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THE INHIBITION OF MILD STEEL CORROSION BY EXTRACTS FROM SEEDS OF *MYRISTICA FRAGRANCE, MONODORA MYSTICA* AND *PARKIA BIGLOBOSA* IN SULPHURIC ACID SOLUTION

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ABSTRACT

Gravimetric and volumetric methods were used to study the corrosion inhibition of mild steel by ethanol extracts from seeds of Myristica fragrance (MF), Monodora mystica (MM) and Parkia biglobosa (PB) in sulphuric acid solution. The results of the investigation revealed that the plant extracts inhibit mild steel corrosion to a reasonable extent in the acidic medium. The inhibition efficiency was found to increase with increase in extract concentration and decrease in temperature. The inhibition efficiencies for all the concentrations and temperatures studied followed the trend: PB > MM > MF. The experimental data were consistent with Langmuir adsorption isotherm and a physical adsorption mechanism was proposed for the adsorption of the extracts on the mild steel surface.

Key words: *Acid corrosion; Adsorption isotherm; Corrosion inhibitor; Mild steel; Monodora mystica; Myristica fragrance; Parkia biglobosa*

1.0 INTRODUCTION

Mild steel has been extensively used under different conditions in chemical and allied industries in handling alkaline, acid and salt solutions. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products [1]. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds [2]. The successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment have been reported [3-9]. The significance of this area of research is primarily due to the fact that natural products are environmentally friendly and ecologically acceptable.

Myristica fragrance belongs to the family Myristicacae and genus Myristica. The tree is about 25 feet tall and has a grayish brown smooth bark. The seed (nutmeg) is a firm, fleshy and whitish transverse by red brown veins abounding in oil [10]. *Monodora mystica* (calabash nutmeg) is a tropical shrub of the annonacease apple family. The flower looks like those of orchid hence it is also known as African orchid nutmeg. The fruit is nearly spherical in shape about the same size as an orange [11]. *Monodora mystica* (African locust bean) is of the family leguminoseae. The tree is about 10-20 m high. The fruit is a slightly covered pod that contains seeds which are embedded in a sweet yellow pulp [10].

As a contribution to the current interest on environmentally friendly corrosion inhibitors, the present study investigates the inhibiting effect of ethanol extracts from the seeds of some local spices: *Myristica fragrance, Monodora mystica* and *Parkia biglobosa* on the corrosion of mild steel in sulphuric acid solution.

2.0 Methodology

2.1 Materials preparation

Materials used for the study were mild steel sheet of composition (wt %) Mn (0.64), P (0.06), C (0.19) S (0.05), Ni (0.09), Cr (0.08). Mo (0.02), Cu (0.27), Si (0.26) and the rest Fe. The sheet was mechanically pressed, cut to form different coupons, each of dimension, 5.00 x 4.00 x 0.08 cm and 1.33 x 4.00 x 0.08 cm for the weight loss and hydrogen evolution techniques, respectively. Each coupon was degreased by washing with ethanol, rinsed with acetone, dried and preserved in a desiccator. All reagents used for the study were Analar grade and distilled water was used for their preparation.

2.2 Extraction of plant

Samples of *Myristica fragrance, Monodora mystica* and *Parkia biglobosa* were collected from a local market in Ikot Ekpene and identified in the herbarium of the Department of Biological Sciences of the University of Calabar. The leaves were shredded using a kitchen knife and dried in an oven (N53C- Genlab) at 50 °C. They were then ground into powder using porcelain mortar and pestle. A portion of 80g of the powder was extracted continually with 250 cm^3 of absolute ethanol for 24 hrs. The solvent was then evaporated and 10 g of the jelly extract obtained was soaked in 1 liter of H_2SO_4 solution, kept for 24 hrs, filtered and stored. From this stock (10.0 g/L) solution serial dilution to concentrations of 0.5, 1.0, 2.0, 4.0 and 6.0 g/L was done.

2.3 Phytochemical screening

Phytochemical screening was carried out on the ethanolic extracts from the seeds of *Myristica fragrance, Monodora mystica, Parkia biglobosa* following the methods described by Trease and Evans [12]. The plants were screened for alkaloids, saponins, tannins, flavonoids, polyphenols and antraquinones.

2.4 Gravimetric method

In the weight loss experiment, the pre-cleaned mild steel coupons were dipped in 250 mL of the respective inhibitor or blank solutions maintained at 303 K. The weight loss was determined by retrieving the coupons at 2hr intervals progressively for 8hrs. Prior to measurement, each coupon was washed in 20% NaOH solution (containing 100 g/L of zinc dust), rinsed in deionized water, cleaned and dried using acetone. The difference in weight was taken as the weight loss of mild steel. From the weight loss, the inhibition efficiency (%I) of the extract and surface coverage (è) of mild steel were calculated using Equations 1 and 2, respectively.

$$\% I = \frac{R_b - R_i}{R_b} x\, 100 \qquad 1$$

$$\theta = \frac{R_b - R_i}{R_b} \qquad 2$$

R_b and R_i are the corrosion rates for the uninhibited and inhibited solutions, respectively.

2.5 Gasometric method

Gasometric measurements were carried out at 303 and 313 K as previously described [13, 14]. The rates of hydrogen evolution were obtained from the slope of the graph of volume of hydrogen evolved per surface area against time and the inhibition efficiency and surface coverage determined using Equations 1 and 2, respectively.

3.0 RESULTS AND DISCUSSION

3.1 Trend of inhibition efficiency with concentration and temperature

The corrosion rate, surface coverage and inhibition efficiency for mild steel coupons in 5 M H_2SO_4 solutions in the absence and presence of *Myristica fragrance* (MF), *Monodora mystica* (MM) and *Parkia biglobosa* (PB) using weight loss method are presented in Table 1. Table 1 clearly reveals the corrosion inhibiting effect of MF, MM and PB in the corrodents, which becomes more pronounced with increasing inhibitor concentration. This implies a dependence of the inhibition process on the amount of the inhibiting species present in the system. The order for the corrosion inhibitive effects is PB > MM > MF. The plot in Figure 1 suggest that PB exerted a greater inhibiting effect than MM and MF in 5 M H_2SO_4. The results obtained from the gasometric technique at 303 and 313 K are presented in table 1.

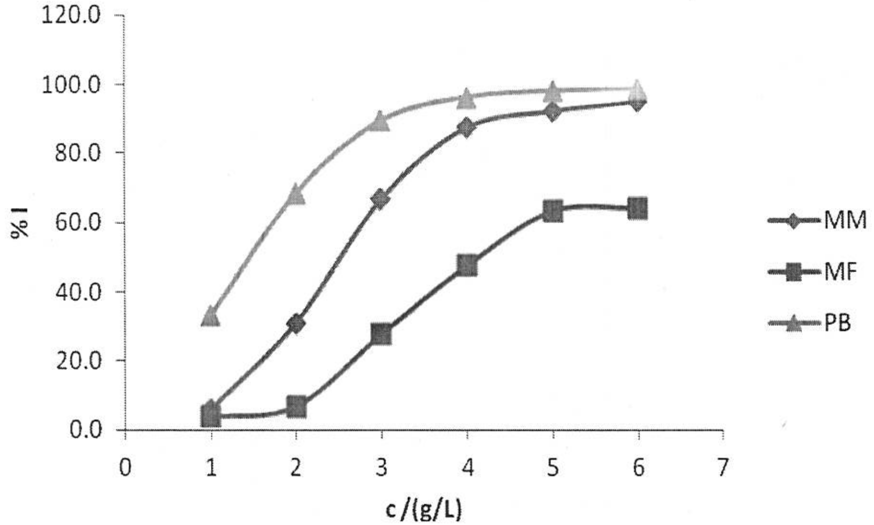
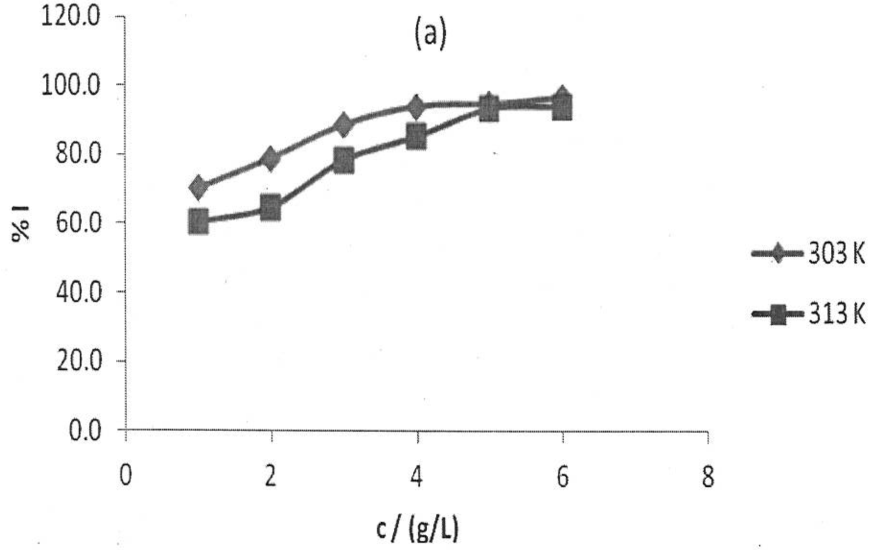


Figure 1: Variation of inhibition efficency (% I) with extract concentration for mild steel in 5.0 M H_2SO_4 solution in the presence of *Myristica fragrance* (MF), *Monodora mystica* (MM) and *Parkia biglobosa* (PB) using weight loss method.



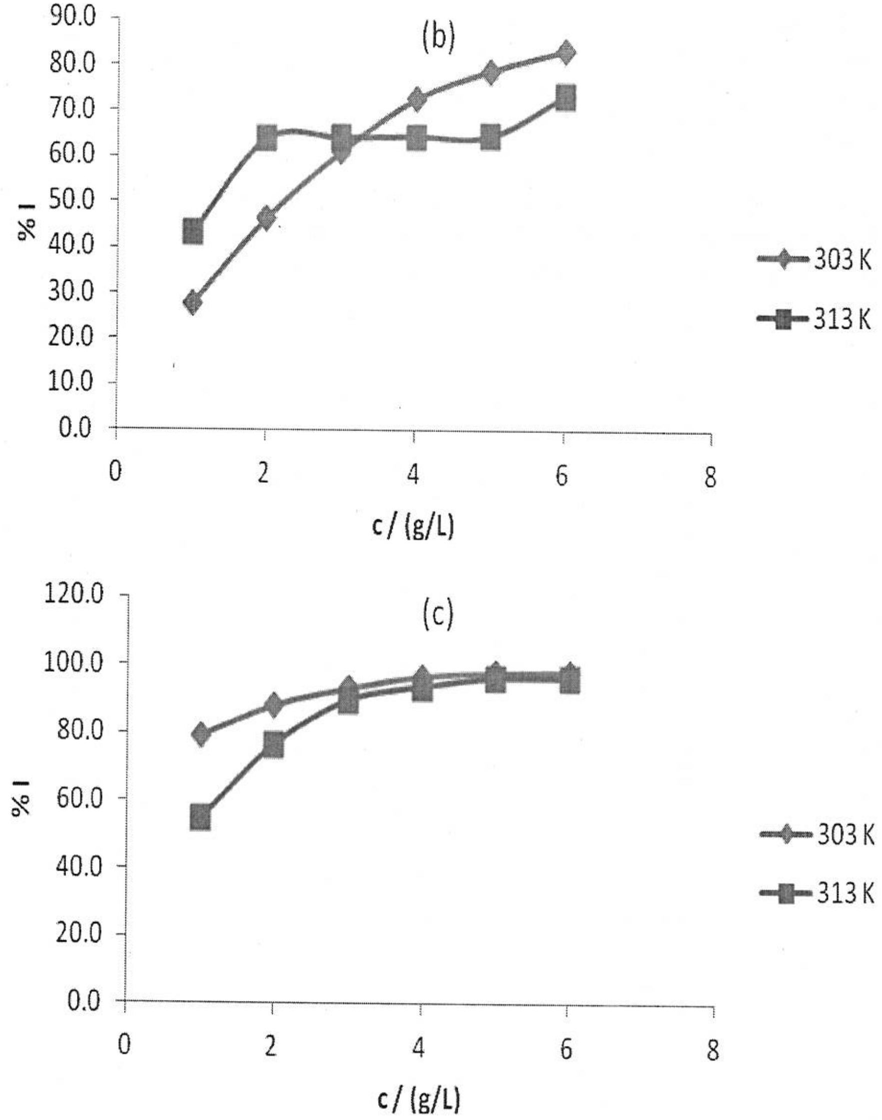


Figure 2: Variation of inhibition efficiency (%I) with extract concentration for mild steel in 5.0 M H_2SO_4 solutions in the presence of (a) MF (b) MM and (c) PB using gasometric technique at different temperatures.

Figure 2 shows the effect of temperature on % I which decreases with increase in temperature; this suggests a physical interaction between the metal surfaces. Although the inhibition efficiency of

MM was observed to be higher at a comparatively lower inhibitor concentration there was a swift swap of the tendency at about 3.0 g/L of MM thus reconfirming to physical interaction between the inhibitor and the metal surface.

Table 1: Corrosion rate, surface coverage and inhibition efficiency for mild coupons in 5 M H_2SO_4 solution in the absence and presence of inhibitors using the weight loss technique at 30°C

	Concentration (g/L)	Corrosion rate ($mg/cm^2/hr$)	Surface coverage, θ	Inhibition efficiency (%)
	Blank	0.0332	-	-
Monodora mystica (MM)	0.5	0.0312	0.0602	6.0
	1.0	0.0229	0.3102	31.0
	2.0	0.0111	0.6657	66.6
	4.0	0.0042	0.8735	87.3
	6.0	0.0026	0.9217	92.2
	10.0	0.0017	0.9487	94.8
Myristica fragrance (MF)	0.5	0.0319	0.0392	3.9
	1.0	0.0309	0.0693	6.9
	2.0	0.024	0.2771	27.7
	4.0	0.0174	0.4759	47.6
	6.0	0.0122	0.6325	63.3
	10.0	0.0119	0.6415	64.2
Parkia biglobosa (PB)	0.5	0.0222	0.3313	33.1
	1.0	0.0106	0.6807	68.1
	2.0	0.0036	0.8916	89.2
	4.0	0.0013	0.9608	96.1
	6.0	0.0007	0.9789	97.9
	10.0	0.0005	0.9849	98.5

Table 2:Phytochemical screening of the ethanol extracts fron the seeds of *Myristica fragrance,Monodora mystica* and *Parkia biglobosa*

Chemical constituents	Screening		
	Myristica fragrance	*Monodora mystica*	*Parkia biglobosa*
Anthranoids	-	-	-
Alkaloids	+	+	+
Saponins	-	-	-
Flavonoids	+	+	-
Tannins	-	-	-
Polyphenols	+	+	+
Antraquinones	-	-	-

The phytochemical screening of *Myristica fragrance, Monodora mystica* and *Parkia biglobosa* is presented in Table 2. From Table 2 it can be seen that alkaloids, polyphenols and flavonoids are present in MM and MF while only alkaloids and polyphenols are present in PB. The corrosion inhibiting effect of the extracts can be attributed to phytochemical constituents including alkaloids, polyphenols and flavoniods. The greatest inhibitive effect exhibited by PB is in line with reports given by Ikeuba *et al.* [4] confirming the efficacy of alkaloid active components. This can be explained on the basis of lower intermolecular interactions between the active principles present in the extract. This also suggests that that there may be an antagonistic interaction between the natural products present in the extract [4].

3.2 Adsorption behavior

The adsorption characteristics of ethanol extract from MF, MM and PB were also investigated by fitting data obtained for the degree of surface coverage into different adsorption isotherms. The tests indicate that Langmuir adsorption isotherm best describes the adsorption behaviour of the extracts. The Langmuir adsorption isotherms may be formulated as:

$$\frac{c}{\theta} = \frac{1}{K_{eq}} + c \qquad 3$$

where *c* is the concentration of the inhibitor in the solution, *è* is the degree of surface coverage of the inhibitor and K_{eq} is the adsorption equilibrium [15]. Figure 3 shows Langmuir adsorption isotherm for the adsorption of ethanol extracts (MM, MF and PB) on mild steel surface. Values of adsorption parameters deduced from the isotherms are presented in Table 3. From the results obtained, it is significant to note that the R^2 values of the plots are very close to unity, which indicates a strong adherence of the adsorption data to the Langmuir adsorption isotherm. Values of adsorption equilibrium constant determined from the slope of the Langmuir adsorption isotherms were used to calculate the free energies of adsorption of ethanol extract of MM, MF and PB on mild steel surface using Equation 4

$$K_{eq} = \frac{1}{55.5} \exp\left(\frac{-\Delta G^{o}_{ads}}{RT}\right) \quad 4$$

where ΔG^{o}_{ads} is the free energy of adsorption, *R* is the gas constant, *T* is the temperature and 55.5 is the molar concentration of the acid in the solution. Calculated values are between -13.86 and -15.34 at 303 K and -11.75 and -13.18 at 313 K, respectively. The values are negative and are less than the threshold value of -40 KJ/mol required for chemical adsorption, hence the adsorption of ethanol extracts from *Myristica fragrance, Monodora mystica* and *Parkia biglobosa* on mild steel surface is spontaneous and is consistent with the mechanism of physical adsorption.

Increase in temperature decreased the inhibition efficiencies of the plant extracts suggesting physical adsorption of the components of the extracts on the surface of the metals. In order to affirm this, the apparent activation energies (E_a) for the corrosion reaction of mild steel in the absence and presence of various concentrations of the extracts were calculated from the condensed Arrhenius equation (Equation 5)

$$\log\frac{R_2}{R_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad 5$$

where R_1 and R_2 are taken to be the corrosion rates at T_1 and T_2 respectively [8]. The values are listed in Table 5. These values in the presence of the extracts are larger than the value for the blank (44.64 KJ/mol) confirming that the extracts from *Myristica fragrance, Monodora mystica* and *Parkia biglobosa* retards the corrosion of mild steel in H_2SO_4 via a physical adsorption of the components of the extracts on the metal surface.

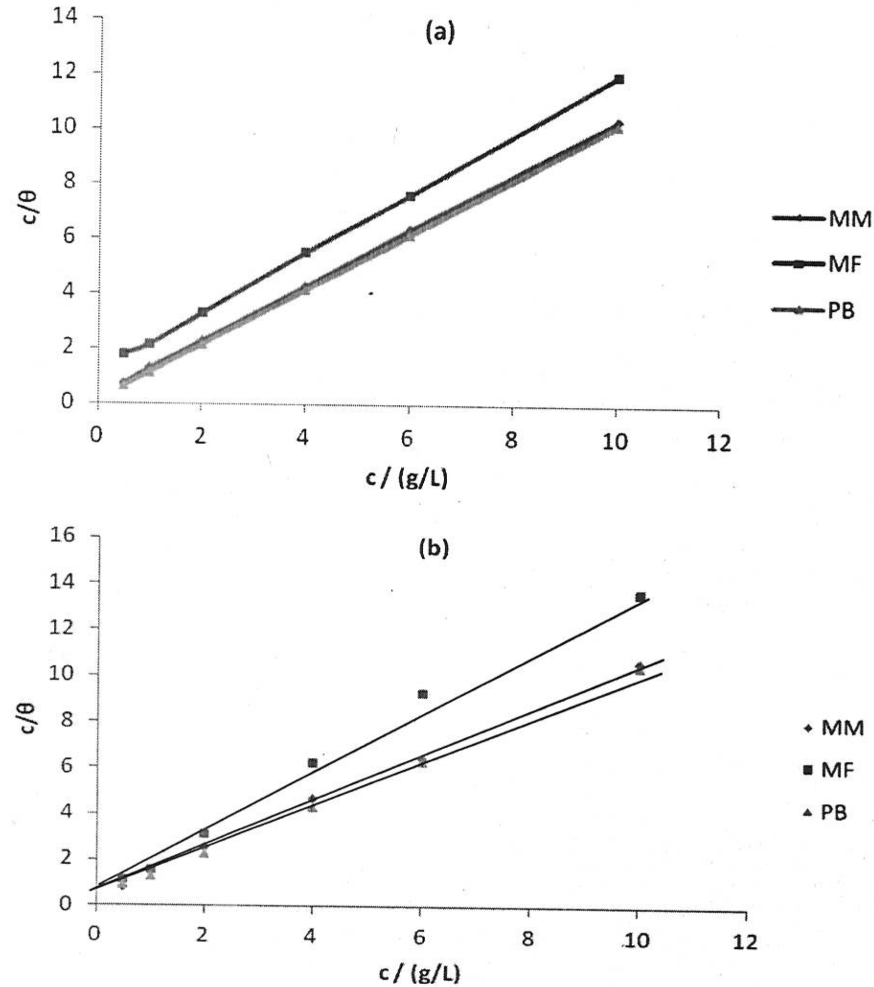


Figure 3: Langmuir isotherm for the adsorption of ethanol extract of *Myristica fragrance* (MF), *Monodora mystica* (MM) and *Parkia biglobosa* (PB) on the surface of mild steel at (a) 303K and (b) 313 K

Table 4: Adsorption equilibrium constant, adsorption free energy and correlation factors for mild steel in the presence of the inhibitors at different temperatures.

Temperature	Inhibitors	K_{ads}	ΔG_{ads}	R^2
303 K	MM	4.42	-13.86	1.000
	MF	0.87	-9.77	0.999
	PB	7.94	-15.34	1.000
313 K	MM	2.15	-12.05	0.998
	MF	1.91	-11.75	0.994
	PB	3.37	-13.18	0.999

Table 5: Calculated activation energy for mild steel in the presence of different concentrations of ethanol extracts from *Myristica fragrance* (MF), *Monodora mystica* (MM) and *Parkia biglobosa* (PB) Ea/ (kJ/mol)

	Ea/ (kJ/mol)		
Inhibitors	MM	MF	PB
Blank	44.64	44.64	44.64
0.5 g/L	25.67	66.86	105.98
1.0 g/L	13.50	84.67	99.52
2.0 g/L	38.10	93.73	81.35
4.0 g/L	65.25	112.53	98.18
6.0 g/L	85.34	62.61	101.81
10.0 g/L	81.30	85.08	109.72

4.0 CONCLUSION

- Ethanol extracts from *Myristica fragrance* (MF), *Monodora mystica* (MM) and *Parkia biglobosa* (PB) are good inhibitor for the corrosion of mild steel in H_2SO_4 solution and the inhibition efficiencies followed the trend: PB > MM > MF.

- The inhibition efficiency of the extracts increases with increase in concentration and with decrease in temperature.
- The adsorption characteristic of the inhibitor is best described by Langmuir adsorption isotherm and a physical adsorption mechanism is proposed for the adsorption of the extracts on the metal surface.

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