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Corrosion Inhibition on Austenitic Stainless Steel in Sea Water Using Onion (*Allium Cepa*) as Corrosion Inhibitor

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ABSTRACT

The corrosion inhibition of austenitic stainless steel in sea water in the presence of *Allium cepa* extract was studied using weight loss technique at room temperature. Austenitic stainless steel samples obtained were immersed completely in their various media of varying concentrations with and without the onion extract as inhibitor (i.e. 0.1 to 0.6g of inhibitor in 500ml of sea water). The weight loss data was recorded every 4 days for a period of 28 days. The results from the experiment showed that the weight of the stainless steel samples decreased with an increase in time exposure of the steels in the sea water. Stainless steel samples immersed in the presence of the inhibitor decreased at a lower rate as compared to the control experiment. The solution containing the onion extract also inhibited the corrosion rate of the austenitic stainless steel sample to an extent depending on the medium type. The results also revealed that the higher the concentration of the inhibitor, the higher the inhibition efficiency. The optimum inhibition efficiency was 76.43% when *Allium cepa* was present at 0.6g per 500ml demonstrating the onion extract as a good corrosion inhibitor that can be applied in industries which makes use of the austenitic stainless steel for their operations as well as other metals. Three adsorption isotherm models were investigated in this study namely; Langmuir adsorption isotherms was used to determine the adsorption properties. The results showed that the extract adsorb on the surface of the austenitic stainless steel through physical adsorption of which Langmuir adsorption isotherm gave the best fit and the process was spontaneous.

KEYWORDS: Corrosion, Austenitic Stainless Steel, Corrosion rate, *Allium cepa*, corrosion inhibitor, weight loss, adsorption.

I. INTRODUCTION

The ISO 8044 standard, defines corrosion as ‘the physical-chemical interaction between a metal and its environment, leading to modifications of the metal properties and leads to a significant alteration of the metal function, its environment or the technical system involved’. (Duret-Thual, 2014). It is an irreversible interfacial reaction of a material (metal, polymer, ceramic) with its environment which results in consumption of material or dissolution into the material of a component of the environment (IUPAC 2012).

Materials corrosion is of a major concern and importance in process engineering and materials technology, often taking into considerations the environmental conditions that play an important role on metals exposed to such corrosive media. It is the chemically induced damage to a material that results in deterioration of the material and its properties (Oluwole, 2014). It is a universal phenomenon; it is everywhere, air, water, soil and in every environment we encounter. It is an inevitable phenomenon and the only way to avoid corrosion totally is to operate in a vacuum but conditions make it impossible (Roberge, 2000, Obiukwu et al., 2013).

The deterioration of the material and/or the technical system usually takes different forms, from generalized to localized, visible to hidden with adverse consequences on the technical system operation and safety, for human beings and environment. The economic consequences are also huge. Corrosion in industrial process systems affects the gross domestic product of developed countries (Duret-Thual, 2014). A significant percentage of engineering systems depend upon corrosion protection for performance reliability, enhanced performance and safety. A recent cost of corrosion study estimated that in 2002, corrosion drained about 3.1% of the GDP from the US economy. On this basis, the direct economic loss from corrosion in US in 2004 was put at $364 billion (Sinnot, 2004). Steel is one of the most preferred materials for the construction and fabrication of process equipment and machinery (Sinnot, 2004). Due to its ease and excellent physical properties, it has been used extensively and considerably under different conditions in chemical and allied industries, it is suitable for use with most organic solvents. (Nwabanne and Okafor, 2012).

Steels materials used in process equipment in industries suffer from corrosion attack due to metal degradation and attacks such as pitting corrosion. These has resulted in loss of production, costly maintenance and high operating cost. In addition, leaks of process fluids may also lead to unacceptable health and safety hazards, risk of damage to the environment, as well as the associated clean-up costs (Loto and Loto, 2016). These corrosion associated expenditures can have a huge financial impact on company's operating costs.

Austenitic stainless steel are iron-chromium-nickel alloys (nickel provides malleability and weldability to this series of alloys). They are characterized by their high corrosion resistance due to a high percentage of the chromium content present in its composition (at least 17%) which make the steel completely austenitic in the presence of low carbon contents (Oluwole, 2010). Austenitic stainless steel has found its major application in marine environments, desalination plants, food processing industries, oil and gas (onshore and offshore) which makes it susceptible to corrosion attack.

II. ALLIUM CEPA AS CORROSION INHIBITOR

A significant percentage of engineering systems depend upon corrosion protection for Performance reliability, enhanced performance and safety. A recent cost of corrosion study estimated that in 2002, corrosion drained about 3.1% of the GDP from the US economy. On this basis, the direct economic loss from corrosion in US in 2004 was put at $364 billion (Sinnot, 2004). Corrosion inhibitors uses protective metal covering or coatings to protect and prevent metal surfaces from corrosion. A common mechanism for inhibiting corrosion involves the formation of a coating surface often a passivation layer which prevents access of the corrosive substance to the metal. Alternatively, the corrosion inhibitor could be introduced as an additive to the fluid that surrounds the metal surface (Grafen et al, 2002).

Most industrial grade commercial corrosion inhibitors are multi-component inhibitor systems which consist of nitrogen and sulfur functionalities (Elron, 2015). These inhibitors are stable and provide suitable protection in corrosive environments (Lopez *et al*, 2005, Abbasov *et al*, 2010), However due to high cost, health and environmental toxicity concerns, as a result of the presence of heavy metals, chromates, and phosphates in these inorganic inhibitors, recent trends in corrosion studies has been geared towards the use of more environmentally friendly natural and organic, non-toxic, biodegradable and readily available inhibitor materials (Mahmood 2012, Benton, 1997).

Allium cepa commonly called bulb onion or common onion is a vegetable that is readily available in every part of Nigeria which is consumed on a daily basis by everyone. It is the most widely cultivated specie of the genius *Allium*. It is used as a food item for preparing our local dishes and can also be eaten raw. Extract of onion (*Allium cepa)* is investigated in this work. *Allium cepa* extracts on analysis was discovered to contain Vitamin C, Vitamin B6, folic acid, phenolic, flavonoids as well as quercetin and glycosides (Loto and Loto, 2016). Hence, this study is aimed at the possibility of using this specie as a corrosion inhibitor of austenitic steel immersed in sea water.

III. MATERIALS AND METHODS

Materials

Austenitic stainless steel was purchased from Hand Rails Integrated steel company in Yenagoa, sea water was sourced from Nembe River, Bayelsa state. Ethanol used as the extraction solvent was obtained from the Chemistry Research Laboratory, Niger Delta University, Amassoma. *Allium cepa* commonly known as onion which will serve as the inhibitor was gotten from Amassoma local market.

IV. METAL PREPARATION

The stainless steel sample was cut into coupons of different rectangular dimensions using a grinding machine and filed to ensure better shaping. Specimen steel coupons were polished and cleaned with abrasive paper, degreased with Acetone, washed in distilled water and air dried. A total of 7 metal coupons samples were weighed using a digital weighing balance to get their initial weight before immersion into the corrosive medium.

V. PREPARATION OF *ALLIUM CEPA* EXTRACT

Allium cepa commonly known as onion which was used in this study was obtained from Amassoma local market. The allium cepa extract was prepared following procedure described by Loto and Loto, 2016. Using methanol as the organic extractor- Different quantities of onion (0.1 – 0.6g) of the onion was chopped into pieces together with bark and soaked in 1000ml of methanol for 5 days. At the end of the soaking period, the chopped onion was filtered to obtain a liquid solution of methanol and onion organic matter. The liquid was separated with the use of a rotary evaporator which extracted the methanol from the liquid solution leaving behind the solution of onion organic matter. The organic solutions were stored in a refrigerator until it was used for the experiments. (Loto and Loto, 2016)

VI . WEIGHT LOSS EXPERIMENT

The varying concentrations of the corrosive environment with and without the inhibitor was separately measured into seven different plastic beakers which was labelled according to the specimen above (i.e. from A to G) using a paper tape. The prepared austenitic stainless steel samples were immersed totally in their various solution with specimen G as our control solution (i.e. without the inhibitor). The experiment was conducted at room temperature.

The weight loss of each austenitic stainless steel sample was determined at intervals of four days for a total of twenty-eight days. Samples for weight loss measurements are removed, rinsed in water, sun dried for 2 hours, weighed to get their new weights before re-immersing them in their respective solutions. This process was repeated continuously until the final result was obtained.

VI . RESULTS AND DISCUSSION

Determination of Corrosion rates

Corrosion rate was calculated using the equation below

$$CR = 87.6\left(\frac{W}{DAT}\right) \quad (1)$$

Where:

CR = corrosion rate in mm/yr.

W = weight loss in grams

A = area of specimen, in cm^2

t = exposure time, hr.

D = density of specimen, g/cm^3

Calculation of Inhibition Efficiency

The inhibitor efficiency was calculated using the follow equation:

$$E_f = [(Ro - Ri)/Ro]\,(100) \quad (2)$$

Where,

E_f is inhibitor efficiency (percentage),

R_i is corrosion rate of metal with inhibitor and

R_o is corrosion rate of metal without inhibitor.

The results obtained from the experiment are presented below;

Table 1. Weight Loss Of Austenitic Stainless Steel Samples Sea Water

Concentration in 500ml	Metal Sample	Weight loss Of Samples(g) Initial	Day 4	Day 8	Day 12	Day 16	Day 20	Day 24	Day 28
0.1g	A	6.47	0.02	0.03	0.04	0.06	0.96	1.02	1.07
0.2g	B	5.40	0.01	0.02	0.03	0.06	0.82	0.88	0.96
0.3g	C	6.20	0.02	0.04	0.05	0.08	0.70	0.76	0.82
0.4g	D	5.42	0.01	0.03	0.05	0.08	0.38	0.44	0.50
0.5g	E	5.60	0.01	0.02	0.05	0.10	0.36	0.42	0.47
0.6g	F	6.05	0.01	0.02	0.05	0.07	0.35	0.41	0.46
0.0g	G	6.58	0.01	0.02	0.06	0.10	0.97	1.03	1.11

The loss in weight of austenitic stainless steel samples in sea water in the presence and absence of *Allium cepa* extract after 28 days of immersion was determined. Tables 1 shows the respective values of weight loss of the various steel samples with time for all the media. From the results obtained and presented in the tables, it was observed that the weight loss of the steel samples is dependent on the concentration of the inhibitor as well as the time of exposure in the sea water. The weight of the steel decreased with the time of exposure. It was also observed that the weight loss obtained increased as the concentration of the inhibitor reduces. Generally, the control experiments (i.e. the medium without *Allium cepa* extract) recorded higher weight loss more than those media with different concentrations of the inhibitor.

The results obtained showed that the rate of corrosion was dependent on the concentration of inhibitor used. From the plot in figure 1, the higher the concentration of the inhibitor, the lower the corrosion rate of the steel in the sea water. Corrosion rate was highest in the medium without the inhibitor. It was observed that the steel sample in the control solution began to rust on the 12th day while the rusting process was reduced in medium A and B since their inhibitor concentration is not high enough, while in the other media at higher inhibitor concentration there was no visible rusting process taking place. This is due to the fact that the passive film on the steel was more effective at concentrations above 0.2g in 500ml of the sea water.

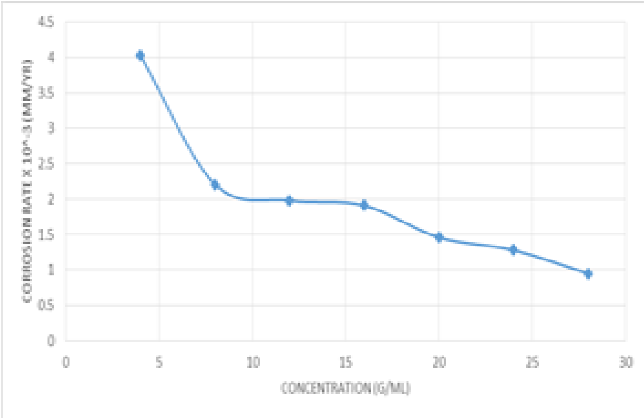


Figure 1: Overall Rate of corrosion x 10^{-3} (mm/yr.) Vs. Concentration (g/ml) of Austenitic Stainless Steel exposed to Sea Water.

%inhibitor efficiency of the Various Inhibitor Concentration

The calculated values of inhibition efficiency of the extract on the corrosion of austenitic stainless steel are presented below. From figure, it is clearly seen the inhibition efficiency increased in the presence of the inhibitor compared to the control solution. The maximum inhibition efficiency was found to exist for the medium with 0.6g per 500ml 0f the extract. Also from Figure 2, it is observed that the higher the inhibition efficiency of the extract, the lower the corrosion rate on the steel sample.

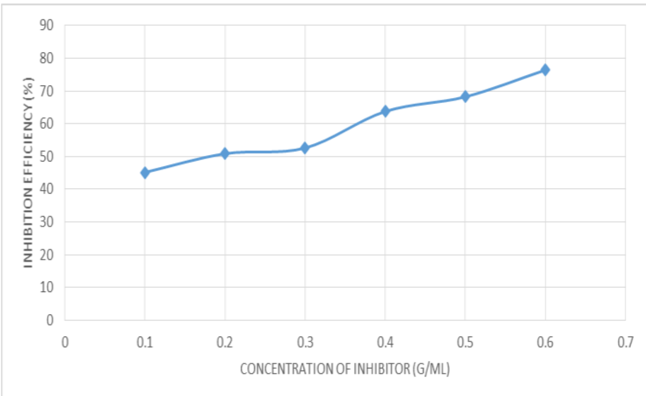


Fig 2. % Inhibition Efficiency Vs. Inhibitor Concentration (g/ml) of Austenitic Stainless Steel in Sea Water.

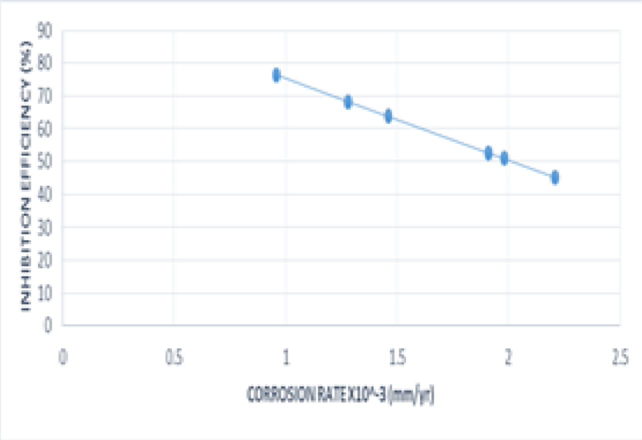


Fig 3. % Inhibition Efficiency Vs. Corrosion Rate x 10^{-3}(mm/yr) of Austenitic Stainless Steel in Sea Water.

VI. ADSORPTION ISOTHERM AND ADSORPTION PARAMETERS

Adsorption isotherms are important in understanding the mechanism of corrosion reaction of mild steel. The most frequently used isotherm is the Langmuir isotherm. Weight loss and surface coverage results are used to calculate adsorption isotherm parameters (Obot et al, 2009). Mathematically the Langmuir isotherm is given as

$$\frac{C}{\theta} = C + \frac{1}{K_{ads}}$$

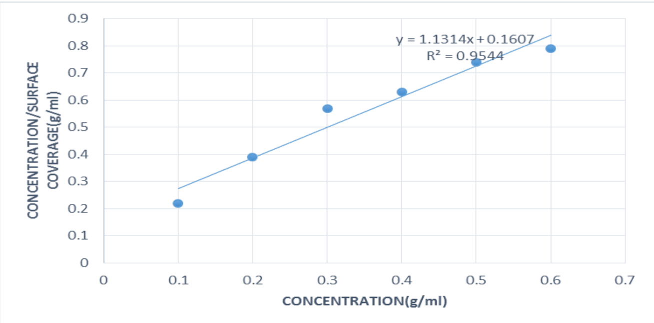
$$\theta = \left(\frac{w_0 - w}{w_0}\right) \textit{Where } \theta \textit{ is the surface coverage}$$

k_{ads} *is the adsorption constant*

C *is the concentration of inhibitor*

w_0 *and* w *are the corrosion rates in the absence and in the presence of inhibitor respectively*

Figure 3: Plot of C/θ against C is shown in figure below.



Ebenso *et al* (1999) recognized that a corrosion inhibitor may function by reaction with the metal ion newly produced in the corrosive environment but in a plane very near or on the metal surface, and by adsorption. Adsorption further offers data about the relations amongst the absorbed molecules specifically and in addition to their metal surface interaction. This means that the adsorption isotherm can be said to be an expedient approach that promotes the interpretation of the process of corrosion or electrochemical reactions in the adsorption process (Singh and Quraishi, 2010). An adsorption isotherm offers explanation for the relation between the metal exposed surfaces to the coverage of an interface with adsorbed species. Adsorption is of two types viz- physical adsorption (physisorption) and chemical adsorption (chemisorption).

The interaction between the onion extract which adsorbed on the austenitic stainless steel surface can be best described by adsorption isotherm. The degree of surface coverage, θ, for varying inhibitor concentration at room temperature was used to elucidate the adsorption isotherm in order to establish the adsorption processes involved. To achieve these, three adsorption isotherms were fitted to the experimental data to determine which one will best explain the metal surface-inhibitor interaction through the R^2 value of the various graphical plots.

The thermodynamic parameters associated with the various adsorption isotherms were derived using the relationship between the adsorption equilibrium K and the Gibbs Free energy of adsorption using the expression below:

ΔG_{ads} = -RT In (55.5K)

Where R is the molar gas constant given as 8.314J/molK, T is the thermodynamic temperature in kelvin (K), K is the adsorption constant and 55.5 represents the molar concentration of the solvent which is used for the case of water. The results obtained from the isotherm plots alongside the thermodynamic parameters are presented in the table below:

Table 2: Adsorption parameters of the corrosion plot of austenitic stainless steel in sea water in the presence of *Allium cepa.*

Isotherm	Slope	Intercept	R^2	K	ΔG_{ads} (KJ/mol)
Langmuir	1.1314	0.1607	0.9544	6.2228	-32.13

From table 2 it is observed that negative values of the standard free energy of adsorption were obtained which indicates a spontaneous adsorption of inhibitor molecules and strong interaction between the surface of the austenitic stainless steel and the allium cepa. Generally values of – ΔG_{ads} around $-20Kj/mol$ or lower are indicative of the electrostatic interaction between charged organic molecules and charged metal surface (Physical adsorption). Values around $-40kj/mol$ or higher are indicative of charge sharing or charge transfer from organic molecules to the metal surface to form a coordinated bond (Chemical-adsorption). (Popova et al 2003, Nnanna et al 2013, lalitha et al, 2005). The values ΔG_{ads} obtained in this study for the adsorption of allium cepa on austenitic stainless steel is less than $-40Kj/mol$ which supports previous assumption of physical adsorption. The calculated adsorption values for the studied inhibitor show that the adsorption is of physical in nature, and there is no chemisorption between the inhibitor molecule and the metal surface.

From the results obtained, Langmuir isotherm model gave the best fit having its correlation regression value close to unity and slope approximately about unity. The negative values of the Gibbs free energy of adsorption (ΔG_{ads}) indicates clearly the spontaneity of the adsorption process. The adsorption constant (K) values were calculated from the various equations of lines of the three models and were used to further calculate the Gibbs free energy of adsorption for the Langmuir models.

The values of ΔG_{ads} obtained for the three models were of magnitudes less than 40KJ/mol. It is well known that the values of ΔG_{ads} in the order of −20kJ mol-1 or lower indicate a physisorption while those about −40kJ mol−1 or higher involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a co-ordinate type of bond (Abiola *et al.*, 2004).

CONCLUSION

On the basis of this study, the following conclusion are drawn

- The weight loss of austenitic stainless steel in sea water increased as the time of exposure increased and also as the concentration of the inhibitor in the sea water reduces.
- The sea water used was corrosive to a large extent. From the experimental set up, the corrosion rate of the stainless steel increased more in the control medium (i.e. without the inhibitor) and as time increases, the rate of corrosion on the steels also increased.
- The inhibition efficiency increased with increase in concentration of the onion extract. The phytochemical constituents present in the extract contributed to the inhibitive action of the extract. In this paper, the investigation of corrosion inhibition on austenitic stainless steel was studied using *Allium cepa.*
- Austenitic stainless steel is naturally resistant to corrosion to a measurable extent due to its nickel and chromium content.
- Three adsorption isotherm models were studied. It was observed that the sorption data fitted into Langmuir, Freundlich and Temkin isotherm of which Langmuir isotherm was found to have the highest regression value and hence having the best fit.
- The results showed that *Allium cepa* acts as a good corrosion inhibitor.

REFERENCES

1. Abiola O. K., Oforka N. C. and Ebenso E. E. (2004) Bulletin of Electrochemistry 2004(20): 409.
2. Abbasov, V.M., Gadjiyeva, S.R., Magerramov, R.S., Akhmedov, N.S. and Rasulov, S.R (2010) "Influence of potassium salts of nitro derivative high α-olefins in 1% NaCl solution saturated with CO_2 on steel corrosion." *Azerbaijani Oil Industry*, vol. 8, pp. 1-4, 2010.
3. Aluko, S.O. (2010). Corrosion and Fatigue Behavior of Welded Austenitic Stainless Steel in Different Environments. MSc. Dissertation, Ahmadu Bello University, Zaria, 5-7, 11-19.
4. Arab, S.T. and Turkustuni, A.M. (2006). Inhibition of the corrosion of steel in phosphoric acid By phenacyl dimethyl sulfonium bromide and some of its para substituted derivatives. *Portugaliae Electrochimica Acta,* 2006 (24):53-69.
5. Benton, W.J. and Koskan, L.P. (1997) "Inhibtion of carbon dioxide corrosion of metals." US Patent 5607623 A, Mar. 4, 1997.
6. Ebenso, E.E., Ekpe, U.J., Ita, B.I., Offiong, O.E. and Ibok, U.J. 1999. “Effect of molecular structure on the efficiency of amides and thiosemicarbazones in hydrochloric acid 1,” *Mater. Chem. Phys.* 1999 (60): 79-90.
7. Gomes, E.E. (2015). Green Inhibition of Mild Steel Corrosion in a CO_2 Saturated Saline Solution. MSc. Dissertation, Sharjah United Arab Emirates, Zaria, pp. 20.
8. Grafen, H., Horn, E.M., Schlecker, H. and Schindler H. ‘corrosion’ Ullmans’ encyclopaedia of industrial chemistry. Wiley VCH: Weinheim 2002.
9. IUPAC (2012) ‘Compendium of Chemical Terminology. Gold Book ’. Version 2.3.2. 2012-0819, (Available from: http://goldbook.iupac.org/PDF/goldbook.pdf).
10. Iyasara, A.C. and Ovri, J.E. (2013). Corrosion Inhibition of Stainless Steel (314L) using molasses. *International Journal of Engineering and Science,* 2(1): 346-352.
11. Khaled K.F., Abdel-Rehim, S.S., Hazzazi, O.A., and Amin, M.A. (2008) *Corros. Sci.*, 50: 2258.
12. Lalitha. R., Ramesh S. and Rajeswari. S. (2005) Surface protection of copper in acid medium by azoles and surfactant. *Electrochemical acta 51:47-55.*
13. Lopez, D.A., Simison, S.N. and De Sanchez. S.R. "Inhibitors Performance in CO2 corrosion: EIS Studies on the Interaction between their Molecular Structure and Steel Microstructure." *Corrosion Science*, vol. 47, no. 3, pp. 735-755, Mar. 2005.
14. Loto, C. A. and Loto, R.T. (2015). Pitting Corrosion inhibition of Type 304 Austenitic Stainless Steel by 2-Amino-5-ethyl-1,3,4-thiadiazole in Dilute Sulphuric Acid. *Protection of metals and physical chemistry of surfaces*, 51(4):693-700.

15. Loto, C.A. and Loto, R.T. (2016). Corrosion inhibition effect of *Allium cepa* extracts on mild Steel in H_2SO_4. *Der Pharma Chemica*, 8(20): 63-73.
16. Mahmood M. E. (2012) Corrosion Inhibitors Effects and adsorption properties of Theobromine for the Corrosion of Iron in Hydrochloric Acid Medium. Journal of Kerbala University. 10(3): 152-162.
17. Nnanna, L. A., Owate, I. O., Nwadiuko, O C., Ekekwe, N.D. and W. J. Oji, W.J. (2013) Adsorption and Corrosion Inhibition of Gnetum Africana Leaves Extract on Carbon Steel. *International Journal of Materials and Chemistry. 3(1): 10-16.*
18. Nwabanne, J.T and Okafor, V.N. (2012) Adsorption and Thermodynamics Study of the Inhibition of Corrosion of Mild Steel in H_2SO_4 Medium Using Vernonia amygdalina. *Journal of Minerals and Materials Characterization and Engineering, 11:885-890.*
19. Obiukwu, O.O., Opara, I.O. and Oyinna, B.C. 2013. "Corrosion Inhibition of Stainless Steel Using Plant Extract *Vernonia amygdalina* and *Azadirachta indica*". *Pacific Journal of Science and Technology*. 14(2):31-35.
20. Obot, I.B., Obi-Egbedi, N.O., and Umoren. S.A. (2009). Adsorption Characteristics and Corrosion Inhibitive Properties of Clotrimazole for Aluminium Corrosion in Hydrochloric Acid. *Int. J. Electrochem. Sci., 4: 863 – 877.*
21. Oguzie, E.E. (2005). Inhibition of acid corrosion of mild steel by Telfaria occidentalis extract. Pigment and Resin Technology. 34 (6): 321- 326.
22. Popova, A., Sokolova, E., Raicheva, S., Christov, M. 2003. AC and DC study of the temperature effect on mild steel corrosion in acid media in the presence of benzimidazole derivatives. Corrosion Science, 45(1): 33-58.
23. Quraishi, M.A., Singh, A., Singh, V.K., Yadav, D.K., & Singh, A.K. (2010). Green Approach to Corrosion Inhibition of Mild Steel in Hydrochloric Acid and Sulphuric Acid Solutions by the Extract of *Murraya koenigii* Leaves. *Materials Chemistry and Physics*, *122 (1)*, 114-122.
24. Rajendran, S., Joany, M.R., Apparao, B.V., Palaniswamy, N. 2000. Synergistic effect of Calcium gluconate and Zn2 on the inhibition of corrosion of mild steel in neutral aqueous environment. Transactions of Society for Advancement of Electrochemical Science and Technology. 35(3 & 4):113.
25. Roberge, P.R (ed). 2000. *Handdook of Corrosion in Engineering (8 edition)*. McGraw-Hill:New York, NY. 1300.
26. Sinnot, R.K. "Coulson and Richardson's Chemical Engineering," Vol.6, 3rd Edition, Elsevier, India, 2004, p. 294.
27. Water Research Foundation (2015), Guidelines for the use of Stainless Steel in the Water and Desalination Industries, pp. 1-12.