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Eco-Friendly Corrosion Inhibitors: Adsorption And Inhibitive Action Of Ethanol Extracts Of *Mallotus Oppositifolius Leaves* For The Corrosion Of Mild Steel In 1m Hydrochloric Acid Solution.

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ABSTRACT

The effect of Mallotus oppositifolius leaf extract was investigated as corrosion inhibitor of mild steel in acid using the weight loss and hydrogen evolution methods in the temperature range 298K-318K. The results obtained indicated that inhibitor efficiency (IE%) increased with increasing inhibitor concentration but decreased with increase in temperature. At 800g/dm^3 concentration of the extract, the percentage inhibition reached about 97 % at 298K and 93.1 % at 318K for the weight loss method and 92 % at 298K and 75.2 % at 318K for the hydrogen evolution method. The thermodynamic parameters for the adsorption of this inhibitor on the metal surface was calculated using the Langmuir adsorption isotherm, activation energy (Ea) and the heat of adsorption (Qads). The increase in activation (Ea) energy and the negative values of heat of adsorption (Qads) of the corrosion inhibitior and its ability to fit the Langmuir isotherm suggest that the Mallotus oppositifolius molecules are physically adsorbed on the metal surface. The Mallotus oppositifolius leaves extract was found to be an excellent potential corrosion inhibitor because of the presence of phytochemicals in the leaf extract.

KEYWORDS: *Corrosion inhibitor, Mallotus Oppositifolius, mild steel, adsorption isotherm.*

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I. INTRODUCTION

Mild steel (MS) has been extensively used under different conditions in chemical and allied industries in handling alkaline, acid and salt solutions (Vimala *et al,* 2011). One of the most challenging and difficult tasks for industries are the protection of metals from corrosion. Corrosion involves the deterioration of a material as it reacts with its environment. It is a natural process that commonly occurs because unstable materials, such as refined metals want to return to a more stable compound. Corrosion is an ubiquitous problem that continues to be of great relevance in a wide range of industrial applications and products; it results in the degradation and eventual failure of components and systems both in the processing and manufacturing industries and in the service life of many components. Corrosion control of metals and alloys is an expensive process and industries spend huge amounts to control this problem. Using inhibitors is an important method of protecting materials against corrosion especially in acidic media (Trabanelli,1991).

The use of synthetic compounds for corrosion inhibition is diminishing due to the strict environmental regulations and toxic effects of synthetic compounds on human and animal life. The toxicity may manifest either during the synthesis of the compound or during its applications; Consequently, there exists the need to develop a new class of corrosion inhibitors with low toxicity, eco-friendliness and good efficiency**.** These natural organic inhibitors can be extracted or synthesized from potential herbs, spice and medicinal plants (Li *et al,* 2007, 2008; Ramesh *et al,* 2003; Stupnisek-Lisac and Podbrscek, 1994). They are non toxic, bio degradable, naturally occurring and are readily available. Most of these organic inhibitors are compounds with nitrogen, sulphur and oxygen, hetero-atoms having higher electron density, making them the reactions centers. (Li *et al,* 2008).

Other authors have also shown that the inhibitive effect of some plants solution extract is due to the adsorption of molecules of phytochemicals present in the plant on the surface of the metal (Zakvi and Mehta, 1988; Oguzie and Ebenso, 2006; El-Etre and El-Tantawy, 2006), which protect the metal surface and thus do not permit the corrosion process to take place. In this paper, gravimetric and gasometric techniques are applied to investigate the ability of *Mallotus oppositifolius* to inhibit the corrosion of mild steel in acidic environment in furtherance of my quest to explore naturally occurring substances as corrosion inhibitor.

II. EXPERIMENTAL

2.1 Material Preparation

Mild steel sheets of composition (0.05% C, 0.32% Mn, 0.027% P, 0.030% S, 0.004% Si and balance Fe) and 0.05 cm thickness were used in the study. The sheets were mechanically press cut into 3×3 cm coupons. These coupons were used as cut with further polishing. However, they were rinsed with ethanol and degreased in acetone prior to their use in corrosion studies.

2.2 SOURCE of *Mallotus oppositifolius* leaves

The plant materials used were collected from Ntigha in Isiala Ngwa North L.G.A of Abia state, Nigeria (lat 5.1°N, Long 7.43°E). Samples of the plant were authenticated by the Department of Forestry, Michael Okpara University of Agriculture Umudike, Nigeria.

2.3 PREPARATION OF *Mallotus oppositifolius* EXTRACT (MOE)

The fresh green leaves of MO collected were washed thoroughly with distilled water, air dried and oven dried at (46 ±2°C). The dried leaves were pulverized using a grinding machine. About 30g of the dried sample was macerated in 95% ethanol in 1000ml round bottom flask at room temperature (27±2 °C).
The flask was covered left in a cool dried cupboard for 72hrs. The content of the flask was filtered using a handkerchief (11.9g). The filtrate were used to prepare the different concentrations of the plant extract needed (200, 400, 600 and 800 g/dm^3).

2.4 WEIGHT LOSS METHOD (Gravimetric Method)

In the weight loss experiments, the pre-cleaned mild steel coupons were first weighed using Adventural pro Analytical weighing balance AV313 model; least count of 0.001g labeled and suspended in the test solution. The weight loss was determined by retrieving the coupons for 3 hours, washed with distilled water cleaned with bristle brush, rinsed with acetone, dried and reweighed. The weight loss was taken to be the difference between the weight at a given time and the original weight of the coupons. The measurements were carried out at different temperatures and concentrations of the MO extract with and without the inhibitor.

The corrosion rate was computed using the expression:

Corrosion rate (CR) = $\frac{W1-W2}{At}$ …………………………………. (1)

Where;
W_1 and W_2 are the weight loses (g) before and after immersion in the test solutions, respectively,
A is the surface area of the specimens (cm^2)
t is the exposure time (hour).

The Inhibition Efficiency (IE%) of MOE was evaluated using the following equation:

$IE\% = 1 - \frac{CRinh}{CRblank} \times 100$…………………………….. (2)

Where, CR_{blank} and CR_{inh} are the corrosion rate in the absence and presence of the inhibitor, respectively in HCl and at the same temperature, the degree of surface coverage (θ) was calculated from the equation:

$\theta = 1 - \frac{CRinh}{CRblank}$ ………………………… (3)

2.5 HYDROGEN EVOLUTION MEASUREMENTS

The mild steel coupons were pre-cleaned and weighed in same way as done in the gravimetric method. A 250ml test solution of 1M HCl was introduced into the Buckner flask connected to the gasometry apparatus and the initial volume of air was recorded. The volume of hydrogen gas evolved when mild steel coupons were dropped into the solution was monitored by the volume change in the level of paraffin oil. The change in paraffin oil level was monitored at fixed time interval of 3 hours. The experiment was performed with and without inhibitors at different concentrations (200, 400, 600 and 800 g/dm^3) and MO extract acting as inhibitors in acidic media.

For hydrogen evolution method, the rate of corrosion was calculated using the following equation:

$CR = \frac{\Delta VH}{t}$………………………………… (4)

Where;
CR is the rate of corrosion
ΔV_H change is the volume of hydrogen in ml
t is the immersion time.

The Inhibition Efficiency (IE%) was calculated using the equation:

$$IE\% = 1 - \frac{CRinh}{CRblank} \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. (5)$$

Where, CR_{blank} and CR_{inh} are the corrosion rate in the absence and presence of the inhibitor, respectively in HCl and at the same temperature.

The Degree Of Surface Coverage (θ) was calculated from the equation:

$$\theta = 1 - \frac{CRinh}{CRblank} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

III. RESULTS AND DISCUSSION

3.1 WEIGHT LOSS MEASUREMENTS

The corrosion rate, inhibition efficiency and surface coverage for mild steel exposed to 1M HCl at 298K and 318K as a function of concentration of inhibitor is shown in Table 1 and 2 respectively.

Table 1: The corrosion parameters for mild steel in 1MHCl with *Mallotus oppositifolius* extract from weight loss measurements at 298K

Conc (g/dm^3)	Initial Weight(g)	Final Weight(g)	Weight Loss(g)	CR (mdd)	Surface Coverage(θ)	IE(%)
Blank	3.327	3.174	0.153	0.067	_	_
200	3.527	3.484	0.043	0.019	0.716	71.6
400	3.573	3.543	0.030	0.013	0.806	80.6
600	3.575	3.559	0.016	0.007	0.896	89.6
800	3.670	3.665	0.005	0.002	0.970	97.0

Table 2: The corrosion parameters for mild steel in 1MHCl with *Mallotus oppositifolius* extract from weight loss measurements at 318K

Conc (g/dm^3)	Initial Weight(g)	Final Weight(g)	Weight Loss(g)	CR (mdd)	Surface Coverage(θ)	IE(%)
Blank	3.605	3.013	0.592	0.261	-	-
200	3.465	3.250	0.215	0.095	0.636	63.6
400	3.471	3.319	0.152	0.067	0.743	74.3
600	3.504	3.407	0.097	0.043	0.835	83.5
800	3.457	3.415	0.042	0.018	0.931	93.1

3.2 HYDROGEN EVOLUTION MEASUREMENTS

The calculated values of corrosion rate, inhibition efficiency and surface coverage for mild steel corrosion in 1M HCl in the presence of different concentration of the MO extract from the hydrogen evolution method are presented in Table 3 and 4 at 298K and 318K respectively

Table 3: The corrosion parameters for mild steel in 1MHCl with *Mallotus oppositifolius* extract from hydrogen evolution measurements at 298K

Conc	Initial Volume(ml)	Final Volume(ml)	Volume Change(ml)	CR (mdd)	Surface Coverage(θ)	IE(%)
Blank	9.500	19.500	10.000	80.000	_	_
200	17.800	19.900	2.100	16.800	0.79	79
400	11.500	13.100	1.600	12.800	0.84	84
600	9.600	10.800	1.200	9.600	0.88	88
800	9.800	10.600	0.800	6.400	0.92	92

Table 4: The corrosion parameters for mild steel in 1MHCl with *Mallotus oppositifolius* extract from hydrogen evolution measurements at 318K.

Conc	Initial Volume(ml)	Final Volume(ml)	Volume Change(ml)	CR (mdd)	Surface Coverage(θ)	IE(%)
Blank	3.600	47.600	44.000	352.000	-	-
200	9.400	30.700	21.300	170.400	0.516	51.6
400	6.000	23.800	17.800	142.400	0.595	59.5
600	2.300	16.700	14.400	115.200	0.673	67.3
800	3.600	14.500	10.900	.87.200	0.752	75.2

3.3 EFFECT OF INCREASE IN CONCENTRATION

It is observed from table 1 and 2 that the inhibition efficiency of mild steel increased with increasing concentration of inhibitor. This behavior could be attributed to the increase in adsorption of inhibitor on the metal or at the solution interface on increasing its concentration. The corrosion rate decreased with increase in concentration. The weight loss decreased as the concentration of the extract increased. Table 3 and 4 shows that the rate of hydrogen evolution decreased with the introduction of the leaves extract, the volume of hydrogen evolved decreased further as the concentration of inhibitor is increased. From fig. 4.1 and 4.2, the inhibition efficiency increased as the concentration is increased; this trend may results from the fact that inhibition efficiency and surface coverage increased with the increase in concentrations.

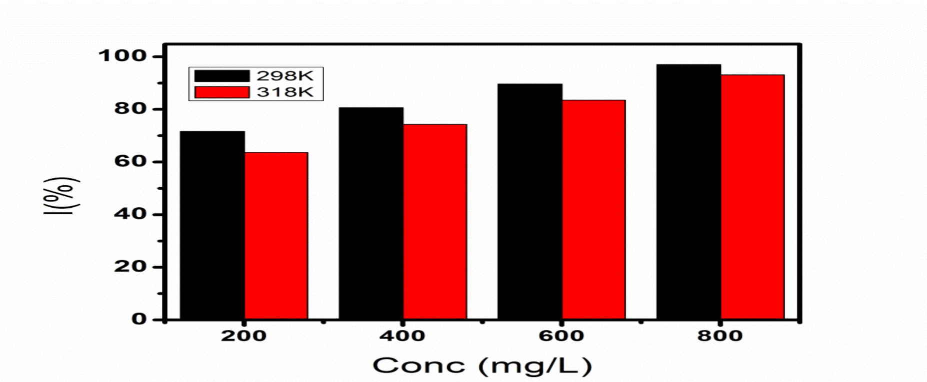

Figure 4.1: Variation of inhibition efficiency with *Mallotus oppositifolius* concentration for mild steel in 1M HCl (weight loss measurements)

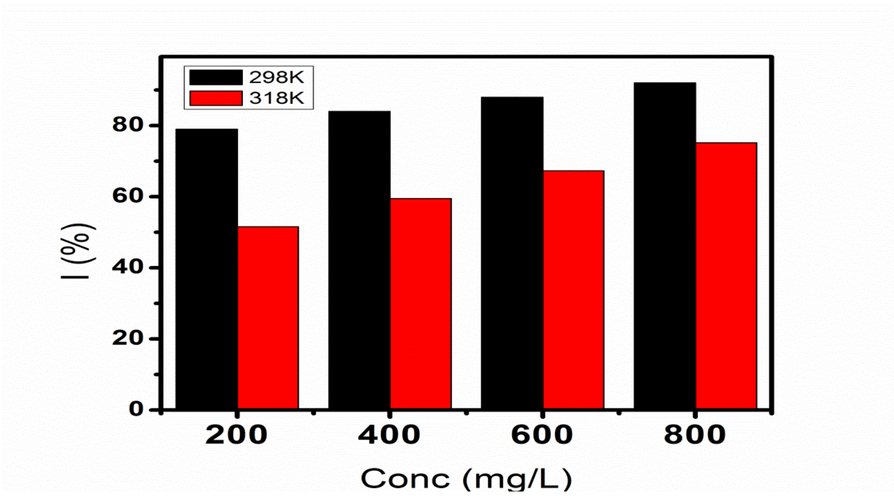

Figure 4.2: Variation of inhibition efficiency with *Mallotus oppositifolius* concentration for mild steel in 1M HCl (hydrogen evolution measurement)

3.4 EFFECT OF INCREASE IN TEMPERATURE

From table 2 the weight loss increased as the temperature increased; it was also observed from table 4 that increase in temperature increased the rate of hydrogen evolution; indicating that the rate of corrosion of mild steel in 1M HCl increases as temperature increases. It can also be shown from fig. 4.1 and 4.2 that the inhibition efficiency decreases with an increase in temperature. Such behavior can be interpreted in terms of the fact that the phytochemical molecules are physically adsorbed on the surface of metal (Obot and Obi, 2008) such that an increase in temperature resulted in the desorption of some adsorbed phytochemical molecules from the metal surface. Since, a physisorption mechanism is indicative of a weak adsorption bond, it may be possible that at higher temperatures, the decrease in inhibition efficiency may be a result of the increased agitation of the solution resulting from higher rates of hydrogen evolution, thereby reducing the ability of the molecules to be adsorbed on the surface of the metal (Okafor *et al*, 2007).

3.5 THERMODYNAMICS STUDIES

The apparent activation energies (Ea) for the corrosion process in absence and presence of inhibitor were evaluated from the condensed Arrhenius equation as follows;

$$log\frac{R2}{R1} = \frac{Ea}{2.303R}\left(\frac{1}{T1} - \frac{1}{T2}\right)$$

Where R_1 and R_2 are the corrosion rates at temperatures T_1 andT_2 respectively.

An estimate of the heat of adsorption (Qad) was obtained from the trend of surface coverage with temperature as follows

$$Qad = 2.303R\left[\log\left(\frac{\theta 2}{1-\theta 2}\right) - \log\left(\frac{\theta 1}{1-\theta 2}\right)\right] x\ \frac{T1\,T2}{T2-T1}$$

Where θ_1 and θ_2 are the degree of surface coverage at temperatures T_1 and T_2 respectively.

Table 5: Calculated values of activation energies (Ea) and heat of adsorption (Qad) for mild steel corrosion in 1M HCl with MO extract as inhibitor (using the gasometric technique)

System	Activation energy (KJ/mol)	Heat of adsorption (KJ/mol)
Blank	58.375	-
1M HCl + 200g/dm^3 extract	91.281	- 16.781
1M HCl + 400g/dm^3 extract	94.923	- 13.586
1M HCl + 600g/dm^3 extract	97.907	- 10.566
1M HCl + 800g/dm^3 extract	102.910	- 7.944

The results obtained from table 5 indicated that activation energy in the presence of the MO extract increases. This behavior is an indication of physisorption of the component of MO extract on the surface of metal. Table 5 showed that the value of Ea for inhibited solution is higher than that for uninhibited solution, suggesting that dissolution of mild steel is slow in the presence of inhibitor and can be interpreted as due to physical adsorption (Villamil et al., 1999). The negative values of heat of adsorption are consistent with the phenomenon of inhibitor physisorption.

3.5 ADSORPTION ISOTHERM

Basic information on the interaction between the inhibitors and the mild steel surface can be provided by the adsorption isotherm. In order to obtain the isotherm, the surface coverage values (θ) defined in equation (3) was evaluated by using the %IE values obtained from hydrogen evolution measurements. The θ values increased with increasing inhibitor concentration as a result of more inhibitor molecules adsorption on the metal surface. The θ values for different concentrations of the tested MO have been applied using the langmiur adsorption isotherm equation below;

$$\frac{C}{\theta} = c + \frac{1}{Kad}$$

Where c = concentration of inhibitor,

θ = surface coverage defined in equation 3

Kad = equilibrium constant for the adsorption reaction related to the free energy of adsorption (Singh and Dey, 1993)

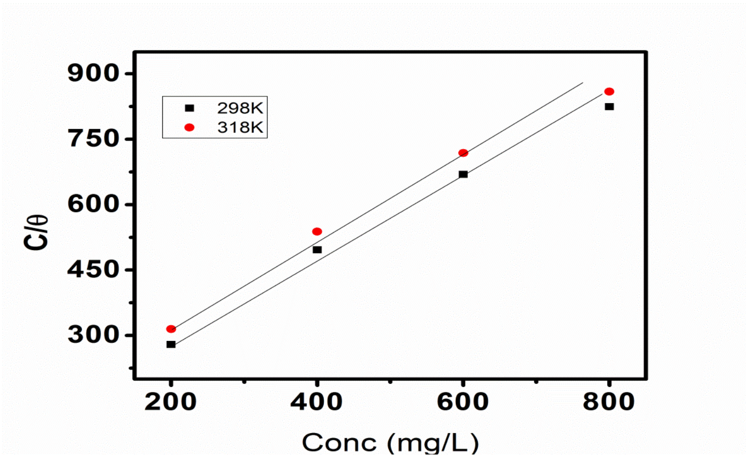

Figure 4.5: Langmuir adsorption isotherm for the inhibition of corrosion of mild Steel by MO in 1M HCl.

Figure 4.3 gives the result of Langmuir's plot for corrosion inhibition data of the inhibitors.

The ability to fit Langmuir isotherm show that the plant is physically adsorbed on the mild steel coupon. Therefore, the plant extract can be considered as a source of relatively cheap, eco-friendly and effective green corrosion inhibitor in acid medium.

3.6 MECHANISM OF INHIBITION

The inhibition of corrosion by MO extract can be attributed to the phytochemicals present in the plant extract since these compounds contain oxygen and nitrogen atoms and unsaturated bonds which are the centers of adsorption.

The isotherm depicted in Figure 4.3 characterizes the spontaneous physisorption of phytochemical composition of extract on mild steel surface. Thus, the mechanism of corrosion inhibition of steel in HCl polluted solution by the phytochemical compounds of the extract can be explained on the basis of adsorption on the metal surface. The adsorption of the inhibitor molecules on the steel surface is due to the donor - acceptor interaction between electrons of donor atoms and aromatic rings of inhibitors and the acceptor, i.e., vacant d orbital of iron surface atoms. The inhibitor molecules can also be adsorbed on the metal surface in the form of negatively charged species which can interact electrostatically with positively charged metal surface, which led to increase the surface coverage and consequently protect efficiency even in the case of low extract concentration.

IV. CONCLUSION

From the evaluation of *Mallotus oppositifolius*, the following conclusions were made;

1. The inhibition efficiencies of the *Mallotus oppositifolius* extracts evaluated was found to increase with increase in the concentration of the plant extract and decreases with increase in temperature of the system.
2. The addition of inhibitor increases the adsorption of phyto-constituents over the metal surface and results in the formation of a protective layer; which may decrease the electron transfer between the metal surface and the corrosive medium.
3. The corrosion rate of mild steel in 1MHCl decreases with increase in concentration of *Mallotus oppositifolius* extract.
4. The maximum inhibition efficiency of *Mallotus oppositifolius* extract was found to be 97% and 93.1% at 298 K and 318 K respectively for the weight loss method.

5. The maximum inhibition efficiency of *Mallotus oppositifolius* extract was found to be 92% and 75.2% at 298 K and 318 K respectively for the hydrogen evolution measurement.
6. The increase in the energy of activation values indicated a physical adsorption of the inhibitor on mild steel surface with increase in concentration
7. The negative values of heat of adsorption indicated that the *Mallotus oppositifolius* is physically adsorbed on the surface of mild steel.
8. The adsorption of inhibitor on mild steel surface from the acid solution fits Langmuir adsorption isotherms

From the efficiency values we can firmly say that the extract from the leaves of *Mallotus oppositifolius* inhibit the corrosion of mild steel in acidic environment to a reasonable extent. Therefore, the plant extract can be considered as a source of relatively cheap, eco-friendly and effective green corrosion inhibitor in acid medium. *Mallotus oppositifolius* was observed to be an efficient corrosion inhibitor and we recommend that it should be used as corrosion inhibitor.

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