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The inhibitory properties of the boiling extracts from *Malus sylvestris* and *Syringa vulgaris* flowers on the corrosion of stainless steel in sulphuric acid medium

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Abstract: The inhibitory properties of the *Malus sylvestris* flower and *Syringa vulgaris* flower boiling extracts against the stainless steel EN Fe37-3FN corrosion in 0.5 M sulphuric acid medium were studied using electrochemical methods, including open circuit potential measurement, potentiodynamic polarisation and EIS. The addition of 10 mg/l of the *Malus sylvestris* flower extract slows the corrosion by 15%, and that of of 10 g/l – by 65%, while the addition of 10 mg/l of the *Syringa vulgaris* flower extract slows the corrosion by 30%, and that of of 1 g/l and more – by 65%. The Langmuir absorption model describes the adsorption of the components of the extracts on a surface of the steel, and the adsorption is physical in its nature. The *Malus sylvestris* flower and *Syringa vulgaris* flower extracts reveal themselves as interesting and environmentally safe substances for the steel corrosion rate reduction in acidic environments.

INTRODUCTION

In recent years, researchers have become increasingly interested in the use of chemicals derived from natural products as green corrosion inhibitors (Raja, Ghoreishiamiri, Ismail 2015; Nasab et al. 2022). The use of natural chemicals, which are typically eco-friendly, lowers the expenses associated with the search for and special manufacturing of inhibitors. Typically, plant extracts from the roots, leaves, flowers, fruits, and seeds are employed (Alrefaee et al. 2021; Umoren et al. 2019). Additionally, it creates a new opportunity for the utilisation of food waste and products made from biomass (Marzorati, Verotta, Trasatti 2018).
The wild crabapple (*Malus sylvestris*) and the common lilac (*Syringa vulgaris*) are very popular ornamental plants in gardens and parks both in Europe and Asia because of their attractive flowers. Their flowers contain several flavonoids (Mustafa, Nebija, Hajdari 2018) and phenols (Mustafa, Nebija, Hajdari 2018; Hanganu et al. 2021). However, both flavonoids (Bhardwaj, Sharma, Kumar 2021; Kadhim et al. 2021) and phenols (Kadhim et al. 2021) exhibit inhibitory properties on metal oxidation, and therefore, the boiling extracts of both *Malus sylvestris* and *Syringa vulgaris* flowers might be useful corrosion inhibitors safe for the environment. However, the inhibitory properties of flower extracts of the lilac or the wild crabapple on the metal corrosion were never examined, and there are no published studies in the literature.
Therefore, in the present study, the inhibitory ability of the boiling extracts of the *Malus sylvestris* and *Syringa vulgaris* flowers against the corrosion of stainless steel EN Fe37-3FN in 0.5 M sulphuric acid medium are aimed to be investigated.

MATERIAL AND METHODS

Reagents and Equipment

Ethanol (analytical grade) and sulphuric acid (pure grade) were purchased from LLC "Lenreaktiv". Steel electrodes were manufactured from cylindrical ingots made of stainless 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.

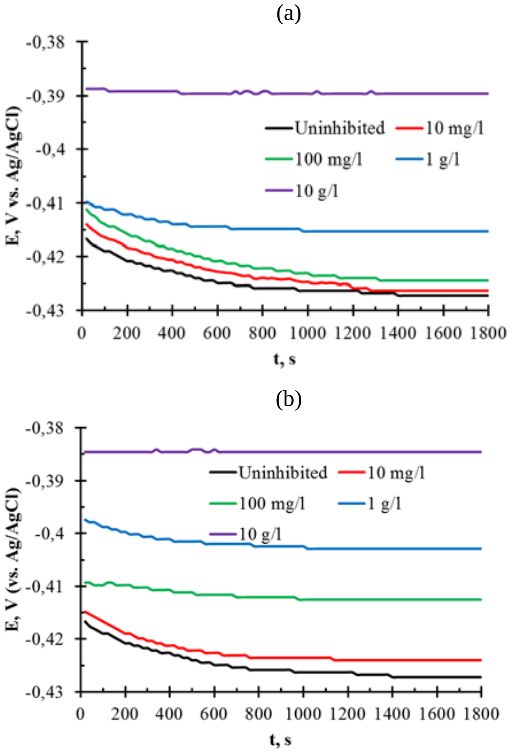

Figure 1: The open circuit potential of steel in 0.5 M H_2SO_4 with the different additions of (a) the *Malus sylvestris* flower extract, (b) the *Syringa vulgaris* flower extract after 30 min of exposure.

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 flowers of *Malus sylvestris* and *Syringa vulgaris* were harvested during the blooming period in mid-May from the several wild trees growing on the streets of Kurgan, Russia. The flowers were air-dried during three months.

A total of 100 g of dried *Malus sylvestris* flowers and of 100 g of dried *Syringa vulgaris* flowers were weighted, immersed into a liter of the distilled water, heated and boiled under the reflux condenser during 3 h. The boiling extracts were cooled, the flowers 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 *Malus sylvestris* flower extract and those of the *Syringa vulgaris* flower extract with the concentrations ranging from 0.02 to 20 g/l were prepared by the appropriate dilutions. The solutions were then equally diluted by 1 M sulphuric acid to finally produce a series of acidic solutions of *Malus sylvestris* flower extract and of *Syringa vulgaris* flower extract in 0.5 M H_2SO_4 with concentrations ranging from 0.01 to 10 g/l.

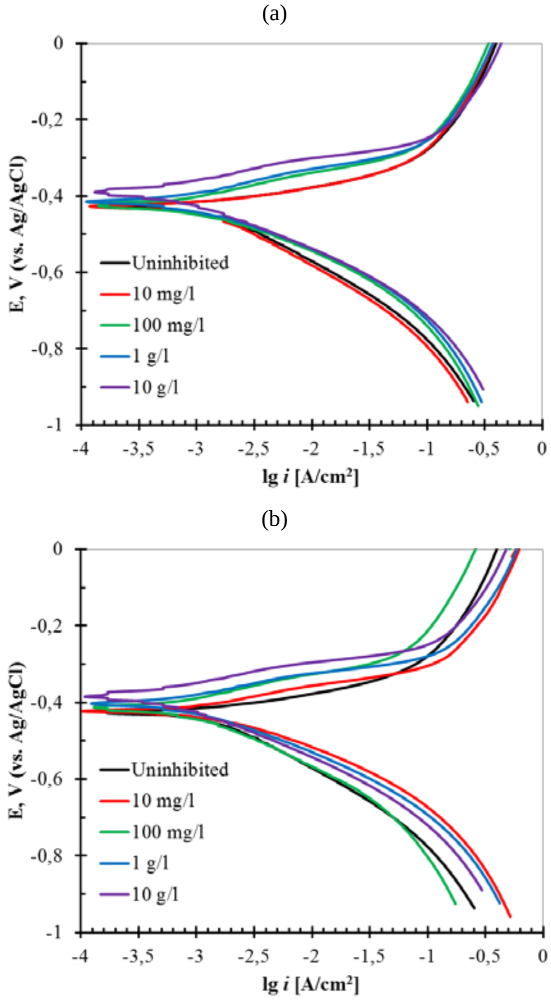

Figure 2: The polarisation curves of steel in 0.5 M H_2SO_4 with the different additions of (a) the *Malus sylvestris* flower extract, (b) the *Syringa vulgaris* flower extract after 30 min of exposure.

RESULTS

Polarisation studies

For polarisation tests, solutions of 0.5 M sulphuric acid and 0.5 M sulphuric acid with the addition of different concentrations of *Malus sylvestris* flower or *Syringa vulgaris* flower extract ranging from 0.01 to 10 g/L were prepared. Electrodes made of EN Fe37-3FN stainless 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 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. Each experiment was performed in triplicate. The obtained polarisation curves were presented in the coordinates $E(\lg i)$, and the Tafel slopes, the corrosion current density, and the polarisation resistance were evaluated from them (Kadhim et al. 2021). 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 = $(i_0 - i) / i_0 \cdot 100\%$, and also from the ratio of the polarisation resistances in the presence (R) and in the absence (R_0) of the inhibitor: IE = $(R - R_0) / R \cdot 100\%$ (Kadhim et al. 2021). The results are presented in Figure 2 and in Table 1.

Table 1: 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	R_p, Ohm ·cm^2	IE, %	i_{cor}, mA/cm^2	IE, %
0	–427	73.9	–179.6	13.2	–	1.72	–
		***Malus sylvestris* flower extract**					
0.01	–426	69.9	–175.8	15.0	11.8	1.45	16.1
0.1	–424	60.7	–157.8	16.6	20.1	1.15	33.5
1	–415	55.6	–148.5	18.9	30.0	0.93	46.0
10	–390	42.6	–150.2	24.4	45.9	0.59	65.6
		***Syringa vulgaris* flower extract**					
0.01	–424	59.3	–159.5	16.5	19.7	1.14	33.8
0.1	–412	47.3	–123.8	19.6	32.4	0.76	55.9
1	–402	40.1	–132.3	22.3	40.6	0.60	65.0
10	–385	39.7	–141.1	32.8	59.7	0.41	76.1

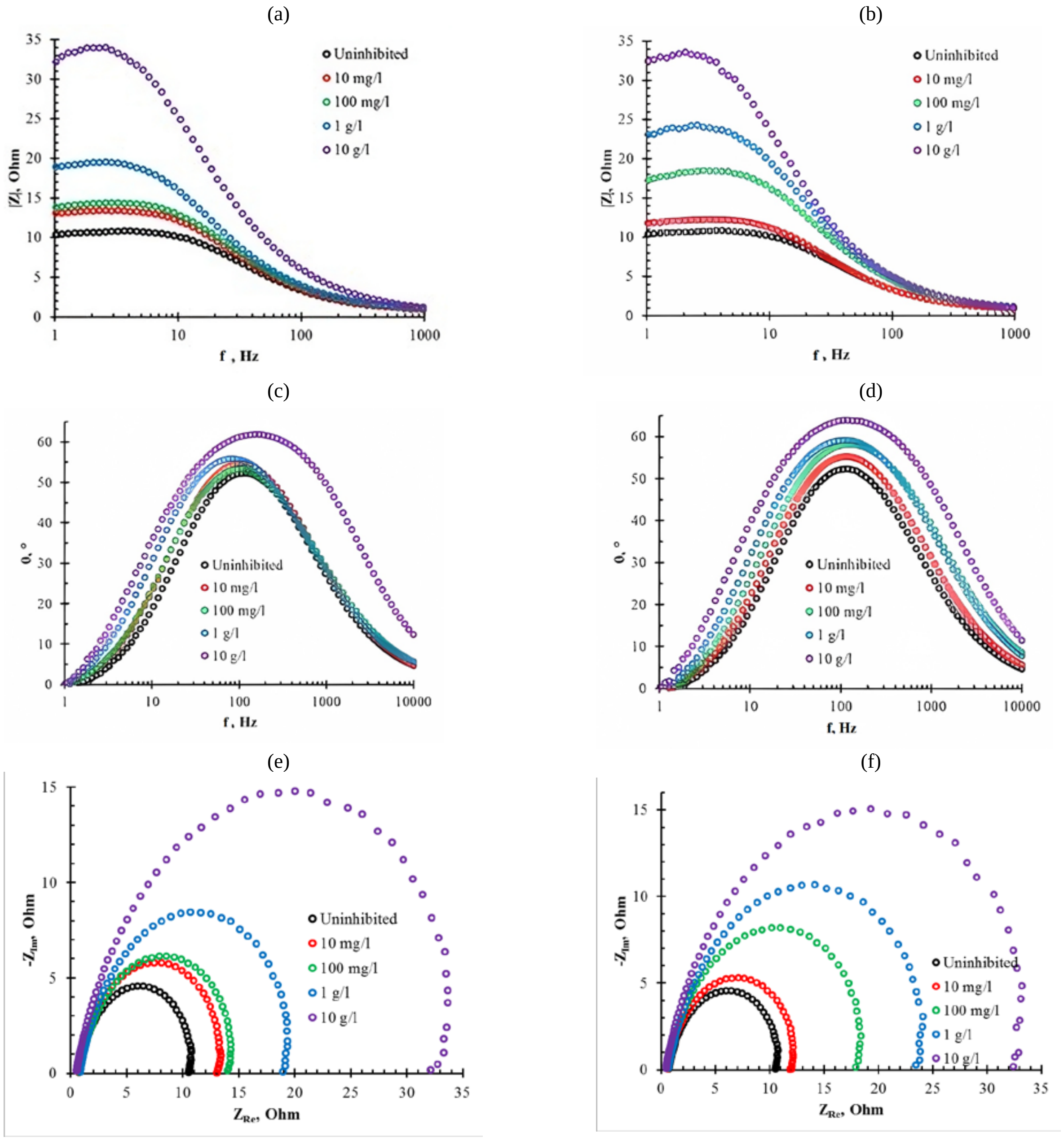

Figure 3: The Bode plots of steel in 0.5 M H_2SO_4 with the different additions of (a), (c) the *Malus sylvestris* flower extract, (b), (d) the *Syringa vulgaris* flower extract, and the Nyquist plots of steel in 0.5 M H_2SO_4 with the different additions of (e) the *Malus sylvestris* flower extract, (f) the *Syringa vulgaris* flower extract after 30 min of exposure.

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	C_{dl}, μF	d, nm	R_{ct}, Ohm	IE, %
0	0.7	1.3	0.85	374	7.4	11.7	–
***Malus sylvestris* flower extract**							
0.01	0.7	1.25	0.85	357	7.8	12.6	7.1
0.1	0.8	1.2	0.84	332	8.3	15.8	25.9
1	0.8	1.15	0.85	316	8.7	21.5	45.6
10	0.6	0.75	0.84	172	16.1	37.8	69
***Syringa vulgaris* flower extract**							
0.01	0.6	1.2	0.85	332	8.3	13.6	13.9
0.1	0.6	0.95	0.85	253	10.9	20.9	44.0
1	0.6	0.9	0.84	214	13.1	27.5	57.4
10	0.4	0.85	0.84	185	15.0	38.7	69.8

EIS Studies

For EIS tests, solutions of 0.5 M sulphuric acid and 0.5 M sulphuric acid with the addition of different concentrations of *Malus sylvestris* flower or *Syringa vulgaris* flower extract ranging from 0.01 to 10 g/L were prepared. Electrodes made of EN Fe37-3FN stainless 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 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 (Yuan et al 2010). For the estimation of the impedance parameters, a simplified Randles equivalent electrical circuit (Yuan et al 2010), 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 $1 / Z = P \cdot (i \cdot f)^n$, where f 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 (Bondarenko, Ragoisha 2005). In addition, the capacitance and the thickness of the double electric layer were estimated. 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: $\text{IE} = (R - R_0) / R \cdot 100\%$ (Kadhim et al. 2021). The results are presented in Figure 3 and in Table 2.

Langmuir Adsorption Model

The description of the adsorption of the flower 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 *Malus sylvestris* flower or *Syringa vulgaris* flower 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 3.

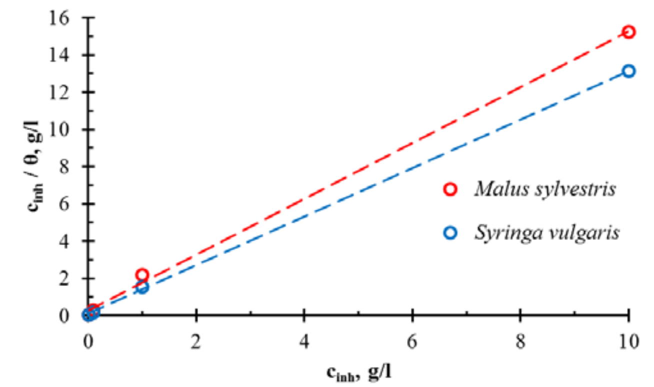

Figure 4: The plots of c_{inh} / θ vs. c_{inh} for the adsorption of the *Malus sylvestris* flower extract and the *Syringa vulgaris* flower extract on the steel surface.

DISCUSSION

From the results of the electrochemical and EIS measurements it is evident that the concentration of the extract from *Malus sylvestris* flowers equal to 10 mg/l in the sulphuric acid solution leads to the inhibition efficiency ~15% on the corrosion of stainless steel EN Fe37-3FN, and at theconcentration of 10 g/l the inhibition efficiency increases up to ~65%.

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
***Malus sylvestris* flower extract**					
0.01	0.161	0.062	$c_{inh} / \theta = (1.50 \pm 0.04) \cdot c_{inh} + (0.3 \pm 0.2)$; $R^2 = 0.998$	3 ± 2	–20 ± 5
0.1	0.335	0.298			
1	0.460	2.171			
10	0.656	15.236			
***Syringa vulgaris* flower extract**					
0.01	0.338	0.029	$c_{inh} / \theta = (1.30 \pm 0.01) \cdot c_{inh} + (0.09 \pm 0.07)$; $R^2 = 0.999$	11 ± 4	–23 ± 8
0.1	0.559	0.179			
1	0.650	1.537			
10	0.761	13.131			

In addition, the extract from *Syringa vulgaris* flowers has even stronger corrosion inhibition properties, and its inhibition efficiency is ~30% at the concentration level of 10 mg/l, and ~65% at the concentrations greater than 1 g/l. The Langmuir adsorption model fairly describes the adsorption of the components from the extracts on the steel surface. The estimated Gibbs energies of sorption for both *Malus sylvestris* flower and *Syringa vulgaris* flower extracts are in the range ~ –20 kJ/mol, and it characterises the physical nature of the adsorption. In any case, *Malus sylvestris* flowers and *Syringa vulgaris* flowers are widely cultivated in several countries, and the raw material are easily available. This study reveals a possible new usage of the boiling extracts of these flowers as environmentally benign corrosion inhibitors.

CONCLUSIONS

Commercial essential oil of pink pepper fruit, bought in a market in Tuzla, shows a cytotoxic effect on the HeLa cell line. The antibacterial potential of the oil is extremely high, and the mechanism of the inhibitory effect is connected to its hydrophobicity, which enables it to bind to cell membranes, which leads to disruption of cell integrity and cell death. The antioxidant potential of EO of pink pepper fruit is extremely weak compared to the results of antioxidant capacity obtained for vitamin C. The mentioned *in vitro* studies need to be further expanded in order to gain a better insight into the biological action of this essential oil.

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Summary/Sažetak

Inhibicijska svojstva vodenih ekstrakata cvijeta *Malus sylvestris* i cvijeta *Syringa vulgaris* protiv korozije nehrđajućeg čelika EN Fe37-3FN u 0,5 M sumpornoj kiselini proučavana su korištenjem elektrokemijskih metoda, uključujući mjerenje potencijala otvorenog strujnog kruga, potenciodinamičku polarizaciju i EIS. Dodavanje 10 mg/l ekstrakta cvijeta *Malus sylvestris* usporava koroziju za 15%, a dodavanje 10 g/l usporava koroziju za 65%, dok dodavanje 10 mg/l ekstrakta cvijeta *Syringa vulgaris* usporava koroziju za 30%, a dodavanje 1 g/l i više usporava koroziju za 65%. Langmuirov model adsorpcije opisuje adsorpciju komponenti ekstrakata na površini čelika, a adsorpcija je fizičke prirode. Ekstrakti cvijeta *Malus sylvestris* i *Syringa vulgaris* su zanimljivi i ekološki sigurne supstance za smanjenje stope korozije čelika u kiselim sredinama.