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Investigation of Piperanine as HCl Ecofriendly Corrosion Inhibitors for C38 Steel

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Isolated from black pepper (BP) extract, piperanine was tested as corrosion inhibitor of C38 steel corrosion in 1 M HCl solution. Piperanine was identified by NMR techniques. The corrosion tests were conducted by weight loss method at various temperatures varying from 298 to 353 K. Results obtained from weight loss measurements indicate that the natural compounds tested exhibit higher efficiency exceeding 97.5% at 10^{-3} M piperanine. Piperanine adsorbs on the steel surface according Langmuir isotherm. Adsorption enthalpy were determined and discussed. Effect of temperature was also investigated and activation parameters were evaluated.

Keywords: Corrosion; Acid solutions; Green inhibitor; Piperanine; Adsorption

1. INTRODUCTION

In a modern business environment, successful enterprises cannot tolerate major corrosion failures, especially those involving personal injuries, fatalities, unscheduled shutdowns and environmental contamination. For this reason considerable efforts are generally expended in corrosion control at the design stage and in the operational phase. Corrosion can lead to failures in plant infrastructure and machines that are usually costly to repair, costly in terms of lost or contaminated product, in terms of environmental damage, and possibly costly in terms of human safety [1]. The use of inhibitors is one of the most practical methods for protection against corrosion especially in acid descaling bathes to prevent not only metal dissolution but also acid consumption. It is well known that many organic compounds are able to reduce the corrosion rate of metals significantly [2–4]. Inhibitors reduce the rate of either or both of the partial reactions of the corrosion process, the anodic metal dissolution and the cathodic oxygen reduction. The most synthetic corrosion inhibitors are known by their hazardous effects and the research of ecofriendly inhibitors to prevent environment receives more attention of scientists and industrials. Naturally extracts and oil issued from plants to use naturally occurring products as corrosion inhibitors as they are inexpensive, readily available and renewable sources of materials, environmentally friendly and ecologically acceptable [5–10].

In our laboratories, many studies have been investigated on the corrosion inhibition by natural plant extract and their oils on steel in acidic solutions [11-20]; however, the constituents that provide inhibitive action, the mechanisms and the best condition for inhibition are still unclear. But, data on the composition of both oil and extract may give information on the molecules which can adsorb on the metallic surface and hence secure from corrosion. The present study is aimed to isolate piperanine and to test its inhibitive action as ecofriendly on C38 steel corrosion in 1 M HCl. The work was conducted through weigh loss measurements. The effect of temperature (298 to 353 K) was also investigated to get more data on activation process.

2. EXPERIMENTAL

2.1. Isolation of Piperanine from Black Pepper

Piperanine can be isolated in good yield from ground black pepper as described elsewhere [21-24]. Two methods of extractions of the piperanine were used: extraction involving refluxing with C_2H_5OH (95%) or CH_2Cl_2 and by means of a device of soxhlet (C_2H_5OH 95%). With the extraction involving refluxing, two alkaloid (principal) amide products (piperine and piperanine) were obtained. Recrystallisation from ethanol gave pure piperine soluble in the cold ethanol (PF: 128 °C), and pure piperanine soluble at hot temperature (PF: 135 °C). We notice during these various manipulations of extractions, that the piperine is soluble in the dichloromethane and in the cold ethanol and the piperanine is soluble in the dichloromethane and in the hot ethanol. The isolated piperanine (Fig.1) was purified and characterised by (^{1}H and ^{13}C) NMR spectroscopies.

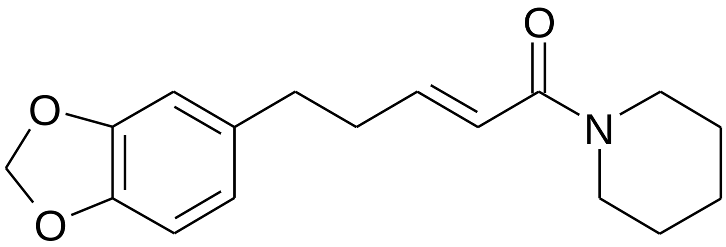


Figure 1. Molecular structure of piperanine

2.3. Specimen preparation

The composition of C38 steel used in this study is: 0.179% C, 0.165% Si, 0.439% Mn, 0.203% Cu, 0.034% S and Fe balance were used. Samples were cut into 2 × 2 × 0.5 cm dimensions used for weight loss measurements. The exposed area was mechanically abraded with various emery papers up to 1000 grades. They were degreased with acetone and rinsed by distilled water before each experiment. Molar HCl solutions were prepared by dilution of 37% HCl analytical grade using distilled water. The concentration range of piperanine varied from $2.5\text{x}10^{-8}$ to 10^{-3} M. The electrolyte used was 100 ml for each experiment.

2.4. Weight loss measurements

Corrosion tests were conducted in molar HCl at different concentrations of the inhibitor. The immersion time for the weight loss is 6 h at 35°C and 1h at other temperatures. The results of the weight loss experiments are the mean of three runs, each with a fresh specimen and 100 ml of fresh acid solution. The inhibition efficiency *IE*% was calculated using the following equation:

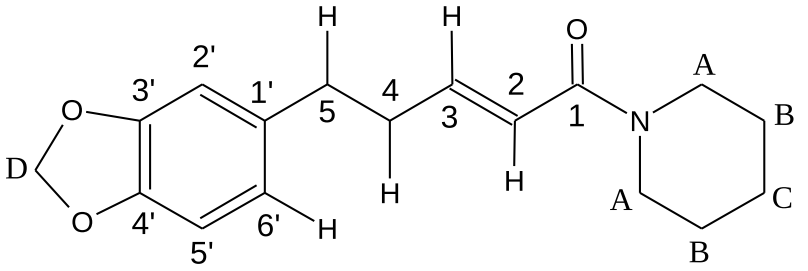
$$E_W \% = \frac{W_{corr} - W_{corr/inh}}{W_{corr}} \times 100 \qquad (1)$$

where, $W_{corr/inh}$ and W_{corr} are the corrosion rate of steel in inhibited and uninhibited solution, respectively.

3. RESULTS AND DISCUSSION

The common procedure for the isolation of piperanine involves extraction using ethanol (95%) soluble at hot temperature and KOH; however, the procedure below involving refluxing with CH_2Cl_2 also gives good yield of piperanine.

- Molecular structure of piperanine isolated from black Pepper



- Data of piperanine isolated

Yield: 30%; Mp: 135°C

We remark that the data obtained by ^{1}H and ^{13}C NMR (Tables 1 and 2) are comparable to those obtained by Wu et al. and Ekanem et al. [25,26]

Table 1. Chemical Schifts (ppm) of ^{1}H NMR

Protons	**A**	**B**	**C**	**D**	**2**	**3**	**4, 5**	**2'**	**5'**	**6'**
δ ^{1}H ($CDCl_3$)	3,50 (4H,m)	1,65 (4H,m)	1,56 (2H,m)	5,90 (2H,s) (2H,s)	6,20 (1H,d) J= 15	6,82 (1H,m)	2,46 – 2,73 (4H, m)	6,70 (1H,d) J=1,2	6,73 (1H,d) J=7,90	6,63 (1H,d) J=7,91)

Table 2. Chemical Schifts (ppm) of ^{13}C NMR

Atom	**A**	**B**	**C**	**D**	**1**	**2**	**3**	**4**	**5**
δ ^{13}C ($CDCl_3$)	44,2	26,1	23,8	100,8	165,5	122,2	143,8	33,8	34,5

Atom	**1'**	**2'**	**3'**	**4'**	**5'**	**6'**
δ ^{13}C ($CDCl_3$)	134,8	107,8	144,8	146,8	109,1	122,2

The average weight loss data obtained for the C38 steel specimen in triplicates for various concentrations of inhibitor tested are presented in table 3. The variation of both corrosion rate and efficiency issued from table 3 are depicted in figure 2. From the weight loss data, it is clear that the loss in weight of mild steel specimens decreases with increasing piperanine concentration. Hence the inhibition efficiency (E_w%) increases with the increase in concentration to attain 97.5% at 10^{-3} M.

Table 3. Effect of piperanine on the steel corrosion in molar HCl solution

Inhibitor	Concentration (M)	W (mg cm^{-2} h^{-1})	Ew %
Blank	1	1.13	-
Piperanine	$2.5x10^{-8}$	0.87	22.8
	$5x10^{-8}$	0.502	55.5
	$1x10^{-6}$	0.277	75.5
	$2x10^{-5}$	0.111	90.2
	$4x10^{-4}$	0.074	93.4
	10^{-3}	0.028	97.5

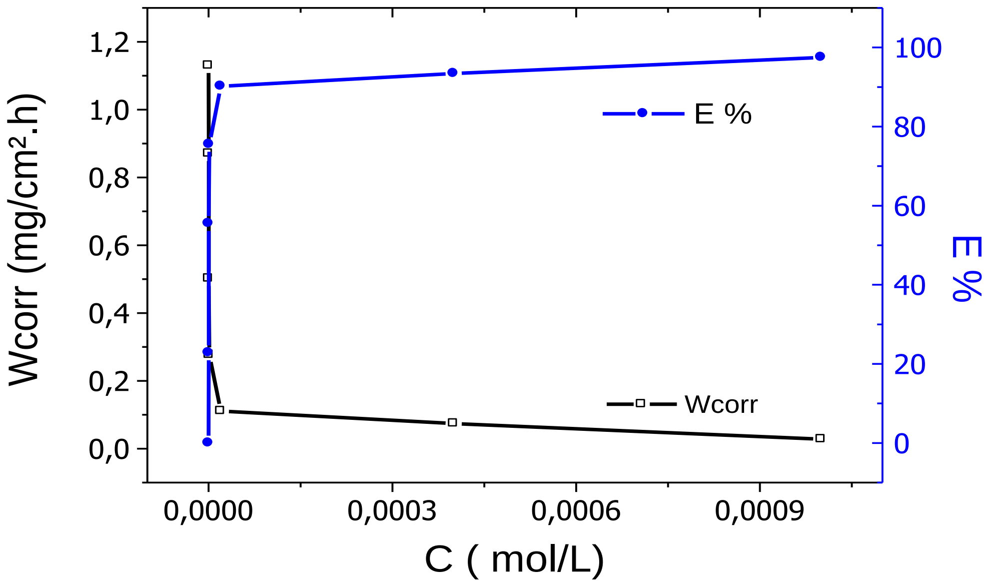
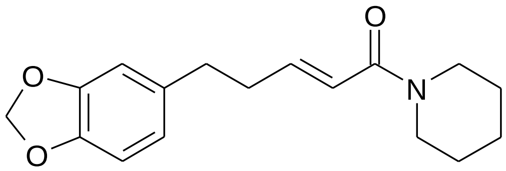
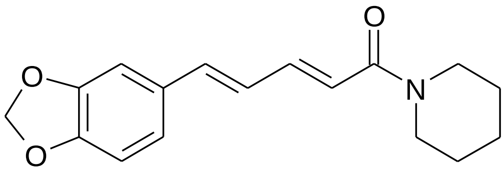


Figure 2. Variation of the corrosion rate and inhibitive efficiency against the piperanine concentration

The examination of moleculare structure of piperanine shows the presence of amide function as well as 1,3-benzodioxole separated by aliphatic chain containing double bond activates the adsorption phenomenon. Amide compounds exhibited excellent inhibitory effect on steel in acidic media [27-29]. In previous work, the piperine exhibited 98.7% at 10^{-3}M compared to piperanine; this slight difference may be explained by the presence of supplementary double bond in the aliphatic chain which reinforced the adsorption process:



piperanine
E % = 97.5 at 10^{-3}M



piperine
E % = 98.7 at 10^{-3}M [23]

The effect of temperature on the corrosion rate was studied in 1 M HCl at temperature range 40 – 70 °C in the absence and presence of piperanine by Weight loss measurements at 1 h of immersion. The results obtained from these studies were listed in Table 4. Inspection of Table 3 shown that, as the temperature increased, the corrosion rate shifted to higher values in both uninhibited and inhibited acid solutions.

This is due on to the increase of the rate of metal dissolution. It is clear from the figure that inhibition efficiency decreased with increase in temperature. This may be probably due to increased rate of desorption of piperanine from the mild steel surface at higher temperature. A decrease in inhibition efficiencies is generally related to weakening of physical adsorption. It is then interesting to determine the activation energy of the corrosion process.

Table 4. Corrosion data of steel in 1M HCl without and with 10^{-3} mol L^{-1} of piperanine in the temperature range 40–70 °C at 1 h.

	Temperature °(C)	W_{corr} (mg.cm^2.h^{-1})	E_w (%)
1M HCl	40	2.604	-
	50	4.834	-
	60	9.781	-
	70	13.235	-
Piperanine	40	0.180	93.1
	50	0. 382	92.0
	60	0.886	88.6
	70	4.140	68.8

The activation energies (E_a) for the corrosion of C38 steel in the absence and presence of piperanine at 10^{-3}M were calculated using Arrhenius-type equation:

$$W_{corr} = Ae^{-\frac{E_a}{RT}} \tag{2}$$

where E_a is the activation corrosion energy; R is the universal gas constant; A is the Arrhenius pre-exponential factor, T is the absolute temperature and W_{corr} is corrosion rate.

Arrhenius plots for the corrosion rate of C38 steel in 1 M HCl are shown in Fig. 3. Values of E_a for C38 steel in were evaluated from the slope of log W versus $1/T$ plots and given in Table 4.

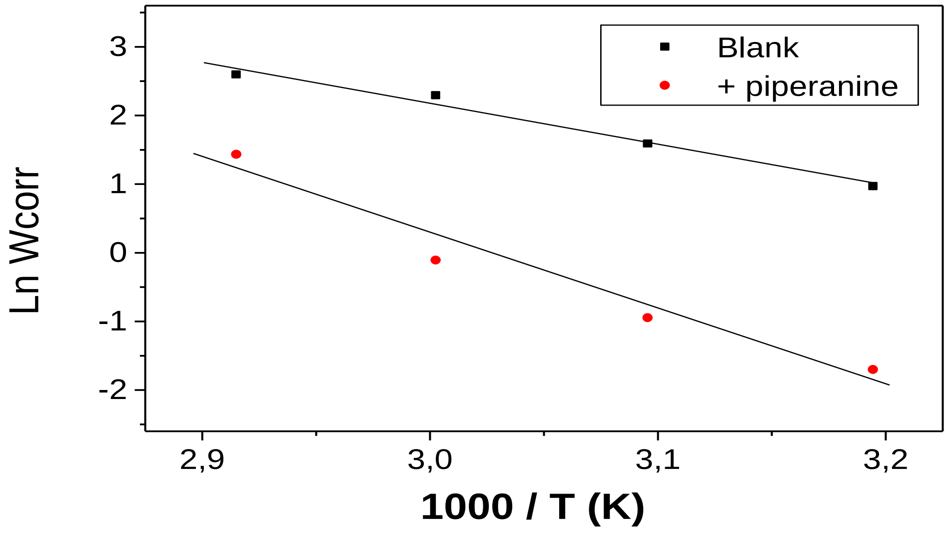


Figure 3. Arrhenius plots of log(W) versus $1/T$ at different concentrations of piperanine.

Values obtained in the absence 49.97 kJ/mol and presence of piperanine 90.99 kJ/mol indicate that the presence of inhibitor increases the activation energy of the metal dissolution reaction. The increase in activation energy can be attributed to an appreciable decrease in the adsorption of the inhibitor on the metal surface with increase in temperature and a corresponding increase in corrosion rates due to the fact that greater area of metal is exposed to the acid environment [30]. The higher value of E_a in the presence of inhibitor compared to that in its absence and the decrease in the inhibition efficiency with rise in temperature is interpreted as an indication of physisorption without excluding the chemisorption mode. The adsorption study may give more details.

In spite of this it is generally possible to divide all adsorption phenomena involving solid surfaces into two main classes: physical adsorption and chemical adsorption (or chemisorption). Physical adsorption arises from intermolecular forces involving permanent dipole, induced dipole, and quadrupole interactions. It involves van der Waals or secondary valence forces. It is akin to condensation. Chemisorption, on the other hand, involves a chemical interaction with attendant transfer of electrons between the adsorbent and the adsorbing species (adsorbate). The adsorbed species are held to the surface by valence forces that are the same as those that hold atoms together in a molecule [31]. Physical adsorption is a readily reversible process, and alternate adsorption and desorption stages can be carried out repeatedly without changing the character of the surface or the adsorbate. Since chemisorptions is a chemical reaction confined to the surface of a solid and since the possibility of chemical reaction is highly specific to the nature of the species involved, chemisorption can take place only if the adsorbate is capable of forming a chemical bond with the adsorbent. Moreover, because it requires a chemical interaction, chemisorptions is limited to a maximum of one layer of molecules on the surface (a monolayer). It frequently involves lower coverage. The valence forces holding the molecules on the surface fall off very rapidly with distance and become too small to form chemical bonds when the distance from the solid surface exceeds normal bond distances.

The Langmuir adsorption isotherm provides a simple mechanistic picture of the adsorption process and gives rise to a relatively simple mathematical expression. The Langmuir adsorption isotherm may written in the following rearranged form:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (5)$$

where C is the concentration of inhibitor, K is the adsorptive equilibrium constant, θ is the surface coverage. The standard adsorption free energy (ΔG_{ads}) may be estimated using :

$$K = \frac{1}{55.5}\exp(-\frac{\Delta G^{\circ}_{ads}}{\mathrm{RT}}) \qquad (6)$$

Figure 4 is presented the relationship between C/θ and C (Fig. 6). The curve obtained shows a linear behaviour with slope almost equals unity (1.028). The strong correlation factor $R^2=0.99986$ suggests that the adsorption of piperanine on metal surface obeys well the Langmuir adsorption isotherm. The reciprocal of intercept of the straight lines C_{inh}/θ-axis is K = 379391.5 L/mol. The standard free energy of adsorption (ΔG_{ads}) value deduced is -43.18 kJ/mol. Generally, values of ΔG_{ads} up to -20kJ/mol are consistent with electrostatic interactions between the charged molecules and the metal (physisorption) while those around -40kJ/mol or higher are associated with chemisorptions as a result of sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of bond (chemisorptions) [32].

The too negative values of ΔG_{ads} indicate the stability of the adsorbed layer on the steel surface and spontaneity of the adsorption process and also chemical and physical adsorption can occur together, but any adsorbed layers beyond the first must be physically adsorbed [31].

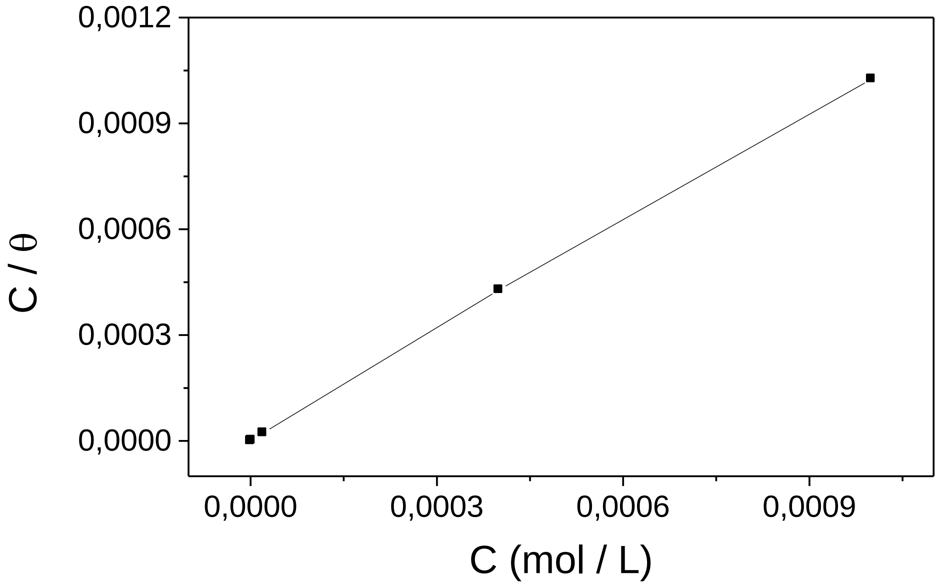


Figure 4. Langmuir adsorption plots for C38 steel in 1 M HCl at 35 °C.

4. CONCLUSION

Piperanine was isolated and characterised by NMR and tested on the corrosion of steel in molar HCl using weight loss method, the following conclusions may be made:

1. Piperanine reduced the corrosion rate of of C38 steel in HCl medium.
2. The inhibition efficiency increases with increase of inhibitor concentration to attain a maximum value of 97.5% at 10^{-3} mol/L.
3. The inhibition efficiency decreases with increase of Temperature.
4. Piperanine adsorbs on the metal surface according to the Langmuir isotherm.
5. Activation and adsorption data show that inhibitor may act by both chemisorptions and physical adsorption.

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