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Tomato peels extract as a green corrosion inhibitor for carbon steel in acetic acid solution

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Abstract

The active components in tomato peels were extracted using alcohol, and FTIR was measured to clarify the structure. Electrochemical impedance spectroscopy (EIS), potentiodynamic polarization (PP), and weight loss (WL) measurements were used to investigate the corrosion inhibition of carbon steel in acetic acid solution. The corrosion rate decreased as the extract content increased. Additionally explained were the rise in charge transfer resistance and the fall in polarization current densities; an indication for the inhibitory effect. The findings demonstrated that the inhibitory effect was caused by the physical adsorption of molecules on the carbon steel surface majorly at the cathodic locations, forming a barrier that protected the steel from the corrosive medium. This adsorption followed Langmuir isotherm. Also, the temperature effect showed a tendency of tomato peels extract to inhibit the corrosion, cathodically.

Keywords: Corrosion, adsorption, carbon steel, Tomato peels, acetic acid.

1. Introduction

Because of its good physical qualities and ease of availability, carbon steel is often regarded as one of the best materials for industry. However, because of its sensitivity to corrosion, its usage is limited in acidic environments [1]. However, among the lower carbon acids in the aliphatic series, acetic acid is by far the most significant organic acid from a commercial standpoint. It is used in the production of pharmaceuticals and medications, as well as in the rubber, silk, rayon, and plastics industries. It makes sense for industries that produce or utilize acetic acid as a reactant to employ carbon steel for reaction vessels or storage tanks [2]. Investigation is necessary into the complicated and significant issue of how acetic acid affects the kinetics of carbon steel corrosion [3]. Because they are unable to totally block the surface sites for anodic dissolution, short chain length carboxylates have been found to be ineffective at inhibiting the corrosion of carbon steel in aqueous solution [4]. There aren't many articles that discuss how iron behaves in neutral and weakly acidic liquids. Finding new sources for emphasizing anticorrosive active chemicals and obtaining "green" organic molecules for their future usage as corrosion inhibitors is an intriguing and practical task. The literature claims that food extracts and fruit-based wastes, contain a variety of green active chemicals that show promise in preventing corrosion under various circumstances [5-8]. In place of synthetic chemicals, food waste is regarded as a sustainable and possibly renewable resource. These days, researchers are creating more environmentally friendly corrosion prevention techniques based on "green chemistry" [9-14]. Using organic solvents or water/organic solvent it is combinations, easy to extract sustainable and environmentally friendly organic molecules.

In this work, tomato peels extract was tested as a green corrosion inhibitor for carbon steel in acetic acid solution at different temperatures.

2. Experimental

2.1. Materials and extraction

The composition of carbon steel used in this investigation is: 0.13% C, 0.25% Si, 0.34% Mn, 0.010% S, 0.013% P, 1.02% Cr, 0.50% Mo, 0.70% W, 0.47% V, and Fe is the remainder. Acetone, ethanol (99%) and acetic acid were purchased from AL-Nasr Chemicals Co., Egypt.

The tomato peels were washed well, dried in the sun, refluxed for one hour with ethanol (99%), then filtered and let the filtrate concentrate, dry in the open air to leave the extract (a red paste). FTIR is acquired by Thermos Nicolet IS10 FT-IR Spectrophotometer. IR spectrum (KBr) showed characteristic bands at 3635 cm⁻¹ (v_{OH}), 3044, 3023 cm⁻¹ (v_{CH} Ar), 2951, 2922 cm⁻¹ (v_{CH} Alkane), 1748 cm⁻¹ ($v_{C=O}$), 1573 cm⁻¹ ($v_{C=C}$ Ar), 1068 cm⁻¹ (v_{CH} Ar), **Figure 1**.

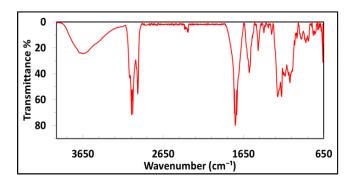


Figure 1: FTIR spectrum of the tomato peels extract.

2.2. Weight loss (WL) measurements

The carbon steel specimens were weighed before and after immersion in acetic acid solution every day for five days, at different tomato peels concentration from 50 ppm to 500 ppm.

The inhibition efficiency is calculated using the corrosion rate in mg.h⁻¹.cm⁻² [15]:

$$\% IE_{WL} = \left(1 - \frac{CR_{EXT}}{CR_{Free}}\right) \times 100 \tag{1}$$

2.3. Electrochemical measurements

Potentiodynamic polarization (PDP) curves as well as electrochemical impedance spectroscopy (EIS) of carbon steel in acetic acid solution without and with different peels concentrations tomato were investigated at different temperatures. The inhibition efficiency using i_{EXT} and i_{Free} (the corrosion current density of carbon steel in acetic acid solution with and without the tomato peels extract), and R_{EXT} and R_{Free} (the charge transfer resistance in acetic acid solution with and without the tomato peels extract), was calculated using the following equations [16]:

$$\% IE_{PDP} = \left(1 - \frac{i_{EXT}}{i_{Free}}\right) \times 100$$
 (2)

$$\% IE_{EIS} = \left(1 - \frac{R_{Free}}{R_{EXT}}\right) \times 100$$
(3)

3. Results and Discussion

3.1. Weight loss (WL) outcomes and adsorption isotherm

Figure 2 shows that the rate of corrosion of carbon steel increases with time in the acetic acid solution. However, the corrosion rate decreases and thus the inhibition efficiency increases with time in the presence of tomato peels extract. It is also shown that the inhibition efficiency increases with increasing concentration of tomato peels extract. When the concentration rose, the quantity of protective molecules on the metal's surface grew as well, improving the extract's effectiveness. The FTIR spectrum revealed distinctive bands for heteroatoms, such as the benzene ring, O, and π electrons, which are in charge of the inhibitor molecules' attraction to the metal surface, which is followed by the adsorption and inhibition process [17].

The values of surface coverage (θ = IE/100) at different tomato peels extract concentrations were calculated. The results are fitted satisfactorily with Langmuir adsorption isotherm with R² ≈ 1, Figure 3 [18]:

$$C / \theta = (1 / K_{ads}) + C \tag{4}$$

where, K_{ads} and C are the equilibrium constant of adsorption process and the extract concentration, respectively. The standard free energy of adsorption ΔG°_{ads} is calculated [19]:

$$K_{ads} = 1 / C_{H_2O} exp \left(-\Delta G_{ads}^0 / RT\right)$$
(5)

where, C_{H2O} is the concentration of water $\approx 10^6$ ppm. The calculated values of ΔG_{ads} are small negative values, indicating that the adsorption process of the tomato peels

extract molecules on the metal surface is spontaneous and physical in nature. The heteroactive centers in the tomato peels extract molecules cause the molecules move towards the oppositely charged carbon steel surface and adsorb on it, resulting in corrosion inhibition from the attacking of acetic medium.

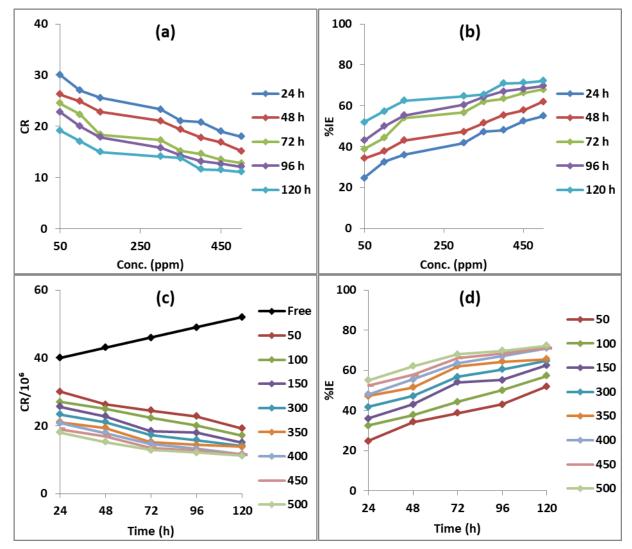


Figure 2: Change of corrosion rate and inhibition efficiency with tomato peels extract concentration (a-b) and with immersion time (c-d), in acetic acid solution.

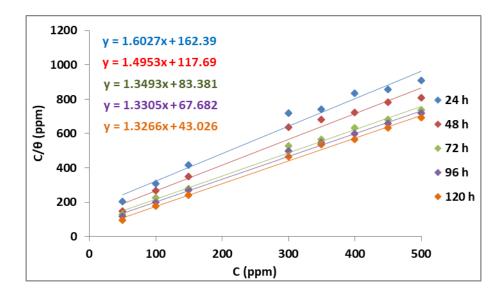


Figure 3: Langmuir adsorption isotherm for tomato peels extract on carbon steel in acetic acid solution.

3.2. Potentiodynamic polarization (PDP) measurements

In addition to the severity of the reaction or the rate of corrosion, the polarization potential curves provide information about the mechanism of the reaction, **Figure 4**. Here, we notice a decrease in current density with an increase in the concentration of the tomato peels extract, which indicates for the efficiency of the extract against corrosion in acetic acid solution.

Table 2: Potentiodynamic polarization parameters of carbon steel without and with different tomato peels

 extract concentrations in acetic acid solution, and at 298 K.

Conc. (ppm)	β _c	β _a	E _{corr}	i _{corr}	%IE	
	(V/dec)	(V/dec)	(mV)	$(\mathbf{mA} / \mathbf{cm}^2)$	/0112	
Blank	-2.7	2.0	-685	91.9	-	
50	-2.8	2.8	-782	32.4	64.7	
100	-2.7	3.6	-767	30.0	67.3	
150	-2.6	3.1	-861	25.8	71.8	
300	-2.5	3.1	-782	20.8	77.2	
350	-2.8	3.3	-767	20.3	77.8	
400	-3.2	2.8	-861	16.9	81.5	
450	-2.8	3.2	-782	15.8	82.7	
500	-2.6	3.4	-767	14.8	83.8	

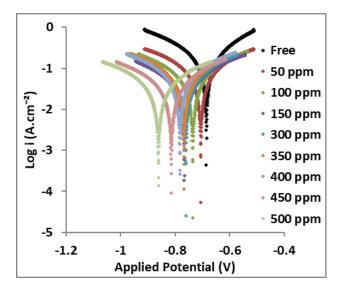


Figure 4: Potentiodynamic polarization curves of carbon steel without and with different tomato peels extract concentrations in acetic acid solution.

Also, we note the similarity of the polarization curve of the corrosion of carbon steel in the acetic acid with it in the presence of the tomato peels extract, which indicates that the tomato peels extract does not affect the reaction mechanism [20].

Moreover, the corrosion potential in the presence of the tomato peels extract changed to more negative values with increasing tomato peels extract concentration and both anodic and cathodic slopes changed slightly, **Table 2**, which indicates for the adsorption of the tomato peels extract on the surface of the metal, as a cathodic type inhibitor [21].

3.3. Electrochemical Impedance Spectroscopy (EIS)

In **Figure 5**, Nyquist plots demonstrated a sharp rise in the charge transfer resistance,

as evidenced by the Nyquist plot diameter, as the concentration of tomato peel extract increased. This suggests that the presence of tomato peel extract is what inhibits corrosion in this experiment with increasing inhibition efficiency.

Additionally, because of its inhibitory function, the solution resistance rose as the dosages of tomato peel extract increased, **Table 3**. Furthermore, the Nyquist plots' shape hardly changes when tomato peel extract is added, indicating that the reaction mechanism remains the same as previously demonstrated. The EIS data was fitted using the equivalent circuit, the Randles circuit [22].

Conc. (ppm)	$R_{S}(\Omega)$	$\mathbf{R}_{\mathrm{ct}}\left(\Omega ight)$	%IE
Blank	659.24	130.13	-
50	670.03	188.46	30.95
100	686.28	406.59	67.99
150	697.66	446.51	70.86
300	715.41	455.94	71.46
350	715.77	479.99	72.89
400	726.67	495.14	73.72
450	695.79	582.86	77.67
500	703.57	603.72	78.45

Table 3: EIS parameters of carbon steel in acetic acid solution without and with different concentrations of tomato peels extract.

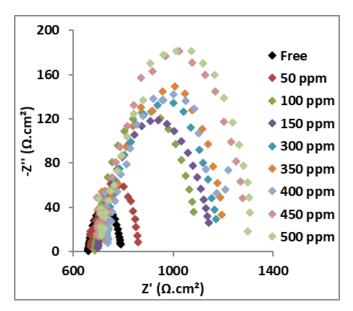


Figure 5: Nyquist plots for carbon steel in acetic acid solution without and with different concentrations of tomato peels extract.

3.4. Temperature effect

As a controlling environmental factor, temperature affects the rate of corrosion and inhibitor adsorption on metal surfaces. Experiments were conducted between 25°C and 50°C to investigate the impact of temperature on inhibitory properties. **Tables 4-5** show the relationship between temperature and inhibition efficiency.

According to the above outcomes, the separation of the tomato peel extract from the carbon steel specimen's surface is the cause of the decrease in inhibitory efficiency with rising temperatures [23].

From the calculated inhibition efficiency, **Table 4**, of tomato peels, a

noticeable decrease in the inhibition efficiency was detected which informs that the adsorption process was physical in action, as one can say that the adsorbed molecules of the inhibitor are being disorbed with elevating the temperature and this behavior can occur only in the case of physical adsorption process [24].

From **Figure 6**, it is obvious that E_{corr} for carbon steel moves toward more negative values with increasing temperature suggesting that the corrosion process is anodically controlled. This shift is observed with the extract presence, an indication for its tendency for cathodic inhibition, at relatively high temperatures [25].

Table 4: Corrosion parameters of carbon steel in acetic acid solution with and without 500 ppm tomato

 peels extract at different temperatures.

System	Conc. (ppm)	β _c	β _a	E _{corr}	i _{corr}	%IE
		(V/dec)	(V/dec)	(mV)	$(\mathbf{mA}/\mathbf{cm}^2)$	
	25°C	-2.7	2.0	-685	91.9	
Blank	30°C	-2.7	2.6	-733	157.9	
	40°C	-2.7	2.6	-757	201.6	-
	50°C	-3.3	2.6	-758	368.6	
	25°C	-2.6	3.4	-767	14.8	83.8
500 ppm	30°C	-2.6	2.6	-778	31.4	80.0
	40°C	-2.6	2.6	-791	40.8	79.7
	50°C	-3.0	-2.1	-916	49.4	78.4

Nyquist plots show clear lower solution resistance and lower charge transfer resistance with elevating temperatures, that a decrease in inhibition efficiency is observed with the tomato peels extract presence as shown in **Table 5**. This is due to the increased molecular kinetic energies of the tomato peels molecules, causing the desorption of them from the carbon steel surface , leaving it uncovered from the corrosive acetic acid solution [26].

Table 5: EIS data of carbon steel in acetic acid solution with and without 500 ppm tomato peels extract at different temperatures.

System	Conc. (ppm)	$\mathbf{R}_{\mathrm{S}}\left(\Omega ight)$	$\mathbf{R}_{\mathrm{ct}}\left(\Omega ight)$	%IE
Blank	25°C	659.2	130.1	
	30°C	599.5	129.0	
	40°C	475.4	127.8	-
	50°C	335.2	125.0	
500	25°C	703.5	603.7	78.4
	30°C	485.1	274.7	52.6
500 ppm	40°C	378.0	189.0	31.1
	50°C	330.2	181.6	28.3

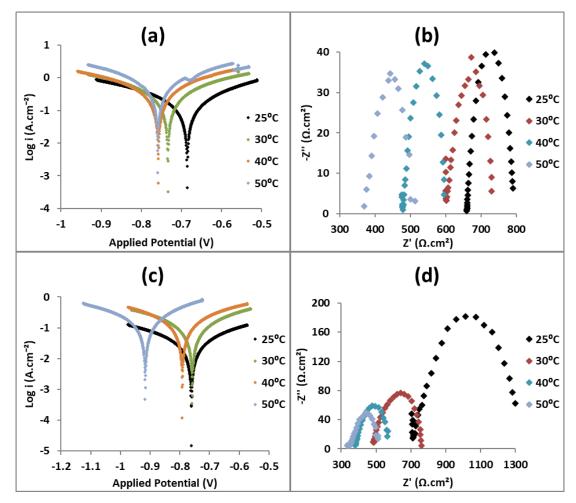


Figure 6: PDP curves and EIS plots for carbon steel in (a-b) uninhibited and (c-d) inhibited acetic acid solution at different temperatures.

4. Conclusion

Tomato peels were successfully extracted using alcohol, and the structure of the resulting extract was examined using FTIR to verify the existence of heteroatoms. When tested at various temperatures in an acetic acid solution, the extract showed good characteristics for inhibiting metallic corrosion cathodically. It was proposed that the inhibitory mechanism was caused by spontaneous physical adsorption.

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