STUDIA UBB CHEMIA, LXIX, 2, 2024 (p. 49-66)
(RECOMMENDED CITATION)
DOI:10.24193/subbchem.2024.2.04

THE INHIBITORY PROPERTIES OF THE *FAGOPYRUM ESCULENTUM* GROATS BOILING EXTRACTS ON CORROSION OF THE MILD STEEL IN ACIDIC ENVIRONMENTS

Pavel Anatolyevich NIKOLAYCHUK[a,b,*]

ABSTRACT. The inhibitory ability of the boiling extracts from the groats of *Fagopyrum esculentum* on the corrosion of mild steel EN Fe37-3FN in 0.5 M hydrochloric acid and 0.5 M sulphuric acid media was investigated using gravimetric, electrochemical, and EIS methods. It was shown that the addition of 100 mg/l of the *Fagopyrum esculentum* groat extract reduces the corrosion rate by 50%, and that of of 1 g/l and more – by 75%. The adsorption of the extract components on a steel surface follows the Langmuir adsorption model, and the nature of adsorption is physical. The *Fagopyrum esculentum* groats extract shows itself as perspective and environmentally friendly substance for reducing the steel corrosion rate in acidic environments.

Keywords: *Fagopyrum esculentum, common buckwheat, acid medium corrosion inhibition, gravimetric study, electrochemical study, Langmuir adsorption isotherm.*

INTRODUCTION

The usage of industrial side products and wastes [1], expired drugs [2], food and biomass waste [3, 4] and compounds extracted from natural products [4] attract a growing interest of the corrosion engineers around the globe. By employing environmentally degradable natural compounds one could drastically reduce the costs and the ecological impact of both production of inhibitors, and their subsequent utilization. A plant's roots, leaves, aerial parts, fruits, and seeds are frequently used as the source of extracted compounds [4].

---

[a] *Kurganskij gosudarstvennyj universitet, Sovetskaya 63/4, 640020 Kurgan, Russian Federation*
[b] *Novosibirskij gosudarstvennyj universitet, Pirogova 2, 630090 Novosibirsk, Russian Federation*
* *Corresponding author: pavel.nikolaychuk@kgsu.ru*

Common buckwheat (*Fagopyrum esculentum*) is a pceudocereal plant cultivated widely for its grain-like seeds, as a cover crop, as a green manure, as a plant for erosion control or as wildlife cover and feed [5]. The porridge made from the ground and roasted buckwheat groats is common for East Europe and Central Asia. During the cooking the groats are boiled in water, which is then usually discarded. However, the cotyledons of the buckwheat plant contain diverse phytochemicals, including rutin [6], tannins, catechin-7-O-glucoside, fagopyrins [7–10], salicylaldehyde and some other aromatic aldehydes [11, 12]. However, both aldehydes, flavonoids and phenols [13, 14] exhibit inhibitory properties on metal oxidation. Moreover, antioxidant activity of the compounds extracted from the buckwheat groats was already reported [15, 16], and there is a clear dependency between the antioxidant and inhibition properties of natural compounds [17]. Therefore, the compounds extracted into the boiling water from *Fagopyrum esculentum* groats during the cooking might be useful and environmentally friendly corrosion inhibitors.

Acidic environments are often employed for the study of the effectiveness of inhibitors, because acids give the most demonstrative results [14]. In addition, the study of the acidic corrosion of metals is important for oil and gas industry, the galvanic electroplating of metals, the development of the solutions for the metal pickling, and for the rust removal [14]. Usually both hydrochloric acid as the non-oxidising acid, and sulphuric acid as the oxidising acid are used for the acidic corrosion testing. Therefore, in the present study, the inhibitory properties of the boiling extracts of the *Fagopyrum esculentum* groats on the corrosion of mild steel EN Fe37-3FN in 0.5 M hydrochloric acid and 0.5 M sulphuric acid media are aimed to be investigated.

RESULTS AND DISCUSSION

Gravimetric studies

From the measured weight losses ($\Delta m = m_0 - m$, mg, where m_0 and m are the weights of the steel sample before and after immersion into corrosive medium, respectively), sample surfaces (S, cm^2), and immersion times (t, h) the average corrosion rates (ω, mg/(cm$^2 \cdot$ h)) were estimated [14]:

$$\omega = \Delta m / (S \cdot t). \qquad (1)$$

An inhibitory ability of the compound according to gravimetric measurements (IE_{grav}, %) was estimated from the ratio of the corrosion rates in the absence (ω_0) and in the presence (ω) of the inhibitor [14]:

$$IE = (\omega_0 - \omega) / \omega_0 \cdot 100\%. \qquad (2)$$

The dependence of the measured inhibition efficiencies at the different inhibitor concentrations (c_{inh}, g/l) is presented in Table 1. The results show that upon addition of the *Fagopyrum esculentum* groats extract the weight loss of the steel plates significantly reduces that confirms its inhibitory effect.

Table 1. The results of the gravimetric measurement of the corrosion rates

Medium	**0.5 M HCl**		**0.5 M H_2SO_4**	
c_{inh}, g/l	**ω, mg/(cm² · h)**	**IE_{grav}, %**	**ω, mg/(cm² · h)**	**IE_{grav}, %**
0	0.89 ± 0.08	–	1.1 ± 0.1	–
0.1	0.42 ± 0.05	52.6	0.54 ± 0.05	51.2
0.3	0.26 ± 0.04	71.2	0.40 ± 0.05	63.8
1	0.17 ± 0.03	80.9	0.32 ± 0.04	71.0
3	0.14 ± 0.02	84.2	0.25 ± 0.04	77.2
10	0.12 ± 0.02	86.3	0.20 ± 0.03	81.4

Polarisation studies

An open circuit potential (E_{corr}, mV) was recorded during 30 min. The results are presented in Figure 1.

As could be seen, the addition of the inhibitor shifts both the initial and the equilibrium values of the open circuit potentials of steel in acid in the more positive direction. This implies that the the *Fagopyrum esculentum* groats extract acts as the anodic type inhibitor, and primarily decreases the rate of the anodic dissolution of metal.

For the measurement of the linear polarisation resistance the polarisation curves were presented in the coordinates E(*i*), and the polarisation resistances (R_p, Ohm · cm²) were evaluated as the slopes of these curves using the least squares technique:

$$R_p = dE / di. \tag{3}$$

The inhibitory ability of the compound according to the linear polarization resistance (IE_{LPR}) was estimated from the ratio of the polarisation resistances in the presence (R_p) and in the absence ($R_{p,0}$) of the inhibitor [14]:

$$IE_{LPR} = (R_p - R_{p,0}) / R_p \cdot 100\%. \tag{4}$$

The results are presented in Figure 2 and in Table 2.

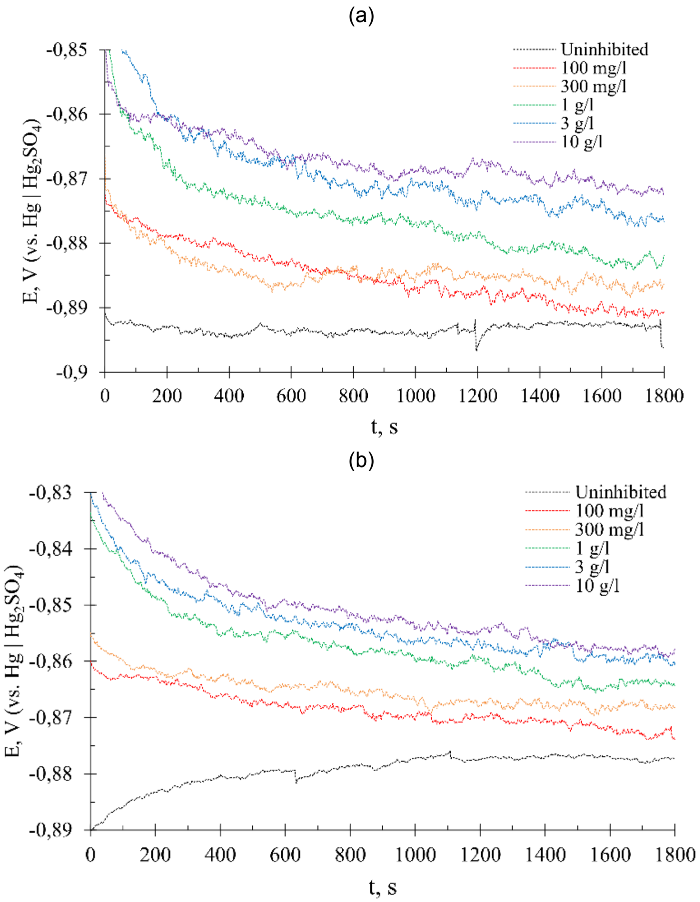

Figure 1. The open circuit potential of steel in (a) 0.5 M HCl, and (b) 0.5 M H_2SO_4 with the different additions of the *Fagopyrum esculentum* groats extract after 30 min of exposure.

Table 2. The measured polarisation resistance of the steel in the solutions of hydrochloric and sulphuric acids with the different additions of the inhibitor

Medium	**0.5 M HCl**		**0.5 M H_2SO_4**	
c_{inh}, g/l	**R_p, Ohm · cm^2**	**IE_{LPR}, %**	**R_p, Ohm · cm^2**	**IE_{LPR}, %**
0	630 ± 10	–	410 ± 10	–
0.1	1420 ± 20	55.8	810 ± 10	49.5
0.3	2430 ± 40	74.1	1150 ± 20	64.2
1	3420 ± 50	81.6	1340 ± 20	69.4
3	4370 ± 70	85.6	1770 ± 30	76.7
10	5460 ± 90	88.5	2810 ± 50	85.3

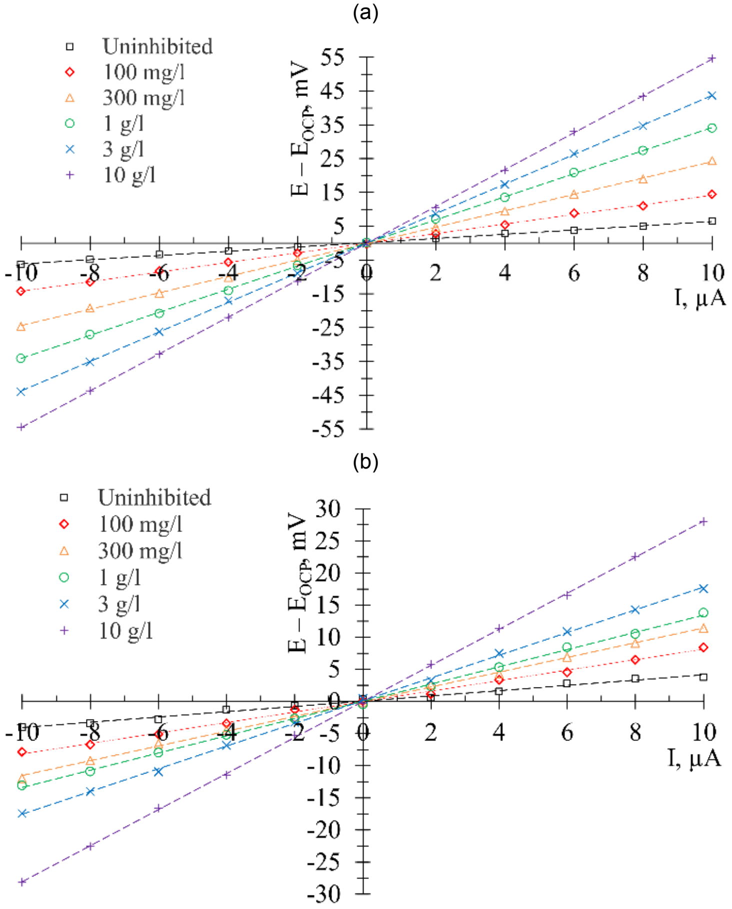

Figure 2. The linear polarisation resistance curves of steel in (a) 0.5 M HCl, and (b) 0.5 M H_2SO_4 with the different additions of the *Fagopyrum esculentum* groats extract

For the measurement of the Tafel slopes [18] and the corrosion current density the polarisation curves were presented in the coordinates $E(\lg i)$, and the Tafel slopes (b, mv/dec) and the corrosion current density (i_{corr}, A/cm^2) were evaluated from them [19]. Subsequently, the polarisation resistances (R_p, Ohm · cm^2) were estimated from the Tafel slopes and the corrosion current densities using the Stern – Geary equation [20, 21]:

$$R_p = b_a \cdot |b_c| / (\ln 10 \cdot i_{corr} \cdot (b_a + |b_c|)), \tag{5}$$

where b_a and b_c are the slopes of the anodic and cathodic branches of the polarisation curve. The inhibitory ability of the compound according to the corrosion current densities (IE_{CCD}) was estimated from the ratio of the corrosion current densities in the absence (i_0) and in the presence (i) of the inhibitor [14]:

$$IE_{CCD} = (i_0 - i) / i_0 \cdot 100\%, \qquad (6)$$

and also from the ratio of the polarisation resistances in the presence (R) and in the absence (R_0) of the inhibitor using equation (4). The results are presented in Figure 3 and in Table 3.

Table 3. The results of the electrochemical measurement of the corrosion rates

c_{inh}, g/l	E_{corr}, mV	b_a, mV/dec	b_c, mV/dec	i_{corr}, μA/cm^2	IE_{CCD}, %	R_p, Ohm·cm^2	IE_{LPR}, %
0.5 M HCl with additions of *Fagopyrum esculentum* groats extract							
0	–896	98.9	–118.8	38.4	–	611	–
0.1	–891	75.6	–127.1	17.4	54.7	1185	48.4
0.3	–886	72.6	–130.0	9.9	74.0	2037	70.1
1	–882	70.5	–134.4	7.0	81.6	2852	78.5
3	–877	75.5	–130.1	4.9	87.1	4183	85.4
10	–873	64.3	–146.5	3.9	89.7	4895	87.5
0.5 M H_2SO_4 with additions of *Fagopyrum esculentum* groats extract							
0	–877	55.1	–117.3	38.8	–	319	–
0.1	–874	37.6	–115.8	21,3	45.2	579	44.8
0.3	–868	31.9	–121.4	15.0	61.3	730	56.2
1	–864	30.9	–126.2	11.9	69.4	903	64.5
3	–860	32.1	–128.6	10.2	73.8	1281	75.0
10	–857	33.1	–128.9	7.8	79.9	1511	78.8

As could be seen from the results, the Tafel slopes of the anodic branches of polarisation curves significantly decrease upon addition of the buckwheat groats extract, whereas the slopes of the cathodic branches of polarisation curves slightly increase. This confirms that the extract acts as the anodic type inhibitor, and decreases the rate of metal anodic dissolution, whereas the rate of the hydrogen production at the cathode remains practically the same. The values of the linear polarisation resistances obtained experimentally and estimated by the Stern–Geary equation coincide well, which confirms the integrity of the experimental data.

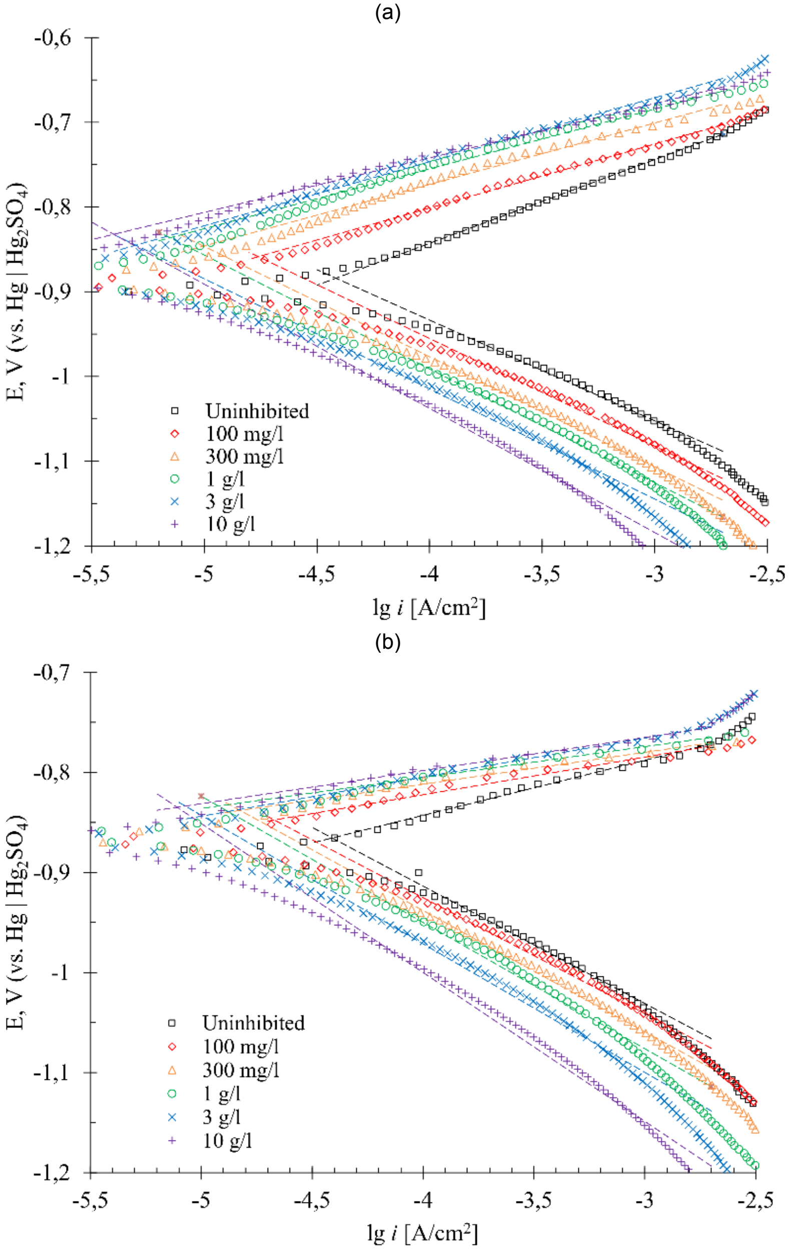

Figure 3. The polarisation curves of steel in (a) 0.5 M HCl, and (b) 0.5 M H_2SO_4 with the different additions of the *Fagopyrum esculentum* groats extract after 30 min of exposure.

EIS studies

For EIS tests, the obtained results were presented in the form of Bode and Nyquist plots [22]. For the estimation of the impedance parameters, a simplified Randles equivalent electrical circuit [23], containing the solution resistance R_s, the consecutive charge transfer resistance R_{ct} of the passivation layer, and the parallel constant-phase element representing the double electric layer, was employed. The impedance (*Z*, Ohm) of the Randles equivalent circuit is expressed by the equation [22]:

$$Z = R_s + 1 / ((1 / R_{ct}) + P \cdot (i \cdot \omega)^n), \tag{7}$$

where ω, Hz is the frequency of the alternate current, i is an imaginary unit, and P and n are the parameters of the constant phase element.

The fitting of the equivalent circuit parameters to the experimental impedance values was performed using the free software EIS Spectrum Analyser [24]. In addition, the capacitance (C_{dl}, F) and the thickness (d, m) of the double electric layer were estimated [25]:

$$C_{dl} = P^{1/n} \cdot (R_s \cdot R_{ct} / (R_s + R_{ct}))^{(1-n)/n}, \tag{8}$$

$$d = (S \cdot \varepsilon_0 \cdot \varepsilon) / C_{dl}, \tag{9}$$

where *S*, m^2 is the electrode surface, ε is the dielectric constant of water, and $\varepsilon_0 = 8.85 \cdot 10^{-12}$ F/m is the dielectric constant of vacuum.

The inhibitory ability of the compound according to the electrochemical impedance spectroscopy (IE_{EIS}) was estimated from the ratio of the charge transfer resistances in the presence (R_{ct}) and in the absence ($R_{ct,0}$) of the inhibitor [14]:

$$IE_{EIS} = (R_{ct} - R_{ct,0}) / R_{ct} \cdot 100\%. \tag{10}$$

The results are presented in Figure 4 and in Table 4.

The Nyquist plots demonstrate a semicircle behaviour typical for the Rangles equivalent circuit. With addition of the inhibitor the semicircle diameter increases, but the form of the plot does not change, which implies that the inhibitor does not alter the corrosion mechanism (which is also confirmed by the almost constant value of the constant phase element parameter n) but increases the resistance of the charge transfer through the metal surface. The constant phase element parameter P decreases upon addition of the buckwheat groats extract, which means the decrease of the double layer capacitance, and the increase of the double layer thickness.

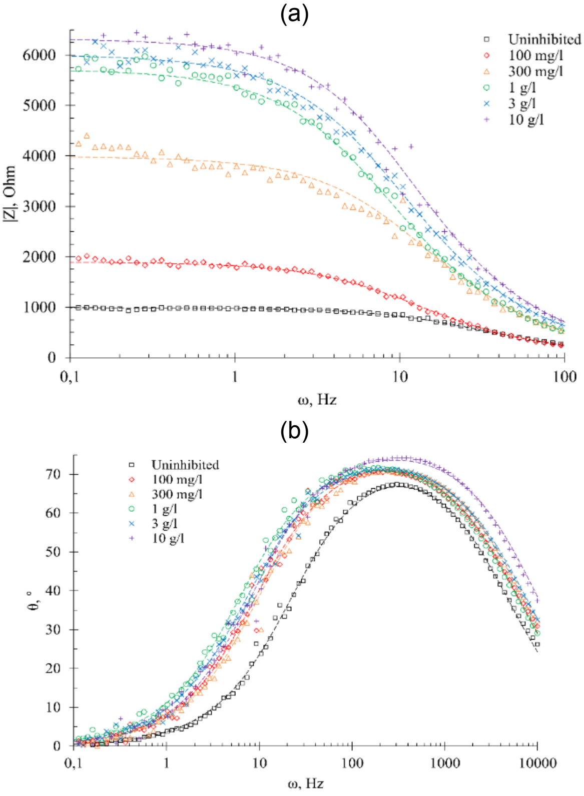

Figure 4ab. The Bode plots of steel in (a), (b) 0.5 M HCl with the different additions of the *Fagopyrum esculentum* groats extract after 30 min of exposure.

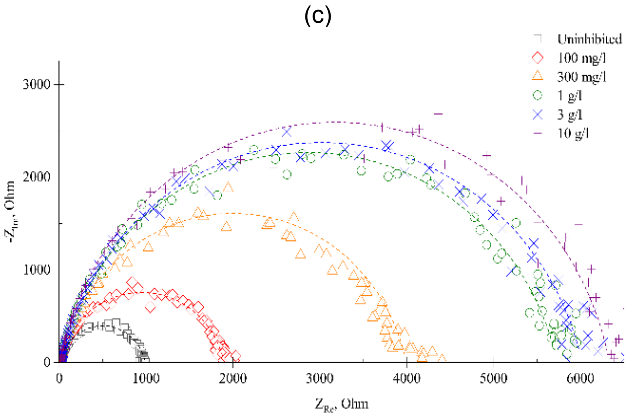

Figure 4c. The Nyquist plots of steel in 0.5 M HCl with the different additions of the *Fagopyrum esculentum* groats extract after 30 min of exposure.

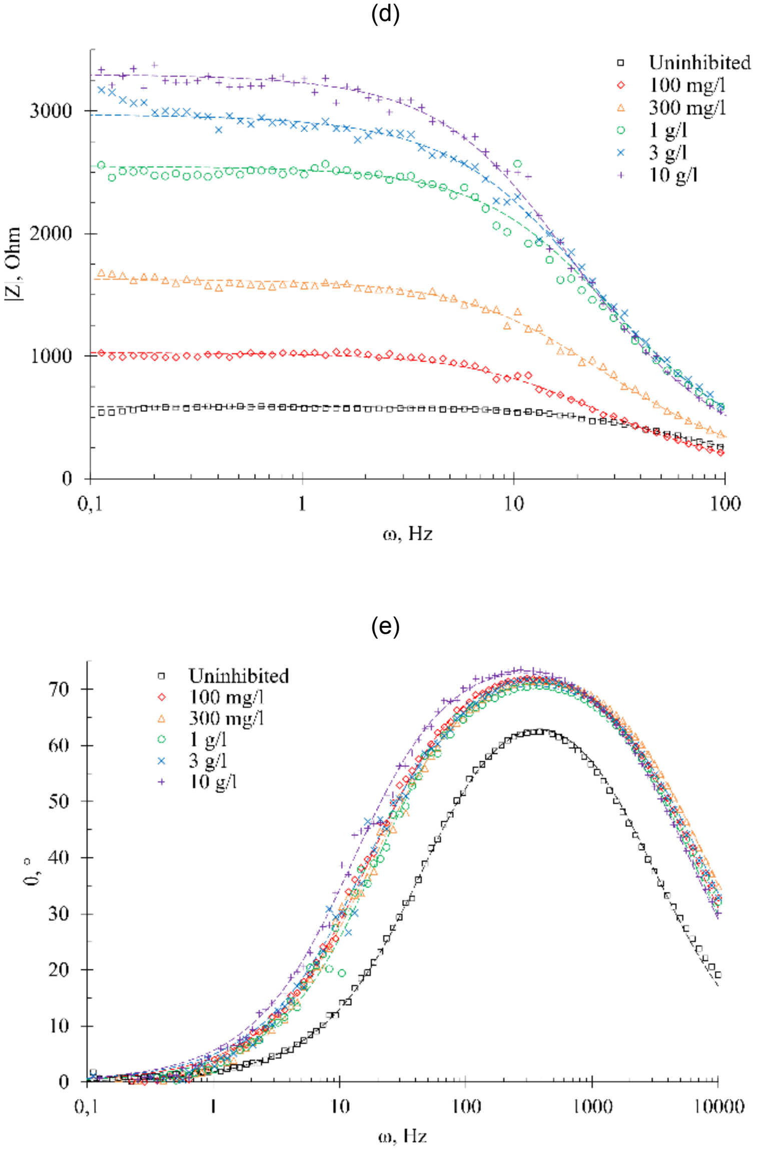

Figure 4de. The Bode plots of steel in (d), (e) 0.5 M H_2SO_4 with the different additions of the *Fagopyrum esculentum* groats extract after 30 min of exposure.

(f)

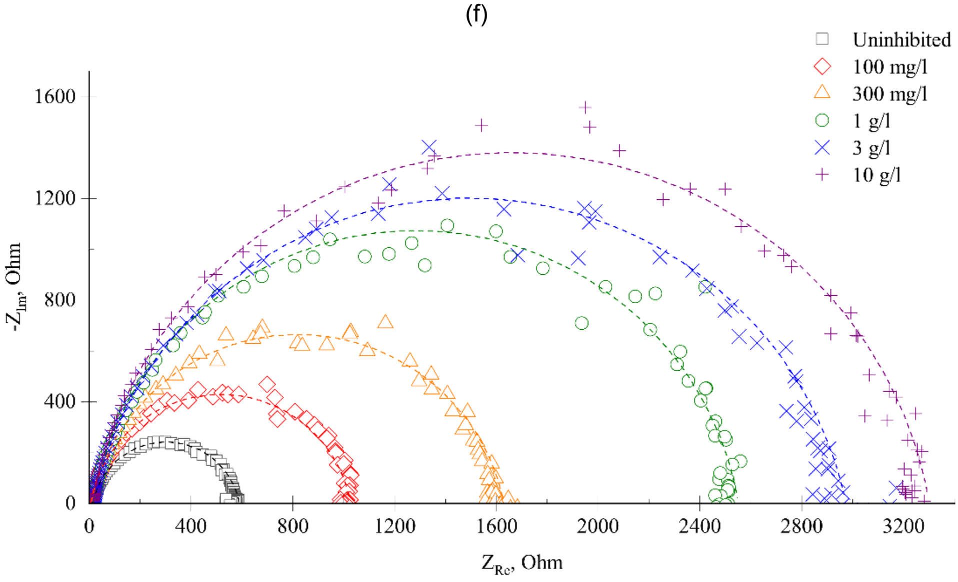

Figure 4f. the Nyquist plots of steel in 0.5 M H_2SO_4 with the different additions of the *Fagopyrum esculentum* groats extract after 30 min of exposure.

Table 4. The results of the EIS measurement of the corrosion rates

c_{inh}, g/l	R_s, Ohm	P, $\mu Ohm^{-1} \cdot s^n$	n	C_{dl}, µF	d, nm	R_{ct}, Ohm	IE_{EIS}, %
0.5 M HCl with additions of *Fagopyrum esculentum* groats extract							
0	9.8	142.6	0.86	710	3.91	983.3	–
0.1	7.1	162.6	0.85	739	3.75	1891.3	48.0
0.3	14.4	69.2	0.87	347	7.99	3979.4	75.3
1	15.9	77.1	0.85	354	7.83	5717.9	82.8
3	16.3	63.8	0.85	285	9.74	6002.9	83.6
10	13.4	48.8	0.88	246	11.30	6319.5	84.4
0.5 M H_2SO_4 with additions of *Fagopyrum esculentum* groats extract							
0	14.8	110.6	0.89	663	4.17	575.8	–
0.1	5.2	150.8	0.89	828	3.34	1022.8	43.7
0.3	7.8	97.9	0.87	472	5.86	1622.4	64.5
1	15.2	51.6	0.89	283	9.77	2535.8	77.3
3	13.9	61.6	0.87	302	9.16	2959.6	80.5
10	14.1	60.4	0.89	335	8.26	3287.3	82.4

Langmuir adsorption model

The description of the adsorption of the groats extract components on the steel surface was performed in terms of the Langmuir adsorption model [26]. The Langmuir adsorption isotherm equation was linearised in the form:

$$c_{inh} / \theta = 1 / K_{ads} + c_{inh}, \qquad (11)$$

where c_{inh}, g/l is the concentration of the *Fagopyrum esculentum* groats extract solution, K_{ads}, l/g is the adsorption-desorption equilibrium constant, and θ is the percentage of the surface covered by the inhibitor, which assumed to be equal to the inhibition efficiency. The dependencies of c_{inh}/θ on c_{inh} are presented in Figure 5 and in Table 5.

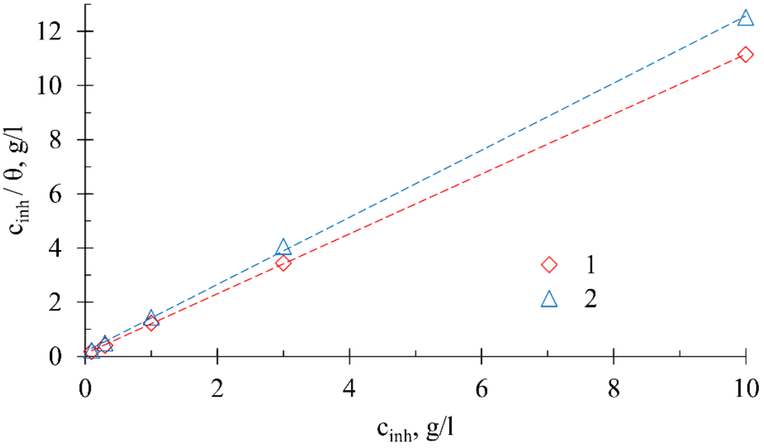

Figure 5. The plots of c_{inh} / θ vs. c_{inh} for the adsorption of the *Fagopyrum esculentum* groats extract on the steel surface from the solution of (1) 0.5 M HCl, (2) 0.5 M H_2SO_4.

The data were processed using the least squares technique [27], and the equilibrium constants K_{ads} were estimated as the intercepts of the regression equations. The Gibbs energy changes of the sorption ($\Delta_{ads}G$, J/mol) were estimated from the equation:

$$\Delta_{ads}G = -RT \ln (K_{ads} \cdot c_{water}), \qquad (12)$$

where $c_{water} = 10^3$ g/l is the water concentration in the extracts. The results are presented in Table 5. The results show that the Langmuir adsorption model describes the inhibitor sorption on the metal surface quite well. The calculated Gibbs energies of sorption do not exceed –20 kJ/mol for both hydrochloric and sulphuric acids, which means the physical nature of the sorption.

Table 5. The parameters of the Langmuir adsorption model

C_{inh}, g/l	θ	C_{inh} / θ, g/l	Regression equation	K_{ads}, l/g	$\Delta_{ads}G$, kJ/mol
0.5 M HCl with additions of *Fagopyrum esculentum* groats extract					
0.1	0.547	0.183	$c_{inh} / \theta = (1.106 \pm 0.003) \cdot c_{inh} + (0.09 \pm 0.02)$; $R^2 = 0.999$	11 ± 2	–23 ± 1
0.3	0.740	0.405			
1	0.816	1.225			
3	0.871	3.444			
10	0.897	11.148			
0.5 M H_2SO_4 with additions of *Fagopyrum esculentum* groats extract					
0.1	0.452	0.221	$c_{inh} / \theta = (1.24 \pm 0.01) \cdot c_{inh} + (0.18 \pm 0.07)$; $R^2 = 0.998$	7 ± 3	–21 ± 2
0.3	0.613	0.489			
1	0.694	1.441			
3	0.738	4.065			
10	0.799	12.516			

The results of the open circuit potential measurements show that with the addition of a *Fagopyrum esculentum* groats extract the potential of the mild steel both in the solution of 0.5 M HCl and 0.5 M H_2SO_4 shifts to the more positive values. In addition, the Tafel slopes of the anodic branches of the polarisation curves decrease with alteration of the extract concentration, whereas the slopes of the cathodic branches only slightly increase. This implies that in the solutions of both acids the buckwheat groats extract acts as the anodic-type inhibitor [28, 29].

The values of the inhibition efficiencies estimated from the data of gravimetric (IE_{grav}), electrochemical (IE_{LPR} and IE_{CCD}) and EIS experiments (IE_{EIS}) coincide well and show the similar trend. The values of the polarisation resistance of the absorbed inhibitor estimated from the data of linear polarisation and from the Tafel slopes also coincide well, which confirms the integrity of the data.

With the increase of the extract concentration from 0.1 to 1 g/l its inhibition efficiency on the corrosion of mild steel EN Fe37-3FN in a 0.5 M hydrochloric acid medium rises from ~50% to ~80%, but the further concentration increase gives no significant improvement of the inhibition efficiency. In contrast, the inhibition efficiency of the extract on the corrosion of the same steel in a 0.5 M sulphuric aicd medium continues to increase with the rise of extract concentration, and approaches ~80% when the concentration of 10 g/l is achieved.

The adsorption of the extracted components on the steel surface fairly obeys the Langmuir adsorption model. The calculated Gibbs energies of sorption are in the range ~ –20 kJ/mol for both hydrochloric and sulphuric acids, which means that the nature of the adsorption is physical due to the electrostatic interactions [30].

Despite the experimental values of the inhibition efficiencies may vary significantly with alteration of both the solution composition and temperature [31], the groats extracts of *Fagopyrum esculentum* showed itself as a perspective natural corrosion inhibitor for steels in acidic environments. The addition of buckwheat groats extracts to a corrosive environment can be used to protect equipment from corrosion in pickling areas of metal processing industries, and in electroplating baths, and also be part of products for removing corrosion products from steel surfaces [32, 33].

CONCLUSIONS

The inhibitory ability of the *Fagopyrum esculentum* groats boiling extracts on the corrosion of mild steel EN Fe37-3FN in 0.5 M hydrochloric acid and 0.5 M sulphuric acid media was investigated using gravimetric, electrochemical, and EIS methods. It was shown that the addition of 100 mg/l of the extract reduces the corrosion rate in HCl by 50% and in H_2SO_4 by 50%, whereas the addition of 10 g/l of the extract further reduces the corrosion rate by 80%. The adsorption of the extract components on a steel surface follows the Langmuir adsorption model, and the nature of adsorption is physical. The *Fagopyrum esculentum* groats extract shows itself as perspective and environmentally friendly substance for reducing the steel corrosion rate in acidic environments.

EXPERIMENTAL SECTION

Reagents and Equipment

Ethanol (analytical grade) and hydrochloric and sulphuric acids (pure grade) were purchased from LLC "Sigma Tek" (Khimki, Russia). Steel electrodes were manufactured from cylindrical ingots made of mild steel EN Fe37-3FN (containing no more than 0.14% C, 0.3% Ni, Cu, and Cr, 0.05% Si, 0.4% Mn, 0.05% P and 0.04% S). The unused flat end surface of the ingots was sealed by the epoxy resin, and the cylindrical working surface immersed in the solution was equal to 0.04 cm^2.

Weighting of the samples was performed using the analytical balance EX224/AD (Ohaus Corp., Parsippany, USA). Electrochemical and EIS measurements were conducted using the potentiostat-galvanostat PS-50 (LLC “SmartStat”, Chernogolovka, Russia). The mercury-mercurous sulphate reference electrode by Schott Instruments GmbH (Meinz, Germany) was used. A water for solution preparation was first distilled using the aquadistiller AE-15 (LLC “Livam”, Belgorod, Russia) and then deionized using the water purification system AkvaLab S18 (LLC “Akvalab”, Moscow, Russia). The magnetic stirrer MS-200 LT (LLC “Labtex”, Moscow, Russia) was used for stirring and heating the solutions. The single-channel laboratory pipettes manufactured by Thermo Fisher Scientific (Waltham, USA) were used for pipetting the solutions. A laboratory glassware of 2nd grade was used.

Preparation of the extracts

The buckwheat grain is collected usually after 90–110 days after seeding, separated from grain shells, processed by steam under the temperature of 120 ^{o}C and pressure of 0.6 MPa during 10 minutes, then air-dried and ground.

The dried and ground groats of the common buckwheat are produced in Russia at the industrial scale, and are commercially available. They were purchased from LLC “Kamelot-A” (Tomsk, Russia).

A total of 100 g of dried and ground *Fagopyrum esculentum* groats were weighted, immersed into a litre of the deionised water, heated and boiled under the reflux condenser during 3 h. The boiling extracts were cooled, the groat material was removed, and the solid residues were filtered off through the filter paper with the pore diameter of 12 μm.

A total of 10 ml of each extract were taken, placed in a beaker and heated to dryness in order to determine the masses of the dissolved substances and the initial concentrations of the extract solutions. Then the working solutions of the *Fagopyrum esculentum* groats extract with the concentrations ranging from 0.2 to 20 g/l were prepared by the appropriate dilutions. The solutions were then equally diluted by 1 M hydrochloric acid or by 1 M sulphuric acid to finally produce a series of acidic solutions of *Fagopyrum esculentum* groats extract in 0.5 M HCl or 0.5 M H_2SO_4 with concentrations ranging from 0.1 to 10 g/l.

Gravimetric studies

For gravimetric tests, rectangular flat plates made of EN Fe37-3FN mild steel with thickness 3 mm, width 20 ± 2 mm, and height 30 ± 2 mm (the plate surface is 15 cm^2) were polished using the P2500 emery paper and degreased by ethanol. The weighted plates were immersed into corrosive media for 2 h, then washed with distilled water, dried, and reweighted. Each experiment was performed in triplicate.

Electrochemical and EIS studies

For electrochemical and EIS tests, electrodes made of EN Fe37-3FN mild steel and sealed with the epoxy resin with the working surface of 0.04 cm^2 were polished using the P2500 emery paper and degreased by ethanol. The measurements were conducted in a standard three-electrode electrochemical cell, consisting of the working electrode (steel sample), auxiliary electrode from the porous graphite, and the mercury-mercurous sulphate reference electrode. An open circuit potential was recorded during 30 min. For the measurement of the linear polarization resistance the polarization curves were recorded in galvanodynamic mode in the current ranges from –10 μA and to +10 μA with the current sweep rate of 2 μA/s. For the measurement of the Tafel slopes [18] and the corrosion current density the polarisation curves were recorded in both directions in the potential ranges from the measured open circuit potential to –500 mV and to +500 mV relatively to it with the potential sweep rate of 10 mV/s. An impedance values were recorded at the open circuit potential value in the alternate current frequency interval from 100 mHz to 10 kHz with the potential amplitude of 10 mV. Each experiment was performed in triplicate.

ACKNOWLEDGMENTS

This work was supported by the state assignments of the Ministry of Science and Higher Education of the Russian Federation (Project Reg. No. 1023041400091-5-3.2.10;2.4.2 and FSUS-2022-0022) and the strategic academic leadership program “Prioritet 2030”.

REFERENCES

1. R. Haldhar; S. C. Kim; E. Berdimurodov; D. K. Verma; C. M. Hussain; Corrosion inhibitors: industrial applications and commercialization. In *Sustainable corrosion inhibitors II: Synthesis, design, and practical applications*, ACS Symposium Series, American Chemical Society, USA **2021**, Volume 1404, pp. 219-235. doi: 10.1021/bk-2021-1404.ch010.
2. N. Vaszilcsin; A. Kellenberger; M. L. Dan; D. A. Duca; V. L. Ordodi; *Materials*, **2023**, *16(16)*, 5555. doi: 10.3390/ma16165555.
3. A. Thakur; S. Sharma; R. Ganjoo; H. Assad; A. Kumar; *J. Phys. Conf. Ser.*, **2022**, *2267(1)*, 012079. doi: 10.1088/1742-6596/2267/1/012079.
4. S. Marzorati; L. Verotta; S. P. Trasatti; *Molecules*, **2018**, *24(1)*, 48. doi: 10.3390/molecules24010048.

5. T. Björkman; R. R. Bellinder; R. R. Hahn; J. Shail; *Buckwheat Cover Crop Handbook*, Cornell University, Ithaca, New York, USA **2008**.
6. S. Kreft; M. Knapp; I. Kreft; *J. Agric. Food Chem.*, **1999**, *47(11)*, 4649–4652. doi:10.1021/jf990186p.
7. K. Eguchi; T. Anase; H. Osuga; *Plant Prod. Sci.*, **2009**, *12(4)*, 475–480. doi:10.1626/pps.12.475.
8. L. Ožbolt; S. Kreft; I. Kreft; M. Germ; V. Stibilj; *Food Chem.*, **2008**, *110(3)*, 691–696. doi: 10.1016/j.foodchem.2008.02.073.
9. E. Tavčar Benković; D. Žigon; M. Friedrich; J. Plavec; S. Kreft; *Food Chem.*, **2014**, *143*, 432–439. doi: 10.1016/j.foodchem.2013.07.118.
10. S. Kreft; D. Janeš; I. Kreft; *Acta Pharm.*, **2013**, *63(4)*, 553–560. doi:10.2478/acph-2013-0031.
11. D. Janes; S. Kreft; *Food Chem.*, **2008**, *109(2)*, 293–298. doi: 10.1016/j.foodchem.2007.12.032.
12. D. Janes; D. Kantar; S. Kreft; H. Prosen; *Food Chem.*, **2009**, *112(1)*, 120–124. doi: 10.1016/j.foodchem.2008.05.048.
13. N. Bhardwaj; P. Sharma; V. Kumar; *Cor. Rev.*, **2021**, *39(1)*, 27-41. doi: 10.1515/corrrev-2020-0046.
14. A. Kadhim; A. A. Al-Amiery; R. Alazawi; M. K. S. Al-Ghezi; R. H. Abass; *Int. J. Cor. Scale Inh.*, **2021**, *10(1)*, 54-67. doi: 10.17675/2305-6894-2021-10-1-3.
15. M. Watanabe; *J. Agric. Food Chem.*, **1998**, *46(3)*, 839-845.
16. I. Sedej; M. Sakač; A. Mandić; A. Mišan; V. Tumbas; J. Čanadanović-Brunet; *J. Food Sci.*, **2012**, *77(9)*, C954-C959. doi: 10.1111/j.1750-3841.2012.02867.x.
17. V. I. Vorobyova; M. I. Skiba; A. S. Shakun; S. V. Nahirniak; *Int. J. Cor. Scale Inh.*, **2019**, *8(2)*, 150-178. doi: 10.17675/2305-6894-2019-8-2-1.
18. J. Tafel; *Z. Phys. Chem.*, **1905**, *50(1)*, 641-712. doi: 10.1515/zpch-1905-5043.
19. F. Mansfeld; *Corrosion*, **1973**, *29(10)*, 397-402. doi: 10.5006/0010-9312-29.10.397.
20. M. Stern; *Corrosion*, **1958**, *14(9)*, 60-64. doi: 10.5006/0010-9312-14.9.60.
21. M. Stern; A. L. Geary; *J. Electr. Soc.*, **1957**, *104(1)*, 56-63. doi: 10.1149/1.2428496.
22. X. Z. Yuan; C. Song; H. Wang; J. Zhang; EIS equivalent circuits. In *Electrochemical Impedance Spectroscopy in PEM Fuel Cells: Fundamentals and Applications*, X. Z. Yuan et al. Eds.; Springer, Berlin, Germany, **2010**, pp. 139-192. doi: 10.1007/978-1-84882-846-9_4.
23. J. E. B. Randles; *Disc. Faraday Soc.*, **1947**, *1*, 11-19. doi: 10.1039/DF9470100011.
24. A. S. Bondarenko; G. A. Ragoisha; Inverse problem in potentiodynamic electrochemical impedance spectroscopy. In *Progress in Chemometrics Research*, A. L. Pomerantsev Ed.; Nova Science Publishers, New York, USA, **2005**, pp. 89–102, http://www.abc.chemistry.bsu.by/vi/analyser.
25. A. Lasia; *Electrochemical Impedance Spectroscopy and its Applications*, Springer, New York, USA, **2014**. doi: 10.1007/978-1-4614-8933-7.
26. I. Langmuir; *J. Am. Chem. Soc.*, **1918**, *40(9)*, 1361-1403. doi: 10.1021/ja02242a004.

27. R. Adrain; *The Analyst; Or Mathematical Museum*, **1808**, *1(4)*, 93-109.
28. S.-I. Pyun; *ChemTexts*, **2021**, *7(1)*, 2. doi: 10.1007/s40828-020-00121-y.
29. X. Xie; R. Holze; *ChemTexts*, **2018**, *4(1)*, 5. doi: 10.1007/s40828-018-0057-0.
30. A. Kokalj; *Cor. Sci.*, **2022**, *196*, 109939. doi: 10.1016/j.corsci.2021.109939.
31. A. B. Kičenko; V. M. Kušnarenko; *Praktika protivokorrozionnoj zaŝity*, **2005**, *4(38)*, 17-22.
32. T. J. Harvey, F. C. Walsh; A. H. Nahlé; *J. Mol. Liq.*, **2018**, *266*, 160-175. doi: 10.1016/j.molliq.2018.06.014.
33. M. Goyal; et al. *J. Mol. Liq.*, **2018**, 256, 565-573, doi: 10.1016/j.molliq.2018.02.045.