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Plant Extracts for Inhibitory Protection of Steel

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Abstract—New environmentally friendly corrosion inhibitors for mild steel that are based on plant raw materials, basil, cinnamon, sage, clove, spirulina, and pomegranate are proposed for the protection of industrial equipment. Extracts of clove, sage, and basil at 10 cm^3/dm^3 in tap water provide protection of 91.29–94.65%. In a 0.1 M hydrochloric-acid solution, the maximum anticorrosion action is observed for the extracts of sage and basil at 20 cm^3/dm^3 (90.11%) and for a pomegranate-peel extract at 30 cm^3/dm^3 (93.39%).

Keywords: plant raw materials, hydroalcoholic extracts, basil, cinnamon, sage, clove, spirulina, pomegranate, tap water, hydrochloric acid, steel 20, steel ST3, protective layer, antimicrobial action, nontoxic inhibitors

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Industrial inhibitors are predominantly synthetic organic compounds [1–4]. Their application pollutes the environment and requires increased safety. Therefore, the development of environmentally friendly inhibitors that are based on plant raw materials is an urgent research problem.

Research groups have proposed inhibitors that are based on lipids [5], powder-rust converters, and volatile inhibitors of atmospheric corrosion that are based on fruit-kernel wastes [6]. They have also developed and patented inhibitors that are based on mustard oil and wastes of the fat and oil industry [7]. One promising direction of development is production of inhibitors using extracts of oil radish, rape, garlic, cabbage stumps [8], buckeye fruits [9], hop cones, wormwood, and walnut shells [10].

This study is aimed at increasing the range of highly efficient environmentally friendly inhibitory compositions that are based on plant raw materials.

MATERIALS AND METHODS

The effect of extracts of basil, cinnamon, sage, clove, spirulina, and pomegranate peel on the corrosion of steel was studied. The objects of study were selected on the basis of the availability of the raw materials, the presence in their composition of compounds with active centers that can significantly affect corrosion, and a satisfactory level of sanitary and hygienic requirements during production and application of the corrosion inhibitors.

Dried leaves of basil and sage, cinnamon, clove, spirulina, and pomegranate peel were ground into powder. The extracts were obtained using a hydroalcoholic solution (1 pts wt of the dry powder/25 pts wt of the solvent) and introduced into a corrosive environment at the concentration (C) of 10–30 cm^3/dm^3.

The efficiency of inhibition of corrosion by the obtained extracts was evaluated for steel ST3 by a gravimetric method and for steel 20 by electrochemical methods. The choice of the steel is caused by steel 20 and ST3 being the most widespread construction materials after stainless steel, which are used for manufacturing different equipment, including equipment for the chemical and food industries. This includes steam boilers, distillation devices, presteeping tanks, fermenting and settling vats, plate heat exchangers and shell and tube heat exchangers, pipelines, and parts of dough-handling equipment.

The corrosive environments were a 0.1 M HCl solution and tap water (pH 7.2, mineralization of 372.4 mg/L, total hardness of 4.7 mol/L, and total iron of 0.4 mg/L).

Polarization curves (20 mV/min) were recorded using the stationary potential at the end electrode in a glass three-electrode electrochemical cell with the cathode and anode spaces being separated. The reference electrode was made of silver chloride; the auxiliary electrode was made of platinum. The potential of the working electrode was converted to the standard hydrogen scale. The polarization curves were used to determine electrochemical corrosion currents (I_{corr}) and partial cathodic (I_c at E_c = –0.46 V) and anodic (I_a at E_a = –0.14 V) currents. Inhibition coefficients γ_{corr}, γ_c, and γ_a ($\gamma = I/I'$, where I and I' are the corrosion currents without and with extracts, respectively) and degree of protection Z_{corr}, Z_c, and Z_a, ($Z = (1 - 1/\gamma) \times 100\%$) were calculated.

For the gravimetric method, rectangular ST3 specimens with a size of 50.3 × 22.3 × 3.2 mm were used.

Table 1. Results of gravimetric study of the anticorrosive effect of extracts on ST3 ($T = 295$ K)

Extract	C, cm^3/dm^3	K_m, g/(m^2 h)	Z_m, %	K_m, g/(m^2 h)	Z_m, %
		tap water		0.1 M HCl solution	
Without extracts		0.0570	–	6.27	–
Basil	10	0.0049	91.29	0.69	88.99
	20	0.0105	81.58	0.62	90.11
	30	0.0107	81.28	0.98	84.37
Spirulina	10	0.0107	81.14	0.86	86.28
	20	0.0053	90.64	0.63	89.95
	30	0.0059	89.54	0.65	89.63
Cinnamon	10	0.0047	91.68	1.93	69.21
	20	0.0190	66.50	0.83	86.76
	30	0.0419	26.42	1.09	82.48
Clove	10	0.0035	93.78	1.18	81.18
	20	0.0096	83.07	0.94	85.00
	30	0.0166	70.86	0.95	84.85
Sage	10	0.0030	94.65	0.85	86.44
	20	0.0112	80.25	0.62	90.11
	30	0.0180	68.40	0.64	89.79
Pomegranate peel	10	0.0190	65.00	0.78	87.58
	20	0.0150	72.92	0.55	91.19
	30	0.0280	50.00	0.41	93.39

Their surface was subsequently ground using P240–P1200 emery paper, washed in running water, and degreased. The exposure to tap water was carried out for 216 h. After the exposure, the corrosion products were removed from the specimen surface, and it was degreased and weighted. The corrosion rate was calculated by the formula $K_m = (m_1 - m_2)/St$ (g/(m^2 h)), where m_1 is the mass of the specimen before the exposure, g; m_2 is the mass of the specimen after the exposure, g; S is the area of the specimen surface, m^2, and t is the duration of the exposure, h.

The efficiency of corrosion protection was assessed by degree of protection $Z_m = [(K_m - K'_m)/K_m] \times 100\%$, where K_m and K'_m are the rates of corrosion of steel in the absence and presence of extracts, respectively, g/(m^2 h).

The content and distribution of chemical elements in the surface layer were tested by Auger electron spectrometry using the AES-200 Auger spectrometer of an LAS-2000 multifunctional setup (RIBER, France).

To study the antimicrobial action of the extracts, *Escherichia coli* and *Bacillus subtilis*, which are model objects for studying basic life processes, were used. The sensitivity of these microorganisms to the active components of the extracts was determined by the disc method [11]. Microbiological analysis of water was performed by counting the number of mesophilic aerobic and facultative anaerobic microorganisms (MAFAnM) in 1 cm^3 of the water.

Statistical processing of the results of the study was carried out for a confidence level of 0.95. The number of measurements was $n = 5$ [12].

RESULTS AND DISCUSSION

The results of the experiments are given in Tables 1–3 and Figs. 1–4. All the plant extracts that we selected exhibited an inhibiting action.

We have determined (Table 1) that the optimum concentration in tap water for the extracts of basil, cinnamon, sage, and clove is 10 cm^3/dm^3 and that for the extracts of spirulina and pomegranate peel is 20 cm^3/dm^3. The efficiency of corrosion protection with respect to weight loss in specimens of steel ST3 at the optimum concentrations of the inhibitors is from 72.92 to 94.65% for Z_m and from 3.8 to 18.71 for γ_m.

In a 0.1 M hydrochloric-acid solution, the optimum concentration for the extracts of basil, cinnamon, sage, and clove is 20 cm^3/dm^3, while for pomegranate peel it is 30 cm^3/dm^3. The degree of protection is 85.00–93.39%, and γ_m is 6.67–15.29. The rate of corrosion at the optimum concentrations of the extracts decreases by a factor of 7–10. A further

Table 2. Results of electrochemical study of the anticorrosive effect of extracts ($C = 20$ cm^3/dm^3) in a 0.1 M HCl solution on steel 20 ($T = 291$ K)

Extract	I_a	γ_a	Z_a, %	I_c	γ_c	Z_c, %	I_{corr}	γ_{corr}	Z_{corr}, %
Without extracts	46.77	–	–	24.12	–	–	18.19	–	–
Basil	13.80	3.39	70.49	10.12	2.38	58.04	3.50	5.19	80.75
Clove	13.80	3.39	70.49	7.95	3.03	66.99	2.51	7.24	86.20
Pomegranate peel	15.59	3.00	66.67	10.05	2.40	58.27	4.39	4.14	75.86
Cinnamon	10.07	4.64	78.47	7.95	3.03	66.99	3.17	5.73	82.53
Spirulina	18.19	2.57	61.11	14.45	1.67	40.09	5.00	3.78	72.51
Sage	10.07	4.64	78.47	10.12	2.38	58.04	2.50	7.27	86.25

Table 3. Content of elements in a surface layer of steel 20, at %

Elements	Specimen no.	Distance from the surface, nm									
		0	0.8	1.6	4	12	16	40	80	140	160
Fe	1	16.2	46.2	67.3	76.7	85.3	89.7	91.9	93.5	98.4	98.3
	2	4.6	7.1	8.7	15.5	24.4	31.3	46.2	61.3	72.9	76.1
	3	13.5	41.6	59.7	77.3	83.2	86.1	92.8	96.7	99.1	98.5
C	1	58.4	7.3	5.9	5.3	4.1	3.7	2.7	2.4	0.0	0.0
	2	88.9	85.2	83.4	76.8	65.3	59.2	44.2	22.9	19.8	18.5
	3	67.8	26.9	18.1	9.7	2.8	2.3	1.5	0.0	0.0	0.0
O	1	21.5	42.2	26.2	14.9	5.7	5.1	3.9	2.5	1.2	1.0
	2	3.9	4.8	4.3	4.2	4.9	4.8	5.2	4.7	3.4	3.3
	3	17.2	32.1	23.1	11.5	9.3	8.9	4.6	2.1	1.1	1.0
Cl	2	0.0	0.7	0.4	0.3	0.2	0.2	0.1	0.1	0.1	0.1
	3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

(1) control specimen of steel 20 in air; (2, 3) 0.1 M HCl: (2) without extracts; (3) with extract of pomegranate peel.

increase in the concentration does not enhance the degree of protection.

It should be noted that specimens exposed to a 0.1 M HCl solution without inhibitors are covered with loose gray corrosion products. At the same time, there has been no evidence of destruction on the surface of ST3 specimens in solutions with plant extracts added during the entire period of the study.

Data of electrochemical tests have confirmed the accuracy of the above-mentioned results (Table 2, Fig. 1): all the plant extracts that are used in the study inhibit metal dissolution. The degree of anodic protection of steel 20 increases from 61.11% (spirulina extract) to 84.1% (pomegranate peel extract). The addition of the extract of pomegranate peel to the corrosion medium results in a preferential inhibition of the anodic partial process ($\gamma_a/\gamma_c = 2.2$), which is in agreement with the gravimetric results. The inhibition of the cathodic partial process for all the extracts is insignificant. The maximum degree of cathodic protection ($Z_c = 66.99\%$) is observed for the clove and cinnamon extracts.

The mechanism of action for the developed inhibitors is caused in large part by chemically active components being chemisorbed on the metal surface and forming a film that isolates this surface from the adverse effects of the environment. According to [9, 13, 14], plant components that can significantly affect the corrosion are tannins, carbohydrates, phenols, amino acids, and aldehydes. The pomegranate peel contains tannins, gallotannins and ellagitannins; basil is rich in derivatives of caffeic acid, eugenol, and camphor; cinnamon contains cinnamaldehyde; sage, tannins and terpenoids; clove, eugenol; and spirulina, amino acids (Fig. 2).

Tannins are polyphenols (phenolic hydroxyl groups constitute 15–30% of the molecular mass) [9]. The characteristic features of polyphenols are sorption activity, which is caused by their ability to be adsorbed on a wet metal surface via hydrogen bonds, and the complexing activity, which is caused by hydroxyl and/or carbonyl groups that can form ionic or donor–acceptor bonds with metal cations [12]. Since the reactive groups are in ortho positions with respect to each other, complexes that are formed have a chelate

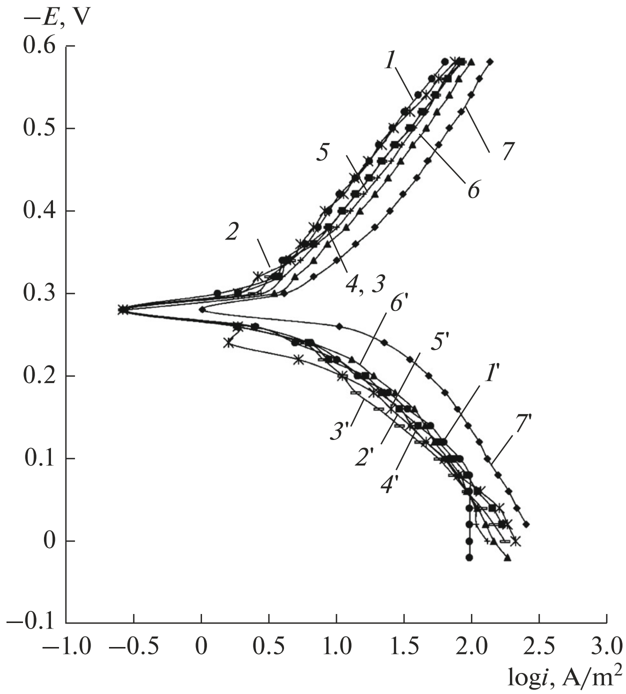

Fig. 1. The (*1–7*) cathodic and (*1'–7'*) anodic polarization curves of steel 20 in (*7.7'*) 0.1 M HCl and with addition of extracts ($C = 20$ cm^3/dm^3): (*1.1'*) clove, (*2.2'*) cinnamon, (*3.3'*) sage, (*4.4'*) basil, (*5.5'*) pomegranate peel, and (*6.6'*) spirulina.

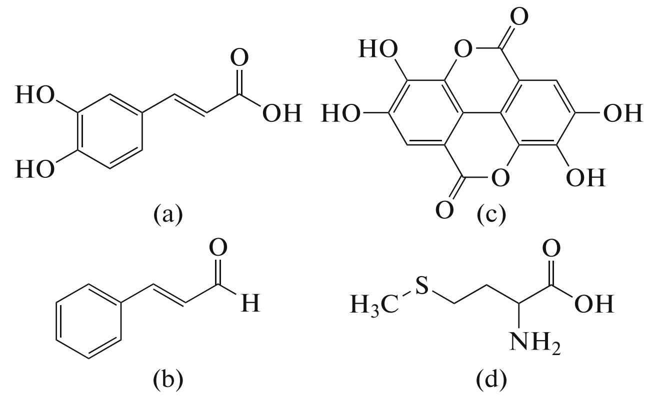

Fig. 2. Structural formulas: (a) caffeic acid, (b) cinnamaldehyde, (c) ellagitannin (the active substance of pomegranate peel), and (d) methionine.

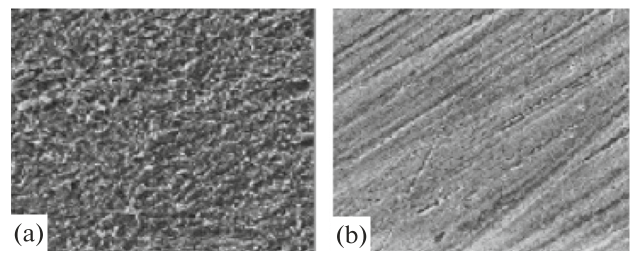

Fig. 3. Surface of specimens of steel ST3 (4000× magnification): (a) after exposure to a 0.1 M HCl solution without extracts; (b) after exposure to a 0.1 M HCl solution that is supplemented with extract of pomegranate peel.

structure and are relatively stable. The protection depends on the orientation of the tannin molecule with respect to a steel surface. With a flat arrangement, tannin hydroxyl groups can form stable chemical bonds with iron atoms. At an increase in the concentration, tannin molecules are arranged perpendicular to the specimen surface and form dark purple easily movable coordination compounds with iron ions. In this case, an increase in the concentration of plant extracts decreases the degree of protection and the corrosion medium becomes purple.

The presence of a protective film is confirmed by photographs of the specimen surface (Fig. 3): corrosion damage is observed on the surface in a 0.1 M HCl solution and a solid film without signs of corrosion is observed in a solution that is supplemented with inhibitors.

Comparison of the Auger spectra of the surface layers of steel 20 specimens ((*1*) in air, (*2*) after exposure to a 0.1 M HCl solution, and (*3*) in an inhibited 0.1 M HCl solution that is supplemented with extracts of pomegranate peel) indicates the presence of a protective film on the metal surface (Table 3, Fig. 4).

Thus, the inhibition of the medium by extract of pomegranate peel increases the iron content at an electron-escape depth of 4 nm by a factor of 5. The protective film on the steel surface prevents iron release in the form of primary corrosion products. The iron content in the specimen with pomegranate peel (Table 3, specimen 3) almost coincides with its distribution in the control specimen in the air (specimen 1), the surface of which is covered by a formed oxide film.

The inhibitor adsorption can occur both on metals with vacant electron orbitals and on metal oxides that have defects and can accept electrons. Exposure to 0.1 M HCl, when the extract of pomegranate peel is added, increases the oxygen content in the surface layers (Table 3, Fig. 4) at a depth up to 16 nm by a factor of 3–7. This is evidence of formation of a coordination compound at the interaction of the metal with oxygen that enters the composition of the functional groups of compounds from the extract of pomegranate peel.

When the extract of pomegranate peel is used, a chloride ion is not observed as an activator of corrosion in the surface layers of steel, which also confirms the presence of a protective film that makes the diffusion of activator ions to the metal surface difficult.

The carbon content is significantly higher in 0.1 M HCl solutions (both with and without extracts) than in the control specimen in the air. The high carbon content in specimens after exposure to a 0.1M HCl solution is obviously caused by chloride ions activating the steel surface, which becomes covered by a layer of

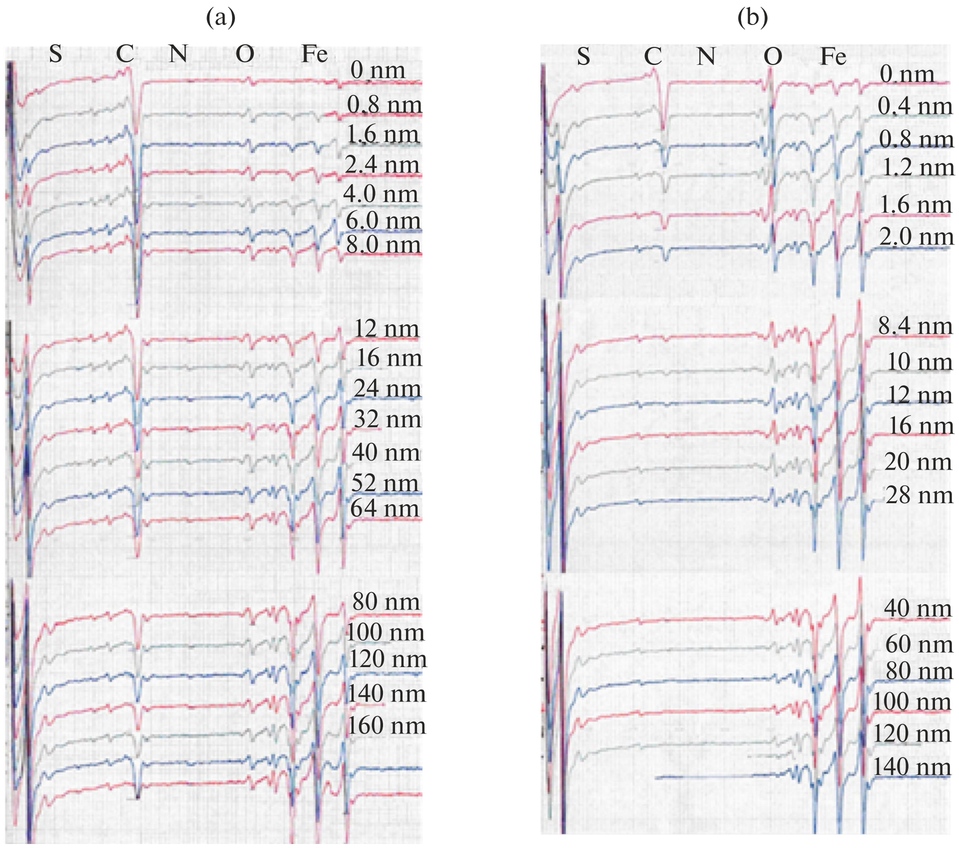

Fig. 4. The Auger electron spectra of the surface of steel 20: (a) after exposure to a 0.1 M HCl solution without extracts; (b) after exposure to a 0.1 M HCl solution that is supplemented with extract of pomegranate peel.

loose corrosion products and absorbs carbon compounds from the solution and the air. Moreover, iron ions are released into the solution in the form of corrosion products and this increases the carbon fraction on the steel surface. Addition of the extract of pomegranate peel elevates the carbon content at a depth of 4 nm, when compared to the control specimen, owing to the chemisorption of active components of the inhibitor on the metal surface (Fig. 2c).

Large technical difficulties are known to be caused by microorganisms, which grow on the walls of reservoirs and pipelines [15]. Therefore, we studied the antimicrobial action of the extracts. It has been found that the best antimicrobial activity is exhibited by the extract of pomegranate peel toward both Gram-positive *Bacillus subtilis* and Gram-negative *Escherichia coli*. The zone of growth inhibition for *Bacillus subtilis* and *Escherichia coli* was 20.5 and 18.2 mm, respectively, which indicates the high sensitivity of these cultures to the extract of pomegranate peel. The microbiological analysis of water supplemented with the extract of pomegranate peel (20 cm^3/dm^3) has demonstrated an eightfold decrease in the MAFAnM.

CONCLUSIONS

The hydroalcoholic extracts of basil, cinnamon, sage, clove, spirulina, and pomegranate peel that we studied exhibit a high anticorrosion activity in tap water and 0.1 M hydrochloric-acid solution and have an antimicrobial effect. The maximum degree of protection is observed for ST3 in tap water after addition of sage extract (94.65%) and in a 0.1 M hydrochloric-acid solution after addition of pomegranate peel (93.39%).

Auger spectrometry demonstrated the existence of a protective film on the steel surface, which is formed owing to adsorption of active components of the extract of pomegranate peel.

The suggested extracts from plant raw materials are environmentally friendly and nontoxic inhibitors of corrosion.

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