International Journal of Chemical and Biochemical Sciences
(ISSN 2226-9614)

Journal Home page: www.iscientific.org/Journal.html

Spectroscopic study on corrosion inhibition of mild steel by tamarind (*Tamarindus indica*) fruit husk in acidic medium

*Linus N. Okoro[1]*and Chiedozie Mbaka[1]*

[1]*Department of Petroleum Chemistry, American University of Nigeria, PMB 2250, Yola, Nigeria

Abstract

The corrosion inhibition of mild steel by *Tamarindus indica* fruit husk extract in 1M H_2SO_4 has been investigated using UV-VIS spectroscopic method. The concentrations of 0.0g/15ml, 0.2g/15ml, 0.4g/15ml and 0.6g/15ml of *Tamarindus indica* fruit husk extract were studied at temperatures of 30, 40, 50 and 60 ˚C. The experimental results obtained revealed that the inhibition efficiency increased with increase in concentration of the inhibitor but decreased with increase in temperature. Adsorption of *Tamarindus indica* fruit husk extract was found to follow the Langmuir's adsorption isotherm. The decrease in inhibition efficiency with increase in temperature suggests that the adsorption mechanism is physiosorption. The negative values of heat of adsorption suggest that the adsorption of *Tamarindus indica* fruit husk extract on mild steel is spontaneous.

Keywords: Corrosion inhibitor, *Tamarindus indica*, Absorbance, Mild steel, Sulphuric acid

Full length article **Corresponding Author*, e-mail: linus.okoro@aun.edu.ng

1. Introduction

Corrosion is the deterioration of substances (usually metals) due to their chemical interaction with their environment. Corrosion on most metals may be said to be inevitable [1]. Corrosion inhibition study has been ongoing for several years. So many researches have been conducted in different mediums and on different metals. Some of these experiments have been done in acidic and alkaline medium. These investigations have been done on different metals like mild steel, carbon steel, aluminum and copper using different plants as corrosion inhibitors. Different techniques have been employed in investigating corrosion inhibition efficiency using weight loss, gravimetric, electrochemical measurement, electrochemical polarization, and spectroscopic methods. One of the ways of combating corrosion is through the use of inhibitors [2]. Corrosion Inhibitors are substances that are added to metals in low concentration as well as in hostile environment to inhibit, reduce or prevent corrosion [3]. The corrosion inhibitor used in this research is an organic inhibitor.

1.1. Mild steel

Mild steel is one of the most significant construction materials, which can be commonly utilized in the oil and gas industries. Mild steel is the most typical type of steel and due to its low cost; it's the primary material for transportation in the oil and gas industry [4].

1.2 Tamarindus indica

Tamarindus indica belongs to the subfamily Caesalpiniaceae and is part of the Dicotyledonous family Leguminosae. Tamarind tree is a tropical fruit found especially in the Indian subcontinent, Africa, Pakistan, Bangladesh, Nigeria and most of the tropical countries. Previous research works done show that medicinal plants exhibit good potentials of being a good corrosion inhibitor. Phytochemical screening shows that *Tamarindus indica* extract has an optimistic result for tannins, flavonoids, alkaloid and glycosides. It is preferred to be used for abdominal pain, diarrhea, dysentery and some bacterial infections [5]. The sour and sweet taste of its fruit pulp is used to add flavor. Moreover, tamarind can also be used in traditional medicine as laxative, diuretic, antibacterial agents in addition to in treatment of fever and malaria infections [6].

The purpose of this research is to determine if *Tamarindus indica* fruit husk can be used to inhibit corrosion of mild steel. This is the first time *Tamarindus indica* fruit husk is being investigated for corrosion inhibition potential. To this effect, the temperature dependence of corrosion inhibition at different temperatures on the mild steel are studied using a spectroscopic analysis and thermodynamic study of corrosion inhibition by tamarind fruit husk in 1M H_2SO_4.

Khadija *et al* carried out a thorough study on the corrosion inhibition of mild steel in formic acid using tamarind leaf extract. The weight-loss technique was the method that was used for this particular research. From their obtained result, they observed increase the inhibition efficiency as concentration of inhibitor and that the Langmuir adsorption isotherm best fits the data from the results that they obtained [6].

2. Experimental

2.1. List of materials

UV/Vis spectrophotometer; Beakers; Thermostat water bath at 40 ˚C; Thermostat for 50 ˚C and 60 ˚C; Aluminum coupons; Oven; *Tamarindus indica* fruit husk from American University of Nigeria; Mild steel; Sand paper; Distilled water; Absolute ethanol JDH 99.7 %; Acetone 99 % Lobal chemie; H_2SO_4.

2.2. Mild steel preparation

The mild steel sheet was mechanically cut with a metal cutter from different coupons of 1cm × 1cm × 1cm thickness. Each coupon was first cleaned with a sand paper and then rinsed with acetone and was allowed to dry. The compositions of the Mild steel (wt%) used in this study are Fe (98.86), Mn (0.6), P (0.36), Si (0.030) and C (0.15).

2.3. Preparation of plant extracts

Tamarindus indica fruit husks were collected from American University of Nigeria in large quantity. It was dried using sunlight and the laboratory oven at 50 ˚C. It was then ground with a blender in the laboratory into powdered form. In every 50 g of the tamarind fruit husk powder, 180 ml of ethanol and 20 ml of distilled water was added and covered with a foil paper. The solution was then left for 24 hours and filtered. The liquid product was heated using the oven in order to remove the ethanol from the liquid product. The evaporation was done in the oven at a temperature of 70 ˚C. The stock solution of the plant extract was then used in preparing the concentrations of 0.2g/15ml, 0.4g/15ml and 0.6g/15ml in 1M sulfuric acid.

2.4. Absorbance difference measurements

The concentrations of blank, 0.2g/15ml, 0.4g/15ml and 0.6g/15ml solutions were prepared from 1M H_2SO_4 and the absorbance readings taken before inserting the mild steel in each of the solutions. The absorbance readings were taken after every two days for ten days (240 hours). This procedure was carried out at temperatures of 30, 40, 50 and 60 ˚C. The absorbance differences obtained after 240 hours were recorded and values used for calculations.

The percentage inhibition efficiency (%IE) was calculated using equation 1:

$$\%\mathrm{IE} = \left[\left(\frac{\mathrm{A}_0^{\circ} - \mathrm{A}_1^{\circ}}{\mathrm{A}_0}\right)\right] \times 100 \ldots\ldots\ldots (1)$$

Where A_0 = the absorbance difference for mild steel in the absence of inhibitors in H_2SO_4 solutions at the same temperature and wavelength. A_1 is absorbance differences for mild steel in the presence of the inhibitors.

The degree of surface coverage (θ) at each concentration of the inhibitor was obtained from equation 2.

$$\theta = \left[1 - \left(\frac{\mathrm{A}_0^{\circ} - \mathrm{A}_1^{\circ}}{\mathrm{A}_0}\right)\right] \ldots\ldots\ldots (2)$$

$$\text{Corrosion Rate}(\mathrm{Adm^{-2}day^{-1}/Add}) = \frac{\Delta \mathrm{A}}{\mathrm{dat}} \qquad (3)$$

ΔA = Absorbance difference, d = density of mild steel; a = area of mild steel; t = time of exposure (hours)

The activation energy values obtained in the study were computed from the transformed Arrhenius equation 4:

$$\mathrm{E_a} = \left[2.303\mathrm{R}\frac{\mathrm{T_1 T_2}}{\mathrm{T_2 - T_1}}\right]\left[\log\frac{\mathrm{p_2}}{\mathrm{p_1}}\right] \ldots\ldots\ldots (4)$$

Where R is the molar gas constant; ρ_1 and ρ_2 are corrosion rates at T_1 and T_2 respectively. The values of heat of adsorption, Qads, for the study were determined from equation 5:

$$\mathrm{Q_{ads}} = 2.303\mathrm{R}[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)] \times \left(\frac{\mathrm{T_1 \times T_2}}{\mathrm{T_2 - T_1}}\right)\mathrm{kJ/mol} \ldots (5)$$

θ_1 and θ_2 are degree of surface coverage at 303K and 313K respectively.

3. Results and discussions

The values in tables 1 to 4 are the absorbance differences (Au), corrosion rates (Ad/m^2/day), inhibition efficiency (%IE) and surface coverage (θ) of mild steel in sulfuric acid solution containing *Tamarindus indica* fruit husk extract respectively, at 30 ˚C (303 K), 40 ˚C (313 K), 50 ˚C (323 K) and 60 ˚C (333 K).

Table 1. Absorbance difference (Au), inhibition efficiency (%IE), surface coverage (θ) and corrosion rate (Ad/m^2/day) in sulfuric acid solution containing Tamarindus indica fruit husk extract at 30^{O}C (303K)

30 ˚C				
Concentrations	**Absorbance difference (Au)**	**Corrosion rate (Ad/m^2/day) x 10^{-4}**	**Inhibition efficiency (% 1E)**	**Surface coverage (θ)**
Blank	4.1050	5.6489	-	-
0.2g/15ml	1.0359	1.4255	74.760	0.7477
0.4g/15ml	0.9704	1.3354	76.360	0.7636
0.6g/15ml	0.8665	1.1924	78.890	0.7889

Table 2. Absorbance difference (Au), inhibition efficiency (%IE), surface coverage (θ) and corrosion rate (Ad/m^2/day) in sulfuric acid solution containing Tamarindus indica fruit husk extract at 40^{O}C (313K)

40 ˚C				
Concentrations	**Absorbance difference (Au)**	**Corrosion rate (Ad/m^2/day) x 10^{-4}**	**Inhibition efficiency (% 1E)**	**Surface coverage (θ)**
Blank	4.8008	6.6064	-	-
0.2g/15ml	1.7132	2.3577	64.31	0.6431
0.4g/15ml	1.4449	1.9883	69.90	0.6990
0.6g/15ml	1.3497	1.8573	71.89	0.7189

Table 3. Absorbance difference (Au), inhibition efficiency (%IE), surface coverage (θ) and corrosion rate (Ad/m^2/day) in sulfuric acid solution containing Tamarindus indica fruit husk extract at 50^{O}C (323K)

50 ˚C				
Concentrations	**Absorbance difference (Au)**	**Corrosion rate (Ad/m^2/day) x 10^{-4}**	**Inhibition efficiency (% 1E)**	**Surface coverage (θ)**
Blank	5.1491	7.0857	-	-
0.2g/15ml	1.9680	2.7082	61.78	0.6178
0.4g/15ml	1.8562	2.5543	63.95	0.6395
0.6g/15ml	1.6146	2.2219	68.64	0.6864

Table 4. Absorbance difference (Au), inhibition efficiency (%IE), surface coverage (θ) and corrosion rate (Ad/m^2/day) in sulfuric acid solution containing Tamarindus indica fruit husk extract at 60^{O}C (333K)

60 ˚C				
Concentrations	**Absorbance difference (Au)**	**Corrosion rate (Ad/m^2/day) x 10^{-4}**	**Inhibition efficiency (% 1E)**	**Surface coverage (θ)**
Blank	5.4652	7.5207	-	-
0.2g/15ml	2.2419	3.0851	58.98	0.5898
0.4g/15ml	2.0973	2.8861	61.63	0.6163
0.6g/15ml	1.9415	2.6717	64.48	0.6447

3.1. Absorbance difference measurements

The absorbance difference results of the mild steel were determined by subtracting the initial absorbance readings of the different concentrations of *Tamarindus indica* fruit husk extract for blank, 0.2g/15ml, 0.4g/15ml and 0.6g/15ml in 1M H_2SO_4 from the final absorbance. The absorbance differences were obtained for the temperatures of 30 ˚C (303 K), 40 ˚C (313 K), 50 ˚C (32 3K) and 60 ˚C (333 K). From tables 3.1, 3.2, 3.3 and 3.4, the absorbance difference was increasing with increase in temperature. At 60 ˚C (333 K), the highest absorbance difference (after blank absorbance values) was observed, and kept decreasing in descending order from 60 ˚C to 30 ˚C. A decrease in absorbance difference was observed with increase in concentration. This indicates that the ethanol extract of *Tamarindus indica* fruit extract inhibited the corrosion of mild steel in 1M sulfuric acid (H_2SO_4) [7].

3.2. Corrosion rate of Tamarindus indica fruit husk

Figure 1 shows the corrosion rate on mild steel in the presence and absence of *Tamarindus indica* against cconcentration of *Tamarindus indica* after 240 hours of exposure at 30, 40, 50 and 60˚C. The corrosion rate of mild steel was determined in IM H_2SO_4 in concentrations of blank, 0.2g/15ml, 0.4g/15ml and 0.6g/15ml as shown in fig 3.5**.** The corrosion rates were increasing with increase in temperature. The corrosion rates were calculated using the corrosion rate formula (equation 3) in the presence and absence of the inhibitor (*Tamarindus indica* fruit extract).

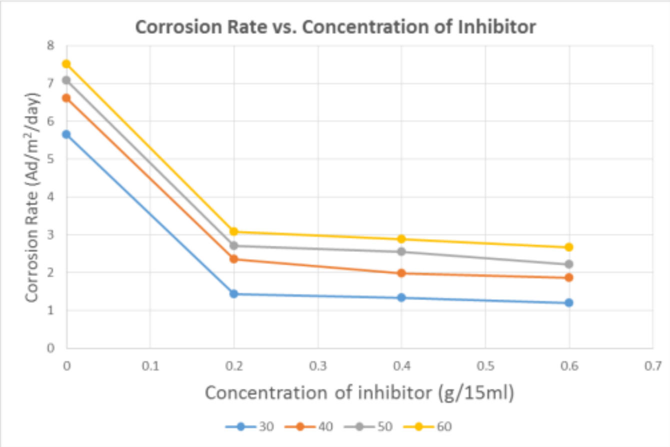

Figure 1. Corrosion rate of sulfuric acid on mild steel in the presence and absence of *Tamarindus indica* fruit extract against concentration of inhibitor after 240 hours at temperatures of 30, 40, 50 and 60 ˚C

3.3. Inhibition efficiency of Tamarindus indica

The inhibition efficiency of *Tamarindus indica* fruit husk at 30, 40, 50 and 60 ˚C in 1M H_2SO_4 of 0.2g/15ml, 0.4g/15ml and 0.6g/15ml is as shown in figure 3.6.

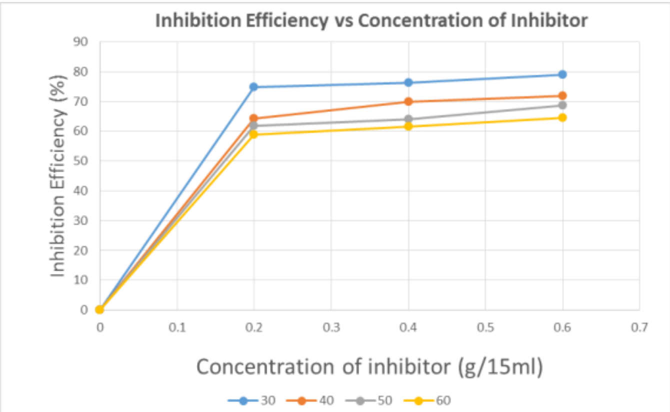

Figure 2. Inhibition efficiency in sulfuric acid on mild steel in the presence of *Tamarindus indica* against concentration of inhibitor after 240 hours for the four temperatures (30, 40, 50 and 60 ˚C)

From figure 2, it is observed that as the concentration of the inhibitor increases, the inhibition efficiency also increases. This can be attributed to the high surface coverage of the inhibitor adsorbed on the mild steel. The presence of some antioxidants like tannins, flavanoids, alkaloids and phenols discovered from the phytochemical analysis are adsorbed on the surface of the mild steel. These antioxidants are known to exhibit inhibition potentials. It is also observed from figure 2 that increase in temperature resulted to decrease of the inhibition efficiency [8]. We therefore propose adsorption mechanism as physiosorption due to decrease of inhibition efficiency with rise in temperature. The peak value of 78.89% at 0.6g/15ml concentration of *Tamarindus indica* fruit husk was observed at 30°C in sulfuric acid; attributed to the increase in the number of adsorbate being adsorbed on the adsorbent.

3.4. Thermodynamic considerations/adsorption isotherm

From table 5, the heat of adsorption ($Q_{ads)}$) values are negative and range from -39.239 to -29.914kJ/mol. The heat of adsorption negative values is an indication that adsorption and inhibition efficiency decreases with increase in temperature [8]. The heat of adsorption negative values also shows that the adsorption of the inhibitor molecules on mild steel is spontaneous. The E_a values for the inhibited were greater than the uninhibited solution. The E_a values of mild steel were less than 40kJ/mol; adsorption decreases with increase in temperature. This assertion agrees to the findings of Ebenso *et al* [9] that, it is physical adsorption mechanism.

Table 5. Thermodynamic Data for Mild Steel Corrosion in 1M H_2SO_4 containing *Tamarindus indica* fruit husk extract from Absorbance Difference Measurements

Concentration (g/ml)	**Activation energy, Ea (kJ/mol)**	**Heat of Adsorption, Q_{ads} (kJ/mol)**
Blank	5.329	-
0.2	11.655	-39.239
0.4	10.924	-26.025
0.6	16.489	-29.914
Average	11.0993	-31.726

3.4.1. Langmuir isotherm

The table 6 shows the values calculated for Langmuir adsorption isotherm using C/θ against concentration. Where C is concentration of the inhibitors and θ is the surface coverage. C/θ was plotted against concentration.

Table 6. Langmuir adsorption isotherm of ethanol extract of *Tamarindus indica* at 30, 40, 50 and 60 ˚C

Temperature	**Concentration**	**C/θ**
30 ˚C	Blank	0
	0.2g/15ml	0.2675
	0.4g/15ml	0.5238
	0.6g/15ml	0.7606
40 ˚C	Blank	0
	0.2g/15ml	0.3109
	0.4g/15ml	0.5723
	0.6g/15ml	0.8346
50 ˚C	Blank	0
	0.2g/15ml	0.3237
	0.4g/15ml	0.6255
	0.6g/15ml	0.8741
60 ˚C	Blank	0
	0.2g/15ml	0.3391
	0.4g/15ml	0.6490

	0.6g/15ml	0.9307

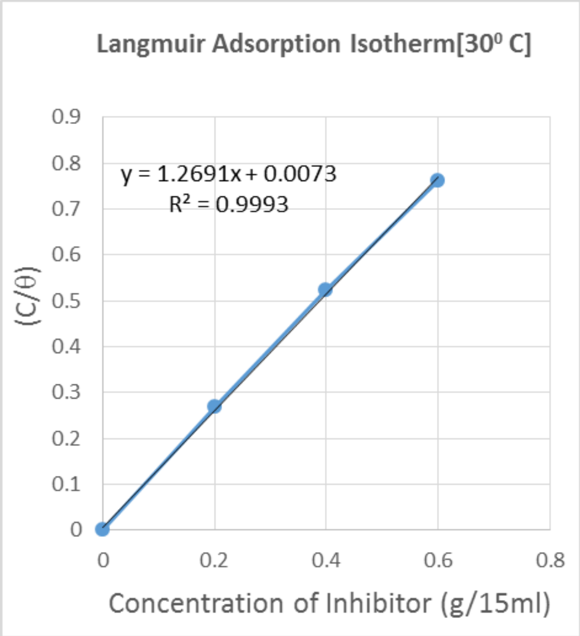

Figure 3. Langmuir adsorption isotherm of Tamarind fruit husk at 30 ˚C

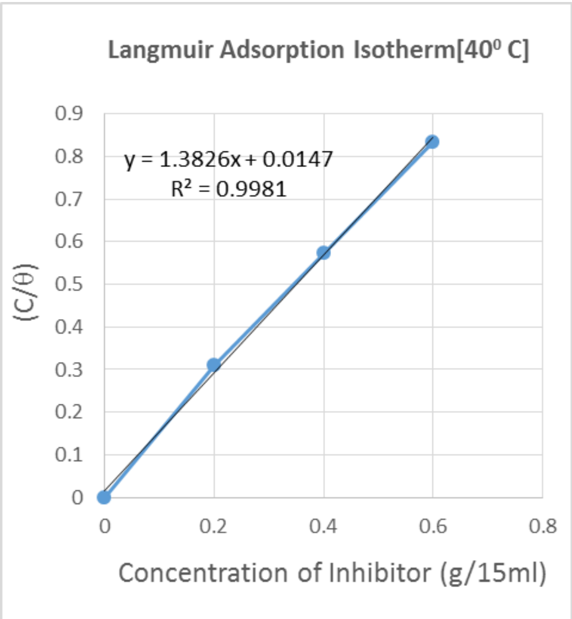

Figure 4. Langmuir adsorption isotherm of Tamarind fruit husk at 40 ˚C

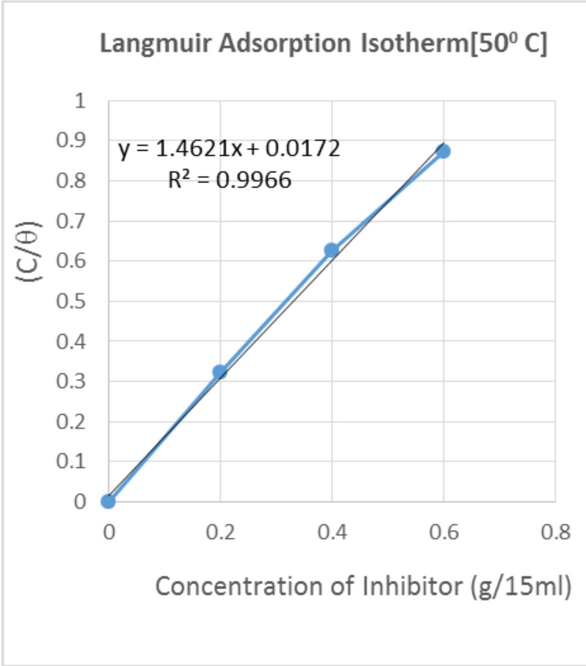

Figure 5. Langmuir adsorption isotherm of Tamarind fruit husk at 50 ˚C

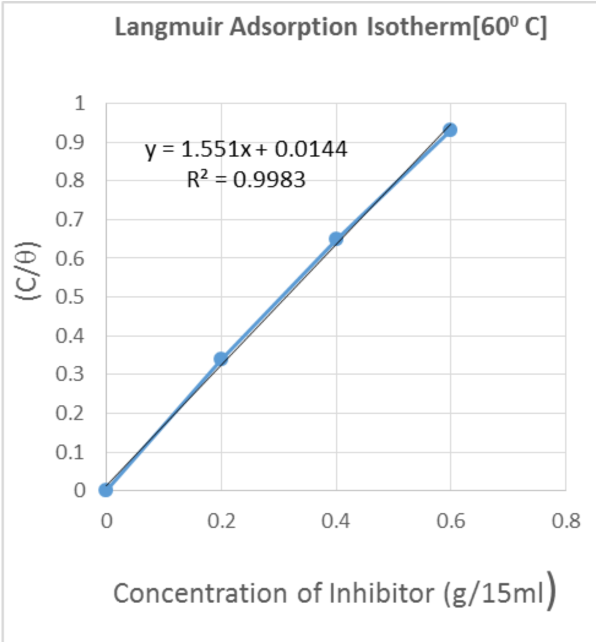

Figure 6. Langmuir adsorption isotherm of Tamarind fruit husk at 60 ˚C

Figures 3-6 shows a linear relationship of *Tamarindus indica* fruit extract on mild steel in 1M sulfuric acid. The slopes obtained from the plots correspond to Langmuir isotherm prediction because it is very close to unity (one).

Conclusions

We have shown in this study that the addition of *Tamarindus indica* fruit husk extracts to 1M H_2SO_4 reduces the corrosion rate of mild steel. The corrosion rate increases with increase in temperature and reduces with increase in inhibitor concentration. The inhibition efficiency (%IE) of *Tamarindus indica* fruit husk increases with increase in concentration and reduces with increase in temperature. The activation energy (E_a) values obtained in this study are below 40kJ/mol which indicates that the mechanism of inhibition is by physiosorption. The negative values of heat of adsorption show that the inhibitor is strongly adsorbed on mild steel surfaces. It also shows that the adsorption is spontaneous. The adsorption mechanism of the extract on the surface of mild steel conforms to the Langmuir adsorption isotherm.

Acknowledgement

We acknowledge the support given to us by the American University of Nigeria (AUN) in providing the laboratory facilities for sample analysis

References

[1] Shaw, B. A.; Kelly, G. Robert. What is corrosion? The Electrochemical Society interface. 2006, 15, 24-27.
[2] Mohammed, N. Rahuma.; Mohammed, B. EL-Sabbah.; Imperiyka, M. Hamad. Effect of Serine and Methionine on Electrochemical Behavior of the Corrosion of Mild Steel in Aqueous Solutions. 2013, 2013, 1-7.
[3] Camila, G. Dariva.; Alexandre, F. Galio. Corrosion Inhibitors–Principles, Mechanisms and Applications. 2014.
[4] Kumar, H.; V. Yadav. American Journal of Materials Science and Engineering. 2013, 1, 34-39.
[5] Kuru, P. Asian pacific journal of tropical biomedicine. 2014, 4, 676-681.
[6] Sivasankar, V.; S. Rajkumar; S. Murugesh.; A. Darchen. Journal of Hazardous Materials. 2012, 225, 164-172.
[7] Okoro, N. Linus.; Khadijah, I. Khalid.; O'Donnell, P. Sylvester. Research Journal of Chemical sciences. 2016, 6, 32-35.
[8] Garai, Subhadra.; Garai, Saraswati.; Jaisankar, Parasuraman.; Singh, J. K.; Elango, Adirajan. Corrosion Science. 2012. 60, 193-204.
[9] Ebenso, E. E., Eddy, N. O. and Odiongenyi, A. O.; African Journal of Pure and Applied Chemistry, 2008, 2 (11),107-115.