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Inhibitive Action and Adsorption Character of Water Extract of Solanum Melongena for the Corrosion of Mild Steel in 0.5 M H_2SO_4

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Abstract: *The inhibitive action and adsorption character of water extract of Solanum melongena (SM) on mild steel in 0.5 M H_2SO_4 was investigated using gravimetric and electrochemical techniques. The results revealed that the water extract of SM effectively inhibited mild steel corrosion in 0.5 M H_2SO_4 environment, with the effect becoming more vivid as water extract of SM extract concentration increased and as immersion time lengthened, from the polarization results, water extract of SM was seen to reduce the cathodic and anodic reactions as a result of the adsorption of the organic species from the extract on the metal/solution interface. Experimental data was seen to fit the Langmuir isotherm, the result obtained showed that water extract of SM could serve as an effective corrosion inhibitor for mild steel in 0.5 M H_2SO_4.*

Keywords: *Corrosion Inhibition, Mild Steel, Gravimetric and Electrochemical Techniques, Adsorption, Solanum melongena.*

I. Introduction

The control and prevention of corrosion of metallic materials put to use in aggressive environments such as extensive engineering, industrial, and scientific research applications represents an important and fundamental problem. This is often associated with considerable safety hazards and economic losses since massive breakdown of engineering structures resulting from the corrosion of metals do occur. A practical approach to reduce corrosion damage in hostile fluid environments involves the use of corrosion inhibiting additives to protect the metal surface in contact with the harsh environment. One of the methods commonly used is the addition of organic corrosion inhibitors to the corrosive media. [1-3]

Some heteroatom-containing organic compounds as well as compounds with extensive conjugation have been reported to effectively inhibit the corrosion of metals in acidic environments. [4-5] addition of such organic inhibitors functioned via the adsorption of the molecules unto the metal/solution interface where the adsorbed species acts as a protective barrier between the metal surface and the corrodent deactivating the active corrosion sites. The extensive use of these organic corrosion inhibitors is often limited because it is cost effective and quite toxic. As a result, great interest and focus is been directed towards organic corrosion inhibitors of plant origin that are eco-friendly, inexpensive, readily available, and renewable. These plant extracts are known to be highly effective in the inhibition of corrosion of metals and its alloys. This has been linked with the organic constituents in these plant extracts with molecular structures bearing close similarities with those of conventional organic inhibitors. Such plant extracts could thus serve as sources of non-toxic and inexpensive corrosion inhibiting additive in acidic environments. The use of natural products of plant origin as corrosion inhibitors has been widely investigated by so many researchers [6-12]. Ulaeto et al. [13] reported the mechanism of corrosion inhibition of mild steel in hydrochloric acid using acid extracts of *Eichhornia crassipes* as inhibitors, the research showed that the plant extracts effectively inhibited the corrosion rate of mild steel in that acidic environment, with the inhibition efficiency becoming more pronounced as the extracts concentration was increased.

(SM) used for this experiment belongs to the solanaceae family; it is commonly called Garden egg or eggplant, cultivated in various parts of Nigeria and other West African Countries. It has a bitter taste, nutritive value and phytochemical composition. It is useful in traditional medicine for treatment of toothache, skin disease, sexual weakness, high blood pressure, and glaucoma. It is very easy to grow and readily available. Some research was reported about SM [14-15]. This present study investigates the inhibitive action and adsorption character of water extract of SM on mild steel in 0.5 M H_2SO_4 using the gravimetric and electrochemical techniques.

II. Experimental Section

1.1 Materials Preparation

Mild steel used for these experiments had weight percentage composition as of carbon - 0.05: Manganese - 0.6, phosphorus - 0.36: silicon - 0.03; and the balance Fe, Each sheet had thickness of 0.14cm. The blank corrodent was 0.5 M H_2SO_4 solution. Stock solution of the plant extract were prepared by boiling weighed amount of the dried and ground leaves of (SM) in water under reflux for 3 h. The resulting solution was cooled to room temperature and triple filtered. The amount of plant material extracted into solution was quantified by comparing the weight of the dried residue with the initial weight of the dried plant material before extraction. Inhibitor test solutions were prepared in concentrations of 400 mg/L, 800 mg/L and 1600 mg/L respectively by diluting the stock solution with the aggressive solution.

1.2 Gravimetric Experiments

Test coupons of dimension 3 x 3 x 0.14cm, were abraded using Silicon carbide paper (up to 1000 grit), rinsed with distilled water, dried in acetone and warm air, weighed and stored in moisture free desiccators prior to use, these were suspended using glass rods and hooks under total immersion conditions in 300ml beaker containing the test solution at room temperature. All tests were made in aerated and unstirred test solutions. In order to ascertain the weight loss with respect to time, test coupons were retrieved at 24 h intervals progressively for 96 h, to determine weight loss after prolonged period, another set was retrieved after 720 h. Immersed in 20% NaOH solution containing 200g/L of zinc dust, scrubbed with bristle brush, washed, dried and reweighed. The weight loss was taken as the difference between the initial and final weights of the coupons. Measurements were undertaken using a FAJA weighing balance of range 0.0001 to 200g. All the reagents used are of analytical grade, all test were run in triplicate to ascertain the reproducibility of the data with standard deviation ranging from 0 to 0.0006

1.3 Electrochemical Measurements

Metal samples for electrochemical measurements were machined into test electrodes of dimension of 1 × 1 cm^2 and fixed in polytetrafluoroethylene (PTFE) rods by epoxy resin in such a way that only one surface of area 1 cm^2 was left uncovered. The exposed surface was cleaned using the procedure described above. Electrochemical experiments were conducted in a conventional three electrode glass cell of capacity 400 mL using a VERSASTAT 400 Complete DC Voltammetry and Corrosion System, with V3 Studio software. A graphite rod was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. The latter was connected via a Luggin's capillary. Measurements were conducted in aerated and unstirred solutions at the end of 1 h of immersion at 30 ± 1 °C. Potentiodynamic polarization study was carried out in the potential range ±250 mV versus corrosion potential at a scan rate of 0.333 mV/s. Each test was run in triplicate and the data showed good reproducibility.

III. Results And Discussion

3.1 Gravimetric Results

3.1.1 Weight Loss and Water Extract Of SM Concentrations With Respect To Time

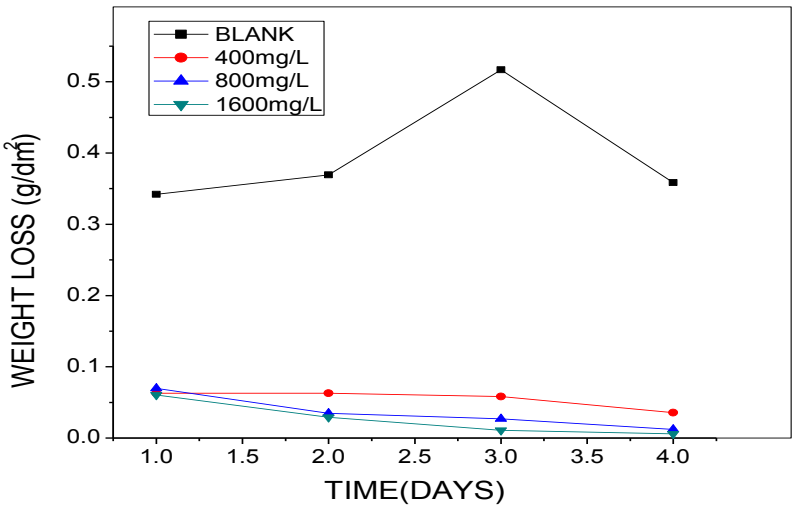

Fig 1 : Weight loss against time for mild steel in 0.5 M H_2SO_4 in the absence and presence of 400 mg/L, 800 mg/L and 1600 mg/L of water extract of SM leaves.

Fig 1 shows weight loss of mild steel in 0.5 M H_2SO_4 for 96 h, the values for the uninhibited system is quite high increasing from 0.34 g/dm^2 to 0.51 g/dm^2 on the third day and sloped to 0.36 g/dm^2 by the fourth day, weigh loss was decreasing in the presence of 400 mg/L concentration of the inhibitor from 0.063 g/dm^2 to 0.03 g/dm^2 by the fourth day, and is highest in the 1600 mg/L concentration from 0.061 g/dm^2 to 0.006 g/dm^2. Weigh loss decreased appreciably compared to the blank values as can be seen in fig 1. Showing the inhibition of mild steel corrosion.

3.1.2 Inhibition Efficiency IE (%) And Water Extract Of SM Concentrations With Respect To Time.

The inhibiting effect of SM on mild steel corrosion was quantified and assessed by evaluating the inhibition efficiency IE (%) as given:

$$IE(\%) = \left(1 - \frac{W_1}{W_2}\right) x\ 100 \qquad (1)$$

Where W_1 and W_2 are the weight losses in inhibited and uninhibited corrodent respectively

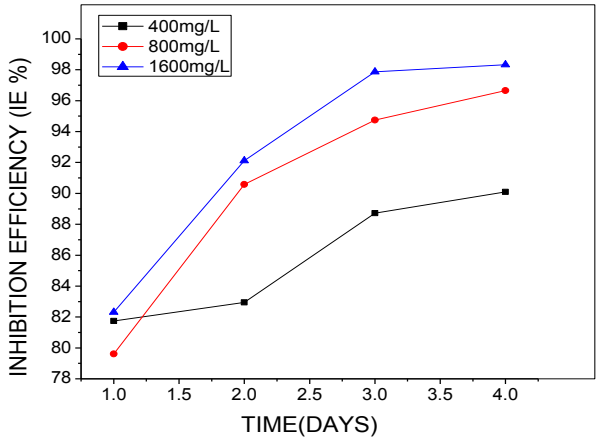

Fig 2: Inhibition efficiency against time for mild steel in 0.5 M H_2SO_4 containing 400 mg/L, 800 mg/L and 1600 mg/L of water extract of SM leaves.

Fig 2 illustrates the inhibition efficiency for mild steel after 96 h, the values for the inhibition efficiency is quite high in the presence of 400 mg/L concentration of the inhibitor from 81.74% to 90.10% by the fourth day, and is highest in the 1600 mg/L concentration from 82.31% to 98.33%. Effect of increasing the concentration of water extract of SM was distinct as corrosion inhibition of mild steel was more in the 1600mg/L concentration. Showing good inhibition efficiency, as has been studied by some authors [16-20]

3.1.3 Effect Of Prolonged Immersion Time On Mild Steel In 0.5 M H_2SO_4 In The Presence And Absence Of Water Extract Of SM. Mild steel was kept in 0.5 M H_2SO_4 corrodent for 720 h without retrieval in the presence and absence of 1600mg/L concentration of water extract of SM. The results are as follows;

In 0.5 M H_2SO_4 corrodent:

Weight loss of mild steel after 720 h	2.8759
Weight loss of mild steel containing 1600mg/L of water extract of SM after 720 h	0.2469
Inhibition efficiency of mild steel containing 1600mg/L of water extract of SM after 720 h	91.41 %

We observed that weight loss was high in 0.5 M H_2SO_4 corrodent and very low with the introduction of SM water extract. Showing that water extract of SM was able to retain its inhibitory abilities after such a prolonged time, giving an inhibition efficiency of 91.41%.

3.2 Electrochemistry results

Electrochemical experiments were carried out to ascertain the effect of water extract of SM on the electrochemical corrosion behavior of mild steel in 0.5 M H_2SO_4 using 400 mg/L and 1600mg/L of water extract of SM concentrations. This was done using the Potentiodynamic polarization technique.

Potentiodynamic Polarization

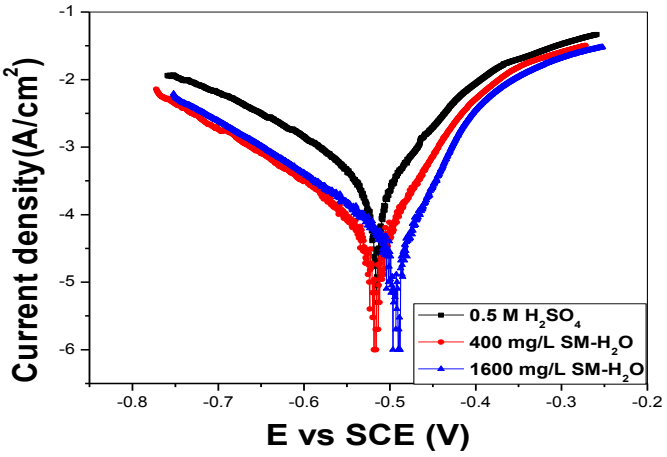

Fig 3 Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4 in the absence and presence of 400mg/L and 1600mg/L SM- water extract.

Potentiodynamic polarization tests were then used to determine the effect of water extract of SM on the anodic dissolution of mild steel and cathodic hydrogen ion reduction. The electrochemical parameters derived from the polarization curves are summarized in table A. The values of the corrosion current densities in the absence (i_{corrbl}) and the presence $i_{corrinh}$ of the inhibitor were used to calculate the inhibition efficiency $\eta\%$ from the polarization data as follows:

$$\eta\% = \left(\frac{I_{corrbl} - i_{corrin\ h}}{i_{corrbl}}\right) \text{X } 100 \qquad (2)$$

Where i_{corrbl} and $i_{corrinh}$ are the corrosion current density in the absence and presence of the inhibitor.

Table A. Tafel Polarization Parameters for Mild Steel in 0.5 M H_2SO_4 in the Absence and Presence of Water Extract of SM Concentrations

System	E_{corr} (mV vs SCE)	i_{corr} (µA/cm^2)	η%
0.5 M H_2SO_4			
Blank	-515.0	462.6	
400mg/L	-516.4	58.7	87.3
1600mg/L	-491.9	54.5	88.2

Fig 3 describes the Potentiodynamic polarization curves for mild steel in 0.5 M H_2SO_4. The corrosion potential, E_{corr}, of the 400mg/L and 1600mg/l concentrations of the water extract of SM in 0.5 M H_2SO_4 containing mild steel are -516.4mV and -491.9mV respectively as shown in figure 3 and in table A. The corresponding i_{corr} values are 58.65mA/cm^2 and 54.5mA/cm^2 for the 400mg/L and 1600mg/L concentrations respectively. The result shows that the presence of the inhibitor reduces both the cathodic and the anodic corrosion current densities, thus implying that the corrosion rate of the mild steel was reduced when compared to the blank values where E_{corr} is -515mV and I_{corr} is 462.6mA/cm^2. Also, the E_{corr} of the 1600mg/L is more positive (anodic) than the 400mg/L. Inhibition efficiency is higher in the 1600mg/L giving 88.2% while the 400mg/L gave 87.5%. Showing that water extract of SM is more effective at higher concentrations. This kind of phenomenon has been studied by several authors [21-25]

3.4 Adsorption Considerations

Surface coverage data are very useful in determining inhibitor adsorption characteristics, such data are applied in construction of adsorption isotherm. Which give detailed information on adsorption mechanism?

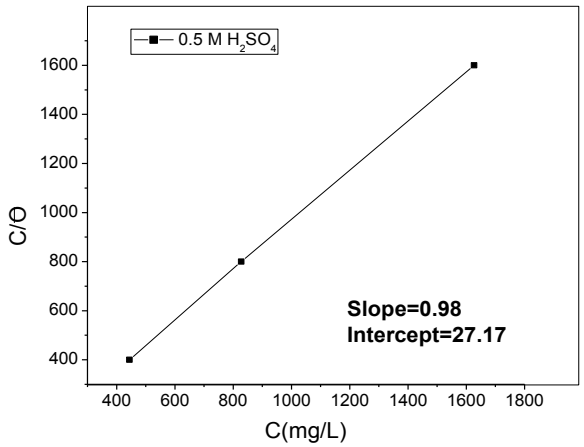

Fig 4. Langmuir adsorption isotherm for water extract of SM on mild steel in 0.5 M H_2SO_4.

The data obtained from gravimetric measurements can be used to determine the adsorption characteristics of water extract of SM on mild steel in the 0.5 M H_2SO_4 according to the Langmuir equation:

$$C/\Theta = 1/b + C \quad (3)$$

Where 1/b is the intercept, C is the inhibitor concentration and Θ is the surface coverage.

And $\Theta = (IE\ \%)\ /100$

The plot of C/Θ against C is shown in Fig. 4 which illustrates Langmuir adsorption isotherm for water extract of SM on mild steel in 0.5 M H_2SO_4 A linear plot was obtained with a slope of 0.98 and intercept of 27.17 suggesting the adsorption of extract organic matter follows the Langmuir adsorption isotherm and confirms adsorption of the extract species on the corroding metal surface, slight deviation of the slope from unity suggest mild interaction between adsorbed species on the metal surface, changes in the heat of adsorption with increasing surface coverage.

In the water extract used in this study, the majority of the organic constituents should exist as protonated species and others in the molecular form. The protonated species could be adsorbed onto cathodic sites on the corroding metal surface and reduce H_2 evolution, while the molecular species can be chemisorbed at active anodic sites and hinder the anodic dissolution reaction. It is possible that at low concentrations of 400mg/L the amount of the surface active organic matter of the extracts was insufficient, as the concentration increases, more of the organic matter becomes available for complex formation which subsequently diminishes the solubility of the surface layer leading to improved corrosion inhibition[26-30]. The trend of inhibition efficiency with immersion time and increase in concentration can be related to the adsorbability of the extract organic matter on the metal surface. This implies that increasing the concentration of water extract of SM in this environment gradually enhanced the adsorbability of the extract, possibly because certain constituents of the extract become available in sufficient amount for chemical interaction with the metal surface, thereby minimizing the adverse effect of increasing corrosion rate with prolonged immersion time. The chemical interaction of some of the extract constituents with the mild Steel surface at high concentrations is attributed to chemisorptions of inhibitor species at anodic and cathodic sites on the corroding metal surface.

IV. Conclusion

This research work aimed at the inhibitive action and adsorption character of water extract of *Solanum melongena* for the corrosion of mild steel in 0.5 M H_2SO_4. The results showed that water extract of SM effectively reduced the corrosion rates of mild steel in 0.5 M H_2SO_4 solution, better results were obtained at higher concentrations of the extract and at prolonged immersion time. Weight loss was high in the uninhibited 0.5 M H_2SO_4 corrodent compared to the inhibited system in which it was low in the 400mg/L, lower in the 800mg/L and much lesser in the 1600mg/L concentrations, indicating that 0.5 M H_2SO_4 was very aggressive on mild steel. Water extract of SM presented highest inhibition efficiency of 90.10% in the 400mg/L concentration, 96.65% for 800mg/L while 1600mg/L concentration was 98.33% for the gravimetric analysis. Polarization measurements showed that the adsorbed extracts organic matter inhibited the corrosion process via a mixed-inhibition mechanism, affecting both the anodic metal dissolution process and the cathodic hydrogen evolution process. Extract adsorption which was due to the formation of a film on the metal/acid solution interface was further corroborated by the experimental data to fit the Langmuir isotherm. The data obtain from the gravimetric and electrochemical measurements demonstrated that water extract of SM can serve as a very good, cheap and readily available inhibitor for mild steel corrosion in 0.5 M H_2SO_4.

References

[1]. Villamil, R. F. V.; Corio, P. Agostinho,; S. M. L. Rubim, J. C. Effect of sodium dodecylsulphate on copper corrosion in sulphuric acid media in the absence and presence of benzotriazole. J. Electroanal. Chem., 1999, 472, 112.

[2]. Heinz, H.; Farmer, B. L.; Pandey, R. B.; Slocik, J. M.; Patnaik, S. S.; Pachter, R.; Naik, R. R. J. Nature of molecular interactions of peptides with gold, palladium, and Pd-Au bimetal surfaces in aqueous solution. Am. Chem. Soc., 2009, 131, 9704.

[3]. Fu, J. J.; Zang, H. S.; Wang, Y.; Li, S. N.; Chen, T.; Liu, X. D. Computational and electrochemical studies of some amino acid compounds as corrosion inhibitors for mild steel in hydrochloric acid solution. Ind. Eng. Chem. Res. 2012, 51, 6377.

[4]. Ashassi-Sorkhabi, H.; Seifzadeh, D.; Hosseini, M. G. EN, EIS and polarization studies to evaluate the inhibition effect of 3H-phenothiazin-3-one, 7-dimethylamin on mild steel corrosion in 1 M HCl solution. Corros. Sci. 2008, 50, 3363.

[5]. Tang, L.; Mu, G.; Liu, G. the effect of neutral red on the corrosion inhibition of cold rolled steel in 1.0 M HCl. Corros. Sci., 2003, 45, 2251.

[6]. Chidiebere, M. A.; Ogukwe, C. E.; Oguzie, K. L.; Eneh, C. N.; Oguzie, E. E. Corrosion inhibition and adsorption behavior of Punica granatum Extract on Mild steel in acidic environment: Experimental and Theoretical studies. Ind. Eng. Chem. Res., 2012, 51, 668 – 677.

[7]. Oguzie, E.E. Corrosion inhibition of aluminium in acidic and alkaline media by Sansevieria trifasciata extract, Corrosion Science, 2007, 49, 1527-1539.

[8]. Quaraish, M. A.; Ambrish, S.; Vinod, K. S.; Yadav, D. K.; Singh,A. K. Green approach to corrosion inhibition of mild steel in hydrochloric acid and sulphuric acid solutions by the extract of Murraga koenigii leaves. Mater. Chem. Phys., 2010, 122, 114.

[9]. Okafor, P. C.; Ebenso, E. E.; Ekpe, J. U. Azadirachta indica extracts as corrosion inhibitor for mild steel in acid medium. Int. J.Electrochem Sci, 2010, 5, 978.

[10]. Ekanem, U. F.; Umoren, S. A.; Udousoro, I. I.; Udoh, A. P. Inhibition of mild steel corrosion in HCl using pineapple leaves (Ananas comosus L.) extracts. J. Mater. Sci., 2010, 45, 5558.

[11]. Obi-Egbedi, N. O.; Obot, I. B.; Umoren, S. A. Spondias monbin L. as a green corrosion inhibitor for aluminium in sulphuric acid correlation between inhibitive effect and electronic properties of extracts major constituents using density functional theory. Arab. J.Chem., 2010, 10, 1076.

[12]. Oguzie, E. E.; Oguzie, K. L.; Akalezi, C. O.; Udeze, I. O.; Ogbulie, J. N.; Njoku, V. O. Natural Products for Materials Protection: Corrosion and microbial growth inhibition using Capsicum frutescens biomass extracts. ACS Sustain. Chem. Eng., 2013, 1, 214.

[13]. Ulaeto, S. B.; Ekpe, U. J.; Chidiebere, M. A.; Oguzie, E. E. Corrosion inhibition of mild steel in hydrochloric acid by acid extracts of Eichhornia crassipes. International Journal of Materials and Chemistry. 2012, 2 (4) 158-164.

[14]. Lester R. N.; Hazan S. M. Z. Origin and domestication of the brinjal eggplant, Solanum melongena, from Solanum incanum. Kew., 1991, 38, 369-387

[15]. Mace E. S.; Lester R. N.; Gebhardt C. G. AFLP analysis of genetic relationships amongst the cultivated eggplant, Solanum melongena and wild relatives (solanaceae). Theor Appl. Genet. 1999, 99, 626-633.

[16]. Oguzie Emeka E.; Maduabuchi A. Chidiebere; Cynthia E. Ogukwe; Kanayo L. Oguzie; Chukwuemeka N. Eneh. The adsorption and corrosion inhibiting effect of aqueous extracts of Punica granatum (PNG) on mild steel in 1 M HCl and 0.5 M H_2SO_4. Ind.and Eng. Chem. Research, 2011, 51, 668-667.

[17]. Abdallah, M. The effects of extract of chamomile (Chamae –melum mixtum L.) Halfabar (Cymbopogen proximus), Black cumin (Nigella sativa L), and kidney bean (phasesolus vulgaris L.) extract on the corrosion of mild steel in aqueous I M sulphuric acid. Corrosion Science, 2004, 46, 1981.

[18]. Okeke, P. I., Maduka O. G., Emereonye R. U., Akalezi C. O., Mughele K., Achinihu I. O., Azubuike N. E. Corrosion inhibition efficacy of Cninodosculus chayamansa extracts on aluminuim metal in acidic and alkaline media. International Journal of Science and Technoledge, 2015,3, 3, 227-234

[19]. E.E. Oguzie; K.I. Iyeh; and A.I. Onuchukwu. Inhibition of mild steel corrosion in acidic media by aqeous extracts from Garcinia kola seed, Bulletin of Electrochemistry, 2006b, 22, (2), 63-68.

[20]. Oguzie, E. E. Influence of halide ions on inhibitive effect of congo red dye on the corrosion of mild steel in sulphuric acid solution. Mater. Chem. Phys. 2004, 87, 212.

[21]. Oguzie, E. E; Enenebeaku, C. O.; Akalezie, O. C.; Okoro, S. C.; Ayuk, A. A.; Ejike, E. N. Adsorption and Corrosion inhibiting effect of Dacryodis edulis extract on low carbon steel corrosion in acidic media. J Colloid interface Sci., 2004, 349, 283-292.

[22]. Villamil, W. M. C.; Gonzales-Rodriguez, J. G.; Martinez, L. An EIS study of the effect of the pedant group in imidazolines as corrosion inhibitors for carbon steel in CO_2 environments. Mater. Corros., 2006, 57, 692.

[23]. Oguzie, E. E.; Li, Y.; Wang, F. H... Corrosion inhibition and adsorption behaviour of methionine on mild steel in sulphuric acid and synergistic effect of iodide ion. Electrochim. Acta, 2007, 52, 6988.

[24]. Morelti, G.; Guids, F; and Gron, G. Toyptamine as a Green iron corrosion inhibitor in 0.5 M Dearected sulphuric acid, Corrosion Science. 2004, (46) 387-403.

[25]. Oguzie, E. E.; Li, Y.; Wang, F. H. J. Corrosion inhibition and adsorption behaviour of methionine on mild steel in sulphuric acid and synergistic effect of iodide ion. Colloid Interface Sci., 2007, 310, 90.

[26]. I.B. Obot; N.O. Obi-Egbedi. Adsorption properties and inhibition of mild steel corrosion in sulphuric acid solution by ketoconazole: Experimental and theoretical investigation. Corrosion Science, 2010, 52, 198.

[27]. Kokalj, A.; Peljhan, S. Density Functional Theory Study of ATA, BTAH, and BTAOH as Copper Corrosion Inhibitors: Adsorption onto Cu (111) from Gas Phase. Langmuir, 2010, 26, 14582.

[28]. M. A. Ameer; E. Khamis; G. Al-Sanani.. Adsorption studies of the effect of thiosemicarbazides on the corrosion of steel in phosphoric acid. Adsorption Science. & Technology, 2000, 18, 177

[29]. Oguzie, E. E. Adsorption and corrosion inhibitive properties of Azadirachta indica in acid solutions. Pigm. Resin Technol., 2006, 35, 334.

[30]. Ebenso, E. E.; Eddy, N. O.; Odiongenyi, A. O. Corrosion inhibitive properties and adsorption behavior of ethanol extract of Piper guinensis as a green corrosion inhibition for mild steel in H_2SO_4. Afr. J. Pure Appl.Chem. 2008, 11, 107.