Inhibitive Behaviour of Methyl Red (2, 4-Dimethylamino-2'-carboxylazobenzene) on Corrosion of Mild Steel in Alkaline Medium

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Abstract   The corrosive behaviour of mild steel in 1M NaOH solutions contaminated with methyl red (2, 4-Dimethylamino-2'-carboxylazobenzene), an organic compound at room temperature 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 alkaline 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 alkaline environment with general decrease in corrosion rate as the concentration of the organic compound increases. The Langmuir adsorption isotherm was found to be the best description of the adsorption behaviour of Methyl red on the mild steel surface.

Keywords   Corrosion, Mild Steel, Methyl Red, NaOH, Optical Emission Spectrometer

1. Introduction

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 [1]. 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 etc. 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 life 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 [2]. The cost to the Nigeria economy is not available. However, a guess could be haphazard; and this is in the corridor of $3.2 billion [3].

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 [4]. Organic inhibitors in particular are of great use in the control of corrosion in sea water. Mild steel corrosion in acidic solution has also been effectively controlled by the use of organic substances containing nitrogen, oxygen or sulphur in the conjugated system as inhibitors [5]. Successful use of naturally occurring inhibitors in both acidic and alkaline environments has been extensively reported [6]. This method of corrosion control is fraught with the challenges of high cost and toxicity. The efficiency of several synthetic organic compounds such as methylsulfiny, carbanion-dimethyl sulfoxide, hydroxyl radicals and alkyl nitrates has been investigated [7]. Corrosion mitigation of structures by these synthetic compounds is significant. However, the known hazardous effects of most synthetic organic inhibitors still pose a great challenge. Most of the efficient inhibitors used in industry are organic compounds having multiple bonds in their molecules which mainly contain nitrogen and sulphur atoms through which they are adsorbed on the metal surface. Compounds with functional groups containing oxygen, nitrogen and sulphur have ability to form complexes with iron. They have been reported to act as effective inhibitors to the surface of steel by means of their competitive adsorption through the surface complex formation [8].

Organic compounds used as inhibitors act through a process of surface adsorption, so the efficiency of an inhibitor depends on (i) the chemical structure of the organic compound, (ii) the surface charge of the metal, and (iii) the type of interactions between the organic molecule and metal surface. Existing data reveal most inhibitors to act by adsorption on the metal surface through heteroatoms such as nitrogen, oxygen and sulphur, double bonds, triple bonds or aromatic rings which tend to form stronger coordination bonds. Compounds with π-bonds generally exhibit good inhibitive properties, the electrons for the surface interaction being provided by the π-orbital [9].

The corrosion inhibition of steels has received a considerable amount of attention as a result of its industrial concern [10, 11]. Steel passivation in alkaline environments is due to the formation of a very thin, but highly protective oxide/hydroxide layer [12]. It has been proved that, in alkaline media, the film corresponds basically to a double-layer model consisting of an inner magnetite and an outer ferric oxide according to a Fe_3O_4/Fe^{3+} structure [13 – 19]. The most internal layer is composed of Fe^{2+} oxides in contact with the substrate. The thermodynamic instability of both Fe^{2+} oxides and magnetite in the presence of oxygen leads to the formation of an outer layer of Fe^{3+} oxides and continuous exposure to oxygen and humidity promotes film growth and a progressive enrichment of the passive film in Fe^{3+}, either in oxide form or oxo-hydroxide form, depending on the potential. The passivity breakdown occurs by addition of Cl^- to the alkaline solution [20]. In practice, corrosion can never be stopped but can be hindered to a reasonable level. Among many methods of corrosion control and prevention, the use of organic inhibitors is the most frequently used. 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 [21]. In this research, the effect of the inhibition efficiency of methyl red on the corrosion of mild steel in alkaline medium using 1M sodium hydroxide solution (NaOH) is experimentally investigated and presented.

2. Experimental Details

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 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 15mm. 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 5.25cm 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 5.25cm and diameter 15mm were used for the experiment and were denoted as A, B, C, D, E, F and G.

2.2. Inhibitor and Alkaline

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 $C_{15}H_{15}N_3O_2$. It was prepared by dissolving 0.1g of Methyl red in 75ml of 95% ethanol and distilled water was added to make 100 ml. Various concentrations of 1%, 2%, 3%, 4%, 5% and 6% weight of each alkaline medium were used as the inhibiting compound. 40g of NaOH was dissolved in $1000cm^3$ of distilled water to get 1M NaOH. The NaOH used as corrosive medium was from Analar grade and bi-distilled water was used for its preparation.
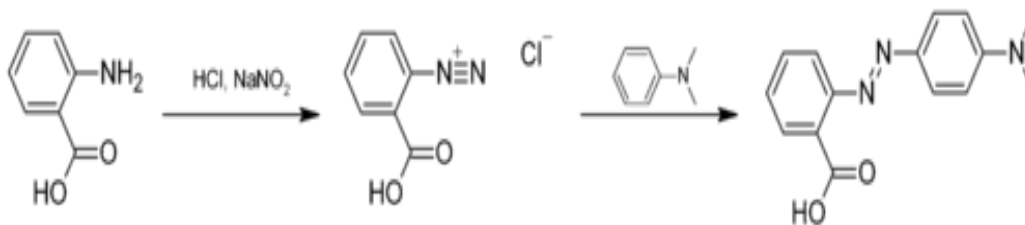
Figure 1. Chemical structure of Methyl Red (2, 4-Dimethylamino-2'-carboxylazobenzene)

Table 1. Spectrometric Compositional Analysis of Specimen

Elements	C	Si	Mn	P	S	Cr	Mo	V	Ni	Cu	Al	Fe
Composition (Wt. %)	0.278	0.210	0.870	0.030	0.040	0.118	0.018	0.008	0.079	0.044	0.003	98.350

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_1 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 NaOH. The inhibitor (Methyl red) under test was mixed with the NaOH 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_2. The weight loss (W_L) 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 [22]

$$Corrosion\ rate\ \ R = \frac{87.6W}{DAT} \qquad (1)$$

Where:

W = Weight loss = Initial weight (W_1) – Final weight (W_2) in milligrams.

A = Total surface area of specimen in cm^2.

T = Total time sample was immersed in hours.

D = Density of the specimen in g/cm^3.

R = Corrosion rate in millimeters per year.

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

$$A = 2\pi r(l + r) \qquad (2)$$

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:

$$P = \frac{R1 - R2}{R1}\ \ X\ 100 \qquad (3)$$

where V_1 and V_2 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 (Ө) was calculated from equation:

$$Ө = \frac{R1 - R2}{R1} \qquad (4)$$

The area and density of the specimen used are 28.28cm^2 and 7.86g/cm^3.

3. 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 residued 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_L in 0% - 6% concentration of Methyl Red in 1M NaOH at every 72hrs for 504hrs

Specimen	Inhibitor Concentration, C (%)	72 hrs W_L (g)	144 hrs W_L (g)	216 hrs W_L (g)	288 hrs W_L (g)	360 hrs W_L (g)	432 hrs W_L (g)	504 hrs W_L (g)
A	0	0.04	0.06	0.20	0.35	0.50	0.63	0.78
B	1	0.02	0.04	0.08	0.14	0.22	0.27	0.33
C	2	0.01	0.06	0.08	0.12	0.18	0.25	0.31
D	3	0.01	0.03	0.06	0.10	0.13	0.18	0.22
E	4	0.03	0.05	0.08	0.10	0.14	0.17	0.18
F	5	0.00	0.02	0.04	0.07	0.09	0.11	0.13
G	6	0.00	0.01	0.01	0.04	0.07	0.09	0.11

Table 3.   Weight losses, W_L in 0% - 6% concentration of Methyl Red in 1M NaOH at 504hrs

Specimen	Inhibitor Concentration, C (%)	W_1(g)	W_2 (g)	W_L (g)
A	0	30.64	29.86	0.78
B	1	30.94	30.61	0.33
C	2	30.49	30.18	0.31
D	3	30.47	30.25	0.22
E	4	31.88	31.70	0.18
F	5	30.94	30.81	0.13
G	6	32.24	32.13	0.11

Table 4.   Inhibition efficiency and surface coverage of Methyl Red on mild steel at 504 hrs

Specimen	Inhibitor Concentration, C (%)	Corrosion Rate (mpy)	Inhibition Efficiency (1%)	Surface Coverage (Ө)
A	0	0.610	0	0
B	1	0.258	57.7	0.577
C	2	0.242	60.3	0.603
D	3	0.172	71.8	0.718
E	4	0.141	76.9	0.769
F	5	0.102	83.3	0.833
G	6	0.086	85.9	0.859
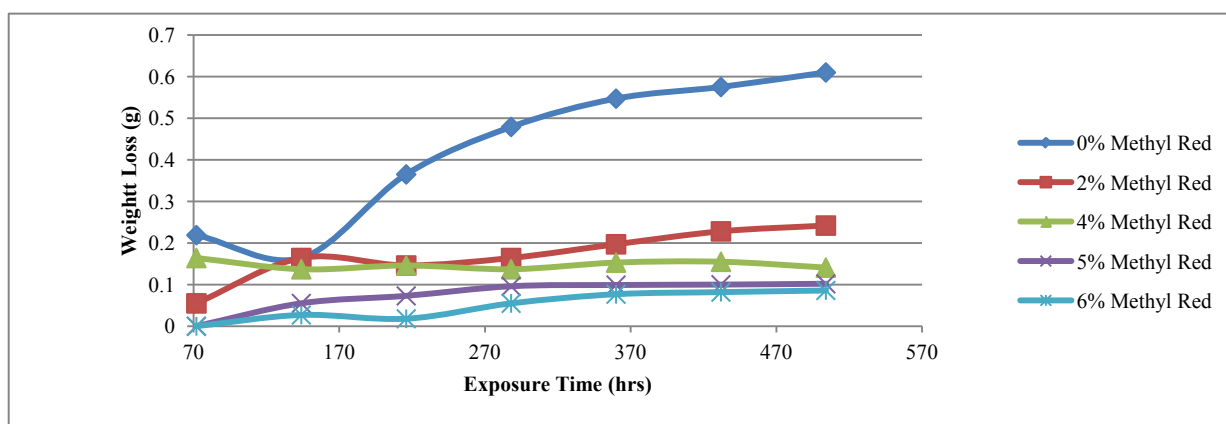
Figure 2.   Variation of weight-loss with exposure time for specimens A, C, E, F & G in 0%, 2%, 4%, 5% & 6% Methyl red concentrations
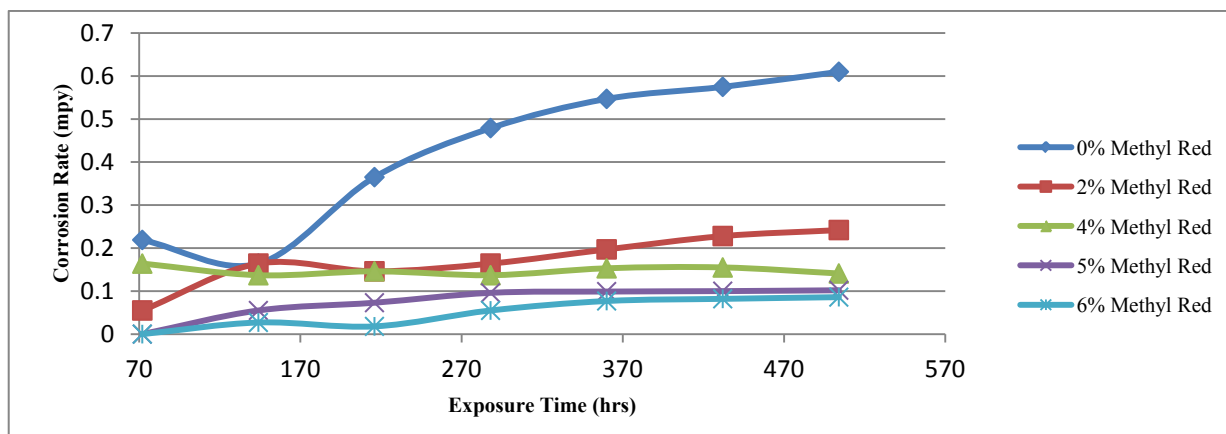
Figure 3.   Effect of percentage concentration of Methyl red on the corrosion rate of mild steel specimen A, C, E, F & G
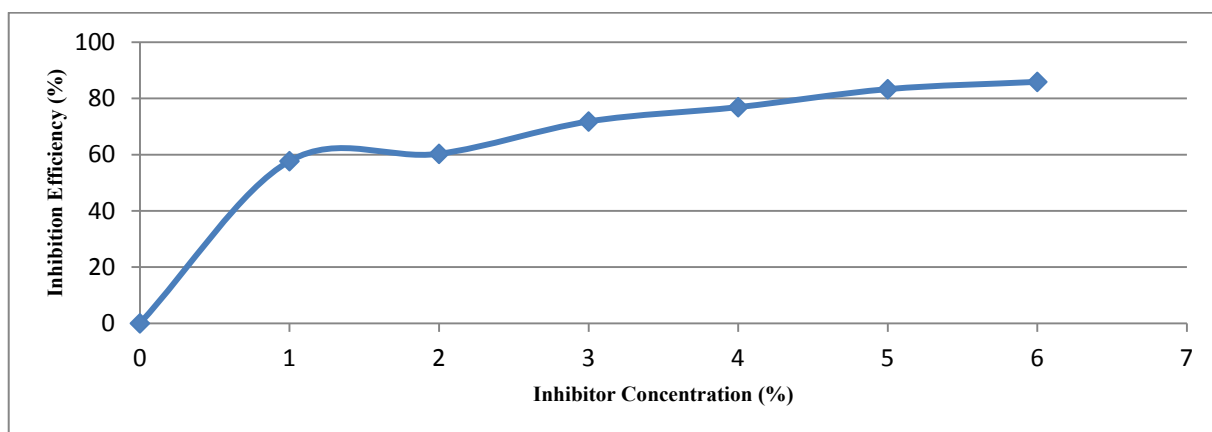
Figure 4. Variation of percentage inhibition efficiency with Methyl red at concentrations at 504 hrs
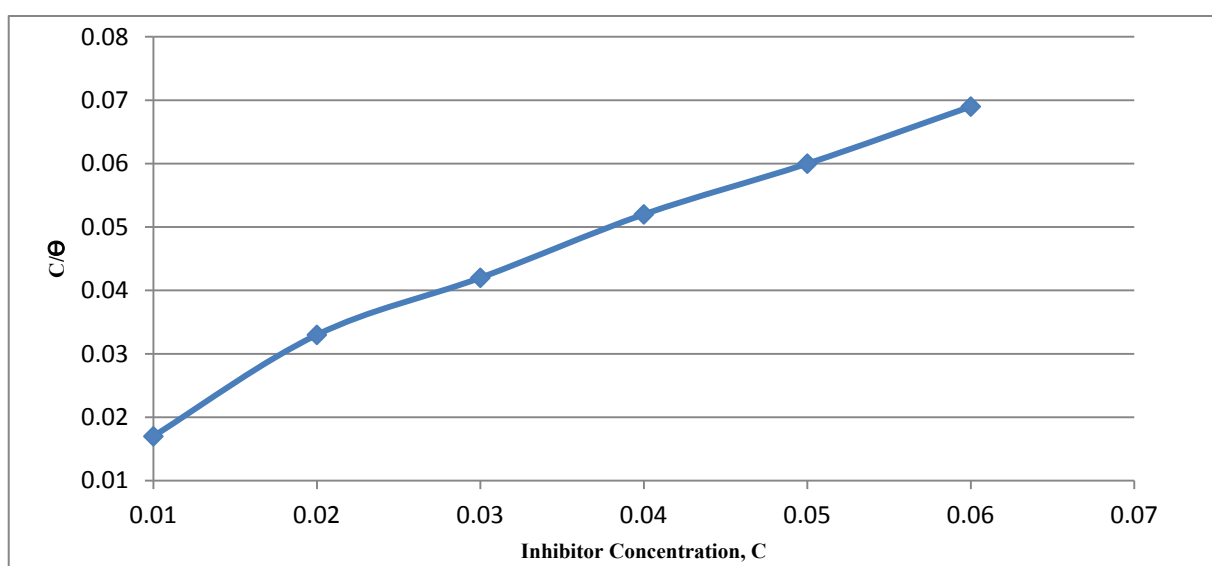

Figure 5. Langmuir isotherm adsorption model on the Mild steel surface in 1M NaOH solution containing different concentrations of inhibitor at 504 hrs

The weight-loss of mild steel was studied at various time intervals from 72 hrs to 540 hrs in the absence (control) and presence of stated concentrations of Methyl red in 1M NaOH. The values of weight-loss (W_L), corrosion rate (R) and the percentage inhibition efficiency and surface coverage are presented in Tables 2, 3 and 4. 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. Weight loss and corrosion rate in specimen A to which no inhibitor was added (control) were the highest. The specimen corroded in the solution (control) by an electrochemical mechanism involving its oxidation as ions according to:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (5)$$

The excess electrons generated in the aqueous solution created hydroxyl ions [OH⁻] by the reduction of dissolved oxygen according to:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (6)$$
$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2 \qquad (7)$$
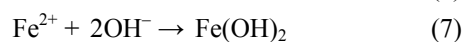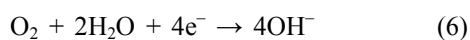
The reaction continues as the $Fe(OH)_2$ reacts with oxygen which enhances uniform corrosion at the cathodic site on the specimen's surface according to:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (8)$$
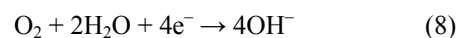
The corrosion rate of the specimen is associated with the flow of electrons with the two reactions involving oxidation (in which the specimen ionised) and reduction occurring at the anodic and cathodic sites respectively, on the surface of the specimen. Generally, the specimen's surface consists of both anodic and cathodic sites, depending on segregation, microstructure, stress, etc [23]. Specimen G to which the highest concentration of the inhibitor was added had the lowest weight loss and corrosion rate. The corrosion rate decreased drastically with increase in Methyl red concentrations 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 for specimens B, C, D, E, F and G. It could be seen that increase in the

concentration of Methyl red resulted in increased inhibition efficiency. The highest inhibition efficiency of 85.9% 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 specimen's 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, -NR2 and/or –SR have been reported to inhibit corrosion of metals in alkaline or acidic solutions [24, 25].

In solutions containing specimens B, C, D, E, F and G, competitive adsorption is assumed to occur on the specimens' surface between the aggressive OH⁻ ions and the anions of the inhibitor molecules [26]. The inhibitor molecules are first absorbed on the specimens' surfaces and therefore impede corrosion by blocking the reaction sites of the specimens' surfaces. In this way, the surface area available for the aggressive OH⁻ ions attack is reduced. 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 protection to the mild steel against corrosion. This film reduces the active surface area exposed to the corrosive medium and delays the iron dissolution [27]. 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. 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 [28].

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 [29, 30]. 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 [31, 32].

$$\theta = \frac{KC}{1+KC} \tag{9}$$

Re-arranging,

$$\frac{C}{\theta} = C + \frac{1}{K} \tag{10}$$

where C is the inhibitor concentration, K is the adsorption equilibrium constant, and θ the surface coverage of the inhibitor. The linear relationship of C/θ versus C in different concentration of Methyl red solutions is displayed in Figure 5. However, the slope of the relation shows a little deviation from unity, this might be the result from the interactions between the adsorbed species on the metal surface [33, 34]. The K value may be taken as a measure of the strength of the adsorption forces between the inhibitor molecules and the metal surface [35].

4. Conclusions

In this study, the weight loss technique reveals Methyl red to be an efficient inhibitor for mild steel in the sodium hydroxide corrosive medium. The inhibition efficiency increases with the increase in concentration of Methyl red with maximum inhibition efficiency value of 85.9% at 6% inhibitor concentration. At this value, the lowest corrosion rate value of 0.086 mpy was obtained. This is a mixed type inhibitor whose adsorption on mild steel is physiochemical. 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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