



The inhibitive properties of *Musa sapientum* peels for mild steel corrosion in H₂SO₄ using both gasometric and thermometric technique

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Abstract

The inhibition of the corrosion of mild steel by ethanol extract of *Musa sapientum* peels in H₂SO₄ has been studied using gasometric and thermometric methods. The results of the study reveal s that the different concentrations of ethanol extract of *M. sapientum* peels inhibit mild steel corrosion. Inhibition efficiency of the extract is found to vary with concentration, temperature, period of immersion and pH. Values of activation energy of the inhibited corrosion reaction of mild steel are greater than the value obtained for the blank. Thermodynamic consideration reveals that adsorption of *M. sapientum* peels extract on mild steel surface is spontaneous and occurred according to Langmuir and Frumkin adsorption isotherms. Physical adsorption mechanism has also been proposed for the adsorption of the inhibitor.

Keywords: Corrosion inhibition, mild steel, Inhibition, adsorption, *Musa sapientum*, peels.

INTRODUCTION

The use of inhibitors is one of the best options of protecting metals against corrosion. Several inhibitors in used are either synthesized from cheap raw material or chosen from compounds having hetero atoms in their aromatic or long chain carbon system. However, most of these inhibitors are toxic to the environment. This has prompted the search for green corrosion inhibitors.

Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. The successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment have been reported by some research groups (Abiola et al., 2007; Kliskic et al., 2000; El-Etre, 1998, 2003, 2006; Ebenso et al., 1998, 2004; Ebenso and Ekpe, 1996; Ekpe et al., 1994; Zucchi and Omar, 1985; Umoren et al., 2006a, 2008a-d; Umoren and Ebenso, 2008; Abdallah, 2004; Okafor et al., 2005, 2007, 2008; Okafor and Ebenso, 2007; El-Etre and Abdallah, 2000; Chetouani et al., 2004; Bouyanzer and Hammouti, 2004; Oguzie, 2005, 2006a,b, 2007 ; Oguzie et al., 2006, 2007; Benda-hou et al., 2006; Sethuraman et al., 2005; Rajendran et al.,

2005) to mention but a few. Efforts to find naturally organic substances or biodegradable organic materials to be used as corrosion inhibitors over the years have been intensified in our research group. Our focus in this paper is on *Musa species* peel that is, banana peels. Several studies have been carried out on banana peels for the production of biogas (Ilori et al., 2007), ethanol production by hydrolysis and fermentation (Sirkar et al., 2008), antacid and diuretic activity of the ash and extracts of the peel (Jain et al., 2007), antibacterial and antioxidant activities (Mokbel and Hashinaga, 2005) and biomass production (Essien et al., 2005), to mention but a few. *Musasapientum* Linn (*Musaceae*) commonly called 'Kela' in Hindi (English: Banana) is extensively cultivated in northern part of Maharashtra. It is one of the most popular fruit crop in India and many parts of Asia and Africa. It possesses many curative properties and prevents many kinds of illnesses and conditions. Different parts of plant are used very frequently in different worship ceremonies by the Indians. Every part of the tree is being used for

Table 1. Corrosion rate (from gasometric method) and reaction number (from thermometric method) for the corrosion of mild steel in H₂SO₄ at 303 K

| Concentration of H ₂ SO ₄ (M) | CR (303K) | RN (303K) |
|---|-----------|-----------|
| 1.0 | 0.175 | 0.0500 |
| 1.5 | 0.180 | 0.0267 |
| 2.0 | 0.220 | 0.0167 |
| 2.5 | 0.380 | 0.050 |

some purposes like food, fuel or timber. It is a perennial herbaceous plant, grows to 5 - 9 m in height. It has tuberous subterranean rhizome, from which the leaves are folded within each other producing false stem, from which the long, narrow blades protrude and spread out. In the center of the folded leaf sheaths, a growing point forms the top of rhizomes, grows up and emerges as an overhanging inflorescence with a succession of reddish brown bracts. The bracts unfold from the base to the tip and fall off. Within the lower 1 - 12 bracts arise 14 - 18 female flowers in double rows these develop into fruits. The roots are adventitious. The leaves are large from 1.5 - 3.5 m and 0.6 meter wide. In India hot water extracts of dried fruits, flowers and roots are used orally for diabetes, the dried flower along with dried fruits of *Coccinia indica* is used to prevent conception orally. The roots are used as anthelmintic, aphrodisiac, laxative and tonic. The fresh fruit is used for peptic and duodenal ulcers. The leaf ash is mixed with honey and taken orally for cough. Banana constitutes one of the major food crops in Nigeria and as a result, large quantities of wastes are often generated from peels and have become a perennial problem. Indiscriminate disposal of these wastes may pose serious environmental hazards. We therefore reasoned that channeling these peels into corrosion studies may yield some interesting results.

To the best of our knowledge, nothing has been reported on the use of ethanol extract of *M. sapientum* peels for the inhibition of mild steel corrosion. *M. sapientum* peels is often discarded as waste after the inner fruit has been removed implying that successful utilization of this waste may also provide an option for resource recovery. The present study seeks to investigate the inhibitive properties of *M. sapientum* peels for mild steel corrosion using both gasometric and thermometric technique. The adsorption and thermodynamic studies are also reported.

EXPERIMENTAL

Materials preparation

Materials used for the study were mild steel sheet of composition (wt %) Mn (0.6), P (0.36), C (0.15) and Si (0.03) and the rest Fe. The sheet was mechanically pressed cut to form different coupons, each of dimension, 5 x 4 x 0.11 cm. Each coupon was degreased by washing with ethanol, dried in acetone and preserved in a desiccator. All reagents used for the study were analar grade and double distilled water was used for their preparation.

Extraction of plant

Samples of *M. sapientum* peels were dried, grounded and soaked in a solution of ethanol for 48 h. After 48 h, the samples were cooled and filtered. The filtrates were further subjected to evaporation at 352 K in order to leave the sample free of the ethanol. The stock solutions of the extract so obtained were used in preparing different concentrations of the extract by dissolving 0.1, 0.2, 0.3, 0.4 and 0.5 g of the extract in 1 L of 2.5 M H₂SO₄ respectively.

Gasometric method

Gasometric methods were carried out at 303 and 333 K as described in literature (Oguzie et al., 2006b; Umoren et al., 2006b, 2007). From the volume of hydrogen evolved per minute, inhibition efficiency (%), and degree of surface coverage (θ) were calculated using equations 1 and 2 respectively.

$$\%I = 1 - \frac{V_{H_2}^i}{V_{H_2}^o} \times 100 \quad (1)$$

$$\theta = 1 - \frac{V_{H_2}^i}{V_{H_2}^o} \quad (2)$$

Where $V_{H_2}^i$ is the volume of hydrogen evolved at time t for inhibited solution and $V_{H_2}^o$ is the volume of hydrogen evolved at time t for uninhibited solution.

Thermometric method

This was also carried out as reported elsewhere (Ebenso, 2003b; Umoren et al., 2006b, 2007). From the rise in temperature of the system per minute, the reaction number (RN) was calculated using equation 3:

$$RN \left(^\circ C / \text{min} \right) = \frac{T_m - T_i}{t} \quad (3)$$

where T_m is the maximum temperature attained by the system, T_i is the initial temperature and t is the time. From the above, the inhibition efficiency (%) of the used inhibitor was computed using equation 4:

$$\%I = \frac{RN_{aq} - RN_{wi}}{RN_{aq}} \times 100 \quad (4)$$

Where RN_{aq} is the reaction number of aqueous acid in the absence of *M. sapientum* peels, and RN_{wi} is the reaction number of aqueous acid in the presence of *M. sapientum* peels.

RESULTS AND DISCUSSION

Table 1 shows values of corrosion rate (CR) of mild steel in at all the concentrations of H₂SO₄ studied and it shows that corrosion rate increases with increase in H₂SO₄ concentration. Table 2 shows the corrosion rate and reaction numbers (RN) for the corrosion of mild steel in 2.5 M H₂SO₄ in the absence and presence of *M. sapientum*

Table 2. Corrosion rate (from gasometric method) and reaction number (thermometric method) for the corrosion of mild steel in 2.5M H₂SO₄ solutions containing *M. sapientum* peels extract.

| Concentration of <i>Musa sapientum</i> peel in 2.5 M H ₂ SO ₄ (g/l) | RN at303K | CR (mdd) at 303K | CR(mdd) at 333K |
|---|-----------|------------------|-----------------|
| 0.1 | 0.022 | 0.215 | 2.015 |
| 0.2 | 0.025 | 0.175 | 1.945 |
| 0.3 | 0.034 | 0.150 | 1.800 |
| 0.4 | 0.048 | 0.140 | 1.790 |
| 0.5 | 0.062 | 0.110 | 1.685 |

Table 3. Values of inhibition efficiency (%) and degree of surface coverage from gasometric and thermometric methods

| Concentration of <i>Musa sapientum</i> peels (g/l) | Gasometric | | Thermometric |
|--|------------|-----------|--------------|
| | %I (303K) | %I (333K) | %I (303K) |
| 0.1 | 43.42 | 11.23 | 40.80 |
| 0.2 | 53.95 | 14.32 | 50.24 |
| 0.3 | 60.53 | 20.70 | 58.51 |
| 0.4 | 63.16 | 21.15 | 61.24 |
| 0.5 | 71.05 | 25.77 | 70.06 |

Table 4. Some thermodynamic parameters for the adsorption of *Musa sapientum* peels on mild steel surface.

| Conc. of <i>Musa sapientum</i> peel (g/l) | E _a (KJ/mol) | Q _{ads} (KJ/mol) |
|---|-------------------------|---------------------------|
| Blank | 39.1959 | |
| 0.1 | 62.6589 | -50.4177 |
| 0.2 | 67.4329 | -54.4609 |
| 0.3 | 69.5799 | -49.5222 |
| 0.4 | 71.3558 | -51.8796 |
| 0.5 | 76.4159 | -54.6981 |

Table 5. Values of Langmuir and Frumkin parameters.

| Langmuir | Temperature (K) | Log K | Slope | ΔG _{ads} | R ² |
|----------|-----------------|--------|-----------|-------------------|----------------|
| | 303 | 0.0689 | 0.7083 | -10.51939 | 0.9979 |
| 333 | 0.4452 | 0.4819 | -13.9602 | 0.9572 | |
| Frumkin | Temperature (K) | α | Log K | ΔG _{ads} | R ² |
| | 303 | 4.1623 | 0.1239 | -10.83848 | 0.9209 |
| 333 | 0.7096 | 0.7353 | -15.80988 | 0.9893 | |

tum peels extract. The slope of each line of volume of hydrogen gas evolved against time represents the corrosion rate at the specified conditions. Addition of increasing concentration of the inhibitor retards the corrosion rate of mild steel in the solutions. This is clearly seen from the decrease in volume of hydrogen evolved corresponding to decrease in the slope of each line with increase in inhibitor concentration.

Table 3 shows values of inhibition efficiency of the different concentrations of *M. sapientum* peels extract at

303 and 333K for both the gasometric and thermometric methods. Table 4 shows the values of activation energy and Q_{ads} obtained for the corrosion inhibition of *M. sapientum* while Table 5 shows the values of some constants obtained from the Langmuir and Frumkin adsorption isotherm plots.

Effect of concentration and temperature

From Tables 1 and 2, it is found that the rate of corrosion

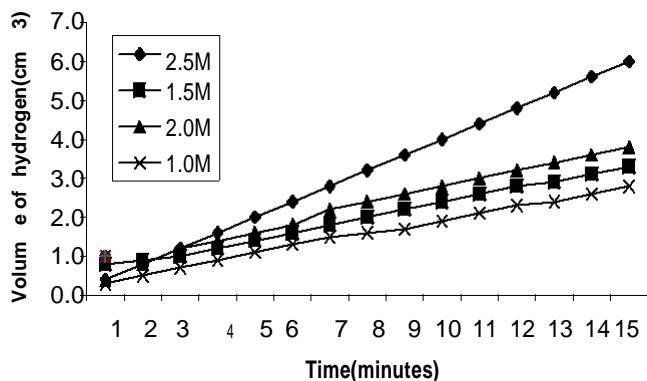


Figure 1. Variation of volume of hydrogen gas evolved with time for corrosion of mild steel in various concentrations of acid

of mild steel is affected by concentration of H_2SO_4 , temperature, concentration of ethanol extract of *M. sapientum* peels and time. The rate of mild steel corrosion increases as the concentration of H_2SO_4 increases and also increases as the temperature is increased. Figure 1 shows the variation of volume of hydrogen evolved with time during the corrosion of mild steel in different concentration of H_2SO_4 . It shows that it increases as the concentration of the acid increases confirming that the rate of corrosion of mild steel in H_2SO_4 increases with concentration.

The volume of hydrogen evolved at different concentrations of ethanol extract of *M. sapientum* peels are lower than volumes evolved for the blank solution (2.5 M H_2SO_4) indicating that different concentrations of this extract retards the corrosion of mild steel. Figure 2 shows gasometric plots for the corrosion of mild steel in the presence of different concentration of *M. sapientum* peels at 303(a) and 333K (b) respectively. Comparing Figure 2 (a) and (b), it is found that at a fixed concentration of the inhibitor, the volume of hydrogen evolved at 333 K is significantly higher than that evolved at 303 K indicating that the inhibition efficiency of *M. sapientum* peels decreases with increase in temperature. The decrease may be due to competition between forces of adsorption and desorption.

From Table 3, it can also be seen that inhibition efficiency of *M. sapientum* peels varies with its concentration. Optimum value of inhibition efficiency (71.05%) was obtained at extract concentration of 0.5 g/l, while the least value was obtained at extract concentration of 0.1 g/l. Figure 3 shows the variation of inhibition efficiency against the different concentrations of *M. sapientum* at both 303 and 333K. The significant difference between values of inhibition efficiency of *M. sapientum* peels obtained at 303 and 333 K suggests that the mechanism of adsorption of inhibitor on mild steel surface is by physical adsorption. For a physical adsorption mechanism, inhibition efficiency of an inhibitor decreases with temperature while for a chemical adsorption mechanism, values

of inhibition efficiency increase with temperature (Ebenso, 2003a, b, 2004). Comparing values of inhibition efficiency obtained from thermometric and gasometric methods, it is seen that values obtained at 303 K from thermometric method were comparable at all concentrations of *M. sapientum* peels with those obtained from the gasometric methods.

Thermodynamic and adsorption considerations

Values of activation energy for the corrosion reaction of mild steel in the presence and absence of different concentration of ethanol extract of *M. sapientum* peels have been calculated using Arrhenius equation (equation 5).

$$CR = A \exp(-E_a/RT) \quad (5)$$

Taking logarithm of both sides of equation 5, equation 6 is obtained:

$$\log CR = \log A - \frac{E_a}{2.303RT} \quad (6)$$

Where CR is the corrosion rate of mild steel, A is Arrhenius constant or pre-exponential factor, E_a is the activation energy of the reaction, R is the gas constant and T is the temperature. Considering a change in temperature from 303 K (T_1) to 333K (T_2), the corresponding values of the corrosion rates at these temperatures are i_1 and i_2 respectively. Inserting these parameters into equation 6, equation 7 is obtained:

$$\log \frac{i_2}{i_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (7)$$

Values of E_a for the inhibited corrosion reaction of mild steel have been calculated using equation 7. The activation energy in the absence of the inhibitor is 39.1959 J/mol and is lower than the values obtained for the inhibited systems. The values in the presence of the inhibitor (presented in Table 4) ranged from 59.9937 to 78.1010 KJ/mol (mean = 69.4820 KJ/mol) supporting the mechanism of physical adsorption. For a physical adsorption, it is expected that the value of E_a should be less than 80.00 KJ/mol (Ebenso, 2003 a, b, 2004; Sheatty et al., 2006).

The values of heat of adsorption of *M. sapientum* peels on mild steel surface were calculated using equation 8 (Ebenso, 2003a, b, 2004; Umoren et al., 2006a, b).

$$Q_{ads} = \frac{\theta_2 T_2}{1-\theta_2} - \frac{\theta_1 T_1}{1-\theta_1} \cdot \frac{T_1 T_2}{T_1 - T_2} \quad (8)$$

Values of Q_{ads} (Table 4) calculated through equation 8 were negative and ranged from -49.5222 to -54.6981 KJ/mol (mean = -52.5917 KJ/mol) indicating that the adsorption of *M. sapientum* peels on mild steel surface is

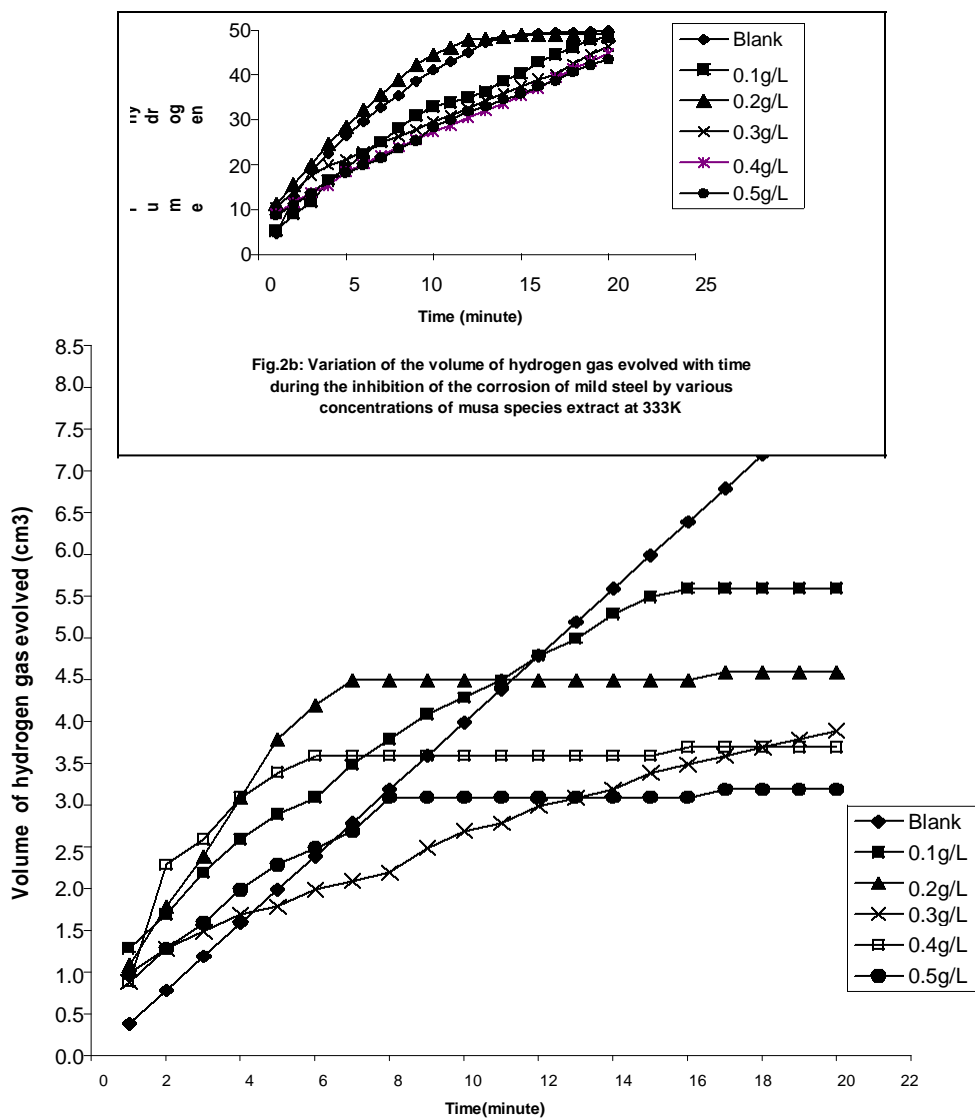


Figure 2a. Variation of volume of hydrogen evolved with time during the inhibition of the corrosion of mild steel by various concentrations of Musa species at 303 K

exothermic. The negative values show that the adsorption and hence the inhibition efficiency decreases with rise in temperature. Similar observation has also been reported by other authors (Ebenso, 2003a, b, 2004; Bhajiwala and Vashi, 2001).

Values of free energy of adsorption of *M. sapientum* peels on mild steel surface were calculated from the plot of the isotherms in Figures 4 and 5. Calculated values of ΔG_{ads} are recorded in Table 5. These values are negative and ranged from -10.51939 KJ/mol at 303 K and -13.9602 KJ/mol at 333 K from the Langmuir isotherm plot and -10.83848 KJ/mol at 303 K and -15.80988 KJ/mol at 333 K from the Frumkin isotherm plot. The values obtained from these plots are quite comparable. This indicates that adsorption of ethanol extract of *M. sapientum* peels is spontaneous and occurs via physical adsorption me-

chanism. Generally, values of ΔG_{ads} up to -20 KJ/mol (as obtained in this study) are consistent with electrostatic interaction between the charged metal and charged molecules which signifies physical adsorption while values more negative than -40KJ/mol signifies chemical adsorption (Ebenso, 2003 a,b,2004; Bhajiwala and Vashi, 2001; Bilgic and Sahin, 2001).

Adsorption isotherms are very important in understanding the mechanism of inhibition of corrosion reactions. The most frequently used adsorption isotherms are Frumkin, Temkin, Freundlich, Florry Huggins, Bockris – Swinkel, El-Awardy and Langmuir isotherms. All these isotherms can be represented as follows,

$f(\theta, x) \exp (-2a\theta) = kC$ (9) where $f(\theta, x)$ is the configuration factor which depends

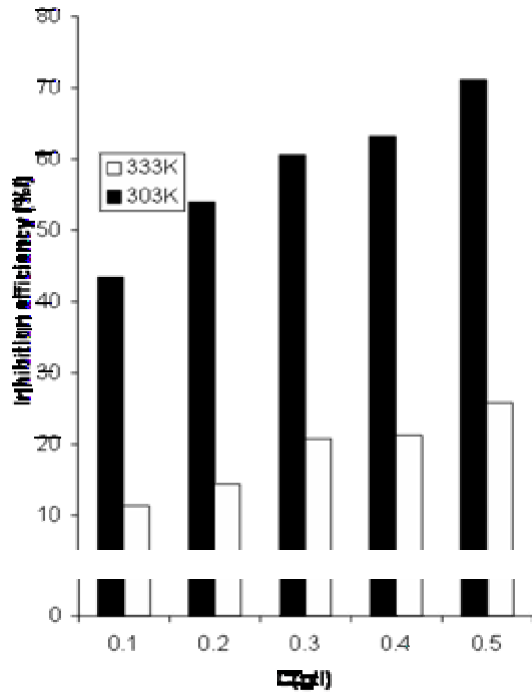


Figure 3. Variation of inhibition efficiency with concentration of Musa sapientum peels extract.

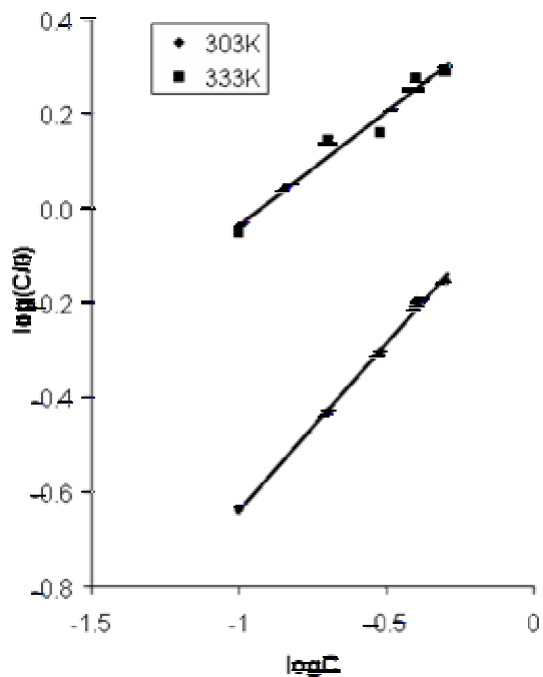


Figure 4. Langmuir isotherm for adsorption of Musaspecies on the surface of mild steel.

upon the physical model and the assumptions underlying the derivation of the isotherm. θ is the degree of surface coverage, C is the inhibitor concentration in the electrolyte, x is the size ratio, a is molecular interaction parameter and k is the equilibrium constant of the adsorption

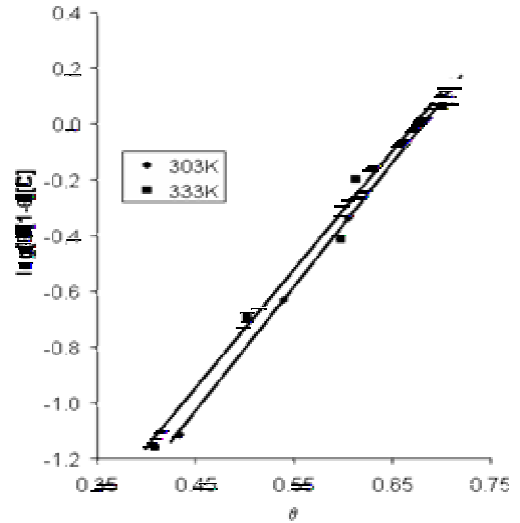


Figure 5. Frumkin isotherm for the adsorption of Musasapientum on the surface of mild steel.

tion process. Adsorption behaviour of *M. sapientum* peels is best explained by Langmuir and Frumkin adsorption isotherms.

Langmuir isotherm is an ideal isotherm for physical or chemical adsorption where there is no interaction between the adsorbate and the adsorbent. Assumptions of Langmuir relate the concentration of the adsorbate in the bulk of the electrolyte (C) to the degree of surface coverage (θ) according to equation 10:

$$\frac{C}{\theta} = \frac{1}{K + C} \quad (10)$$

Where k is the equilibrium constant of adsorption. Taking logarithm of both sides of equation 10, equation 11 is obtained:

$$\log(C/\theta) = \log C - \log K \quad (11)$$

By plotting values of $\log(C/\theta)$ versus values of $\log C$ straight lines graphs were obtained (Figure 4). Applicability of Langmuir adsorption isotherm to the adsorption of *M. sapientum* peels on mild steel confirms the formation of multimolecular layer of adsorption where there is no interaction between the adsorbate and the adsorbent.

Frumkin isotherm equation (equation 12) is obeyed when a plot of $\log(\theta/(1-\theta)[C])$ versus θ produces a straight line with slopes equal to $2\alpha/2.303$.

$$\log(\theta/(1-\theta)[C]) = \log K + 2\alpha\theta/2.303 \quad (12)$$

Where α is lateral interaction term describing the molecular interaction in the adsorbed layer, K is the desorption-adsorption equilibrium constant and C is the concentration of the inhibitor. Figure 5 shows Frumkin plots for the used inhibitor at different temperatures. Values of α calculated from the slopes of lines on the plot were 4.1623 and 0.0709 at 303 and 333 K (presented in Table

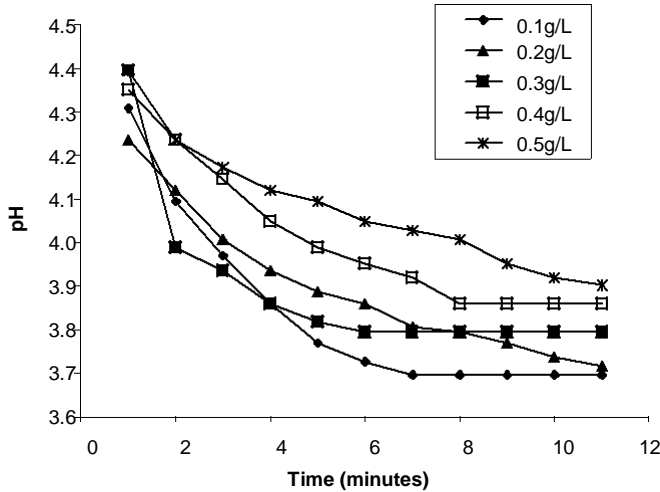


Figure 6. Variation of pH with time for the corrosion of mild steel in the presence of *Musa sapientum* extract at 303 K.

5), respectively indicating attractive behaviour of the inhibitor. Also value of α at 303K is greater than the value obtained at 333 K indicating that the strength of the attractive behaviour of the inhibitor decreases with temperature.

Comparing the degree of linearity of Langmuir and Frumkin adsorption isotherms as measured by values of R^2 (Table 5), it is seen that Langmuir adsorption isotherm is best applicable at 303 K while Frumkin isotherm is best applicable at 333 K. This confirms that the adsorption behaviour of the inhibitor is strongly influenced by temperature. Chemical analysis of the banana peels shows that it contains some antioxidant compounds such as gallic acid, catechin and dopamine which could enhance corrosion inhibition (Mokbel and Hashinaga, 2005). It also contains several other compounds like carbohydrates, crude protein, crude fat, crude fibre etc. (Essien et al., 2005). All these compounds combine to cause corrosion inhibition.

Effect of pH

The dissolution of mild steel in H_2SO_4 occurs according to equation 13:

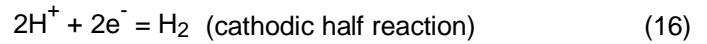
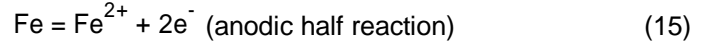


From the above equation, it can be seen that for every two moles of mild steel consumed, one mole of hydrogen gas is evolved. In other word, the dissolution of two mole of mild steel liberates 22400 cm^3 of $H_2 = 1$ mole of H_2 . Therefore if x volume of hydrogen gas is evolved, the number of moles of hydrogen associated with the dissolution is equal to $x/22400$. pH of a solution is defined as follows,

$$pH = -\log_{10}(x/22400) \quad (14)$$

Values of pH calculated through equation 14 have been used to plot Figure 6 which shows variation of pH with time. From Figure 6, it is seen that the pH of the corrodent decreases as the immersion time increases indicating enhancement in the rate of corrosion as the period of immersion increases. This is due to increase in acidity.

Corrosion of mild steel is an electrochemical process involving the following cathodic and anodic half reactions:



Adding equations 15 and 16, the overall cell reaction is obtained as follows,



Nernst equation for the above reaction can be written as follows,

$$E_{Fe} = E^{\circ} + \frac{RT}{nF} \ln(a_{Fe}/a_{Fe^{2+}}) \quad (18)$$

For anodic half reaction, E_{Fe} is independent of pH but for the cathodic half reaction, pH is an important factor. Applying the Nernst equation, the electrode potential for the cathodic half reaction can be written as follow,

$$E_{H_2} = E_{H_2} + \frac{RT}{F} \ln a_{H^+} \quad (19)$$

At $p_{H_2} = 1 \text{ atm}$, equation 19 is rearranged to equation 20 as follow,

$$E_{H_2} = -\frac{RT}{F} \times 2.303pH \quad (20)$$

Where F is the Faraday's constant, R is the gas constant and T is the temperature. The implication of equation 20 is that the variation of E_{H_2} with time during the corrosion of mild steel is expected to follow trend similar to that observed for pH. Therefore, we state that the E_{H_2} of the system decreases as the corrosion of mild steel proceeds. It is also observed that values of electrode potential of the system are expected to vary proportionally with free energy according to equation 21.

$$\Delta G_{ads} = -nFE^{\circ} \quad (21)$$

Where n is the number of electron associated with the redox reaction, F is the Faraday's constant ($F = 96500C$) and E° is the electrode potential. Values of E° calculated through equation 21 were 0.024, 0.033, 0.038, 0.05 and 0.05V at inhibitor's concentration of 0.1, 0.2, 0.3, 0.4 and 0.5 g/l, respectively. From the results, it can also be stated that the variation of inhibition efficiency with concentration of *M. sapientum* peels is partly contributed by differences in values of the electrode potential.

Conclusions

From the present study, it is found that ethanol extract of *M. sapientum* peels can be used as an inhibitor for mild

steel corrosion. The inhibitor acts by being adsorbed on mild steel surface according to classical adsorption models of Langmuir and Frumkin adsorption isotherms. Adsorption characteristics of the inhibitor follow physical adsorption mechanism. It is found that the inhibitive action of *M. sapientum* peels is basically controlled by temperature, pH, period of immersion, electrode potential and concentration of the inhibitor.

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