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RESEARCH ARTICLE

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The effects of black tea extracts on the corrosion inhibition of mild steel in acidic solution

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ABSTRACT

It was examined to evaluate the effectiveness of extracted tea leaves as the green corrosion inhibitor that contains mild steel in acidic solvents. The test specimens were dissolved in an acidic solution with different concentrations of the extracted tea leaves. After 3 hours of immersion, the corrosion rate (CR) was measured. The results showed that a concentration of 1000 mg/l caused a significant inhibition in corrosion rate as compared to control. To see how black tea (BT) extract affected mild steel corrosion in 1 M HCl, it was subjected to a loss of weight procedure. The corrosion level and the inhibitor's performance were examined at five different BT extract concentrations, including 0.4, 1, 1.4, 2, and 2.4 g/l. According to the findings, increased BT concentration at every temperature decreased CR. As a result of the rise in kinetic activities of the metal surface interface, typically, temperature elevation leads to an increase in CR at every concentration of BT extract. The study's findings showed that adding 2.4 g/l of inhibition efficiency resulted in a temperature of 323 K, resulting in 84.95% inhibition efficiency. The small activation energy (Ea) of 8.74 and 11.45 kJ/mole reflected the barrier layer properties of BT extract and its chemical interactions on mild steel surfaces. The thermodynamic parameter revealed the spontaneous interaction between BT extract species and steel surface as k_{ad} rose from 0.929 to 1.728 $(g/l)^{-1}$.

1. INTRODUCTION

Metallic equipment corrosion has always been the biggest challenge in any manufacturing industry. The metal component exposed to a corrosive environment attack may impact the performance of the overall process [1]. Steel is considered one of the most popular alloys used extensively in mechanical equipment and industries like heat exchangers, boilers, and pipelines. The degradation of metal results in economic costs and could cause plants to shut down due to the harmful effect of corrosion on the product quality [2]. Many industries and operations use highly acidic media, especially HCl [3]. Acidity conditions may decline the equipment's service life; therefore, various corrosion control and monitoring techniques are used to prevent component failure [2-4]. Corrosion inhibitors are an essential method commonly used in aggressive environments to reduce, slow down, or delay corrosion of the components [5]. The dosage of the chemical substance should be in a specified treatment to work as an inhibitor, which could significantly improve the corrosion resistance

and is considered a good protection technique for mild steel in various acidic solutions [6]. Chemical inhibitors are either inorganic or organic compounds. As the literature describes, most effective inorganic inhibitors like the sodium salts of chromate, molybdate, and others naturally form a passivation film due to oxidation [4]. These inhibitors, which accumulate on the metal surface and create a barrier film, primarily comprise oxygen, sulfur, nitrogen, alkenes, and phosphorous.

They are costly, dangerous, and may have devastating consequences for the ecosystem and physical health regarding chemical inhibitors. Green corrosion inhibitors have become popular recently because they are naturally safe, biodegradable, cost-effective, accessible, and free of harmful chemicals [7-9]. Various researchers have explored chemical inhibitors such as ferrous sulfate treatment [10], coating [11], and seeds and leaves of plant extracts [12-17]. It was found that green inhibitors could successfully reduce the corrosion rate and impede the growth of various microorganisms and fungi. Previous studies using natural inhibitors have shown that high levels of extract concentration do not affect eliminating corrosion. Thus, the black tea extract is applied as a green inhibitor to protect mild steel against corrosion in an acid solution by measuring the rate of metal removal at different temperatures and low concentrations of black tea extract from (0.4 to 2.4) g/l. The current approach includes the calculation of the kinetics and thermodynamics parameters with and without using inhibitors.

2. EXPERIMENTAL WORK

2.1. Mild steel specimens and solution preparation

A mild steel plate was cut in half to create a standard 30 x 20 x 2 mm size. The findings were pulverized using silicon carbide abrasive paper of (320-1000) grades for the oxide film to be removed. After that, the specimens were cleaned with water, polished, acetone-dried, and kept at 25 degrees Celsius for weight loss checks. Also, aggressive solutions of 1 M hydraulic acid were produced by diluting 37% HCl with distilled water and used as electrolytes for measurements.

2.2. Preparation of BT solutions extract

The packaged tea was bought at a nearby market and used to make black tea. The solution of BT extract was prepared by an aqueous solvent technique. 6 grams of BT was dissolved in 800 milliliters of boiling distilled water for exactly 90 minutes. The extract solution was then filtered and concentrated under a vacuum at 40 degrees Celsius for two hours. The 40ml extract was stored in the refrigerator for future use.

2.3. Weight loss measurements

An appropriate technique to assess corrosion is the analysis of loss of weight. A succession of emery papers was ground with mild steel coupons, then cleaned with acetone and dried at 25 degrees Celsius. The items were then weighed and put in a hundred milliliters of HCl, in the presence and absence of BT extract of different concentrations. A thermostatically regulated water bath was utilized to provide a steady temperature during the research at 293, 303, 313, 323, and 333 K. After three hours, the specimens were extracted and tested again using distilled water. Weight loss data was applied to determine the metal removal rate with Equation 1. [18].

$$CR\ (mm/y) = (87.6\,W)/D.A.T \quad (1)$$

One mm/y denotes 39.37 mpy, and CR represents the rate of corrosion in millimeters/year. W represents mg of weight loss, A reflects the whole opened surface area of the coupon in cm^2, T refers to the time of immersion (hours), and D equals 7.86 g/cm^3 is the specimen density.
Inhibition efficiencies (IE %) were computed from Equation (2) [19].

$$IE\% = \frac{CRo}{CRo - CR_{inh}} \quad (2)$$

Whereas CR_o, CR_{inh} are the corrosion rates in the absence and the presence of an inhibitor.

3. RESULTS AND DISCUSSION

3.1. The rate of corrosion

Table 1. The corrosion parameters were examined with and without different black tea extract concentrations levels after the weight loss was measured in 1 M Hydrochloric acid at different temperature.

BT extract concentration (g/l)	Temperature (K)									
	293		303		313		323		333	
	CR (mm/y)	IE%	CR (mm/y)	IE%	CR (mm/y)	IE%	CR (mm/y)	IE%	CR (mm/y)	IE%
Blank	19.33	-	23.52	-	30.22	-	36.01	-	40.22	-
0.4	12.50	35.33	14.24	39.47	15.35	49.22	16.68	53.66	19.84	50.66
1	11.05	42.82	12.08	48.62	13.40	55.64	15.69	56.42	18.42	54.20
1.4	8.79	54.52	10.50	55.34	10.99	63.62	11.66	67.61	15.96	60.31
2	6.67	65.49	7.24	69.20	8.39	72.23	9.27	74.25	11.95	70.27
2.4	4.33	77.56	4.68	80.08	5.25	82.61	5.41	84.95	8.24	79.51

The explanatory information is listed in Table 1. The CR measured was reduced due to the BT extract concentration increased at all temperatures. For example, the CR fell from 19.33 to 12.50 mm/y when 0.4 g/l BT extract was added to an empty acidic solution at 293 K. Also, in these experiments, the CR was clearly shown to be about five times less than in the use of 2.4 g/l BT. In addition, at all checked temperatures, the corrosion rate declines as the BT extract inhibitor concentration improves. As the BT concentration increases, the corrosion rate drops even at 293 K. In other words, when BT extract is introduced into an acidic solution to inhibit the corrosion process (to lower CR), it increases the protective effects on a steel surface. This confirms that BT extract has antimicrobial activity against various microorganisms and exerts a protective effect on metal surfaces [20]. In addition, when BT extract was present, a significant decline in CR was seen at elevated temperatures. The obtained results confirm the extract's 323 K high-temperature stabilities. This may be due to the high-temperature stability of the BT matrix [21], which resists degradation or interaction with other substances in the solution.

3.2. The inhibition efficiency

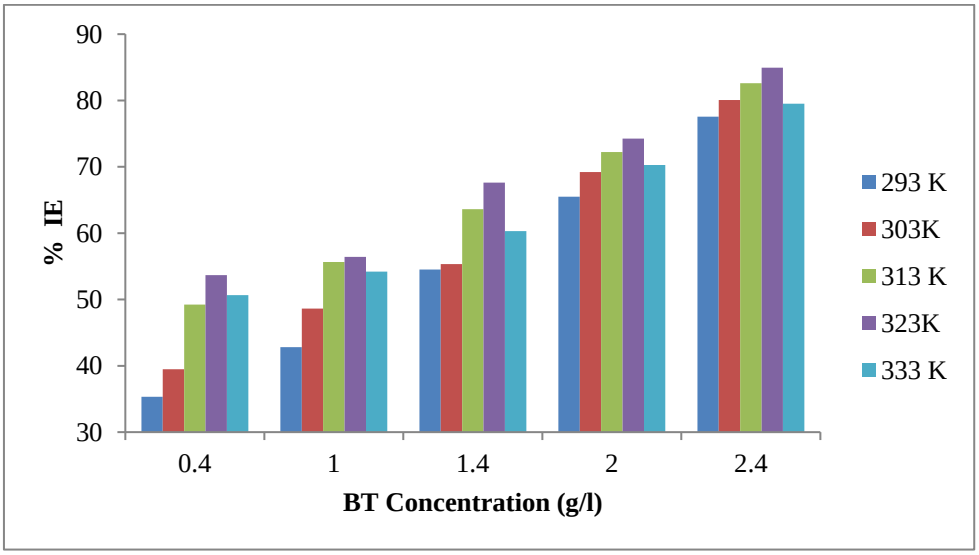

Figure 1. Variation of IE percentage with various BT concentrations and temperatures.

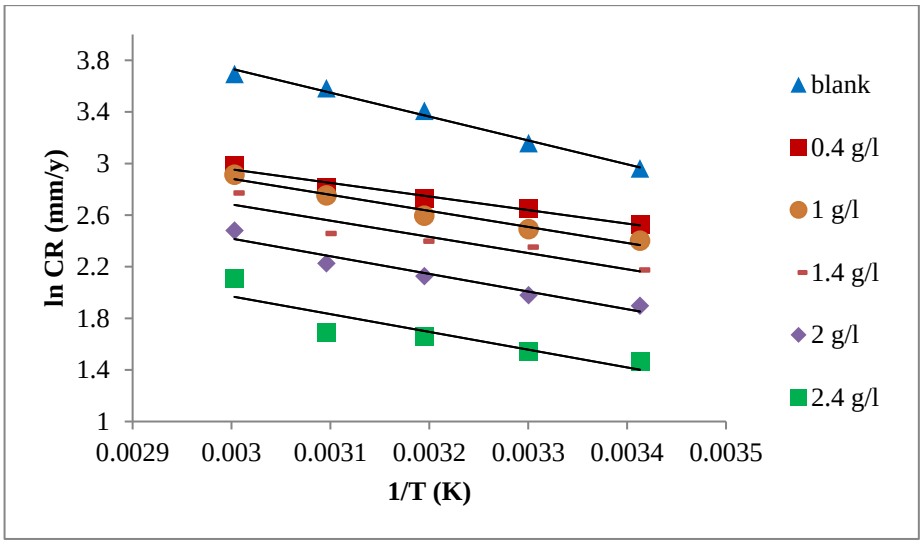

Figure 2. The Arrhenius plots of mild steel corrosion, alone and with conjunction of BT extract, in 1M HCl.

Percentage inhibition efficiency data are presented in Figure 1. via the corrosion rate computation. The obtained results confirmed that IE % increased as the BT extract concentration rose. The absorption of BT extract onto mild steel surfaces, which stopped active metal sites and avoided the corrosive attack by acid solution, is the basis for this increase in the number of components in BT extract. In addition, a temperature increase from 293 to 323K resulted in a substantial increase in the IE % (77.56% - 84.95%), owing to the thermal stability and inhibition performance of BT extract at high temperatures. Further increase in solution temperature to a value of 333 K led to a reduction in IE % (79.51%) which was most closely related to the deterioration of BT extract substance at high temperature. The increased ionic mobility may have influenced the protective activity of BT extract at the metal/electrolyte interface, which was blocked at elevated temperatures [20]. However, the direct link between the inhibitor efficiency and BT extract concentration was seen in the medium of 1 M HCl aggressiveness.

3.3. Kinetic and thermodynamic parameters

To measure kinetic and thermodynamic properties, mild steel corrosion in differing concentrations of BT was employed at various temperatures. The

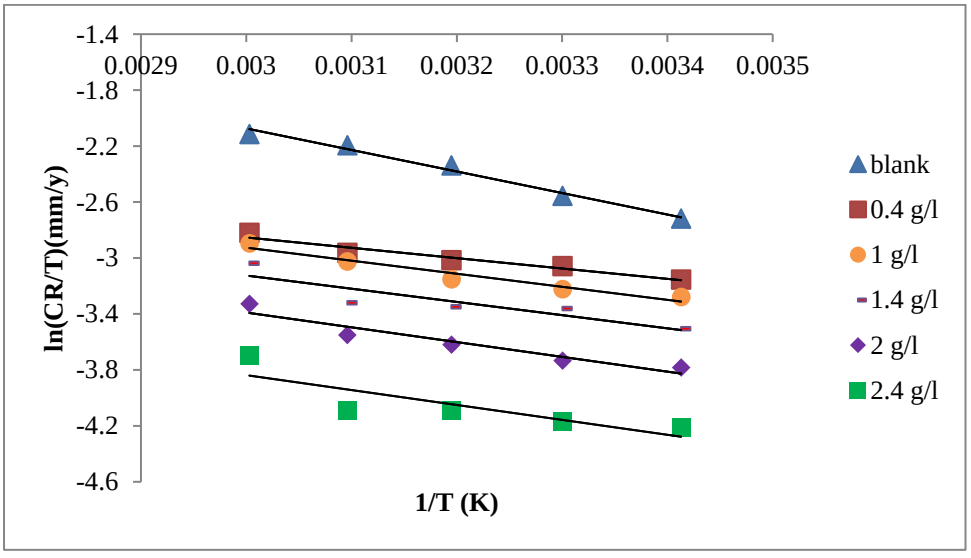

Figure 3. A graph of ln (CR/T) with 1/T with different concentrate levels of BT.

Table 2. Thermodynamic parameters at various BT concentrations.

Concentration of BT(g/l)	Ea (kJ/mol)	ΔH° (kJ/mol)	-ΔS° (J/mol.K)
Blank	15.38	12.79	21.15
0.4	8.74	6.15	5.26
1	10.35	7.76	1.06
1.4	10.45	7.85	2.42
2	11.38	8.78	1.83
2.4	11.45	8.86	5.33

Arrhenius Equation 3 [21] can be utilized to form kinetic information.

$$\ln (CR) = B - \frac{E_a}{RT} \quad (3)$$

B is the metal-dependent Arrhenius constant, whereas R is the 8.314 J/mol.k uniform gas constant. The activation energy (Ea) was computed from a slope of an ln CR against 1/T presented in Figure 2. The enthalpy (ΔH°) and entropy (ΔS°) were computed by the transition state Equation 4.

$$CR = \frac{RT}{Nh} \exp\left(\frac{\Delta S^o}{RT}\right) \exp\left(\frac{-\Delta H^o}{RT}\right) \quad (4)$$

N denotes Avogadro's number, and h refers to Planck's variable. After plotting ln (CR/T) versus 1/T, the magnitude of ΔH° and ΔS° were determined from a straight line with a slope and intercept as shown in Figure 4. Then, the obtained results are demonstrated by Table 2.

In the presence of BT extract, BT molecules absorbed on a metal surface [22] may require relatively low activation energy values. BT extract may also have antioxidant properties [22]. Furthermore, the decrease in Ea values observed in treated specimens was attributed to the coordination compound generated between metal and BT extract molecules. This action effectively ensured that the thick blocking layer was generated by BT extraction. A thick film hampered steel dissolution because of the hydrocarbon chain orientation to the acid solution [23,24].

3.4. Adsorption isotherm and Gibbs energy

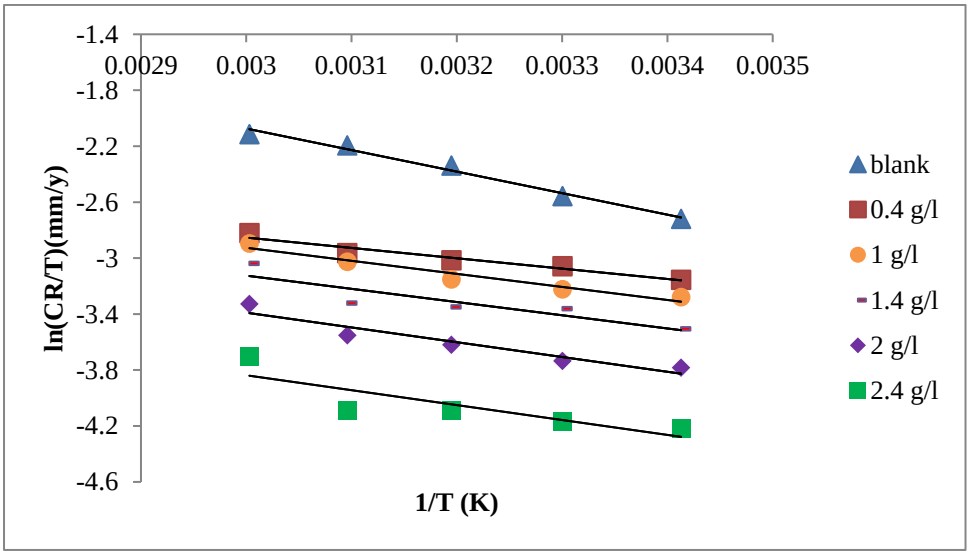

Figure 4. Isotherms mode of black tea extract at various temperature.

Table 3. The adsorption features of BT extract on a mild steel surface at multiple temperatures.

Temperature (K)	K_{ad} $(g/l)^{-1}$	ΔG_{ad} (kJ/mole)	ΔH_{ad} (kJ/mole)	ΔS_{ad} (J/mole. K)
293	0.929	-9.61	-14.014	0.811
303	1.095	-10.38		
313	1.6736	-11.79		
323	1.848	-12.43		
333	1.728	-12.64		

For the corrosion inhibition tendency of organic molecules, meeting inhibitor particles and metal surfaces through the adsorption action can be imperative. The adsorbed film created at a specific temperature, dependent on the concentration of BT extract, was computed using Surface Coverage (Θ) Equation 5.

$$\Theta = IE /100 \quad (5)$$

The surface coverage obtained was used to classify the fitted adsorption isotherm type BT extract's inhibitory properties may be explained by the adsorption of BT extract onto mild steel surfaces, forming a passive film. The surface coverage Θ increased as the extract concentration in all tested temperatures (293 to 333 K) rose. This indicates that BT extracts adsorb onto the surfaces of metal substrates. According to the plot C_{inh}/Θ vs C_{inh} at different temperatures, as shown in Figure 4. a linear trend with slop and correlation coefficient R^2 approximately equal to one, the adsorption type was followed Langmuir adsorption isotherm as given in Equation 6 [26].

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ad}} + c_{inh} \quad (6)$$

The adsorption constant is K_{ad}, while the BT concentration is C_{inh}. By intercepting the lines with the x-axis, the magnitude of K_{ad} and free standard energy ΔG are determined from Equation 7. [26].

$$K_{ad} = \frac{1}{55.5} \exp\left(\frac{\Delta G_{ad}}{RT}\right) \quad (7)$$

The modified Gibbs–Helmholtz Equations 8. [27] applied to compute the thermodynamic properties of adsorption, including enthalpy ΔH_{ad} (kJ/ mol) and entropy ΔS_{ad} (kJ/mol).

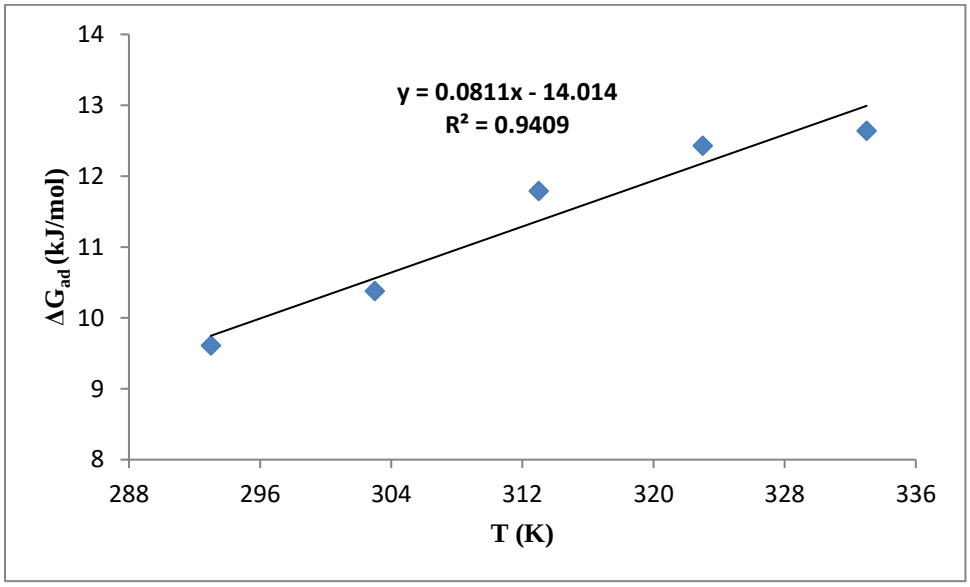

Figure 5. The variation of ΔG (kJ/mol) as a function of temperature (K) for mild steel in 1 M HCl.

$$\Delta G_{ad} = \Delta H_{ad} - T.\Delta S_{ad} \quad (8)$$

The parameter that had been obtained was listed in Table (3). It was deduced that increasing temperature from (293 to 333 K) led to k_{ad} increase from 0.929 to 1.728 $(g/l)^{-1}$. The term referred to the increase in interactions between BT molecules and a mild steel surface [28].

When the ΔG_{ad} was about -20 kJ/mol or even less, it implied a physisorption interaction, demonstrating the moves to the surface of the metal or charge sharing. The data decreased toward more negative values (9.61 to 12.64) kJ/mol as the temperature rose from 293 to 333 K. A protective passive layer in the acid medium was created when BT species adsorbed spontaneously on mild steel surfaces [30]. A linear trend with a coefficient of correlation of 0.9409 as shown by Figure 5, indicated the plot of ΔG_{ad} against the value of temperature. Also, the slope and intercept of the linear relationship depicted in Table 3. have been applied to compute the standard (ΔH_{ad}) and (ΔS_{ad}). In the interaction between mild steel surface and BT extract molecules [28,29], the negative signal of (ΔH_{ad}) suggested an exothermic adsorption procedure. Thus, mild steel dissolution was triggered by ionic species migration to the barrier layer. The study also assisted mild steel surface hydrophilization with a higher temperature and BT concentration [30,31]. The adsorption process of BT extracts on metal surfaces has increased the disorder which can be demonstrated by the obtained positive magnitude of the entropy (ΔS +0.0811). Concerning research, both chemisorption and physisorption are essential for the green inhibitor ability of BT extract on mild steel in 1 M HCl.

4. CONCLUSIONS

- BT extract showed a significant inhibitory effect in the acid solution when the CR of mild steel decreased and IE % improved over all investigations. When the temperature was increased from 293 to 323 K, the IE % rose from 77.56% to 84.95%, with the highest extraction of 2.4 g/l. As the temperature was elevated to 333 K, the IE% decreased to 79.51%, suggesting that the barrier layer deteriorated. However, as the temperature was higher than 333 K, the corrosion rate began to increase; consequently, demonstrating that the barrier layer had deteriorated slightly due to exposure to high temperatures.

- At ambient temperature and various BT concentrations ranging from (0.4 - 2.4 g/l), the results confirmed an enhancement in the IE % value from 35.33 % to 77.51%.

- The adsorption of BT extract on mild steel follows the Langmuir adsorption isotherm.

- A spontaneous adsorbed of the BT particles on the metal surface occurred according to the negative magnitude of ΔG_{ad}.
- Due to the favorable kinetics and thermodynamic characteristics, the action of BT molecules implied chemisorption and physisorption processes on mild steel surfaces.

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