ORIGINAL ARTICLE

The inhibitory properties of the boiling extracts from *Chenopodium album* and *Polygonum aviculare* aerial parts on the corrosion of mild steel in hydrochloric acid medium

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The inhibitory ability of the boiling extracts from the aerial parts of Chenopodium album *and* Polygonum aviculare *on the corrosion of mild steel EN Fe37-3FN in 0.5 M hydrochloric acid medium was investigated using electrochemical methods and EIS. It was shown that the addition of 90 mg/l of the* Chenopodium album *aerial parts extract reduces the corrosion rate by 35%, and that of of 1 g/l and more – by 75%, whereas the addition of 120 mg/l of the* Polygonum aviculare *aerial parts extract reduces the corrosion rate by 40%, and that of of 1 g/l and more – by 85%. The adsorption of the extract components on a steel surface follows the Langmuir adsorption model, and the nature of adsorption is physical. The* Chenopodium album *and* Polygonum aviculare *aerial parts extracts show themselves as perspective and environmentally friendly substances for reducing the steel corrosion rate in acidic environments.*

INTRODUCTION

The use of compounds produced from natural products as corrosion inhibitors has recently attracted experimenters' growing interest [1, 2]. Utilising environmentally degradable natural compounds reduces the costs associated with finding and producing special inhibitors. A plant's roots, leaves, aerial parts, fruits, and seeds are frequently used as extracts [3, 4]. The use of food waste and biomass-based products is also given a new potential by this [5].

The white goosefoot (*Chenopodium album*) and the common knotgrass (*Polygonum aviculare*) are the fast growing annual plants widespread in the fields and wastelands, which makes them very common weed plants in several parts of Europe and Asia. Their aerial parts contain several flavonoids [6–8] and phenols [7]. However, both flavonoids [9, 10] and phenols [10] exhibit inhibitory properties on metal oxidation, and therefore, the boiling extracts of both *Chenopodium album* and *Polygonum aviculare* aerial parts might be useful and environmentally friendly corrosion inhibitors. However, the inhibitory properties of aerial parts extracts of the goosefoot or the knotgrass on the metal corrosion were never examined, and there are no published studies in the literature.

Therefore, in the present study, the inhibitory properties of the boiling extracts of the *Chenopodium album* and *Polygonum aviculare* aerial parts on the corrosion of mild steel EN Fe37-3FN in 0.5 M hydrochloric acid medium are aimed to be investigated.

EXPERIMENTAL

Reagents and equipment

Ethanol (analytical grade) and hydrochloric acid (pure grade) were purchased from LLC "Lenreaktiv". 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 6.3 cm^2.

Weighting of the samples was performed using the analytical balance HT-224RCE (Vibra). Electrochemical and EIS measurements were conducted using the potentiostat-galvanostat P-45X with the frequency response analyser FRA-24M (LLC "Electrochemical Instruments"). The Faraday shield cell SH-3M (LLC "Electrochemical Instruments") was used for shielding the electrochemical cell. The distilled water for solution preparation was produced using the aquadistiller Liston A1204 (LLC "Liston"). The magnetic stirrer RET control-visc (IKA) was used for stirring and heating the solutions. A laboratory glassware of 2nd grade was used.

Preparation of the extracts

The whole plants of *Chenopodium album* and *Polygonum aviculare* were harvested during the bluming perod in early August from the several fields in the outskirts of Kurgan, Russia. The seeds were removed, and the aerial parts including stems, leaves and flowers were air-dried in the absence of the direct sunlight during three months and subsequently ground.

A total of 100 g of dried and ground *Chenopodium album* aerial parts and of 100 g of dried and ground *Polygonum aviculare* aerial parts were weighted, immersed into a litre of the distilled water, heated and boiled under the reflux condenser during 3 h. The boiling extracts were cooled, the plant 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 *Chenopodium album* aerial parts extract with the concentrations ranging from 0.18 to 6 g/l, and those of the *Polygonum aviculare* aerial parts extract with the concentrations ranging from 0.24 to 8 g/l were prepared by the appropriate dilutions. The solutions were then equally diluted by 1 M hydrochloric acid to finally produce a series of acidic solutions of *Chenopodium album* aerial parts extract in 0.5 M HCl with concentrations ranging from 0.09 to 3 g/l, and of *Polygonum aviculare* aerial parts extract in 0.5 M HCl with concentrations ranging from 0.12 to 4 g/L.

Gravimetric studies

For gravimetric tests, solutions of 0.5 M hydrochloric acid and 0.5 M hydrochloric acid with the addition of different concentrations of *Chenopodium album* or *Polygonum aviculare* aerial parts extracts were prepared. Rectangular flat plates made of EN Fe37-3FN mild steel with thickness 3 mm, width 20 ± 2 mm, and height 30 ± ± 2 mm were polished using the P2500 emery paper and degreased by ethanol. The weighted plates (m_0, mg) were immersed into corrosive media for 2 h, then washed with distilled water, dried, and reweighted (m, mg). Each experiment was performed in triplicate. From the measured weight losses ($\Delta m = m_0 - m$, mg), sample surfaces (S, cm^2), and immersion times (t, h) the average corrosion rates (ω, mg/(cm^2·h)) were estimated: $\omega = \Delta m$ / / ($S \cdot$ t). An inhibitory ability (IE, %) of the compound was estimated from the ratio of the corrosion rates in the absence (ω_0) and in the presence (ω) of the inhibitor: IE = $(\omega_0 - \omega) / \omega_0 \cdot 100\%$.

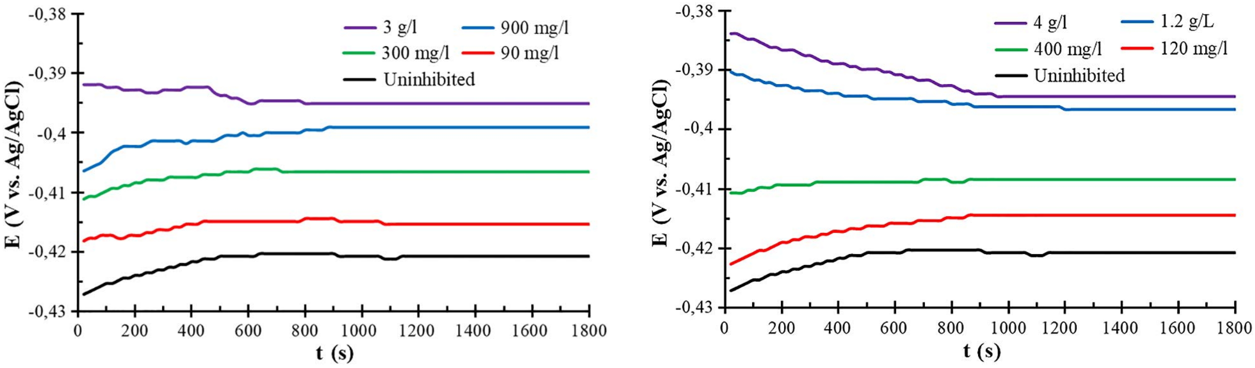
The dependence of the measured inhibition efficiencies at the different inhibitor concentrations (c_{inh}, g/l) is presented in Table 1.

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

c_{inh} [g/l]	ω [mg/(cm²·h)]	IE [%]
0	0.86 ± 0.08	–
Chenopodium album aerial parts extract		
0.09	0.59 ± 0.06	32.0
0.3	0.32 ± 0.05	62.3
0.9	0.24 ± 0.04	71.6
3	0.14 ± 0.03	83.2
Polygonum aviculare aerial parts extract		
0.12	0.51 ± 0.06	41.2
0.4	0.27 ± 0.05	68.4
1.2	0.15 ± 0.04	83.1
4	0.09 ± 0.03	89.5

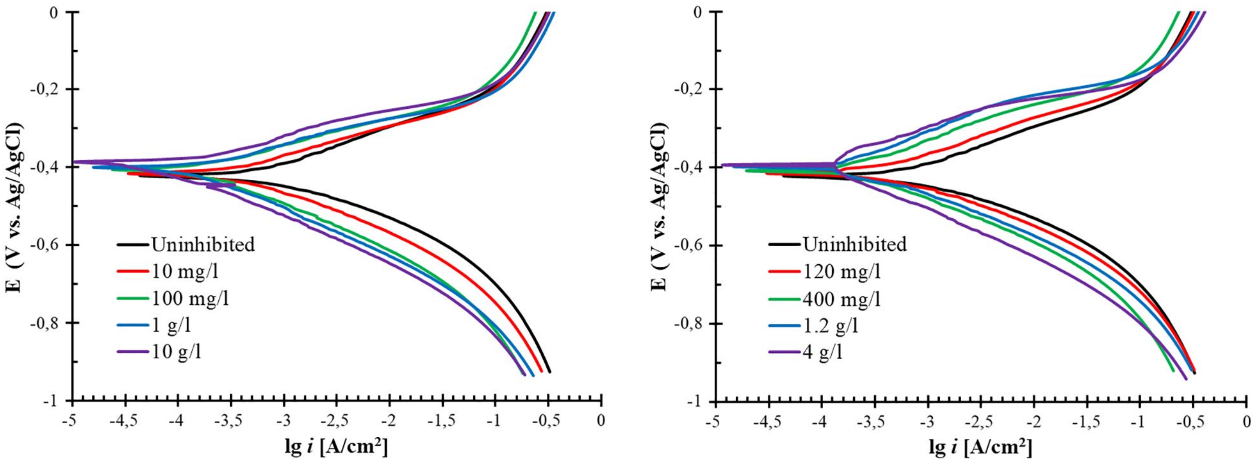
Polarisation studies

For polarisation tests, solutions of 0.5 M hydrochloric acid and 0.5 M hydrochloric acid with the addition of different concentrations of *Chenopodium album* or *Polygonum aviculare* aerial parts extracts were prepared. Electrodes made of EN Fe37-3FN mild steel and sealed with the epoxy resin with the working surface of 6.3 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 from the working electrode (steel sample), auxiliary electrode from the porous graphite, and the silver-silver chloride reference electrode. The cell was placed into the Faraday shield cell. An open circuit potential (E_{corr}) was recorded during 30 min. The results are presented in Figure 1. 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. Each experiment was performed in triplicate. The obtained polarisation curves were presented in the coordinates E (log i), and the Tafel slopes (b) and the corrosion current density (i_{corr}) were evaluated from them



a) b)

Fig. 1. The open circuit potential of steel in 0.5 M HCl with the different additions of: a) the *Chenopodium album* aerial parts extract, b) the *Polygonum aviculare* aerial parts extract after 30 min of exposure



a) b)

Fig. 2. The polarisation curves of steel in 0.5 M HCl with the different additions of: a) the *Chenopodium album* aerial parts extract, b) the *Polygonum aviculare* aerial parts extract after 30 min of exposure

Tab. 2 The results of the electrochemical measurement of the corrosion rates

c_{inh} [g/l]	E_{cor} [mV]	b_a [mV/dec]	b_c [mV/dec]	i_{cor} [mA/cm²]	R_p [Ohm·cm²]	IE [%]
0	–421	92.8	–112.2	0.66	177	–
Chenopodium album aerial parts extract						
0.09	–415	73.9	–129.6	0.43	253	35.4
0.3	–407	69.3	–138.9	0.22	491	67.2
0.9	–399	59.5	–138.0	0.15	623	76.8
3	–395	55.9	–141.8	0.10	945	85.2
Polygonum aviculare aerial parts extract						
0.12	–414	86.6	–113.5	0.40	281	39.2
0.4	–408	79.4	–126.7	0.19	595	71.4
1.2	–397	51.2	–125.7	0.09	968	86.9
4	–394	42.4	–134.6	0.05	1509	92.6

[10]. Subsequently, the polarisation resistances (R_p) were estimated from the Tafel slopes and the corrosion current densities [11]. The inhibitory ability of the compound was estimated from the ratio of the corrosion current densities in the absence (i_0) and in the presence (i) of the inhibitor: IE = $(i_0 - i) / i_0 \cdot 100$ % [10]. The results are presented in Figure 2 and in Table 2.

EIS studies

For EIS tests, solutions of 0.5 M hydrochloric acid and 0.5 M hydrochloric acid with the addition of different concentrations of *Chenopodium album* or *Polygonum aviculare* aerial parts extracts were prepared. Electrodes made of EN Fe37-3FN mild steel and sealed with

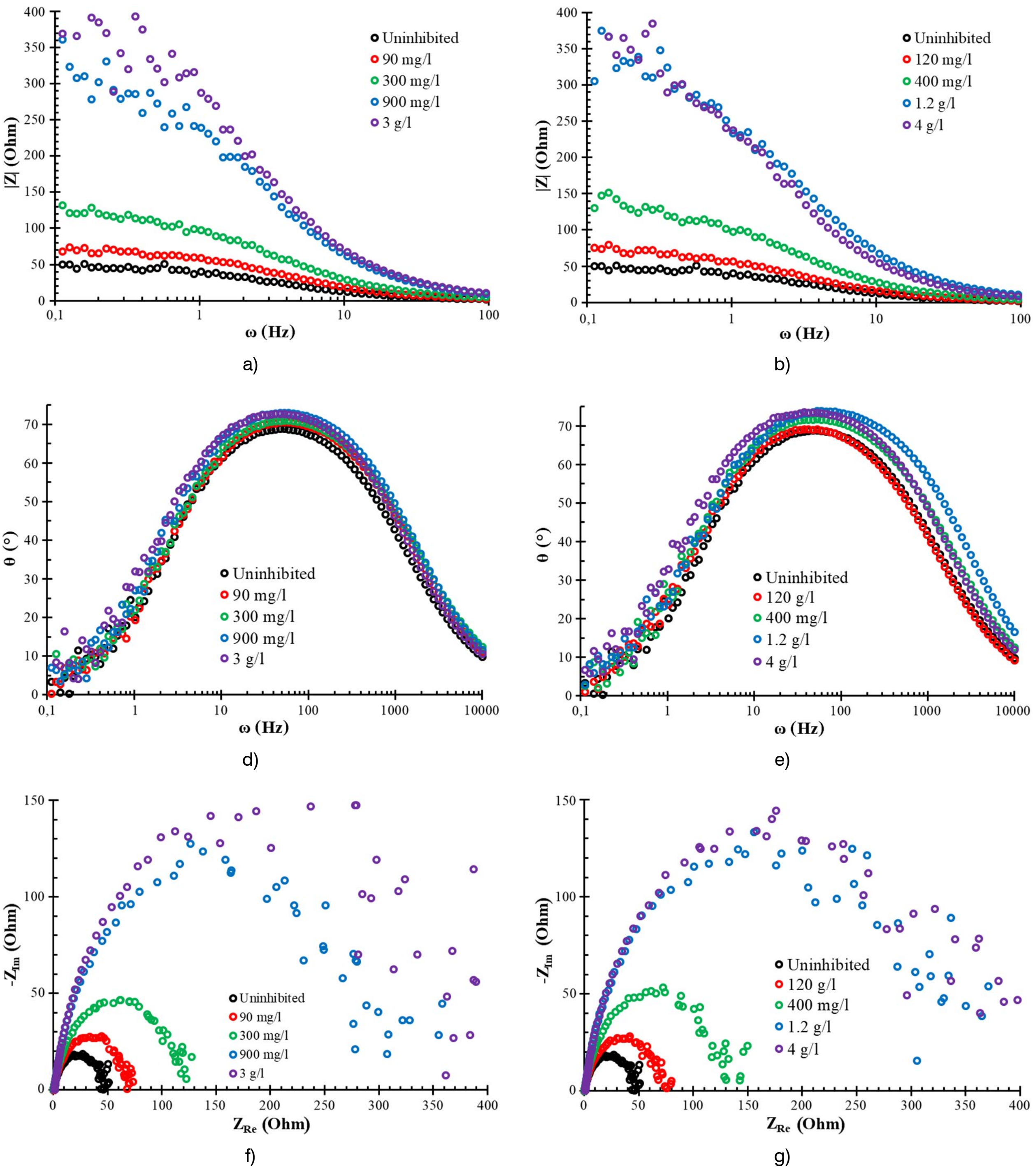


Fig. 3. The Bode plots of steel in 0.5 M HCl with the different additions of: a, c) the *Chenopodium album* aerial parts extract, b, d) the *Polygonum aviculare* aerial parts extract, and the Nyquist plots of steel in 0.5 M HCl with the different additions of: e) the *Chenopodium album* aerial parts extract, f) the *Polygonum aviculare* aerial parts extract after 30 min of exposure

the epoxy resin with the working surface of 6.3 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 from the working electrode (steel sample), auxiliary electrode from the porous graphite, and the silver-silver chloride reference electrode. The cell was placed into the Faraday shield cell. An open circuit potential was recorded during 30 min. An impedance values were recorded at the open circuit potential value in the alternate current frequency interval from 1 Hz to 10 kHz with the potential amplitude of 10 mV. Each experiment was performed in triplicate. The obtained results were presented in the form of Bode and Nyquist plots [12]. For the estimation of the impedance parameters, a simplified Randles equivalent electrical circuit [12], 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 imaginary resistance of the constant-phase element is represented by the equation $1/Z = P \cdot (i \cdot \omega)^n$, where ω is the alternate current frequency, P and n are the adjustable parameters. The fitting of the equivalent circuit parameters to the experimental impedance values was performed using the free software EIS Spectrum Analyser [13]. In addition, the capacitance (C_{dl}) and the thickness (d) of the double electric layer were estimated [12]. The inhibitory ability of the compound was estimated from the ratio of the charge transfer resistances in the presence (R) and in the absence (R_0) of the inhibitor: $IE = (R - R_0) / R \cdot 100\ \%$ [10]. The results are presented in Fig. 3 and in Table 3.

Langmuir adsorption model

The description of the adsorption of the aerial parts extract components on the steel surface was performed in terms of the Langmuir adsorption model. The Langmuir adsorption isotherm equation was linearised in the form $c_{inh}/\theta = 1/K_{ads} + c_{inh}$, where c_{inh} is the concentration of the *Chenopodium album* aerial parts or *Polygonum aviculare* aerial parts extract solution (g/l), K_{ads} is the adsorption-desorption equilibrium constant (l/g), 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 4 and in Table 3. The data were processed using the least squares technique, and the equilibrium constants K_{ads} were estimated as the intercepts of the regression equations. The Gibbs energy changes of the sorption were estimated from the equation $\Delta_{ads}G = -RT \ln (K_{ads} \cdot c_{water})$, where $c_{water} = 10^3$ g/l is the water concentration in the extracts. The results are presented in Table 4.

DISCUSSION

The results of both the gravimetric and the electrochemical measurements show that even the addition of 90 mg of the *Chenopodium album* aerial parts extract to each litre of solution provides the inhibition efficiency ~35% on the corrosion of mild steel EN Fe37-3FN in a 0.5 M hydrochloric acid medium, and the addition of 1 g of the extract to each litre of solution increases the inhibition efficiency up to ~75%. On the other hand, the *Polygonum aviculare* aerial parts extract is a little bit stronger corrosion inhibitor, which provides a ~40% inhibition at the concentration level of 120 mg/l, and at the concentrations greater than 1 g/l also exhibits a moderate inhibition efficiency of ~85%.

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 *Chenopodium album* aerial parts and *Polygonum aviculare* aerial parts extracts, which means that the nature of the adsorption is physical.

Tab. 3 The results of the EIS measurement of the corrosion rates

c_{inh} [g/l]	R_s [Ohm]	P [$mOhm^{-1} \cdot s^n$]	n	C_{dl} [μF]	d [nm]	R_{ct} [Ohm]	IE [%]
0	0.9	0.51	0.86	127.6	0.34	48	–
Chenopodium album aerial parts extract							
0.09	0.8	0.45	0.86	96.6	0.45	71	32.4
0.3	0.7	0.44	0.85	55.8	0.78	124	61.3
0.9	0.7	0.42	0.86	26.0	1.68	298	83.9
3	0.9	0.37	0.89	25.3	1.73	344	86.0
Polygonum aviculare aerial parts extract							
0.12	0.9	0.50	0.86	113.7	0.38	68	29.4
0.4	0.7	0.44	0.86	64.6	0.67	134	69.4
1.2	0.7	0.43	0.88	25.1	1.74	308	84.4
4	0.5	0.41	0.87	24.7	1.76	316	84.8

Tab. 4 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]
Chenopodium album aerial parts extract					
0.09	0.354	0.254	$c_{inh}/\theta = (1.13 \pm 0.01) \cdot c_{inh} + (0.14 \pm 0.02)$; $R^2 = 0.999$	7 ± 2	–22 ± 3
0.3	0.672	0.446			
0.9	0.768	1.172			
3	0.852	3.521			
Polygonum aviculare aerial parts extract					
0.12	0.392	0.306	$c_{inh}/\theta = (1.039 \pm 0.008) \cdot c_{inh} + (0.16 \pm 0.02)$; $R^2 = 0.999$	6 ± 2	–22 ± 3
0,4	0,714	0,560			
1,2	0,869	1,381			
4	0,926	4,320			

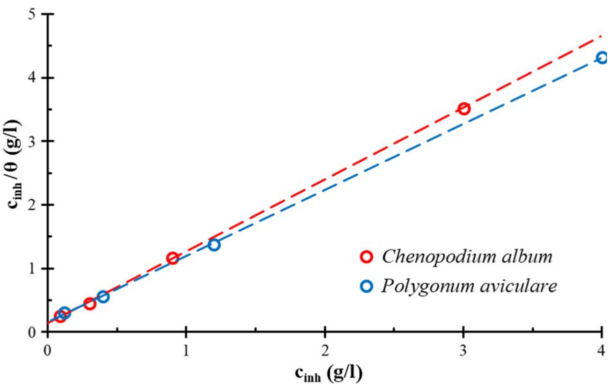


Fig. 4. The plots of c_{inh}/θ vs. c_{inh} for the adsorption of the *Chenopodium album* aerial parts extract and the *Polygonum aviculare* aerial parts extract on the steel surface

In any case, *Chenopodium album* aerial parts and *Polygonum aviculare* aerial parts are widely grown in several countries, and the raw material are easily available. This study shows a possible new implementation of the boiling extracts of these aerial parts as environmentally friendly corrosion inhibitors.

CONCLUSION.

The inhibitory ability of the *Chenopodium album* aerial parts and *Polygonum aviculare* aerial parts boiling extracts on the corrosion of mild steel EN Fe37-3FN in 0.5 M hydrochloric acid medium was investigated using electrochemical methods and EIS. It was shown that the addition of 90 mg/l of the *Chenopodium album* aerial parts extract reduces the corrosion rate by 35%, and that of of 1 g/l – by 75%, whereas the addition of 120 mg/l of the *Polygonum aviculare* aerial parts extract reduces the corrosion rate by 40%, and that of of 1 g/l and more – by 85%. The adsorption of the extract components on a steel surface follows the Langmuir adsorption model, and the nature of adsorption is mostly physical. The *Chenopodium album* aerial parts and *Polygonum aviculare* aerial parts extracts show themselves as perspective and environmentally friendly substances for reducing the steel corrosion rate in acidic environments.

Conflict of interest

The authors declare no conflict of interest.

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