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Ginger and turmeric as green corrosion inhibitors for carbon steel in hydrochloric acid solutions

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Abstract
The effect of green inhibitors extract on the corrosion of carbon steel in 1M HCl solution was studied using weight loss, The results showed that the inhibition efficiency increases with increasing the inhibitor concentration, while it decreases with increasing the temperature, The adsorption of investigated green inhibitors extract on the carbon steel surface obeys the Langmuir adsorption isotherm.

Keywords: green inhibitors, weight loss, inhibition efficiency

Introduction

Corrosion is a fundamental process playing an important role in economics and safety, particularly for metals. The use of inhibitors is one of the most practical methods for protection against corrosion, especially in acidic media [1]. Most well-known acid inhibitors are organic compounds which have π bonds and contains hetero atoms such as sulphur, nitrogen, oxygen and phosphorous which allows the adsorption of compounds on the metal surface [2, 6]. Regarding the chemical structure and chemical behavior, an inorganic compound must be able to oxidize the metal, forming a passive layer on its surface. On the other hand, a molecule of an organic compound must have some features that give it the ability to act as a corrosion inhibitor. Among these, the molecule may have a large structure, double bonds, an active center or group, etc. These features give the molecule the ability to cover a large area of a metal surface with a firmly attached film.1 Apart from the structural aspects, there are also economic and environmental considerations. Thus, since the whole subject of corrosion is about its destructive economical effect, the used inhibitor must be cheap. Furthermore, due to the recent increasing awareness of green chemistry, it must be a nontoxic and environmentally friendly chemical. One of the sources of these cheap and clean inhibitors is plants. Green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment. Several reports are available on the various natural products used as green inhibitors. Low-grade gram flour, natural honey, onion, potato, gelatin, plant roots, leaves, seeds, and flowers gums have been reported as good inhibitors. However, most of them have been tested on steel and nickel sheets. Although some studies have been performed on aluminum sheets, the corrosion effect is seen in very mild acidic or basic solutions (mill molar solutions). Many recent researches [2, 9] have adopted this trend and carried out their work on naturally occurring substances. Promising results were obtained in previous work in this field. It was reported that Khillah extract inhibits steel corrosion in HCl solution with inhibition efficiency as high as 99%,2 while opuntia extract inhibits the corrosion of aluminum in the same acid with efficiency of about 96%.The aim of this work is to study

Experimental

Materials and Solutions

Chemical composition of carbon steel specimens (weight %) is: C 0.2, Mn 0.91, P 0.007, Si 0.002 and the rest is Fe. The carbon specimens before immersion in the test solutions each of them is abraded with emery papers from 300 to 1200 grade size to obtain a smooth surface washed with bidistilled water and then dried using filter papers. AR grade hydrochloric acid (25 %) was used for preparing the corrosive solutions. Appropriate concentration of aggressive solutions used (1 M HCl) was prepared by dilution using bidistilled water.

Weight Loss Measurements

For weight loss measurements, rectangular C-steel specimens of size 20 x 20 x 2 mm were immersed in 100 ml inhibited and uninhibited solutions and allow to stand for several intervals at 25°C in water thermostat. Therefore, the weight losses given by:

$$\Delta m = (m_1 - m_2) \qquad (1)$$

Where m_1 and m_2 are the weights of metal before and after exposure to the corrosive solution, respectively. The percentage inhibition efficiency (% IE) and the degree of surface coverage (θ) of the investigated compounds were calculated from equation (2):

$$\% \text{ IE} = \theta \times 100 = [1 - (\Delta m_{inh} / \Delta m_{free})] \times 100 \qquad (2)$$

Where Δm_{free} and Δm_{inh} are the weight losses per unit area in the absence and presence of additives, respectively.

Results and Discussion

Weight - Loss Measurements

Figure 1-5 shows the effect of concentration of ginger and turmeric extract on the weight loss vs. time of C-steel at 25°C, 35°C, 45°C and 55°C. It is obvious that the weight loss of C-steel in presence of green inhibitors varies linearly with time, and is much lower than that obtained in blank solution. The linearity obtained indicated the absence of insoluble surface film during corrosion and that the inhibitors were first adsorbed onto the metal surface and, therefore, impede the corrosion process [14]. The calculated values of the percentage inhibition efficiency (% IE) at different concentrations of green inhibitors extract in 1 M HCl at different temperatures (25- 45°C) are given in Tables 1 and 2. From these Tables, the inhibition efficiency increases by increasing green inhibitors concentrations and decreases by increasing in temperature. This behavior could be attributed to the increase of the number of adsorbed molecules at the metal surface and desorption of adsorbed molecules from the metal surface occurs by raising the temperature.

Adsorption Isotherms

Basic information on the interaction between the inhibitors and the C-steel can be provided by the adsorption isotherm. Two main types of interaction can describe the adsorption of the organic compound: physical adsorption and chemical adsorption. These are influenced by the chemical structure of the inhibitor, the type of the electrolyte, the charge and nature of the metal. The surface coverage, θ, of the metal surface by the adsorbed inhibitor was evaluated from weight loss measurements using equation (2). The θ values of different inhibitor concentrations at 25°C were tested by fitting to various isotherms including, Frumkin, Langmuir, Temkin and Flory-Huggins. By far the best fit was obtained with the Langmuir isotherm is given as [15]:

$$C/\theta = 1/K_{ads} + C \qquad (3)$$

A plot of (C /θ) against C, for all concentrations of inhibitors (Figure 9-10) a straight line relationship was obtained in all cases with correlation coefficients (R^2) in more than 0.994. Where C is the inhibitor concentration and K_{ads} is the equilibrium constant of adsorption process and is related to the standard free energy of adsorption ΔG°_{ads} by equation (6):

$$K_{ads} = 1/55.5 \exp(-\Delta G^{\circ}_{ads}/RT) \qquad (4)$$

The value of 55.5 is the concentration of water in solution expressed in mole per liter, R is the universal gas constant and T is the absolute temperature .The deviation of the slope from unity as observed from this study could be interpreted that there are interactions between adsorbed species on the metal surface as well as changes in adsorption heat with increasing surface coverage [16, 17], factors that were ignored in the derivation of Langmuir isotherm. The negative ΔG°_{ads} values (Table 3) are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the C-steel surface [18]. It is generally accepted that the values of ΔG°_{ads} up to -20 kJ mol^{-1} the types of adsorption were regarded as physisorption, the inhibition acts due to the electrostatic interaction between the charged molecules and the charged metal, while the values around -40 kJ mol^{-1} or smaller, were seen as chemisorptions, which is due to the charge sharing or a transfer from the inhibitor molecules to the metal surface to form covalent bond [19-20]. The ΔG°_{ads} values obtained in this study range from –36.2 to –36.7 kJ mol^{-1}. It suggested that the adsorption mechanism of investigated inhibitors on C-steel in 1 M HCl solution was typical of physisorption.

Kinetic-Thermodynamic Corrosion Parameters

As noticed previously, the adsorption process was well elucidating by using a thermodynamic model, in addition a kinetic-thermodynamic model was another tool to explain the mechanism of corrosion inhibition for an inhibitor. The apparent effective activation energies (E^*_a) for the corrosion reaction of C-steel in HCl in the absence and presence of different concentrations of investigated compounds were calculated from Arrhenius-type equation [21]:

$$k = A \exp(-E_a^* / RT) \qquad (5)$$

Where A is the Arrhenius pre-exponential factor. A plot of log k (corrosion rate) vs. 1 / T gave straight lines as shown in (Figure 11). The entropy of activation (ΔS^*) and the enthalpy of activation (ΔH^*) for the intermediate complex in the transition state for the corrosion of C-steel in HCl in the absence and presence of different concentrations of investigated compounds were obtained by applying the transition-state equation [22-24]:

$$k = RT / Nh \exp(\Delta S^*/R) \exp(-\Delta H^* / RT) \qquad (6)$$

Where h is the Planck’s constant and N is the Avogadro’s number A plot of log k (corrosion rate) / T vs. 1 / T should give a straight lines (Figure 11), with a slope of ($-\Delta H^*$ / 2.303R), and an intercept of [(log (RT / Nh) + (ΔS^*/2.303R)] [25-26], from which the values of ΔH^* and ΔS^* were calculated, respectively. (Table 4) exhibited values of apparent activation energy, apparent enthalpies ΔH^* and entropies ΔS^* for C-steel dissolution in 1 M HCl solution in the absence and presence of different investigated compounds. The presence of inhibitors decreased the activation energies of C-steel indicating strong adsorption of the inhibitor molecules on the metal surface and the presence of these additives induces the adsorption of theses additives on the surface of C-steel. Values of the entropy of activation ΔS^* in the absence and in presence of the studied compounds are negative. This implies that the activated complex in the rate determining step represents an association rather than a dissociation step [27]. This means that the activated molecules were in higher order state than that at the initial stage [28, 29].

Conclusions

From the overall experimental results the following conclusions can be deduced:

Green inhibitors (ginger and turmeric) are good inhibitors and act as mixed type but mainly act as mixed type inhibitors for carbon steel corrosion in 1 M HCl solution. The results obtained from weight loss measurements showed that the inhibiting action increases with the inhibitors concentration and decreases with the increasing in temperature. Double layer capacitances decrease with respect to blank solution when green inhibitors extract are added. This fact confirms the adsorption of the investigated compounds molecules on the carbon steel surface. The adsorption of green inhibitors on the carbon steel surface at different temperature was found to obey the Langmuir adsorption isotherm and this adsorption is phsicosorption.

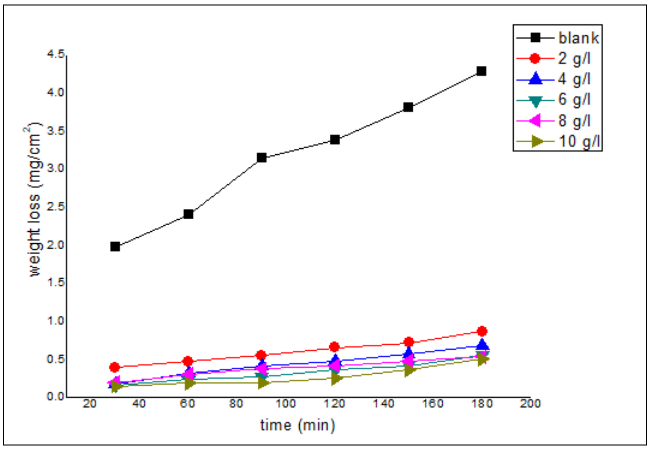

Fig 1: Weight loss-time curves for the dissolution of C-steel in 1 M HCl in the absence and presence of different concentrations of ginger extract at 25 ºC

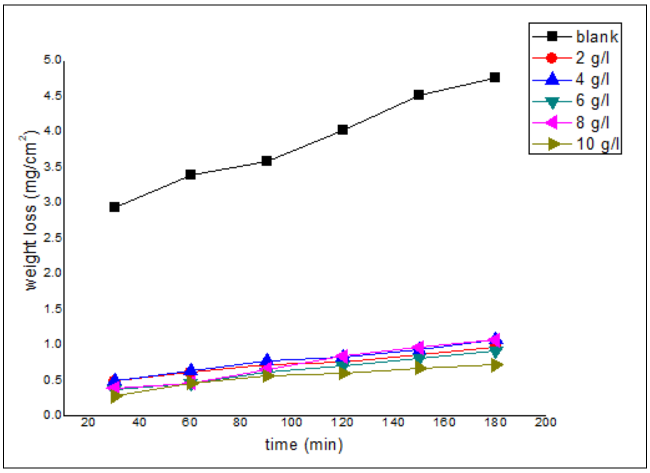

Fig 2: Weight loss-time curves for the dissolution of C-steel in 1 M HCl in the absence and presence of different concentrations of ginger extract at 35 ºC

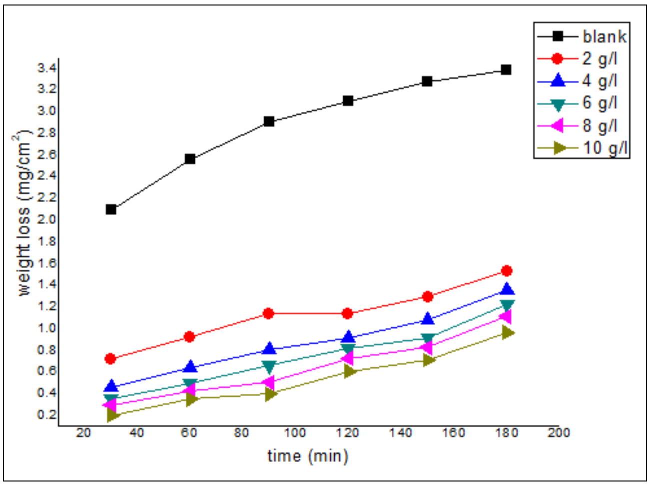

Fig 3: Weight loss-time curves for the dissolution of C-steel in 1 M HCl absence and presence of different concentrations of ginger extract at 45 ºC

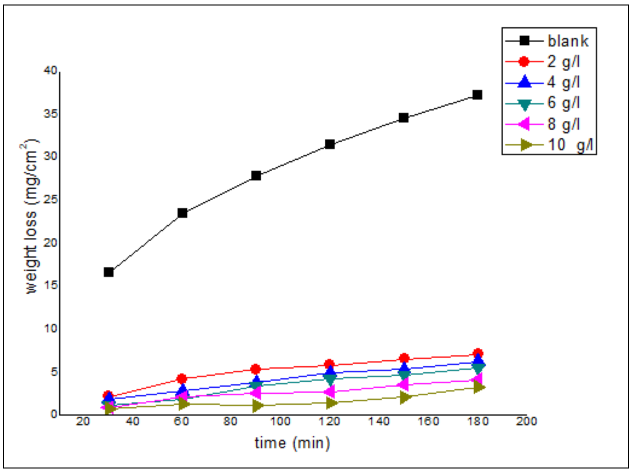

Fig 4: Weight loss-time curves for the dissolution of C-steel in 1 M HCl in the absence and presence of different concentrations of ginger extract at 55 oC

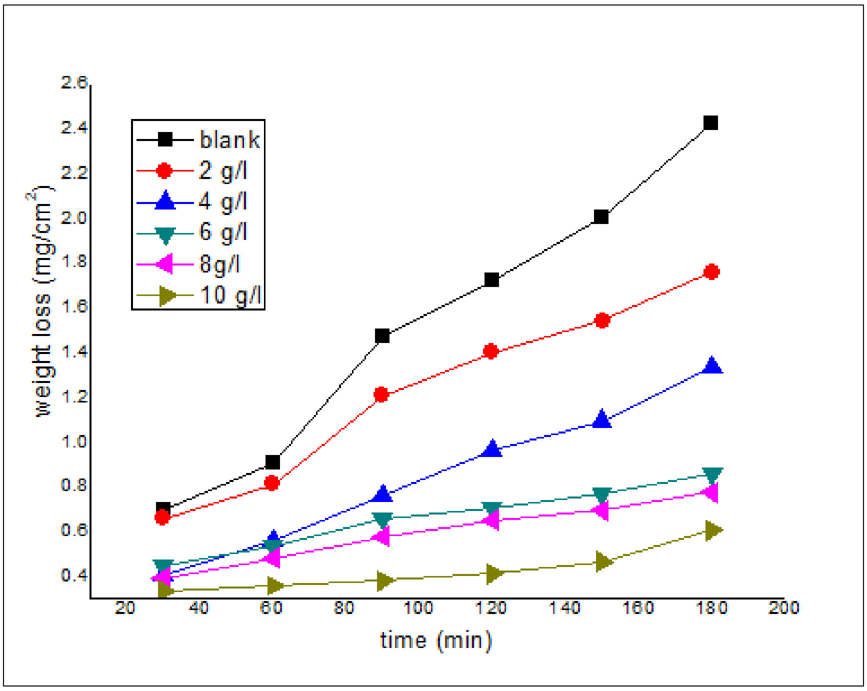

Fig 5: Weight loss-time curves for the dissolution of C-steel in 1 M HCl in the absence and presence of different concentrations of Turmeric extract at 25 ºC

Table 1: Corrosion rate (C.R.) in (mg cm^{-2} min^{-1}) and inhibition efficiency data obtained from weight loss measurements for carbon steel in 1 M HCl solution in the absence and presence of different concentrations of green inhibitors at 25°C

Compounds	**Conc., g/l**	**Corrosion Rate (CR), mg cm^{-2} min^{-1}**	**θ**	**% IE**
1 M HCl		0.0500	----	----
Turmeric	2	0.01166	0.7668	76.68
	4	0.00804	0.8393	83.93
	6	0.00591	0.8824	88.24
	8	0.005424	0.8915	89.15
	10	0.003427	0.9315	93.15
Ginger	2	0.0122	0.756	75.6
	4	0.0101	0.798	79.8
	6	0.00712	0.8576	85.76
	8	0.00633	0.8734	87.34
	10	0.00588	0.8824	88.24

Table 2: Data of weight loss measurements for carbon steel in 1 M HCl solution in the absence and presence of different concentrations of green inhibitors at 35-55°C.

Compound	**Conc., g/l**	**35°C**		**45°C**		**55°C**	
		θ	% IE	θ	% IE	θ	% IE
Turmeric	2	0.7490	74.9	0.7014	70.14	0.6992	69.92
	4	0.7818	78.18	0.7145	71.45	0.7069	70.69
	6	0.8055	80.55	0.7523	75.23	0.7225	72.25
	8	0.8357	83.57	0.7718	77.18	0.7284	72.84
	10	0.858	85.8	0.794	79.4	0.776	77.6
Ginger	2	0.5012	50.12	0.4550	45.50	0.4211	42.11
	4	0.532	53.2	0.471	47.1	0.455	45.5
	6	0.705	70.5	0.602	60.2	0.549	54.9
	8	0.772	77.2	0.662	66.2	0.602	60.2
	10	0.842	84.2	0.713	71.3	0.638	63.8

Table 3: Thermodynamic parameters for the adsorption of three compounds on carbon steel surface in 1 M HCl at different temperatures

Compounds	**Temp., K**	**K_{ads} x10^4, M^{-1}**	**-ΔG°$_{ads}$, kJ mol^{-1}**	**-ΔH°$_{ads}$, kJ mol^{-1}**	**-ΔS°$_{ads}$, J mol^{-1}k^{-1}**
Turmeric	298	85.71	43.89	77.23	109.56
	308	62.53	43.90		107.72
	318	40.23	43.34		107.78
	328	28.81	42.07		110.12
Ginger	298	60.21	42.93	59.81	71.91
	308	28.64	41.86		74.24
	318	17.27	41.02		75.78
	328	13.31	41.06		74.43

Table 4: Activation parameters for the dissolution of carbon steel in the presence and absence of different concentrations of inhibitors in 1 M HCl

Inhibitor	**Conc., g/l**	**Activation parameters**		
		E_a^*	**ΔH***	**-ΔS***
		kJ mol^{-1}	**kJ mol^{-1}**	**J mol^{-1} K^{-1}**
1 M HCl		56.40	23.93	82.16
Turmeric	2	97.86	41.38	42.30
	4	99.27	41.99	46.00
	6	101.36	42.90	52.39
	8	108.45	41.64	42.21
	10	119.79	16.17	167.62
Ginger	2	75.97	31.88	25.55
	4	78.50	32.97	18.30
	6	89.27	31.01	33.86
	8	92.05	31.91	28.40
	10	101.76	18.33	149.32

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