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Corrosion Inhibition of High Carbon Steel in Phosphoric Acid Solution by Extract of Black Tea

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Authors' contributions

This work was carried out in collaboration between both authors. Author FK analysed and interpreted and prepared the manuscript and also read and approved the final manuscript. Author DKV managed the literature searches, analyses of the study performed the spectroscopy analysis and, managed the experimental process, and identified the inhibitor. Both authors read and approved the final manuscript.

Original Research Article

ABSTRACT

Black tea extract was estimated as high carbon steel corrosion inhibitor in 1 M H_3PO_4 solution using non-electrochemical technique (Weight loss, FT-IR and SEM analysis). The maximum inhibition efficiency was found to be 93.79 at 4 g/ L. The results indicated that inhibition efficiency increases as inhibitor concentrations increase. Adsorption studies exhibited that inhibitor adsorbed on the metal surface follow Langmuir adsorption isotherm. The Gibbs free energy of adsorption (Δ G_{ads} = - 9.74 kJ mol^{-1}) values strongly supported the physicochemical adsorption of inhibitor molecules over the high carbon steel surface. Scanning electron microscopy (SEM) was applied to study the high carbon steel surface in the presence and absence of extract. The adsorption mechanism of inhibitor molecule deposited on the metal surface was investigated by Fourier transform infrared spectroscopy.

Keywords: Adsorption; corrosion; mild steel; weight loss.

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1. INTRODUCTION

High carbon steel (HCS) is one of the most frequently used constructional materials in various industries due to its low cost, good tensile strength, and high abundance. Corrosion of metals in acidic solutions is the one of the severe problem in industrial cleaning and pre-treatment process such as acid pickling, acid descaling, and industrial acid cleaning. Hydrochloric acid, Sulphuric acid, and phosphoric acids are the extensively used acidic solutions for these applications [1-7]. Use of corrosion inhibitors is one of the most effective protection method for mild steel in various acidic solutions. Most of the corrosion inhibitors are heterocyclic organic compounds containing nitrogen, phosphorous, sulphur, oxygen and alkenes [4]. The harmful effects of most synthetic organic corrosion inhibitors are the stimulus for the use of natural inhibitors [8]. Recently, various natural plants extracts have become important as they are sustainable, renewable and eagerly available. [9] various researches have been reported using such natural plant extracts. A.M. Abder-Gaber [9] and co-workers reported the inhibitive action of extracts of Chamoline, Black cumin, Halfabar, and Kidney bean plants on the corrosion of steel in different concentrations of sulphuric acid. Taleb Ibrahim and Mehad Habbab [10] studied the inhibitive action of eggplant peel extract in the direction of the corrosion of mild steel in 2M HCl solution at different concentrations and temperatures. They indicated that the extract of the eggplant peel serve as an admirable corrosion inhibitor. Punita Mourya [11] and co-workers have investigated the extract of Tagetes erecta as a mild steel corrosion inhibitor in 0.5 M H_2SO_4 solution. The extreme corrosion inhibition efficiency 99.28% was reported for plant extract at 303 K. Tambi Ramde et al. [12] have inspected the inhibition effect of Camellia sinensis as corrosion inhibitors for Cu65/Zn35 brass alloy in 0.1 N Na_2SO_4 solution with pH 7 and pH 4. Various investigations showed that basic component of plant extracts are alkaloids, steroids, sugars, gallic acid, tannic acid and flavanoids etc. The presence of cellulose, tannins, and polyphenolic compounds have been reported to improve the protection of metal surface, thus decreasing metal corrosion [10-19].

In the present study, the effect of black tea extract was evaluated as green corrosion inhibitor for mild steel in phosphoric acid solution by using weight loss measurement, Scanning Electron Microscope (SEM), and FT-IR techniques.

Thermodynamic data were obtained from various adsorption isotherms. The objective of the present work is to estimate the inhibitive action of black tea extracts as an inexpensive and ecological corrosion inhibitor for high carbon steel in 1 M H_3PO_4 solution.

2. EXPERIMENTAL

2.1 Materials Preparation

High carbon steel specimens containing composition (wt. %) of C = 6.23%, O = 1.99, Si = 0.58%, P = 0.02%, S = 0.01%, Cr = 0.03%, Ni = 0.03 and balance Fe were used for all the experiments. coupons were cut into 5 x 2 x 0.1 cm sizes and used for weight loss measurements and surface analysis. before the measurements, the surface of high carbon steel was abraded using different grades of sic paper. the metal surface was cleaned by washing with double distilled water and acetone respectively, and dried in desiccators before immersing in the corrosive medium. for the corrosion study acidic solution was prepared by dilution of AR grade H_3PO_4 with double distilled water.100 ml volume beaker used in each experiment for concentration range of the extract 1-4 g/l.

2.2 Inhibitor Preparation

Black tea was purchased from local market, weighed and grounded. Black tea powder was refluxed for 3 h in one litre of 1 M H_3PO_4 acid [20]. Then it was filtered and filtrate was made up to one litre using the same 1 M H_3PO_4 acid solution. This solution was taken as stock solution from which solutions of varying strengths were prepared and studied as high carbon steel corrosion inhibitors in acid solution.

2.3 Weight Loss Measurement

Weight loss measurement is the easiest way to find the total weight loss, corrosion rate (ρ), inhibition efficiency (*%I*), and degree of surface coverage (θ). For weight loss measurement, the specimens of 5 x 2 x 0.1 cm size were used. The polished high carbon steel coupons were weighed and suspended in the 100 ml beaker containing test solution in the presence and absence of inhibitor. After 24 h the specimens were taken out and carefully washed with double

distilled water and ethanol, then dried and weighted with the help of metteler Toledo AL204 electronic balance, Accuracy in weighing up to 0.0001 gm.

2.4 Surface Analysis

The surface morphology of high carbon steel specimens was examined by SEM and FTIR analysis. For these studies mild steel specimen first immersed in 100 ml beaker containing 1 M H_3PO_4 solution in the absence and presence of inhibitor for 24 h. FT-IR spectra recorded by using Thermo Nicolet, AVATAR-370-FTIR (USA) over a range of 500-4000 cm^{-1} with a resolution of 4.000 cm^{-1}. Scanning electron microscope images obtained from *ZEISS EVO SEM 18* oxford model.

3. RESULTS AND DISCUSSION

3.1 Weight Loss Measurements

Table 1 shows the value of the inhibition efficiency (*%I*) corrosion rate (*ρ*) and degree of surface coverage (*θ*) with different concentrations of black tea extract for high carbon steel in 1 M H_3PO_4 solution. The corrosion rate (*ρ*) was calculated from the equation given below [5]:

$$\rho = \Delta W / At \tag{1}$$

Where ΔW is the weight loss in mg, *A* is the total area of metal specimen in cm^2, and *t* is the immersion time (24 h).with the calculated corrosion rate Inhibition efficiency (*%I*) was calculated by using the relationship [5,8]:

$$\%I = \left(\frac{\rho 1 - \rho 2}{\rho 1}\right) \times 100 \tag{2}$$

Where ρ1 and ρ2 are the corrosion rates of the mild steel specimens in the absence and presence of inhibitor, respectively.

The values of corrosion rate (*ρ*), inhibition efficiency (*%I*), and surface coverage (*θ*) obtained with high carbon steel specimens in 1 M H_3PO_4 solution. These parameters were evaluated in the absence and presence of inhibitor. From the Table 1, it is evident that inhibition efficiency increases with increase inhibitor concentration. Fig. 1, shows the inhibition efficiency with various concentrations of inhibitors. Study of corrosion rate and weight loss at various experimental with concentration shows in Fig. 2 and Fig. 3 respectively. The variation of inhibition efficiency with temperature is a very important tool as it is used to evaluate the mode of adsorption of inhibitors on the metal surface.

Table 1. Weight loss result of high carbon steel in 1 M H_3PO_4 solution for 24 h immersion time in the presence and absence of different concentrations of inhibitor

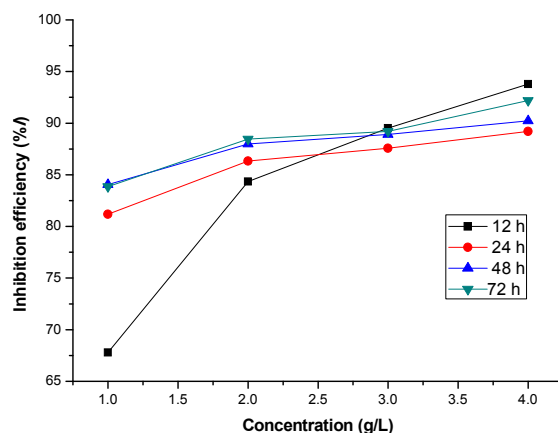| Time (h)	Conc. ($g\ l^{-1}$)	Corrosion rate $\rho(mg\ cm^{-2}h^{-1})$	Inhibition efficiency (*%I*)
12	blank	0.677	-
	1	0.218	67.79
	2	0.106	84.34
	3	0.071	89.51
	4	0.042	93.73
24	blank	1.223	-
	1	0.230	81.19
	2	0.167	86.34
	3	0.152	87.57
	4	0.132	89.21
48	blank	1.524	-
	1	0.243	84.04
	2	0.183	87.99
	3	0.169	88.91
	4	0.149	90.22
72	blank	1.741	-
	1	0.281	83.85
	2	0.201	88.45
	3	0.188	89.20
	4	0.136	92.19

Fig. 1. The relationship between Inhibition efficiency and concentration at different immersion period
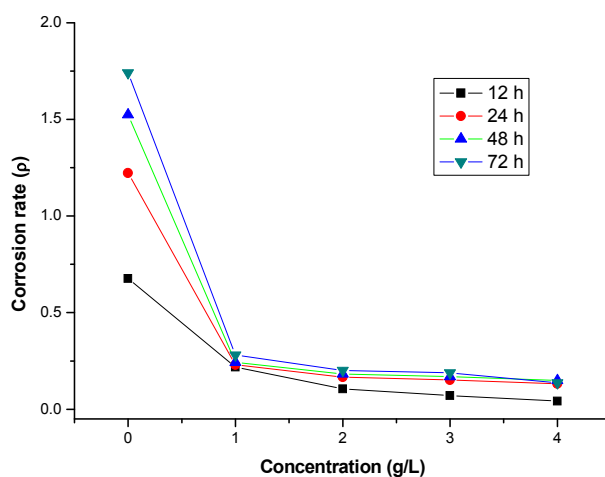

Fig. 2. The relationship between corrosion rate and concentration at different immersion period

3.2 Adsorption Isotherm

The adsorption of the inhibitor molecules on metal surface is influenced by the nature of the metal surface, distribution of the charge in the molecule, the chemical structure of the inhibitor, and the type of electrolyte [7]. The adsorption isotherms provide the basic information on the interaction between the inhibitor and the metal surface [4,21]. The adsorption of main constituents of extract can be attributed to the presence of O, N, P and S atoms, p electrons, and aromatic rings. The inhibitor constituents are present as either neutral or protonated molecules in acid solutions. In general, due to the complex nature of adsorption and the inhibitive action of the inhibitor molecules, single modes of adsorption of the inhibitor on the metal surface are not possible. inhibitor molecules may be adsorbed by the metal surface by one or more of the following mechanisms: 1 electrostatic interaction between the charged molecules and the charged metal; 2 interaction of unshared electron pairs in the molecule with the metal; 3 interaction of p-electrons with the metal; and 4 a combination of 1, 2 and 3 [13]. The degree of the surface coverage (θ) at different concentrations of inhibitors has been calculated for inhibition mechanism. These Calculated θ values were used to determine the adsorption isotherm best

fits the surface coverage data. The correlation coefficient was used to determine the fitting of the experimental data to those isotherms. Linear relationship between θ value and inhibitor concentration C must be found in order to obtain the adsorption isotherm. Several adsorption isotherm models such as Temkin, Frumkin, Langmuir and Flory-Huggins were attempted to fit the θ values. It was found that adsorption of this inhibitor followed the Langmuir adsorption. Usually Chemisorption or physisorption phenomenon attributing to Langmuir adsorption [22]. The Langmuir adsorption isotherm is given by [9,15]:

$$\frac{C}{\theta} = \frac{1}{Kads} + C \qquad (3)$$

Where θ is the surface coverage, K_{ads} is adsorptive equilibrium constant, and C is the equilibrium inhibitor concentration. The plot of C_{inh}/θ versus C_{inh} with slope around unity gives the best fitted straight line [Fig. 4]. Correlation coefficient (r^2) obtained from straight line equation, used to choose the adsorption isotherm that best fit experimental data. K_{ads} value can be calculated from the intercept of the straight lines C_{inh}/θ. The most important thermodynamic adsorption parameters, adsorption free energy (ΔG_{ads}) was evaluated and value shows the physisorption mechanism on metal surface. The relationship between the adsorption constant, K, and the free energy of adsorption, ΔG_{ads} shown in equation given below [6,16].

$$\Delta G_{ads} = -RT \ln (55.5\ K_{ads}) \qquad (4)$$

Where R is gas constant, T is temperature, and K is the binding constant. The negative value of ΔG_{ads} (-9.74 kJ mol^{-1}) indicate the good interaction between the inhibitor molecules and the high carbon steel surface [21,16]. Generally, the standard free energy of adsorption values of -40 kJ mol^{-1} or more negative value involve charge transfer or sharing between inhibitor molecules and metals show the chemical adsorption those of -20 kJ mol^{-1} or less negative value are associated with physisorption [14,11]. Therefore for present study the value of ΔG_{ads} (-9.74 kJ mol^{-1}) has been considered less negative value within the range of physical adsorption.

3.3 FT-IR Analysis

Fig. 5 shows the spectrum of black tea extract and scrapped sample, the broad band at 3446.49 cm^{-1} can be assigned because of stretching mode of a hydroxyl or N–H group. Absorption peak at 1639.08 cm^{-1} may be assigned stretching mode of carbonyl (C=O) group. Therefore, based on above results it is evidence that the extracted organic compounds are stable in 1 M H_3PO_4 [9,23]. In case of scrapped sample (Fig. 5b.) significant changes were observed in the spectrum in comparison to that of inhibitor. Broad band at 3446.49 cm^{-1} shifted to 3392.22 cm^{-1} and peak at 1639.08 cm^{-1} shifted to 1627.00 cm^{-1}. Also the peaks at 1077.03 cm^{-1} shifted to 1022.14 cm^{-1}. All these significant changes in peaks show that the inhibitors interacted on the metal surface [1,22].
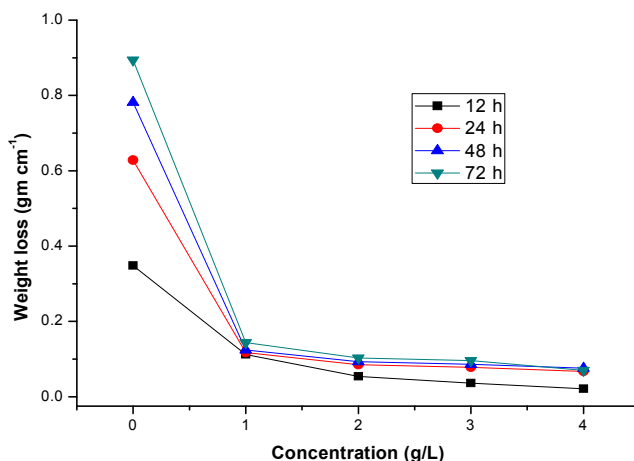

Fig. 3. Variation of weight loss against concentrations for mild steel in 1 M H₃PO₄ solution
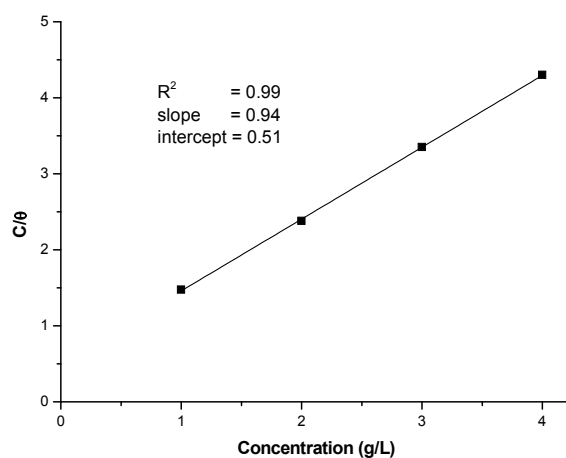
Fig. 4. Langmuir adsorption plot of black tea extract at different concentrations
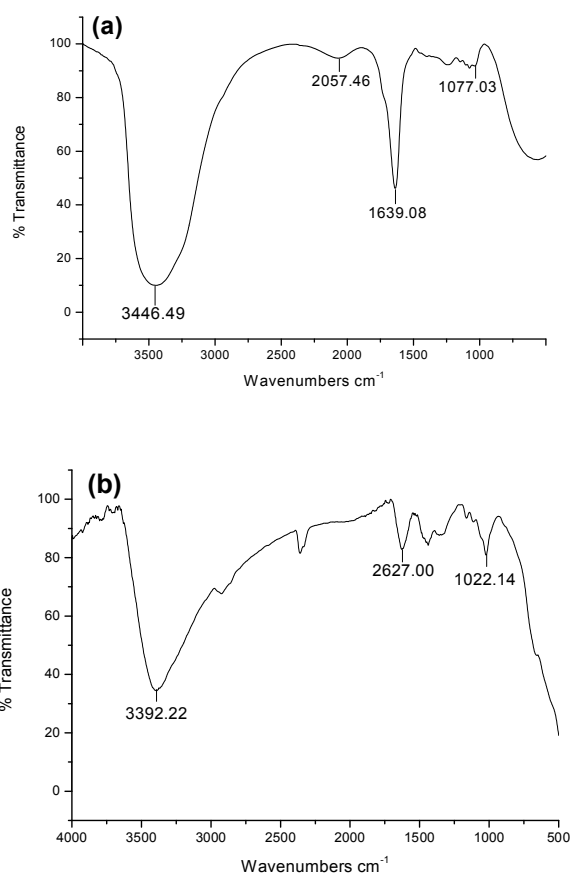

Fig. 5. FT-IR spectra of (a) inhibitor and (b) scrapped samples

3.4 SEM Analysis

The SEM images of metal surface before and after exposing to acidic solution in the absence and presence of inhibitor for 24 h are shown in Fig. 7. It shows the abraded high carbon steel surface before immersion in corrosive solution and Fig. 7b and Fig. 7c shows the SEM images of high carbon steel surface that was immersed in 1 M H_3PO_4 solution in the absence and presence of inhibitor for 24 h, respectively. The SEM image of high carbon steel surface in

Fig. 7a shows the plane surface. Whereas from Fig. 7b it is obviously seen that the metal surface was severely corroded due to presence of corrosive solution. However the appearance of high carbon steel surface is different after the addition of the inhibitor solution shown in Fig. 7c. The uniform distribution of inhibitor on the high carbon steel surface prevent the further corrosion. This protective film is very stable even for 72 h of immersion period [Fig. 7d] [23].

4. MECHANISM OF INHIBITION

Corrosion inhibitors are found to protect mild steel corrosion in acidic solution by adsorbing themselves on mild steel surface. Adsorption can be defined by two main types of interaction: 1 *Chemisorption*, involves charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate type bond. 2 *Physisorption*, involves electrostatic forces between ionic charges on the adsorbed species and the electric charge at the metal/solution interface [2,5]. In case of physisorption the heat of adsorption is low and therefore this type of adsorption is stable only at comparatively low temperatures. Black tea contain caffeine, catechines [Fig. 6], saponin and various organic molecules. This could be explained based on the hypothesis that in the presence of acid solutions polar atoms (N, O, and S) of inhibitor molecules protonated and the negatively charged PO_4^{3-}

would attach to positively charged surface (Fe^{2+}). When inhibitor molecules adsorbs on the steel surface, electrostatic interaction takes place between charged molecules on the metal surface. A close examination of the chemical structure of caffeine and catechines [Fig. 6], exposes that inhibitor molecules have structure characterized by the presence of chelation centres mainly located on nitrogen and oxygen. N and O are the likely locations of complexion of inhibitor molecules with the Fe^{2+} on metal surface, which will result in the formation of a five-membered chelate rings. Such protective film covered the metal surface isolating the metal surface from the corrosive media from further corrosion [19]. In the present study the value of free energy of adsorption, ΔG_{ads} (-9.74 kJ mol^{-1}) has been considered less negative value within the range of physical adsorption [22].

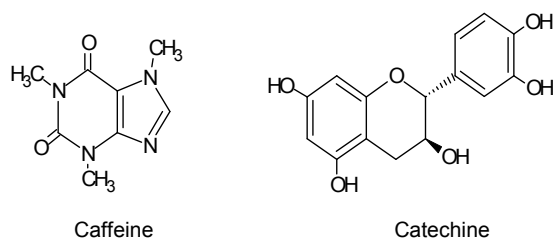Caffeine   Catechine

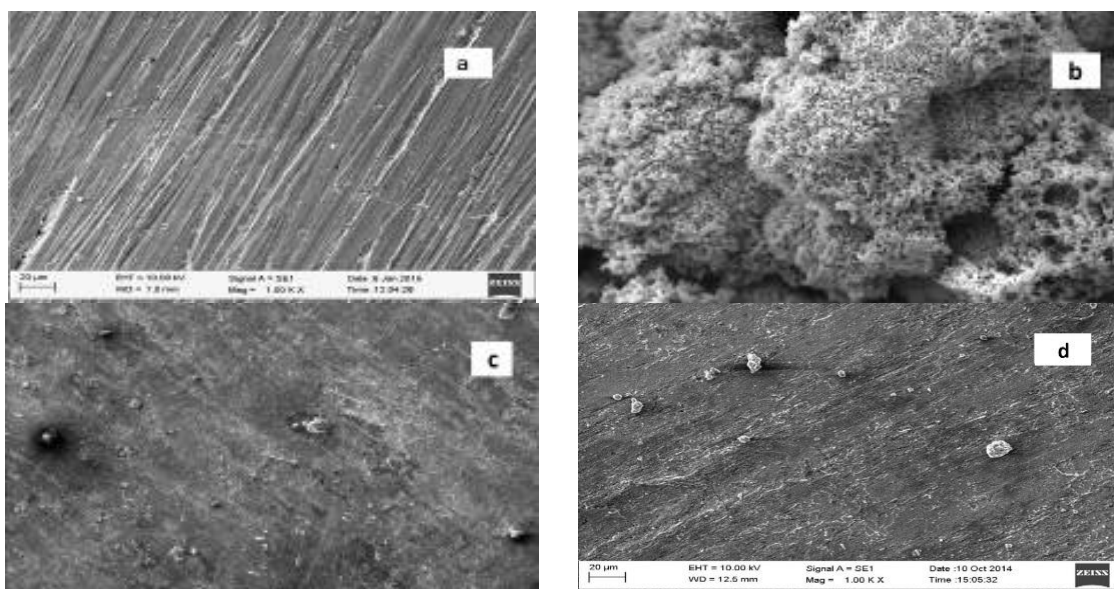**Fig. 6. Molecular structure of main constituents of tea leaves**

Fig. 7. SEM images of high carbon steel surfaces a polished high carbon steel b high carbon steel after immersion in 0.5 M HCl c & d high carbon steel after immersion into inhibitor solution for 24 h and 72 h respectively

5. CONCLUSION

Results of weight loss measurement shows that black tea extract acts as a good high carbon steel corrosion inhibitor in 1 M H_3PO_4. The inhibition efficiency increases with the increase in inhibitor concentration. The maximum inhibition efficiency value of 93.79 was obtained for 4g/l inhibitor concentration. The adsorption of black tea extract follows the Langmuir adsorption isotherm. Values of free energy of adsorption indicates that the adsorption of black tea extract on the high carbon steel surface involves the physical adsorption process. SEM analysis results show that inhibitor molecules form protective layer over the metal surface and prevent from the further corrosion. The result obtained from FTIR spectra provide the strong interaction between inhibitor molecules and high carbon steel surface.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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