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Green Approach to Corrosion Inhibition by Black Pepper Extract in Hydrochloric Acid Solution

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Abstract: In the present work the corrosion inhibition of mild steel in hydrochloric solution by Black pepper extract (*Piper nigrum* fem. *Piperaceae*) was studied. The techniques employed for study were mass loss measurements, potentiodynamic polarisation, linear polarization resistance and electrochemical impedance spectroscopy (EIS). The results obtained revealed that Black pepper extract was a good corrosion inhibitor for mild steel in hydrochloric acid medium and maximum inhibition efficiency (98%) was found at 120 ppm at 35 ºC. Potentiodynamic polarization curves showed that black pepper extract is a mixed-type inhibitor. EIS showed that the charge transfer controls the corrosion process in inhibited solutions. Adsorption of the inhibitor on the mild steel surface followed Langmuir adsorption isotherm. The value of the free energy of adsorption, ΔG_{ads}, indicated that the adsorption of inhibitor molecules was typical of chemisorption. The results obtained show that the Black pepper extract which mainly contains alkaloid 'Piperine' could serve as an excellent green inhibitor for corrosion of mild steel in acid solutions.

Keywords: Corrosion, metals and alloys, inhibition efficiency, black pepper extract, potentiodynamic polarisation.

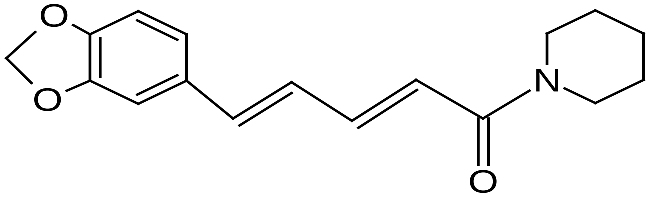
1. INTRODUCTION

Aqueous solutions of acids are among the most corrosive media. The inhibition of iron corrosion by organic additives has been studied widely [1-4]. A considerable amount of interest has been generated in the study of organic compounds as corrosion inhibitors owing to their usefulness in several industries: during the pickling of metals, cleaning of boilers, acidification of oil wells, etc. [5, 6]. Most acid corrosion inhibitors are nitrogen, oxygen and / or sulphur containing organic compounds [7, 8]. But, unfortunately most of them are highly toxic to both human beings and environment. Hence use of natural products which are eco-friendly and are being used as corrosion inhibitors. Now the development of corrosion inhibitors of natural source and non-toxic type has been considered more important and desirable [9].

The extract of black pepper (*Piper nigrum* fem. *Piperaceae*) is a rich source of alkaloid piperine alkaloid and traces of other alkaloids like piperidine, piperettine and piperanine [10]. In continuation of our work on development of green corrosion inhibitors [11-14] we have studied the corrosion inhibition behaviour of Black pepper extract on mild steel in hydrochloric acid solutions.

2. MATERIALS AND METHODS

AR grade HCl (Merck) and deionised water were used for preparing test solutions of hydrochloric acid for all experiments. Preparation of Black pepper extract was made as follows. Placed 30 gm of ground black pepper and 2 gm of calcium carbonate in 500 ml boiling flask add 200 ml of isopropyl alcohol and then refluxed the contents for 1h on steam bath. Filter the mixture and transfer the filtrate in 500 ml boiling flask and distilled off isopropyl alcohol and left 20 ml. Transfer this solution to 50 ml Erlenmeyer flask and make it cool for crystallization of piperine. The filtered product washed with little of methanol; Yield, 1gm [15]. The name and structural formulae of the major constituents present in black pepper extract are given in Fig. (**1**).



Piperine

Fig. (1). Chemical structure of piperine.

Mild steel coupons having composition (wt.%) of C = 0.17; Mn = 0.46, Si = 0.26, S = 0.017, P = 0.019 and remainder as Fe were used for the study. MS coupons of size 2.5 cm × 2.0 cm × 0.025 cm were used for mass loss study. The coupons were degreased with acetone and all experiments for mass loss studies were performed as described earlier [16]. The percentage inhibition efficiency (% IE) was calculated using equation:

$$IE(\%) = \frac{W_0 - W_i}{W_0} \times 100 \qquad (1)$$

where, W_0 and Wi are the mass loss of mild steel coupons in absence and presence of inhibitor respectively. The corrosion rate (CR) was calculated as (mm/ y) using the equation:

$$CR(mm/y) = \frac{k\ w}{ATD} \qquad (2)$$

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where, k is the proportionality constant and equals to 87.6, w = corrosion mass loss in mg, A = exposed area in cm^2, T = immersion time in hour, and D = density of mild steel in g/cm^3.

For electrochemical measurements, mild steel of the same composition coated with commercially available lacquer with an exposed area of 1 cm^2 were used and experiments were carried out in aerated solution without stirring at constant temperature of 30 ± 2 ˚C as per ASTM, American Society for Testing and Materials [17]. The electrochemical experiments were carried out in a conventional three electrodes cell assembly consisting of a mild steel coupon of the size 1 cm^2 as a working electrode, a large rectangular platinum foil was used as counter electrode and saturated calomel electrode (SCE) as reference electrode. All electrochemical measurements were carried out using G300-45050 Potentiostat/Galvanostat (Gamry-Instruments Inc., USA).

The polarization studies were carried out in the potential range -0.25 V to + 0.25 V against the corrosion potential at a sweep rate 0.5 mVs^{-1} to study the effect of inhibitor on the corrosion of mild steel. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (i_{corr}). The inhibition efficiency (%IE) was evaluated from the measured i_{corr} values using the relationship:

$$IE\,(\%) = \frac{i_{corr} - i_{corr\,(inh)}}{i_{corr}} \times 100 \qquad (3)$$

where i_{corr} and $i_{corr\,(inh)}$ is the corrosion current density value in absence and in presence of inhibitor respectively. The linear polarization studies were carried out from cathodic potential of -0.02V *vs* corrosion potential to an anodic potential of +0.02V *vs* corrosion potential at a sweep rate 0.125 mVs^{-1} to study the polarization resistance (R_p).

Electrochemical impedance measurements were performed using A.C. voltage amplitude 10 mV in the frequency range 100 kHz – 0.01 Hz. The values of charge transfer resistance (R_t) and double layer capacitance (C_{dl}) were obtained using Nyquist and Bode plots [18]. The inhibition efficiency was calculated from the charge transfer resistance values using the following equation:

$$IE\,(\%) = \frac{R_{ti} - R_{to}}{R_{ti}} \times 100 \qquad (4)$$

where, R_{t0} and R_{ti} is the charge transfer resistance without and with inhibitor. The double layer capacitance (C_{dl}) values have been estimated from the impedance value using bode plot by the formula:

$$|Z| = \frac{1}{2\pi\, f_{max}\, C_{dl}} \qquad (5)$$

3. RESULTS AND DISCUSSION

3.1. Mass Loss Studies

The values of percentage inhibition efficiency (% I.E.) and corrosion rate (CR) obtained from mass loss measurements at different concentrations of Black pepper extract at 35˚ C are summarized in Table **1**. It was found that extract inhibits the corrosion of mild steel in HCl solution at all the concentrations used in this study viz. 30 ppm to 120 ppm. It was observed that inhibition efficiency increases with increasing concentration of inhibitor and maximum efficiency was observed at 120 ppm. This excellent inhibition efficiency of pepper extract may be attributed to the formation of a barrier film due to adsorption of inhibitor molecules on metal surface involving interactions between pi electrons of inhibitor molecules and vacant d-orbitals of Fe surface atoms [19].

Table 1. Corrosion Parameters for Mild Steel in 1M HCl in Absence and Presence of Various Concentrations of Black Pepper Extract from Mass Loss Measurements at 35˚C for 3 h

Inhibitor	Concentration (ppm)	Mass Loss (mg)	I.E. (%)	Corrosion Rate (mmpy)
1M HCl	0.00	106	0.00	39.34
Black Pepper Extract	30	15	85.85	5.57
	60	4	96.22	1.48
	120	2	98.11	0.74

The variation of inhibition efficiency with acid concentration is shown in Fig. (**2**). It was found that inhibition efficiency slightly decreases (98 % - 94 %) with increase in acid concentration from 1 M to 2 M. The effect of immersion time on inhibition efficiency is shown in Fig. (**3**). It has been observed that increase in immersion time from 3 - 9 h did not cause any significant change in inhibition efficiency, suggesting that inhibitor is effective in acid solution over this immersion range.

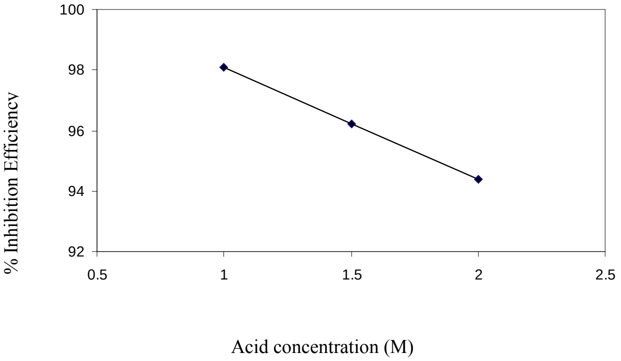

Fig. (2). Variation of inhibition efficiency with acid concentration (M).

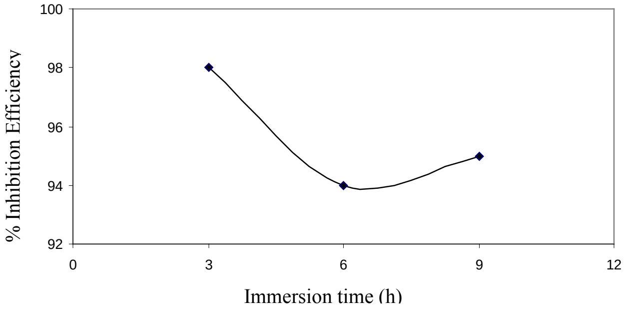

Fig. (3). Variation of inhibition efficiency with Immersion time (h).

The variation of inhibition efficiency with solution temperature is shown in Fig. (**4**). From the figure it is clear that increase in temperature from 35 - 55 ˚C decreases the inhibition efficiency from 98 % - 88 %, again suggesting that inhibitor is effective over this solution temperature.

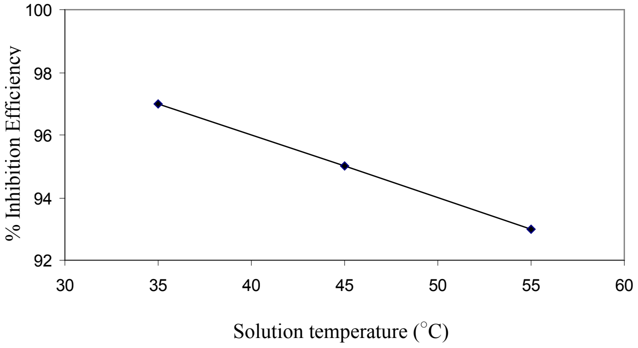

Fig. (4). Variation of inhibition efficiency with solution temperature (ºC).

The values of various thermodynamic parameters (E_a, ΔH°, ΔS° and ΔG_{ads}) evaluated from mass loss measurements [20] is summarized in Table **2**. It is found that the apparent corrosion activation energy (E_a) in inhibited system is higher (57.63 kJ / mol) than that in uninhibited system (22.91 kJ / mol). This indicates that the energy barrier for the corrosion reaction increases in presence of extract. This means that by addition of inhibitor into the acid solution, the corrosion reaction will be further pushed to a surface site, and is characterized by higher value of E_a, indicating that mild steel corrosion occurs at the uncovered part of the surface.

Table 2. Thermodynamic Activation Parameters for Mild Steel in 1M HCl in Absence and Presence of 120 ppm of the Extract

Inhibitor Concentration (ppm)	E_a (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (kJ mol^{-1})	$-\Delta G_{ads}$ (kJ mol^{-1})
1M HCl	22.91	20.29	142.60	----
Black pepper extract	57.63	55.10	62.26	39.33

The values of enthalpy of activation (ΔH°) are 20.29 and 55.10 kJ / mol in free acid solution and in presence of 120 ppm of plant extract, respectively. This indicates that addition of inhibitor retards corrosion process. The values of entropy of activation (ΔS°) are -142.60 and -62.26 kJ / mol in free acid solution and in presence of 120 ppm of extract, respectively. This indicates that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering occurs on going from reactants to the activated complex [21]. Furthermore, the value of ΔS° for inhibited system is small negative indicating that a number of water molecules on the mild steel surface are displaced by inhibitor molecules [22].

The value of free energy of adsorption (ΔG_{ads}) is -39.33 kJ / mol, suggests spontaneous adsorption of inhibitor molecules on the surface of mild steel. Generally, values of ΔG_{ads} up to -20 kJ mol^{-1} are consistent with physisorption while those around -40 kJ mol^{-1} or higher are associated with chemisorption as a result of sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of bond (chemisorption). So the adsorption of molecules of extract on mild steel surface in HCl solution was chemisorption [23].

3.2. Adsorption Isotherm

The degree of surface coverage (θ) for 120 ppm of extract in 1M HCl at 35-55°C for 3 hour immersion time were evaluated from mass loss values. The data were tested graphically by fitting to various isotherms. A straight line was obtained on plotting log θ / (1–θ) versus log C as shown in Fig. (**5**). This indicates that the extract as inhibitor found to obey Langmuir adsorption isotherm [24].

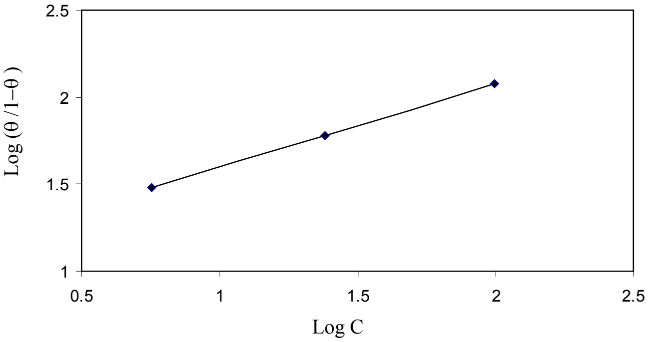

Fig. (5). Langmuir adsorption isotherm plot for the adsorption of active substance of Black pepper extract in 1M HCl on the surface of mild steel.

3.3. Potentiodynamic Polarization Studies

The potentiodynamic polarization curves for mild steel in 1M HCl in free acid solution and in presence of different concentration of extract were shown in Fig. (**6**). The various electrochemical parameters such as corrosion current density (i_{corr}), corrosion potential (E_{corr}), and Tafel constants (β_a and β_c) were given in Table **3**. It is observed that the presence of extract lowers the current density (i_{corr}) values from 501.0 μAcm^{-2} to 34.2 μAcm^{-2} without causing any significant change in corrosion potential (E_{corr}) suggesting that this extract is a mixed type inhibitor. It is also seen from Table **3** that E_{corr} values and Tafel slope constants (β_a and β_c) do not change significantly in inhibited system as compared to uninhibited system.

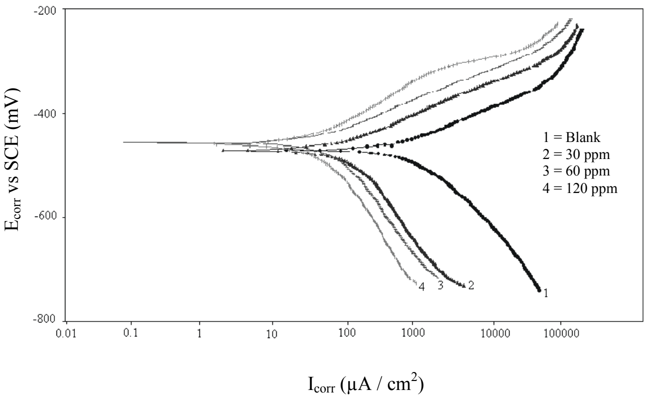

Fig. (6). Potentiodynamic polarization curves for mild steel in 1M HCl in presence of various concentration of Black pepper extract.

Table 3. Electrochemical Polarization Parameters for Corrosion of Mild Steel in 1M HCl in Presence of Various Concentrations of Black Pepper Extract

Inhibitor Concentration (ppm)	I_{corr} ($\mu A/cm^2$)	E_{corr} (mV)	IE (%)	β_a (mV/dec)	β_c (mV/dec)
Blank 1M HCl	501.00	- 476.0	---	60.30	113.40
30	85.60	- 470.0	83 %	76.40	184.80
60	45.30	- 455.0	91 %	74.80	171.80
120	34.20	-458.0	93 %	98.50	198.80

3.4. Linear Polarisation Studies

The values of polarization resistance (Rp) for mild steel in 1M HCl in presence of various concentration of extract are listed in Table **4**. From table it is clear that R_p value increases with increasing inhibitor concentration. The percentage inhibition efficiency were calculated from R_p values using following equation:

$$IE\,(\%) = \frac{R_{P(inh)} - R_P}{R_{P(inh)}} \times 100 \qquad (6)$$

where, $R_{P\ (inh)}$ and R_P are polarization resistance in presence of inhibitor and in free acid, respectively. The values % IE are listed in Table **4**.

Table 4. Linear Polarization Parameters for the Corrosion of Mild Steel in 1M HCl

Inhibitor	Concentration (ppm)	R_P (ohms)	IE (%)
Blank 1M HCl	–	28.37	–
Black Pepper Extract	30	227.30	87.52
	60	353.40	91.97
	120	707.40	95.98

3.5. Impedance Measurements

Fig. (**7**) shows impedance diagram (Nyquist plot) for mild steel in 1 M HCl in presence of various concentration of extract. The impedance data such as R_S, *R*p and C_{dl} were estimated by assuming Randles circuit (Fig. **8**). The values of charge transfer resistance (R_t) and double layer capacitance (C_{dl}) were evaluated from Nyquist and Bode plots as described elsewhere [25]. The values of R_t, C_{dl} and %IE derived from these investigations are given in Table **5**. The existence of single semicircle showed that single charge transfer process occurred during dissolution of mild steel which is unaffected by the presence of extract. It was found that addition of extract increases the values of R_t and reduces the C_{dl} values. The decrease in C_{dl} value is attributed to increase in thickness of electronic double layer [26]. The increase in R_t value is attributed to the formation of protective film on the metal-solution interface [27].

4. MECHANISM OF CORROSION INHIBITION

Corrosion inhibition of mild steel in hydrochloric acid solution by Black pepper extract can be explained on the basis of adsorption. The extract inhibits corrosion by controlling both cathodic and anodic reactions. In acidic solution the active constituent present in the extract exist as protonated species. These protonated species adsorb on the cathodic sites of mild steel and decreases the evolution of hydrogen. The adsorption on anodic sites occurs through π-electrons and lone pair of electrons on nitrogen atom of the active alkaloids found in extracts [28].

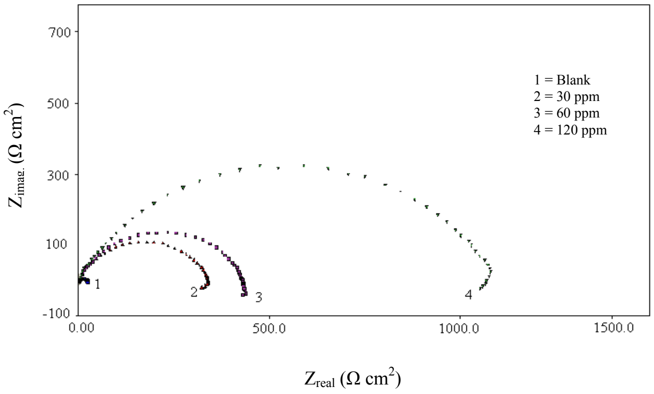

Fig. (7). Nyquist plot for mild steel in 1 M HCl in presence of different concentration of black pepper extract.

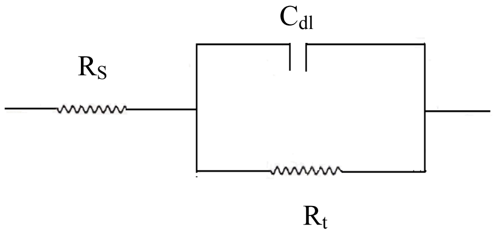

Fig. (8). Randle circuit (R_S = uncompensated solution resistance, R_t = charge transfer resistance, C_{dl} = double layer capacitance).

5. CONCLUSIONS

1. All measurements showed that the Black pepper extract has excellent inhibition properties for the corrosion of mild steel in 1 N HCl solutions. The inhibition efficiency increases with plant extract concentration and reaches its highest value at 120 ppm.
2. The inhibition efficiencies determined by potentiodynamic polarization, EIS, and mass loss methods are in good agreement.
3. Potentiodynamic polarization measurements show that the extract acts as mixed-type inhibitor.
4. EIS measurements indicate that the presence of extract increases the charge transfer resistance and shows that the inhibitive performance depends on ad-

Table 5. Electrochemical Impedance Parameters for Corrosion of Mild Steel in 1M HCl in Presence of Various Concentrations of Black Pepper Extract

Inhibitor	Concentration (ppm)	R_t (Ω cm^2)	f_{max} (Hz)	C_{dl} (μF/cm^2)	IE (%)
Blank 1M HCl	–	25.53	426.9	37.90	–
Black Pepper Extract	30	339.02	50.01	28.17	92.52
	60	431.41	44.13	25.62	94.17
	120	1079.24	33.33	14.70	97.76

sorption of the inhibitor molecules on the metal surface.

5. The adsorption model obeys the Langmuir adsorption isotherm at 35ºC.
6. The value of ΔG_{ads} indicated that the adsorption of alkaloid molecules present in extract was a spontaneous process and was typical of chemisorption.

ACKNOWLEDGEMENT

The authors are grateful to All India Council of Technical Education (AICTE) and Council for Scientific and Industrial Research (CSIR), New Delhi for financial support.

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Received: December 21, 2008 Revised: January 20, 2009 Accepted: February 5, 2009