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Corrosion Inhibition of C38 Steel in 1 M HCl: A Comparative Study of Black Pepper Extract and Its Isolated Piperine

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Corrosion inhibition effect of black pepper (BP) extract and its piperine isolated from BP on corrosion of C38 steel in 1 M HCl solution was investigated by weight loss method. Piperine was isolated by ethanol in yield 6 from ground BP. Results obtained from weight loss measurements indicate that the natural compounds tested exhibit higher efficiency exceeding 95% at 2g/L. The presence of piperine decreases hugely the corrosion rate and its inhibition efficiency (E%) increases with concentration to attain 99 % at 10^{-3}M. Piperine 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, piperine, adsorption

1. INTRODUCTION

The studies of carbon steel corrosion in acidic media receive more and more attention both of academics and industrials because of the wide applications such as acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and the petrochemical processes. The electrochemical corrosion is generally caused by dissymmetry potentials between metal and strong acid. The aggressively of hydrogen ion is inevitable in uninhibited acid. H^+ and Dissolved O_2 are named natural motors of corrosion [1-2]. Facing this problem, the corrosion inhibitors are required. Works on the inhibition are so many so much so that we can not quote them. But scientists are unanimous on the fact that this protection is provided by the adsorption of inhibitors on the metal surface. Then, compounds can adsorb on metal surface and block the active surface sites to reduce the corrosion rate.

Many synthetic compounds offer good anticorrosive action; but most of them risk being highly toxic to both human beings and environment. In these later years, researchers reorient their studies to the use of naturally occurring substances. Plant extracts and oils have became important as an environmentally acceptable, readily available and renewable source of materials for wide range of corrosion prevention; therefore, finding naturally occurring substances as corrosion inhibitors is a subject of great practical significance [3]. The review of Raja and Sethuraman in 2008 [4] may give a vivid account of natural products which are used as corrosion inhibitors for various metal and alloys in aggressive media. They stated that natural plant have become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors. They are the rich sources of ingredients which have very high inhibition efficiency. The studies in these two later years prove that this kind of inhibitor find more and more attention of researchers [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. In the present work, inhibitive action of BP extract as a cheap, eco friendly and naturally occurring substance on corrosion behaviour of C38 steel in 1 M HCl has been investigated through weigh loss measurements. The study is completed by the comparative action of piperine freshly extracted from BP on the corrosion of C38 steel in HCl media.

2. EXPERIMENTAL

2.1. Preparation of BP extract

Dried Black pepper seeds (grounds) were crushed and extracted in boiled water for 2 h. The extracted solution was then filtered and concentrated until the water from the extract evaporates. This solid extract was used to study the corrosion inhibition properties and to prepare the required concentrations of BP.

2.2. Isolation of Piperine from Black Pepper

Piperine can be isolated in good yield from ground black pepper as described elsewhere [21,22]. Two methods of extractions of the piperine 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, we obtain a mixture of two products (piperine and piperanine). During the recrystallizing in the ethanol, the piperine is soluble in the cold ethanol (PF: 128 °C), and the other compound is 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 piperine was purified and characterised by NMR and IR spectroscopies as found in ref. [22].

Figure 1. Black peppercorns

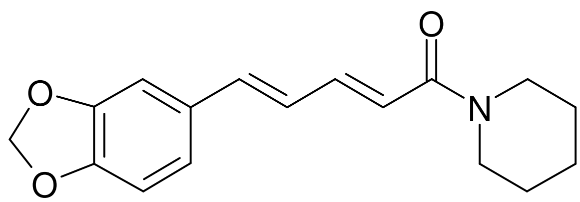

Figure 2. Molecular structure of piperine isolated from black peppercorns

2.3. Specimen preparation

C38 steel specimens having nominal composition of 0.179% C, 0.165% Si, 0.439% Mn, 0.203% Cu, 0.034% S and Fe balance were used. Coupons were cut into $2 \times 2 \times 0.5$ cm dimensions used for weight loss measurements. The exposed area was mechanically abraded with 220, 400, 800 and 1000 grades of emery papers, degreased with acetone and rinsed by distilled water before each experiment. About 1 M HCl solutions were prepared by dilution of 37% HCl (Merck) using distilled water. The concentration range of BP extract employed was varied from 0.008 to 2 g/l and from $7x10^{-8}$ to 10^{-3} M piperine and the electrolyte used was 100 ml for each experiment.

2.4. Weight loss measurements

Experiments were performed with 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} and $W_{corr/inh}$ are the corrosion rate of steel without and with inhibitors, respectively.

3. RESULTS AND DISCUSSION

The corrosion rate and inhibition efficiency for C38 steel in 1 M HCl solution at 35°C in the absence and presence of BP extract are given in Table 1. As the BP extract increases, the corrosion rate decreases. In other words, the inhibition efficiency of natural extract increases with the increase of its concentration to attain 95.8%.

Table 1. Effect of black pepper extract on the steel corrosion in molar HCl solution

Concentration (g / l)	Blanc	0.008	0.04	0.08	0.4	2
W (mg cm^{-2} h^{-1})	1.13	0.83	0.245	0.181	0.0864	0.0479
E %	-	26.5	78.3	84.0	92.4	95.8

The gravimetric data obtained in the absence and presence of piperine at different concentrations are gathered in Table 2. The respective corrosion rate illustrated that the addition of piperine molecule decreases hugely corrosion rate. This finding elucidated by Fig. 3, confirms that piperine adsorbs on steel surface and then inhibits the corrosion process. The inhibition efficiency of P increases with inhibitor concentration to reach higher value (98.9%) at 10^{-3} M (Fig. 3). This behaviour indicates that natural molecule acts as an efficient inhibitor for the corrosion of C38 steel in HCl media.

Table 2. Effect of piperine on the steel corrosion in molar HCl solution

piperine (M)	10^{-3}	5.10^{-4}	$2,8.10^{-4}$	$1,4.10^{-5}$	7.10^{-7}	$7\ .10^{-8}$	blanc
W (mg.cm^{-2}.h^{-1})	0.012	0.027	0.038	0.379	0.784	0.953	1.13
E %	98.9	97.6	96.6	66.4	45.6	15.7	-

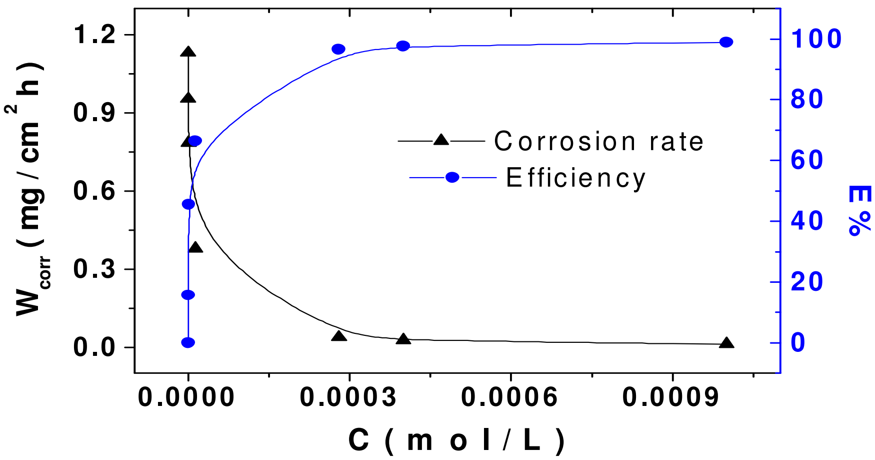

Figure 3. Variation of the corrosion rate and inhibitive efficiency against the piperine concentration

Weight loss measurements for C38 steel in molar HCl without and with 2g/L BP extract or 10^{-3} mol L^{-1} of piperine, in the temperature range 40–70 °C at 1 h of immersion, are shown in Table 3.

Table 3. Corrosion data of steel in 1M HCl without and with 2g/L BP extract or 10^{-3} mol L^{-1} of piperine, 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	-
Black Pepper extract	40	0.143	94.5
	50	0.277	94.2
	60	0.536	93.1
	70	3.257	75.3
Piperine	40	0.150	94.2
	50	0.280	94.1
	60	0.480	93.7
	70	3.890	70.6

The activation energies (E_a) for the corrosion of C38 steel in the absence and presence of different concentrations of BP extract and piperine were calculated using Arrhenius-type equation:

$$W_{corr} = A e^{-\frac{E_a}{RT}} \qquad (2)$$

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. 4. 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. The enthalpy of activation (ΔH^*) and the entropy of activation (ΔS^*) for the corrosion of C38 steel in HCl may be estimated using the transition-state equation:

$$W_{corr} = \frac{k_B T}{h} \exp(\frac{\Delta S^*}{R}) \exp(-\frac{\Delta H^*}{RT}) \quad (3)$$

where k_B is the Boltzmann's constant and h is the Planck's constant. Fig. 5 shows a plot of log(W/T) versus 1/T. Straight lines are obtained with a slope of $-\Delta H^*$ and from the intercepts of log(W/T)-axis, ΔS^* values were calculated and are given in Table 4.

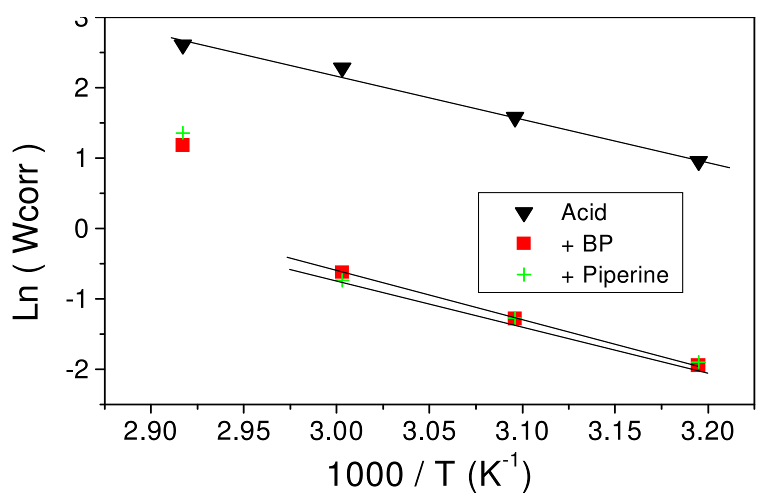

Figure 4. Arrhenius plots of log(W) versus 1/T at different concentrations of BP extract and piperine.

The collected data in Tables 3 and 4 indicate that the addition of both BP extract and piperine leads to an increase in the activation E_a and ΔH^* to values greater than that of the free solution. Moreover, the average difference value of the $E_a - \Delta H^*$ is 2.6 kJ/mol which is approximately equal to the value of RT (2.63 kJ/mol) at the average temperature (238 K) of the domain studied. This result agrees that the corrosion process is a unimolecular reaction as described by the known equation of perfect gas [23]:

$$E_a - \Delta H^* = RT \quad (4)$$

It is pointed out in the literature that positive sign of the enthalpies reflects the endothermic nature of the steel dissolution process. The presence of inhibitors tested reveals that the corrosion process becomes more and more endothermic when compared to blank.

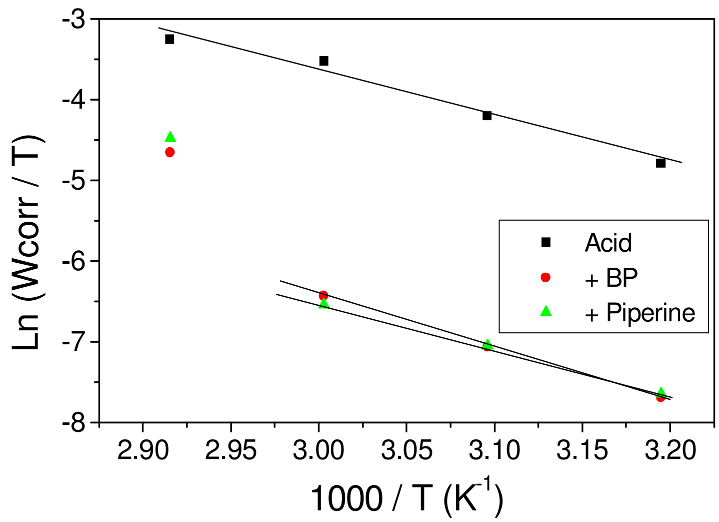

Figure 5. Transition-state plots of log(*W*/*T*) versus 1/*T* in 1 M HCl in absence and presence of various concentrations of BP extract and piperine.

Table 4. Activation data of corrosion reaction of steel in HCl in the absence and presence of piperine.

	E_a (kJ/mol)	$\Delta H°_{ads}$ (kJ/mol)	$\Delta S°_{ads}$ (J/mol.K)
Blank	51.00	48.26	-90.57
BP extract	58.74	56.32	-1,29
Piperine	59.82	57.21	-22.52

Large and negative values of entropies show that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex.

3.1. Adsorption isotherm behaviour

The inhibition process is generally related to adsorption of inhibitor's species onto the metallic surface. Then, as illustrated Do, in his book [24], Adsorption equilibrium information is the most important piece of information in understanding an adsorption process. No matter how many components are present in the system, the adsorption equilibrium of pure components is the essential ingredient for the understanding of how many those components can be accommodated by a solid adsorbent… Various fundamental equations are shown, and to start with the proceeding we will present the most basic theory in adsorption: the Langmuir theory (1918). This theory allows us to understand the monolayer surface adsorption on an ideal surface. By an ideal surface here, we mean that the energy fluctuation on this surface is periodic and the magnitude of this fluctuation is larger than the thermal energy of a molecule (kT), and hence the troughs of the energy fluctuation are acting as the adsorption sites. If the distance between the two neighbouring troughs is much larger than the diameter of the adsorbate molecule, the adsorption process is called localised and each adsorbate molecule will occupy one site. Also, the depth of all troughs of the ideal surface are the same, that is the adsorption heat released upon adsorption on each site is the same no matter what the loading is [25]. The Langmuir adsorption isotherm may be written in the following form:

$$\frac{C}{\theta} = \frac{1}{K} + C \quad \text{with} \quad K = \frac{1}{55.5}\exp\left(-\frac{\Delta G^{\circ}_{ads}}{RT}\right) \qquad (5)$$

where C is the concentration of inhibitor, K is the adsorptive equilibrium constant, θ is the surface coverage and the standard adsorption free energy (ΔG_{ads}).

The relationship between C/θ and C presents linear behaviour at all temperatures studied (Fig. 6) with slopes equal to unity (1.008). The correlation factor is 0.99997. This suggests that the adsorption of henna extract on metal surface followed the Langmuir adsorption isotherm. From the intercepts of the straight lines C_{inh}/θ-axis, K value calculated is 266738 L/mol. The standard free energy of adsorption (ΔG_{ads}) value deduced is -42.31 kJ/mol. The negative values of ΔG_{ads} indicate the stability of the adsorbed layer on the steel surface and spontaneity of the adsorption process.

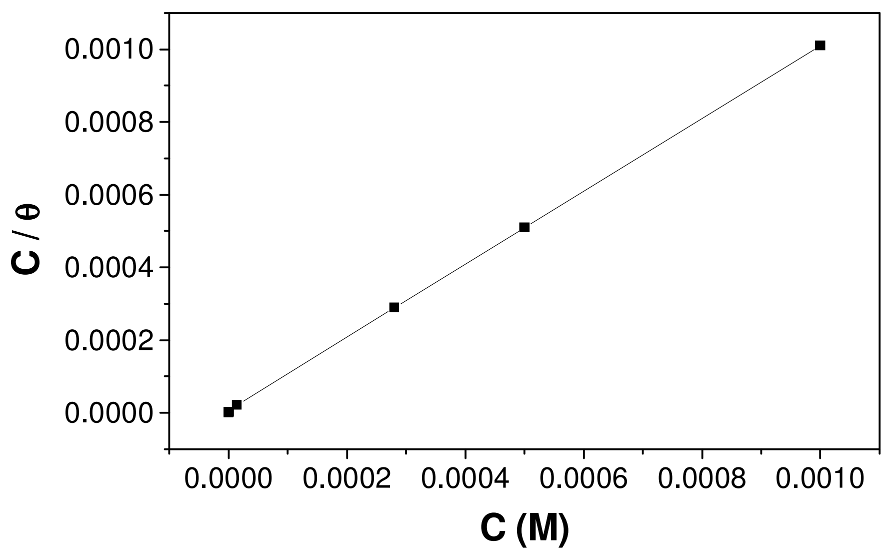

Figure 6. Langmuir adsorption plots for C38 steel in 1 M HCl at 35 °C.

Generally, an adsorption process suggests either physisorption or chemisorption. ΔG_{ads} value lower than -40 kJ/mol are related to the chemisorption between charged molecule and charged metal [26-28].

4. CONCLUSION

The study of effect of black pepper and piperine on the corrosion of steel in molar HCl conducted by weight loss method may draw the following conclusions:

1. The BP extract acts as an efficient inhibitor for corrosion of C38 steel in HCl medium; the inhibition efficiency increases with increase of inhibitor concentration to attain a maximum value of 95.8% at 2 g/L.

2. Addition of isolated molecule of piperine also gives an opportunity to use these natural compounds as efficient inhibitor for C38 steel. Its inhibition attains 99% at 10^{-3}M.

3. Temperature effect shows that piperine exhibits constant efficiency until 60°C which is recommended for industrial descaling.

4. Piperine adsorbs on the metal surface according to the Langmuir isotherm with more probable chemisorption phenomenon.

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Figure 1. Inhibition efficiencies Corrosion rate for mild steel coupons with and without MAB in 1 M HCl at 308 K. The excellent inhibition efficiency of new synthesized corrosion inhibitor for mild steel coupons in corrosive environment was attributed to the existence of a number of heteroatoms (Nitrogen and oxygen), aromatic rings and the system Î±,Î²-unsaturated carbonyl compound in MAB molecule in addition to big molecular structure of MAB.Â 0.2 0.3 0.4 Concentrations (mM). 0.5. Figure 2. Effect of various concentrations of MAB on the inhibition efficiency for mild steel coupons in 1 M hydrochloric acid at 303 K. 3.2. Adsorption Isotherms. The values obtained for surface coverage (Î¸) were used by The acid extract of Digera muricata is controlling the corrosion of mild steel in 1M HCl has been studied by weight loss method and electrochemical impedance spectroscopy in the absence and presence of Digera muricata extract at different time interval and temperature. The inhibition efficiency increases with increase the concentration of Digera muricata extract and immersion period. The inhibition efficiency increased with increasing temperature. The negative value of the free energy of adsorption indicates spontaneous adsorption. The Digera muricata extract obeys Temkin and Frenmdlich adsorp Several studies have investigated the effect of temperature on the inhibition of steel corrosion in acidic environments in the presence of green inhibitors [16, 17]. For instance, Ituen et al. [18] have studied the effect of temperature on the mild steel corrosion in 1 M H2SO4 in the presence of leaves and stems extracts of Sida acuta. Also, Afia et al.Â [21] has assessed the inhibitory potential of Ficus tikoua leaves extract on C-steel corrosion in 1 M HCl media at varying temperatures. On the other hand, the comparison of thermodynamic results obtained on the corrosion process in the presence and absence of inhibitors provides some conclusions regarding the inhibiting mechanism [22]. The present study investigates the inhibitive effect of leaves (ELV) and roots (ERT) extracts of Eichhornia crassipes on mild steel corrosion in HCl solutions using gasometric technique and its modelled structures provides additional insight into the mechanis m of inhib itory action. 2. Materials and Methods. 2.1. Metal S peci men. The mild steel sheets used in this present work have the composition presented in Table 1. Before measurements, the mild steel coupons were mechanically polished with series of emery paper of variab le grades starting with the coarsest and proceeding in steps to the