Journal of the Physical Sciences*, *6*(15), 3616–3623. https://doi.org/10.5897/IJPS11.923

Mustafa, M., & Ahmed, E. (2015). Fundamentals of corrosion mitigations in oil industry. *Sudan Engineering Society Journal*, *60*(January 2014), 8.

Ochigbo, S.S. & Paiko, Y. B. (2011). Effects of Solvent Blending on the Characteristics of Oils Extracted from the Seeds of Chrysophyllum albidum. *International Journal of Science and Nature*, *2*(2), 352–358.

Oloruntoba, D. T., Adesina, O. S., Abraham, O. F., & Akinluwade, K. J. (2019). Corrosion Mitigation of Gray Cast Iron and Aluminum in NaOH Using Water Hyacinth (Eichhornia crassipes) Plant Extract. *Chemical Science International Journal*, *27*(4), 1–15. https://doi.org/10.9734/CSJI/2019/v27i430120

Olufunke O. O. and Adeola E. (2017). Comparative Food Contents of Ripe and Unripe Fruits of African Star Apple, Chrysophyllum albidum G. Don (Syn. Gambeya albida). *Journal Of Research In Forestry, Wildlife And Environment*, *9*(4).

Parameswari, K., Rekha, S., Chitra, S., & Kayalvizhy, E. (2010). Study on the Inhibition of Mild Steel Corrosion by Benzoisoxazole and Benzopyrazole Derivatives in H 2 SO 4 Medium. *Portugaliae Electrochimica Acta*, *28*(3), 189–201. https://doi.org/10.4152/pea.201003189

Raja, P. B., & Sethuraman, M. G. (2008). Natural products as corrosion inhibitor for metals in corrosive media — A review. *Materials Letters*, *62*, 113–116. https://doi.org/10.1016/j.matlet.2007.04.079

Ushie, O. A., Adamu, H. M., Abayeh, O. J., Chindo, I. Y., & Lawal, U. (2014). Phytochemical Screening of (chrysophyllum albidum) Leaf Extracts. *Journal of Applied Chemistry*, *2*(2), 40–46.

William D. Callister, J. & D. G. R. (2009). *Materials Science and Engineering An Introduction*.

Zaki Ahmad. (2006). *Principles of Corrosion Engineering and Corrosion Control* (Issue September).