



## **Corrosion Inhibition of Mild Steel in Acidic Medium by Methyl Red (2, 4-Dimethylamino-2'-carboxylazobenzene)**

**S.I. Durowaye<sup>1</sup>, V.O. Durowaye<sup>2</sup>, B.M. Begusa<sup>3</sup>**

<sup>1</sup>Department of Metallurgical and Materials Engineering, University of Lagos, Akoka, Lagos, Nigeria

<sup>2</sup>Department of Chemistry, International School, University of Lagos, Akoka, Lagos, Nigeria

<sup>3</sup>Department of Chemistry, University of Lagos, Akoka, Lagos, Nigeria

### **ABSTRACT**

The inhibition of corrosion of mild steel in 1M H<sub>2</sub>SO<sub>4</sub> solution at room temperature by methyl red (2, 4-Dimethylamino-2'-carboxylazobenzene), an organic compound was studied using the weight loss technique. The concentration of the methyl red was varied as 1.0%, 2.0%, 3.0%, 4.0%, 5.0% and 6% weight of each acidic medium and their effects were carefully studied on the corrosion rate of mild steel. The results obtained showed methyl red to be an efficient inhibitor in the acid environment with general decrease in corrosion rate as the concentration of the organic compound increases. The adsorption of the inhibitor on the mild steel obeys the Langmuir adsorption isotherm.

**Keywords:** *Corrosion, Mild Steel, Methyl Red, H<sub>2</sub>SO<sub>4</sub>, Optical Emission Spectrometer*

### **1. INTRODUCTION**

The corrosion of metals remains a worldwide scientific problem as it affects the metallurgical, chemical, construction and oil industries. The increasing interest in the manufacture and use of sulphuric acid in applications involving the extensive use of mild steel has created the need for obtaining information on the corrosion resistance of mild steel to sulphuric acid attack. Sulphuric acid is a very important commodity chemical, and indeed, a nation's sulphuric acid production is a good indicator of its industrial strength [1]. Sulphuric acid is widely used in industries such as pickling, cleaning and descaling, industrial cleaning agent, production of chemicals, etc. Mild steel is used in these environments due to its easy availability, low cost and excellent physical properties, but its use and lifespan is restricted in these conditions due to its susceptibility towards corrosion. To complement its low cost and economic value, the most effective means of addressing the corrosion of mild steel is with the use of inhibitors, especially organic compounds. Though many compounds show good anticorrosive activity, most of them are highly toxic to both human beings and the environment. These toxic effects and ecological problems associated with the discharge of such materials have resulted in the development of other efficient and environmentally acceptable inhibitors. Hence, the recent trend is the search for environmentally friendly chemicals. Most natural products are nontoxic, bio-degradable and readily available in abundance for use in aggressive solutions in contact with the steel surface in order to inhibit the corrosion reaction and significantly influence the kinetics of the electrolytic process. A number of organic compounds [2–9] are known to be applicable as corrosion inhibitors for steel in acidic environments. Such compounds typically contain nitrogen, oxygen or sulphur in a conjugated system, and function via adsorption of the molecules on the metal surface, creating a barrier to corrosive

attack [10]. In frequent instances the addition of small quantities of special chemicals to large volumes of corrosive solutions can be quite effective in reducing corrosion. Such chemicals are called corrosion inhibitors. At the simplest level a corrosion inhibitor is a substance which when added in small concentration to an environment effectively reduces the corrosion rate of a metal exposed to that environment. Because of the toxic nature and high cost of some chemicals used like chromate and nitrate, it is necessary to develop environmentally acceptable and less expensive inhibitors [11]. The selection of inhibitor is controlled by its economic availability, its efficiency to inhibit the substrate material and its environmental side effects. Most of the excellent acid inhibitors for corrosion of steel in acidic medium are organic compounds containing nitrogen, oxygen and/or sulphur atoms [12-15]. The inhibiting action of these compounds is attributed as a first stage, to the adsorption of the additives to the metal/solution interface. The adsorption process depends upon the nature and surface charge of the metal, the type of aggressive media, the structure of the inhibitor and the nature of its interaction with the metal surface. Metallic material constitutes a great part of construction material elements in industries, agricultural equipment, oil and gas and petrochemical, medical services, process and allied industries. In these industries, the metallic material as a result of interaction with its environment loses its integrity over a period of time [16]. As such, the material cannot perform the intended function effectively and reliably. Some of these environments are atmosphere, aqueous solution, solids, acids and bases, inorganic solvents, molten salts, liquid metals, human body etcetera. At times, the effect of the loss in integrity may be very severe as to result in loss of valuable production time, accident and in the extreme death. The cost associated with the problem is enormous and its influence in the economy of a nation is

significant. It has been estimated that approximately 5% of industrialised nations' income is spent on corrosion incidental problems. For instance, the cost of the problem to the U.S. economy is put at \$297 billion annually [17]. The cost to the Nigerian economy is not available. However, a guess could be haphazard; and this is in the corridor of \$3.2 billion annually [18]. Corrosion control is an important activity of technical, economical and environmental importance. Thus, the search for efficient corrosion inhibitors has become a necessity to secure metallic materials against unmitigated degradation.

Corrosion of mild steel is of great practical interest because mild steel is widely used in the oil, gas and offshore environments for pipelines, flow-lines, platforms, down-hole tubular equipments, well heads, industrial vessels etc. Corrosion inhibition is being extensively employed in minimising metallic wastage of engineering materials in service [19]. In this research, the effect of the inhibition efficiency of methyl red on the corrosion of mild steel in acidic medium using 1M sulphuric acid (H<sub>2</sub>SO<sub>4</sub>) is experimentally investigated and presented.

## II. EXPERIMENTAL DETAILS

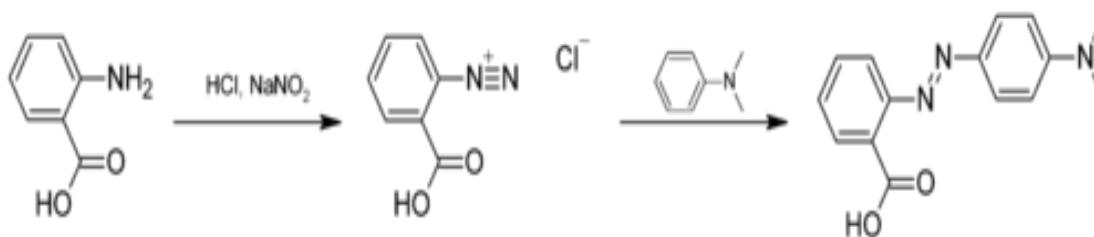


Figure 1. Chemical structure of Methyl Red (2, 4-Dimethylamino-2'-carboxylazobenzene)

Table 1: Spectrometric Compositional Analysis of Specimen

Elements	C	Si	Mn	P	S	Cr	Mo	V	Ni	Cu	Al	Fe
Composition (Wt. %)	0.267	0.250	0.861	0.039	0.033	0.120	0.016	0.003	0.073	0.061	0.031	98.414

### 2.1. Work Materials and Specimen Preparation

The cylindrical mild steel rod used for this study was obtained in the open market and analysed at the Spectrochemical Research Laboratory, Department of Metallurgical & Materials Engineering, University of Lagos, Akoka, Nigeria. It was cut to a length of 30cm and properly machined to diameter 20mm. It was manually polished using silicon carbide grinding papers of grit 60 and 120 to ensure a smooth surface and reduce corrosion attack on the specimen. After polishing, the rod was cut into lengths of 3cm and the edges of these cut pieces were also polished. The rods were kept in a desiccator to prevent corrosion prior to experimentation. Seven specimens of length 3cm and diameter 20mm were used for the experiment and were denoted as A, B, C, D, E, F and G.

### 2.2 Inhibitor and Acid

Methyl Red (2, 4-Dimethylamino-2'-carboxylazobenzene), a reddish powder is the inhibitor used. Its structural formula is shown in figure 1 and its molecular formula is C<sub>15</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>. It was prepared in various concentrations of 1%, 2%, 3%, 4%,

5% and 6%. These were used as the inhibiting compound and 56ml of concentrated H<sub>2</sub>SO<sub>4</sub> was diluted with 944ml of distilled water to get 1M solution of H<sub>2</sub>SO<sub>4</sub>. The H<sub>2</sub>SO<sub>4</sub> used as corrosive medium was from Analar grade and bi-distilled water was used for its preparation.

### 2.3 Test Procedures

The composition analysis of the specimen was determined using an optical emission spectrometer (OES) ARL 3460B model and the chemical composition is shown in table 1. The specimens were degreased in ethanol, air dried and etched in 5% concentrated hydrochloric acid (HCl) for 30 seconds and weighed using an analytical balance. The weight loss was determined by weighting the cleaned samples before and after hanging the sample into 100 ml of corrosive solution in the absence and presence of various concentrations of the inhibitor. The initial weights were recorded as W<sub>1</sub> before immersion in the test environments. Specimens A, B, C, D, E, F and G were immersed in seven separate 150 ml open beakers

containing 100 ml of 1M H<sub>2</sub>SO<sub>4</sub>. The inhibitor (Methyl red) under test was mixed with the H<sub>2</sub>SO<sub>4</sub> solutions in percentage concentrations of 0% (control), 1%, 2%, 3%, 4%, 5% and 6% respectively of the total mixture. The experiment was allowed to run for twenty one days with periodic measurement of weight loss every 72 hours. The specimens were removed from the beakers and scrubbed with a bristle brush, rinsed in distilled water, rinsed in alcohol, air-dried and re-weighed to get the final weight and recorded as W<sub>2</sub>. The weight loss (WL) was calculated in gramme (g) as the difference between the initial weight and the final weight after removal of the corrosion products. The reduction of the thickness as a function of time

was calculated. The experimental readings were recorded to the nearest 0.0001g on a Mettler digital analytical balance (digital analytical balance with sensitivity of ± 1mg. The tests without inhibitors were done for comparison with the tests in inhibited environments to observe the corrosion reactions behaviour of the tested specimens. The corrosion rate (R) in millimeters per year was evaluated using the formula proposed by Krisher [20]

$$\text{Corrosion rate, } R = \frac{87.6W}{DAT} \tag{1}$$

Where:

W = Weight loss (W<sub>L</sub>) = Initial weight (W<sub>1</sub>) – Final weight (W<sub>2</sub>) in milligrams.

A = Total surface area of specimen in cm<sup>2</sup>.

T = Total time sample was immersed in hours.

D = Density of the specimen in g/cm<sup>3</sup>.

R = Corrosion rate in millimeters per year.

The specimens used have cylindrical geometry and each has a total surface area given by:

$$A = 2\pi r(l + r) \tag{2}$$

Where;

l = length of specimen in cm.

r = radius of specimen in cm.

Curves of corrosion rate (calculated) versus time of immersion were also plotted.

The percentage inhibitor efficiency, P, was calculated from the equation:

$$P = \frac{R_1 - R_2}{R_1} \times 100 \tag{3}$$

where R<sub>1</sub> and R<sub>2</sub> are the corrosion rates in the absence and the presence respectively, of a predetermined concentration of inhibitor. The percentage inhibitor efficiency was calculated for all the inhibitors throughout the exposure period. The degree of surface coverage (Θ) was calculated from equation:

$$\Theta = \frac{R_1 - R_2}{R_1} \tag{4}$$

The area and density of the specimen used are 25.143cm<sup>2</sup> and 7.86g/cm<sup>3</sup>.

### III RESULTS AND DISCUSSION

The spectrochemical analysis shown in table 1 reveals that the mild steel specimens used in this study have an iron content of approximately 99% with other trace elements resided from

metal extraction process. The levels of these trace elements are insignificant to influence the chemistry of the behaviour of the steel specimens in the corrosive medium.

**Table 2: Weight losses, W<sub>L</sub> in 0% - 6% concentration of Methyl Red in 1M H<sub>2</sub>SO<sub>4</sub> at every 72hrs for 504hrs.**

Specimen	Inhibitor Concentration, C (%)	72 hrs	144 hrs	216 hrs	288 hrs	360 hrs	432 hrs	504 hrs
		W <sub>L</sub> (g)	W <sub>L</sub> (g)	W <sub>L</sub> (g)	W <sub>L</sub> (g)	W <sub>L</sub> (g)	W <sub>L</sub> (g)	W <sub>L</sub> (g)
A	0	0.30	0.60	0.80	1.06	1.79	2.68	3.16
B	1	0.28	0.40	0.49	0.60	0.69	1.00	1.36
C	2	0.24	0.41	0.52	0.59	0.61	1.27	1.27
D	3	0.21	0.39	0.59	0.83	1.00	1.12	1.20

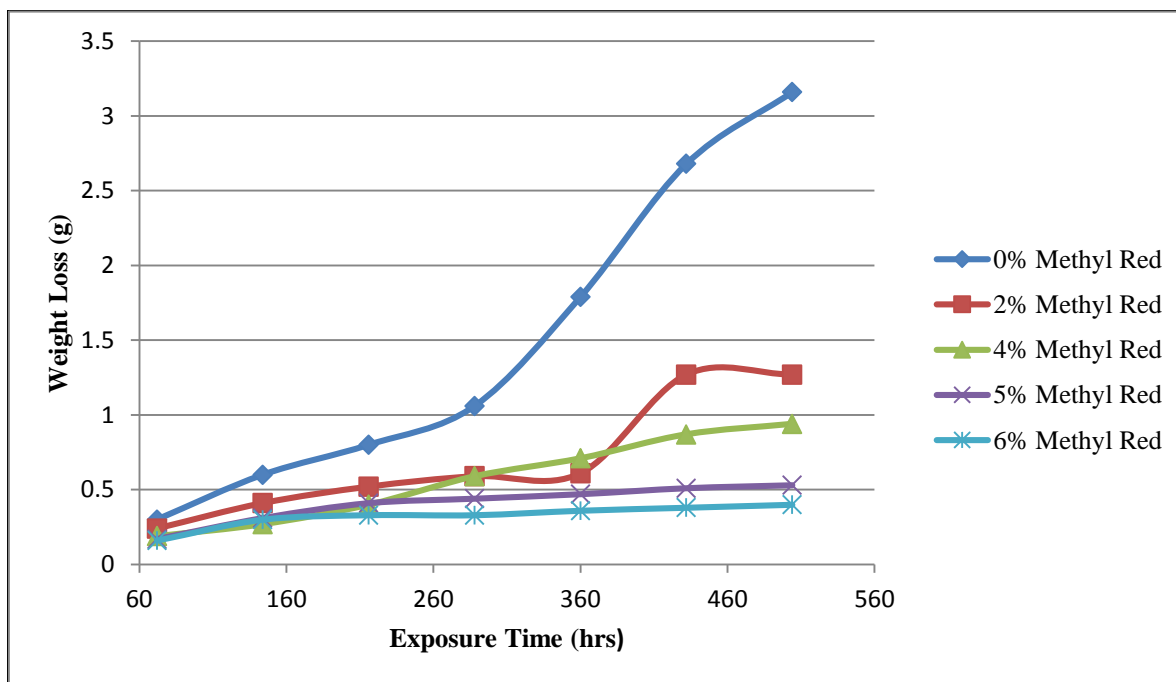
E	4	0.19	0.27	0.40	0.59	0.71	0.87	0.94
F	5	0.17	0.31	0.41	0.44	0.47	0.51	0.53
G	6	0.16	0.30	0.33	0.33	0.36	0.38	0.40

**Table 3: Weight losses,  $W_L$  in 0% - 6% concentration of Methyl Red in 1M  $H_2SO_4$  at 504hrs**

Specimen	Inhibitor Concentration, C (%)	$W_1$ (g)	$W_2$ (g)	$W_L$ (g)
A	0	51.98	48.82	3.16
B	1	51.90	50.54	1.36
C	2	52.12	50.85	1.27
D	3	52.22	51.02	1.20
E	4	52.30	51.36	0.94
F	5	52.66	52.31	0.53
G	6	52.67	52.27	0.40

**Table 4: Inhibition efficiency, Corrosion rate and surface coverage of Methyl Red on mild steel at 504 hrs**

Specimen	Inhibitor Concentration, C (%)	Corrosion Rate (mpy)	Inhibition Efficiency (%)	Surface Coverage ( $\Theta$ )
A	0	2.779	0	0
B	1	1.196	57.0	0.570
C	2	1.117	59.8	0.598
D	3	1.055	62.0	0.620
E	4	0.827	70.2	0.702
F	5	0.466	83.2	0.832
G	6	0.352	87.3	0.873



**Figure 2: Variation of weight-loss with exposure time for specimens A, C, E, F & G in 0%, 2%, 4%, 5% & 6% Methyl red concentrations.**

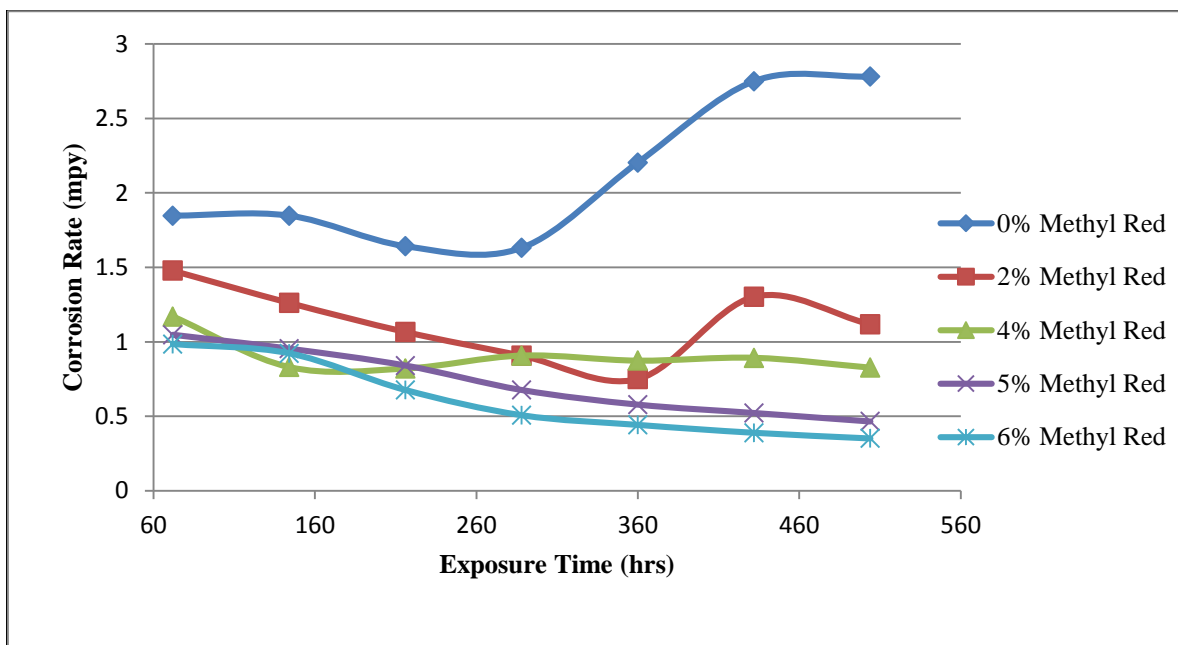


Figure 3: Effect of percentage concentration of Methyl red on the corrosion rate of mild steel specimen A, C, E, F & G.

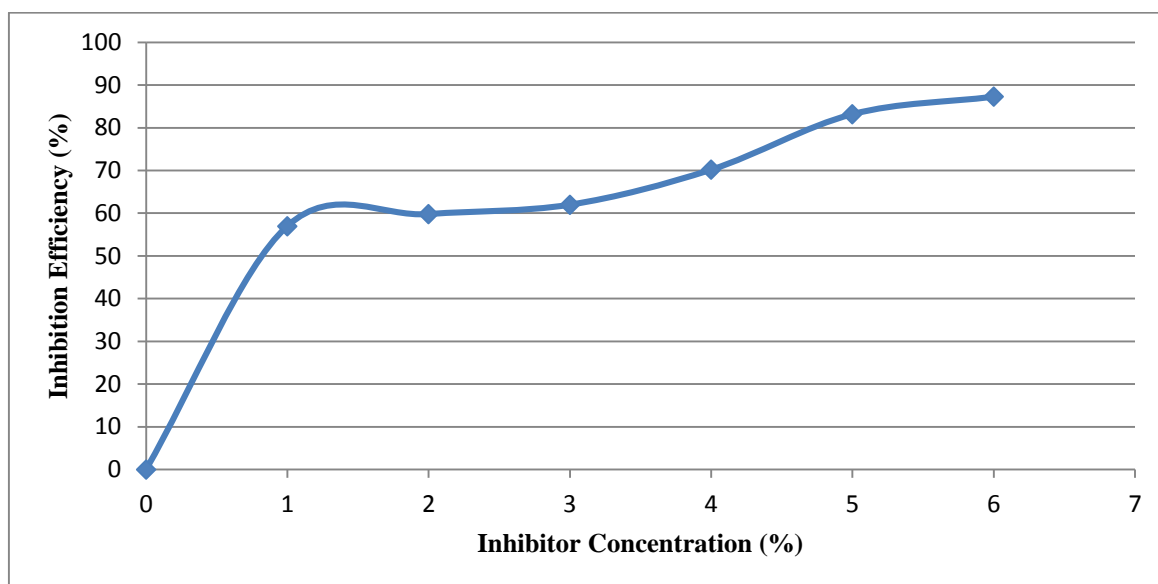


Figure 4: Variation of percentage inhibition efficiency with Methyl red at concentrations at 504 hrs.

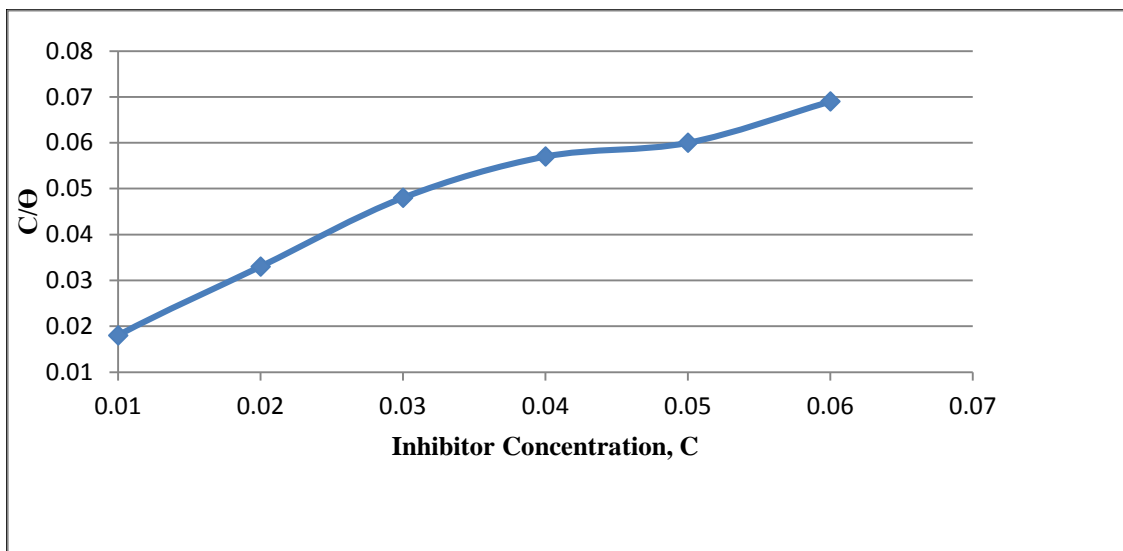


Figure 5: Relationship between  $C/\theta$  and Inhibitor concentration  $C$

The weight-loss of mild steel was studied at various time intervals from 72 hrs to 504 hrs in the absence and presence of stated concentrations of Methyl red in 1M  $H_2SO_4$ . The values of weight-loss ( $W_L$ ), corrosion rate ( $R$ ), the percentage inhibition efficiency and surface coverage are presented in Tables 2, 3 and 4. Weight loss in specimen A to which no inhibitor was added was the highest. Specimen G to which the highest concentration of the inhibitor was added had the lowest weight loss. The corrosion rate decreased drastically with the application of Methyl red due to the interaction of inhibitor molecules with the steel surface. The weight-loss measurements are not linearly proportional to the value of Methyl red concentration most probably due to formation of a protective film which prevents the diffusion of the harmful anions onto the steel irrespective of its concentration. Figures 2 & 3 show the variation of weight-loss and corrosion rate with exposure time at the various inhibitor (Methyl red) concentrations, while Fig. 4 shows the variation of percentage inhibition efficiency with inhibitor concentration. It could be seen that increase in the concentration of Methyl red resulted in increased inhibition efficiency. The highest inhibition efficiency of 87.3% was observed to occur with addition of 6% concentration of Methyl red. This behaviour suggests that the inhibition is due to the adsorption of inhibitor's molecule onto the specimens' surfaces and Methyl red acts as an adsorption inhibitor. The inhibition action of Methyl red is ascribed to the presence of heteroatoms in this compound. Organic compounds that contain functional groups such as  $-OR$ ,  $-NR_2$  and/or  $-SR$  have been reported to inhibit corrosion of metals in alkaline or acidic solutions [21, 22]. The curves obtained indicate similar electrochemical reactions with the addition of Methyl red. A higher coverage of the inhibitor on the surface was obtained in solutions with higher inhibitor concentration. The formation of surface inhibitor film on the mild steel surface provides consideration protection to the mild steel against corrosion. This film reduces the active surface area exposed to the corrosive medium and delays the hydrogen evolution and iron dissolution. The observed phenomenon is generally described as the corrosion inhibition of the metal with the formation of a protective layer of adsorbed species at the metal surface. In the presence of Methyl red, corrosion is inhibited by adsorption of the organic molecules on the metal surface. Protection by Methyl red is generally enhanced by the

presence of iron ions. This is explained by the participation of iron ions in the condensation and polymerization reactions leading to the production of surface films [23]. For an inhibitor to have a high coverage on the surface, a chemical bond between the inhibitor and the metal atom stronger than the one for water molecules should be formed. The adsorption of corrosion inhibitors at the metal/solution interface is due to the formation of either electrostatic or covalent bonding between the adsorbates and the metal surface atoms. To determine the inhibiting properties and the behaviour of the Methyl red molecules adsorbed on the metallic surfaces, it is preferable to suppose that physiochemical reaction is responsible for the main inhibiting effect. Thus, it is a good inhibitor for iron. Furthermore, it is well known that iron corrosion inhibition by organic compounds, particularly those presenting p-bonding, is favoured whenever a strong adsorption process takes place on the metal surface [24]. The nature of inhibitor interaction on the corroding surface during corrosion inhibition of metals and alloys has been deduced in terms of adsorption characteristics of the inhibitor. The adsorption behaviour of the inhibitor molecules on the metal surface can be applied to explain the inhibition mechanism of inhibitors [25, 26]. Several adsorption isotherms can be used to assess the adsorption behaviour of the inhibitor. The Langmuir adsorption isotherm was found to be the best description of the adsorption behaviour of Methyl red on the mild steel surface, which obeys the following equations [27, 28].

$$\theta = \frac{KC}{1+KC} \quad (5)$$

Re-arranging,

$$\frac{C}{\theta} = C + \frac{1}{K} \quad (6)$$

Where  $C$  is the inhibitor concentration,  $K$  is the adsorption equilibrium constant, and  $\theta$  the surface coverage of the inhibitor. The linear relationship of  $C/\theta$  versus  $C$  in different concentration of Methyl red solutions is displayed in Figure 5. The deviation of the slope from unity is attributed to the molecular interaction among the adsorbed inhibitor species, a factor which was not taken into consideration during the derivation of the Langmuir equation. The Langmuir isotherm

assumes that: The metal surface contains a fixed number of adsorption sites and each site holds one adsorbate.

#### IV. CONCLUSIONS

In this study, the weight loss technique reveals Methyl red to be an efficient inhibitor for mild steel in the sulphuric acid corrosive medium. The inhibition efficiency increases with the increase in concentration of Methyl red with maximum inhibition efficiency value of 87.3% at 6% inhibitor concentration. At this value, the lowest corrosion rate value of 0.352 mpy was obtained. This is a mixed type inhibitor whose adsorption on mild steel is physicochemical. It mainly acts by film formation, thus blocking the active sites on the cathodic and anodic regions. The adsorption of this inhibitor obeys Langmuir's adsorption isotherm.

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#### REFERENCES

- [1] Philip.J. Chenier, Survey of Industrial Chemistry (Wiley, New York, 1987), pp. 45–57
- [2] J. Mathiyamsu, I.C. Nebru, P. Subramania, N. Palaniswamy, N.S. Rengaswamy, *Anticorros. Methods Mater.* 48(5), 342 (2001)
- [3] N. Ochoa, F. Moran, N. Pebre, *J. Appl. Electrochem.* 34, 487 (2004)
- [4] E.E. Oguzie, C. Unaegbu, C.N. Ogukwe, B.N. Okolue, A.I. Onuchukwu, *Mater. Chem. Phys.* 84, 363 (2004)
- [5] E.E. Oguzie, *Mater. Chem. Phys.* 87, 212 (2004)
- [6] S. Rajendran, R. Maria Joany, B.V. Apparao, N. Palaniswamy, *Trans. SAEST* 35(3/4), 113 (2000)
- [7] S. Rajendran, B.V. Apparao, N. Palaniswamy, *Anti-corros. Methods Mater.* 44(5), 338 (1998)
- [8] M.N. Shalaby, M.M. Osman, *Anti-corros. Methods Mater.* 48(5), 309 (2001)
- [9] E.E. Ebenso, *Mater. Chem. Phys.* 79, 58 (2003)
- [10] M.A. Quraishi, H.K. Sharma, 4-Amino-3-butyl-5-mercapto-1, 2, 4-triazole: a new corrosion inhibitor for mild steel in sulphuric acid. *Mater. Chem. Phys.* 78, 18 (2002).
- [11] Abiola O.K. and Oforka N.C, (2002), "Inhibition of the Corrosion of Mild Steel in Hydrochloric Acid by (4-Amino – 2 –Methyl-5-Pyrimidinyl Methylthio) Acetic Acid and its Precursor", *Journal of Corrosion Science and Engineering*, vol 3, Pages 1-8.
- [12] M. Abdalla; H. Basim; A.I. Zaaferany and A.S. Fouda: *Int.J.Electrochem Sci.*,7(1) (2012) 282.
- [13] M. Abdel-Aal and M.S. Morad: *Br. Corros. J.* 36, (2001)250
- [14] M. Abdallah and M.M. El-Naggar: *Materials Chem. and Phys.* 71, (2001)291.
- [15] M. Bonkalah, A. Quassini, B. Hammouti and A. El-Idrissi: *Appl. Surf. Sci.*, 252,(2006)2178.
- [16] Callister, W.D. "Materials Science and Engineering". 4th ed. John – Wiley, New York, 1997.
- [17] www.nace.org retrieved Friday July 6, 2007
- [18] CIA-TheWorldfactbook-Nigeria, www.cia.gov/cia/publications/factbook/geos/ni.html. July 2006
- [19] Aver, S.H. (1974): "The Introduction to Physical Metallurgy". 2<sup>nd</sup> Edition McGraw-Hill Inc., New York, pp. 86-92.
- [20] Krisher, A. S., "Technical Information Regarding Coupon Testing in Metal Samples Corrosion Monitoring Systems". Retrieved from www.aispi.com/cpntst.htm, 2006.
- [21] Li, X; Deng, S and Fu, H (2010): "Adsorption and Inhibition effect of Vanillin on Cold Rolled Steel in 3M H<sub>3</sub>PO<sub>4</sub>". *Progress in Organic Coatings* 67, 420 – 426.
- [22] Singh, P; Bhara, K and Singh, G (2008): "Adsorption and Kinetics Studies of Leucine as an Inhibitor on Mild Steel in Acidic Media". *Applied Surface* 254, 5927 – 5935.
- [23] G. Shemit, *Br. Corros. J.* 19, 171 (1984)
- [24] V. Jovancievic, B. Yang, J. O'M Bockris, *J. Electrochem. Soc.* 135, 94 (1988)
- [25] L. Narvaez, E. Cano, D.M. Bastidas, *J. Appl. Electrochem.* 35, 499–506 (2005)
- [26] W.H. Durnie, B.J. Kinsella, R. deMarco, A. Jefferson, *J. Appl. Electrochem.* 31, 1221–1226 (2001)
- [27] Y.H. Tang, W.Z. Yang, X.S. Yin, Y. Liu, R. Wan, J.T. Wang, *Mater. Chem. Phys.* 116, 479–483 (2009).
- [28] M.S. Morad, *J. Appl. Electrochem.* 38, 1509–1518 (2008).