

Sustainable Corrosion Inhibition of Mild Steel in Hydrochloric Acid Using Extracts of *Phaseolus Vulgaris* and *Vicia Faba*



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ABSTRACT

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Phaseolus vulgaris, *Vicia faba*, plant-derived inhibitor, corrosion inhibition, stainless steel, electrochemical study, electrochemical impedance spectroscopy, Langmuir adsorption isotherm

The inhibitory effects of extracts from *Phaseolus vulgaris* and *Vicia faba* beans, obtained from boiled beans, on the corrosion of EN Fe37-3FN mild steel in a 0.5 M hydrochloric acid medium were meticulously investigated utilizing electrochemical techniques and Electrochemical Impedance Spectroscopy (EIS). The corrosion rate was observed to decrease by 40% upon the introduction of 20 mg/L of the *Phaseolus vulgaris* extract, with a notable reduction of 70% when the concentration was increased to 2 g/L and beyond. The *Vicia faba* extract, however, displayed a slightly inferior inhibitory performance, with corrosion rates diminishing by 20% at 20 mg/L and 60% at concentrations of 2 g/L and above. The adsorption of extract constituents onto the steel surface was found to conform to the Langmuir adsorption isotherm model, thereby facilitating the calculation of the sorption equilibrium constant and revealing that the adsorption was primarily physical in nature. These extracts, which are typically discarded by-products of bean cooking, have emerged as cost-effective, readily accessible, and environmentally benign alternatives for mitigating steel corrosion in acidic environments.

1. INTRODUCTION

Compounds extracted from natural products as corrosion inhibitors have garnered significant attention in recent years due to their cost-effectiveness and environmental benefits [1, 2]. Usually, the extracts from roots (e.g., *Rheum ribes* [3]), leaves (e.g., *Acanthopanax senticosus* [4]), flowers (e.g., *Camellia chrysanth* [5]), fruits (e.g., *Punica granatum* [6]), and seeds (e.g., *Persea americana* [7]) of different plants are used [8, 9]. This also opens a new way for the usage of food residues and biomass-derived products [10].

Common beans (*Phaseolus vulgaris*) and fava beans (*Vicia faba*) have been extensively cultivated for both human and animal consumption, given that their beans are rich in several vitamins and polyphenols [11, 12]. Boiling in water is a typical culinary preparation method for these beans, a process that results in the extraction of a portion of the phenols and vitamins into an aqueous phase. The boiling extracts, despite their potential usefulness, are typically discarded and remain underutilized in the food and fodder industries.

Recent studies indicate that polyphenols [13, 14] and vitamins [14] exhibit properties that inhibit metal oxidation. It is thus plausible to hypothesize that the boiling extracts of both *Phaseolus vulgaris* and *Vicia faba* beans could serve as efficient and environmentally friendly corrosion inhibitors. However, the inhibitory properties of bean extracts on metal corrosion have been sparingly studied [15, 16].

Specifically, one study [15] investigated the effects of *Vicia faba* hexane or acetone extracts on the corrosion of mild steel

in a NaCl solution, while another [16] studied the impact of the winged bean (*Psophocarpus tetragonolobus*) hexane extract on the corrosion of reinforced steel in hydrochloric acid. Noticeably, these previous investigations involved the use of organic solvents, leaving the potential of water extracts from beans unexplored. The extensive usage of toxic organic solvents, moreover, raises sustainability concerns for such natural corrosion inhibitors [17].

Given the easy availability of water extracts during the bean cooking process, and the current tendency to simply discard such extracts, the present study aims to investigate the inhibitory properties of the boiling extracts of the black Russian varieties of *Phaseolus vulgaris* and *Vicia faba* on the corrosion of mild steel EN Fe37-3FN in a 0.5 M hydrochloric acid medium. This research hopes to uncover new, sustainable ways of utilizing these bean boiling extracts.

2. EXPERIMENTAL

2.1 Reagents and equipment

Ethanol (analytical grade) and hydrochloric acid (chemically 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% either Ni, and Cu, and Cr, 0.05% Si, 0.4% Mn, 0.05% P and 0.04% S). The cylindrical working surface of the ingots, which was immersed

in the solution, was left exposed with a surface area of 6.3 cm². The unused flat end surface of the ingots was sealed using epoxy resin.

Weighting of the samples was performed with the 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 (the relative standard deviation of the sampled solution volume of 0.1%) was used.

2.2 Preparation of the extracts

The seeds of *Phaseolus vulgaris* of the variety "The black opal", and of the *Vicia faba* of the variety "Russian black" were purchased at the local market. The plants were cultivated in Kurgan, Russia during May to August. The beans were air-dried during three months protected from the direct sunlight irradiation.

A total of 100 g of dried *Phaseolus vulgaris* beans and *Vicia faba* beans were weighted, immersed into the distilled water and soaked overnight. Then the water was drained off, discarded, and replaced by one litre of the fresh one, and the beans were heated and boiled at 100 °C under the reflux condenser during 3 h until the beans are completely cooked. The boiling extracts were cooled, the beans were removed, and the solid residues were filtered off through the filter paper with the pore diameter of 12 µm.

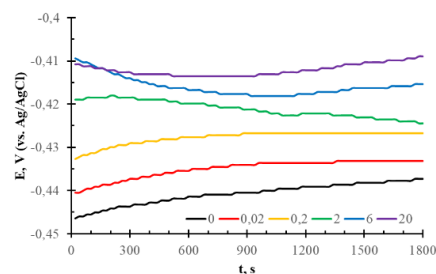
A total of 10 mL of each extract were taken, placed in a beaker and heated to dryness in order to determine the masses of the dissolved substances and the initial concentrations of the extract solutions. Then the working solutions of the *Phaseolus vulgaris* bean extract and those of the *Vicia faba* bean extract with the concentrations ranging from 0.04 to 40 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 *Phaseolus vulgaris* bean extract and of *Vicia faba* bean extract in 0.5 M HCl with exact concentrations ranging from 0.02 to 20 g/L.

3. RESULTS

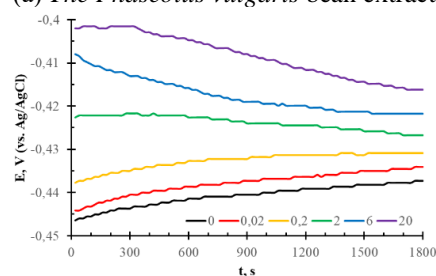
3.1 Polarisation studies

The polarisation tests were performed in hydrochloric acid with and without the additions of inhibitors. Electrodes 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 graphite electrode, 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. The results are presented in Figure 1. Polarisation curves were recorded in the potential range from -500 to +500 mV relatively to the measured open circuit potential with the potential sweep rate of 10 mV/s, which allows the clear estimation of the Tafel slopes. Each

experiment was performed in triplicate. The obtained polarisation curves were presented in the coordinates E(lg *i*), and the Tafel slopes and the corrosion current density were evaluated from them [14]. 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: $IE = (i_0 - i) / i_0 \cdot 100\%$ [14]. The results are presented in Figure 2 and in Table 1.

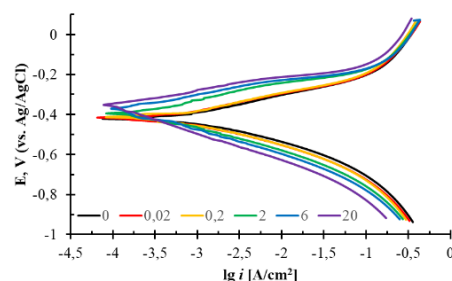


(a) The *Phaseolus vulgaris* bean extract

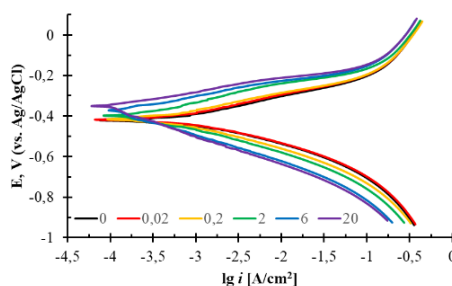


(b) The *Vicia faba* bean extract after 30 min of exposure

Figure 1. The open circuit potential of steel in 0.5 M HCl with the different additions (g/L)



(a) The *Phaseolus vulgaris* bean extract



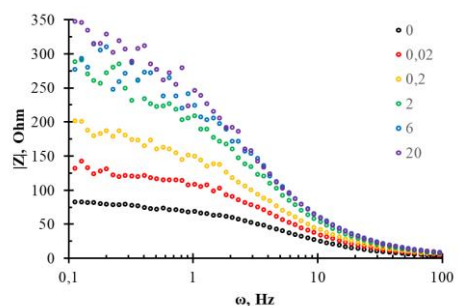
(b) The *Vicia faba* bean extract after 30 min of exposure

Figure 2. The polarisation curves of steel in 0.5 M HCl with the different additions (g/L)

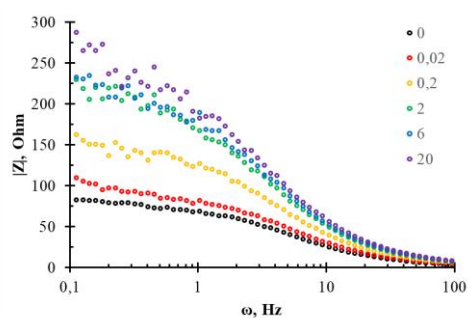
3.2 EIS studies

The EIS tests were performed in hydrochloric acid with and without the additions of inhibitors. Electrodes were polished using the P2500 emery paper, and degreased by ethanol. The

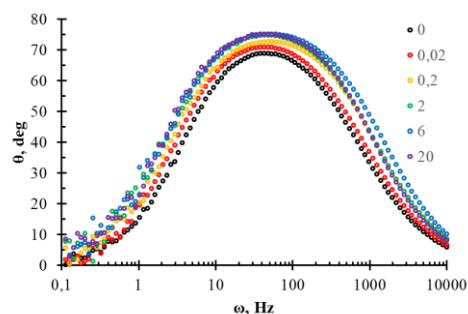
measurements were conducted in a standard three-electrode electrochemical cell, consisting from the working electrode (steel sample), auxiliary electrode from the porous graphite, and the silver-silver chloride reference electrode. The cell was placed into the Faraday shield cell. An open circuit potential was recorded during 30 min. An impedance values were recorded at the open circuit potential value in the alternate current frequency interval from 100 mHz 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 [18]. For the estimation of the impedance parameters, a simplified Randles equivalent electrical circuit [18], 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 fitting of the equivalent circuit parameters to the experimental impedance values was performed using the free software EIS Spectrum Analyser [19]. 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: $IE=(R-R_0)/R \cdot 100\%$ [14]. The results are presented in Figure 3 and in Table 2. The impedance spectra of both inhibitors are very similar to each other.



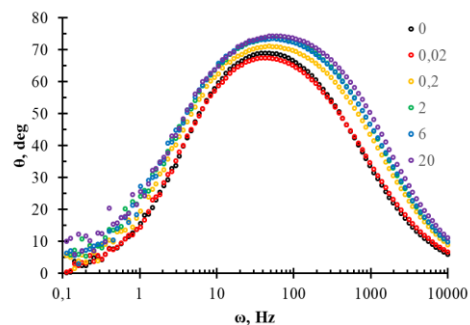
(a)



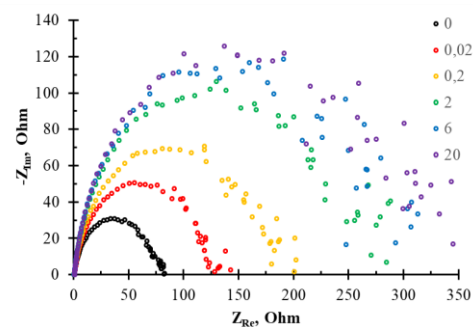
(b)



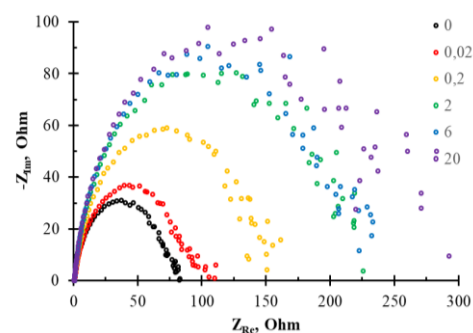
(c)



(d)



(e)



(f)

Figure 3. The Bode plots of steel in 0.5 M HCl with the different additions (g/L) of (a), (c) the *Phaseolus vulgaris* bean extract, (b), (d) the *Vicia faba* bean extract, and the Nyquist plots of steel in 0.5 M HCl with the different additions (g/L) of (e) the *Phaseolus vulgaris* bean extract, (f) the *Vicia faba* bean extract after 30 min of exposure

3.3 Langmuir adsorption model

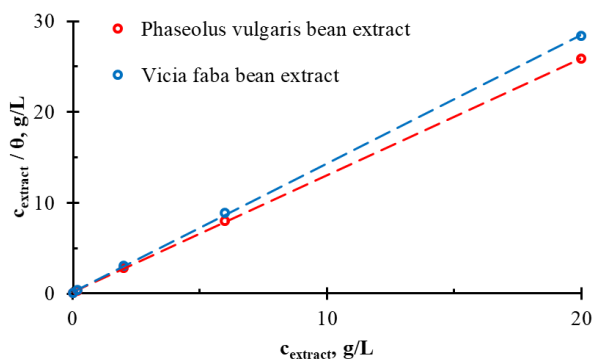


Figure 4. The plots of c_{inh}/θ vs c_{inh} for the adsorption of *Phaseolus vulgaris* bean and *Vicia faba* bean extract on the steel surface

The description of the adsorption of the bean extract components on the steel surface was performed in terms of the Langmuir adsorption model, which assumes that an adsorbate behaves like an ideal gas at isothermal conditions [20]. 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 *Phaseolus vulgaris* bean or *Vicia faba* bean 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 [21], and the equilibrium constants K_{ads} together with their confidence intervals were estimated as the intercepts of the regression equations. The Gibbs energy changes of the sorption and their confidence intervals 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 3.

Table 1. 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} , mA/cm ²	IE, %
0	-0.437 ± 0.002	0.513 ± 0.005	-0.192 ± 0.006	24.77 ± 0.08	–
Addition of <i>Phaseolus vulgaris</i> Bean Extract					
0.02	-0.433 ± 0.002	0.406 ± 0.006	-0.141 ± 0.007	11.28 ± 0.07	54.50
0.2	-0.427 ± 0.001	0.382 ± 0.005	-0.134 ± 0.008	7.64 ± 0.09	69.17
2	-0.424 ± 0.002	0.328 ± 0.004	-0.126 ± 0.006	5.1 ± 0.1	79.35
6	-0.415 ± 0.003	0.277 ± 0.006	-0.112 ± 0.007	3.3 ± 0.1	86.60
20	-0.409 ± 0.003	0.246 ± 0.008	-0.101 ± 0.006	3.1 ± 0.1	87.61
Addition of <i>Vicia faba</i> Bean Extract					
0.02	-0.434 ± 0.002	0.471 ± 0.005	-0.162 ± 0.006	20.56 ± 0.07	17.01
0.2	-0.431 ± 0.001	0.447 ± 0.004	-0.154 ± 0.009	18.07 ± 0.09	27.05
2	-0.427 ± 0.002	0.418 ± 0.007	-0.143 ± 0.007	14.72 ± 0.09	40.57
6	-0.422 ± 0.003	0.394 ± 0.006	-0.137 ± 0.006	8.4 ± 0.1	66.27
20	-0.416 ± 0.002	0.317 ± 0.009	-0.121 ± 0.008	4.7 ± 0.1	81.16

Table 2. The results of the EIS measurement of the corrosion rates

c_{inh} , g/L	R_s , Ohm	P , mOhm ⁻¹ · s ⁿ	n	R_{ct} , Ohm	IE, %
0	0.52 ± 0.04	1.02 ± 0.02	0.86 ± 0.02	77.3 ± 0.6	–
Addition of <i>Phaseolus vulgaris</i> Bean Extract					
0.02	0.25 ± 0.04	0.64 ± 0.02	0.89 ± 0.02	127.2 ± 0.9	39.23
0.2	0.42 ± 0.05	0.59 ± 0.03	0.84 ± 0.01	191.8 ± 0.8	59.70
2	0.78 ± 0.07	0.53 ± 0.02	0.88 ± 0.02	260.3 ± 0.5	70.30
6	1.0 ± 0.1	0.48 ± 0.01	0.84 ± 0.03	307.5 ± 0.7	74.86
20	1.3 ± 0.1	0.42 ± 0.02	0.89 ± 0.02	339 ± 1	77.22
Addition of <i>Vicia faba</i> Bean Extract					
0.02	0.91 ± 0.06	0.74 ± 0.02	0.86 ± 0.02	98.4 ± 0.4	21.44
0.2	0.73 ± 0.05	0.61 ± 0.02	0.87 ± 0.03	152.0 ± 0.8	49.14
2	1.1 ± 0.1	0.56 ± 0.02	0.86 ± 0.01	218.6 ± 0.7	64.64
6	1.2 ± 0.1	0.52 ± 0.01	0.87 ± 0.02	234.9 ± 0.9	67.09
20	1.3 ± 0.1	0.47 ± 0.01	0.87 ± 0.02	261.1 ± 0.9	70.39

Table 3. 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
Addition of <i>Phaseolus vulgaris</i> Bean Extract					
0.02	0.392	0.051	$c_{inh}/\theta = (1.290 \pm 0.008) \cdot c_{inh} + (0.15 \pm 0.07); R^2=0.9999$	7 ± 3	-22 ± 5
0.2	0.597	0.335			
2	0.703	2.845			
6	0.749	8.015			
20	0.772	25.900			
Addition of <i>Vicia faba</i> Bean Extract					
0.02	0.214	0.0933	$c_{inh}/\theta = (1.41 \pm 0.01) \cdot c_{inh} + (0.2 \pm 0.1); R^2=0.9998$	5 ± 3	-21 ± 8
0.2	0.491	0.4070			
2	0.646	3.094			
6	0.671	8.943			
20	0.704	28.413			

4. DISCUSSION

The results of the electrochemical and EIS measurements show that even the addition of 20 mg of the *Phaseolus vulgaris* bean extract to each litre of solution provides the inhibition

efficiency ~40% on the corrosion of mild steel EN Fe37-3FN in a 0.5 M hydrochloric medium, and the addition of 2 g of the extract to each litre of solution increases the inhibition efficiency up to ~70%.

On the other hand, the *Vicia faba* bean extract is a much

weaker corrosion inhibitor, which provides only ~20% inhibition at the concentration level of 20 mg/L, but at the concentrations greater than 2 g/L also exhibits a moderate inhibition efficiency of ~65%.

The adsorption of the extracted components on the steel surface fairly obeys the Langmuir adsorption model [20]. The calculated Gibbs energies of sorption are in the range ~ -20 kJ/mol for both *Phaseolus vulgaris* bean and *Vicia faba* bean extracts, which means that the nature of the adsorption is mostly physical [22].

The estimated inhibition efficiencies are comparable with those reported for the fava bean hexane or acetone extracts against the corrosion of mild steel in the NaCl solution [15], and for the winged bean hexane extract against the corrosion of reinforced steel in hydrochloric acid [16]. However, in the present study no toxic organic solvents were used to obtain the extracts. The *Phaseolus vulgaris* beans and *Vicia faba* beans boiling extracts are the by-products of bean cooking, which are usually discarded. This study shows a possible new implementation of these extracts as environmentally friendly corrosion inhibitors for the food and agricultural industries, where these extracts are produced in significant quantities.

5. CONCLUSIONS

The inhibitory ability of the *Phaseolus vulgaris* bean and *Vicia faba* bean 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. The inhibition efficiencies at the different inhibitor concentrations were estimated. The adsorption of the extract components on a steel surface follows the Langmuir adsorption model, and the nature of adsorption is mostly physical. The *Phaseolus vulgaris* bean and the *Vicia faba* bean extract, as the discarded by-products of bean cooking, are identified as promising and environmentally friendly substances for reducing the steel corrosion rate in acidic environments. Given the increasing need for environmentally friendly solutions in industry, the discovery that these commonly discarded by-products can act as effective corrosion inhibitors is of significant importance. The future studies on exploring other potential environmentally friendly inhibitors based on commonly discarded natural products are beneficial.

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NOMENCLATURE

b	tafel slope, $V \cdot \text{dec}^{-1}$
c	concentration, $\text{kg} \cdot \text{L}^{-1}$
E	electrochemical potential, V
G	gibbs energy, $\text{J} \cdot \text{mol}^{-1}$
IE	inhibition efficiency, dimensionless
i	current density, $\text{A} \cdot \text{m}^{-2}$
K	adsorption-desorption constant, $\text{L} \cdot \text{kg}^{-1}$
n	impedance parameter, dimensionless
P	impedance parameter, $\text{Ohm} \cdot \text{s}^n$
R	electrical resistance, Ohm

Greek symbols

θ	percentage of the adsorbent surface covered by the adsorbive, dimensionless
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Subscripts

a	anode
ads	adsorption
c	catode
corr	corrosion
ct	charge transfer
inh	inhibitor
s	solution