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Electrochemical properties of pigment extracts from dark red corn grains

Elektrohemijska svojstva ekstrakata pigmenta iz zrna kukuruza tamnocrvene boje

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Abstract

Electrochemical properties of pigment extracts from dark red corn grains was investigated by means of cyclic voltammetry (CV) and square wave voltammetry (SWV) on glassy carbon electrode (GC) in 0.1 M H₂SO₄. The shape of CV was typical for the oxidation of polyphenols. The antioxidant capacity of pigment from dark red corn grains was established from the charge under the anodic peaks. Quantitative determination of dark red corn pigments was performed by SWV. The linear polarization resistance (LPR) examinations were conduced in order to study the corrosion effect of polyphenolics on mild steel. Calculated corrosion inhibition efficiency ranged from 30% to 70%. Determination of the corrosion inhibition efficiency revealed that the red corn pigments have anti-corrosion effect on mild steels.

Keywords: polyphenols; antioxidant capacity; linear polarization resistance; corrosion inhibitor

Izvod

Elektrohemijska svojstva ekstrakata pigmenta iz zrna kukuruza tamnocrvene boje ispitivana su pomoću ciklične voltametruje (CV) i voltametrije pravougaonih talasa (SWV) na elektrodi od staklastog ugljenika (GC) u 0.1 M H₂SO₄. Dobijeni oblik CV je tipičan za oksidaciju polifenola. Antioksidativna kapacitivnost je utvrđena određivanjem naelektrisanja ispod anodnih pikova. Pigmenti iz zrna kukuruza tamnocrvene boje su kvantitativno određeni primenom SWV metode. Linearna polarizaciona otpornost (LPR) je sprovedena na niskougljeničnom (može i mekom, ali ovo je bolji izraz) čeliku kako bi se ispitalo koroziono ponašanje polifenola. Izračunata efikasnost inhibicije korozije je bila između 30 % i 70 %. Određivanje ove efikasnosti pokazalo je da pigmenti tamnocrvenog kukuruza imaju antikorozivno dejstvo na niskougljeničnom čeliku.

Ključne reči: polifenoli; antioksidativna kapacitivnost;linearna polarizaciona otpornost;inhibitor korozije

Introduction

Corn grains are source of nutrients and they are known to have high antioxidant capacity due to the presence of (poly)phenolic compounds such as carotenoids, flavonoids, anthocyanins [1]. In plants, these compounds protect the cells from the effect of UV light and high radiance conditions. Pigmented corn, as compared to the yellow ones, are considered as potential sources of health-promoting compounds (carotenoids and flavonoids) due to antiinflammatory, anticancer, and hypoglycemic effect [2]. The antioxidant capacity detection of polyphenolic compounds is usually based on electrochemical, spectroscopic, chromatographic or some other technique [1, 3, 4]. The phenolic groups of flavonoids can be electrochemically oxidized, showing an oxidation peak and then redox potentials determined by voltammetric methods have been used for the evaluation of antioxidant capacity of those compounds [5,6]. The total phenolic content obtained by

electrochemistry was proposed as a screening method to determine polyphenolics in food [7] or in vine [8]. The determined antioxidant activity of polyphenolics was accompanied with the corrosion inhibiting examination, since the most of the green corrosion inhibitors are recently found in the group of these organic molecules [9].

The aim of present study was to investigate the electrochemical behavior of dark red corn in acid solution. By varying the concentration of dark red corn the quantity of antioxidant activity was examined. The corrosion inhibitive test of dark red corn grains was also conducted.

Results and discussion

CV of dark red corn pigments on GC electrode in 0.1 M H₂SO₄ along with the voltammetric response of GC electrode in blank solution (dash line) is presented in Fig. 1. The electrochemical oxidation of examined pigments was depicted by two peaks in forward direction and two peaks on the backward scan, indicating a quasi-reversible process. First peak was attributed to the oxidation of the polyphenolic compounds containing a flavonoid structure, while the second one was attributed to anthocyanins [8]. The observed electrochemical behavior can be attributed to the well-described path for the oxidation of phenols, hydroquinones, and derivatives [10] and it is in accordance with biochemical properties of tested dark red corn seeds [11].

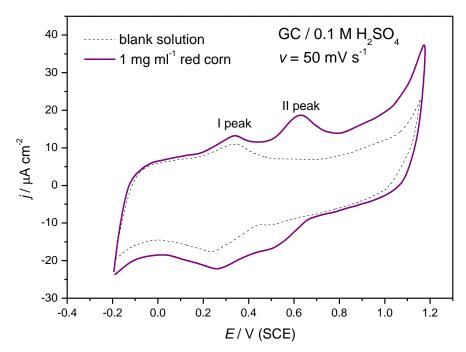


Figure 1. CV of GC electrode in 0.1 M H_2SO_4 (dash line) and after the addition of 1 mg ml⁻¹ red corn pigments (solid line); $v = 50 \text{ mV s}^{-1}$

Electrochemical methods can be used for a facile test of the antioxidant activity of many compounds [3]. So by calculating the charge under the anodic peaks (Q) it was possible to determine the quantity of antioxidants. For several concentrations of red corn pigments (Fig. 2a), that charge under the anodic peaks vs concentration was presented in Fig. 2b. Highest Q value was obtained for the most concentrated solution, which has larger amount of phenolic compounds. The results obtained by CV measurements are consistent with total phenolic and flavonoid contents and with spectrophotometric antioxidant assay (DPPH test) which confirms the same high antioxidant activity [11]. Our results are in accordance with literature data showing higher concentration of phenolic compounds in kernels of darker red and blue flour coloration [4], or of black maize kernels [12] as compared to light colored maize.

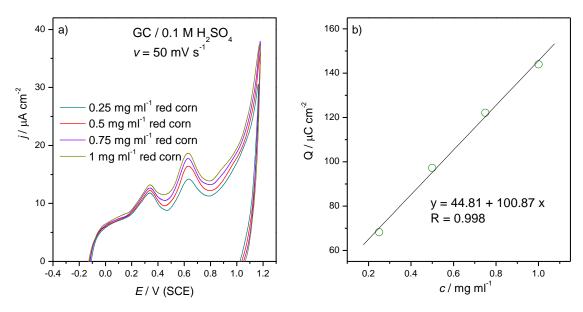


Figure 2. CVs of GC electrode in $0.1 \, M \, H_2 SO_4$ with different concentrations of dark red corn pigments (a); the dependency of charge from concentration (b)

Cyclic voltammetry revealed electrochemical activity and concentration dependency of dark red corn grains using 0.1 M H₂SO₄ solution and thus possibility for its quantitative determination by SWV as is presented in Fig. 3.

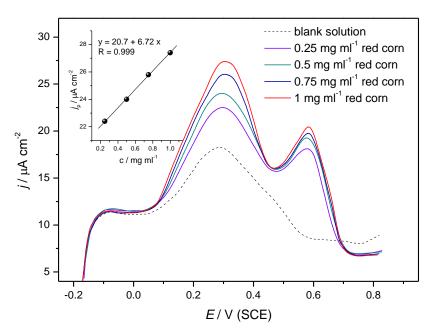


Figure 3. Dark red corn pigments determined by SWV at GC (the concentrations added in electrolyte are presented in legend). Step size 5 mV, pulse size 50 mV and scan rate 50 mV s⁻¹, accumulation time 60 s, at the potential -200 mV

In SWV experiments deposition times of 30 and 120 s and deposition potentials of -100 mV and 0 V as well as pulse size of 20 mV were tested but better results were obtained under conditions presented in Fig. 3. The SWV response showed that the oxidation peak currents for the dark red corn pigments were linearly dependent on its concentration in the range from 0.25 to 1 mg ml-1 as

it is presented in Fig. 3. The obtained regression equation is $j_p/\mu A$ cm⁻² = 20.7 + 6.72 c / mg ml⁻¹ with an excellent correlation coefficient (R = 0.999) according to dependency given in inset of Fig. 3.

The linear polarization resistance measurements on mild steel were performed examining the corrosion inhibitive behavior of dark red corn grains. In order to estimate the inhibiting action of investigation compound, the polarization resistance (Rp) was determined as a slope of the potential versus current curve from LPR data after measurement in the potentials range of -0.01 V - 0.01 V relative to Eoc. the corrosion inhibition efficiency, η_{inh} , was calculated according to equation (1):

$$\eta_{inh} = \left(1 - \frac{R_{p,Me}}{R_{p,inh}}\right) * 100 \tag{1}$$

 $R_{P,Me}$ and $R_{P,inh}$ are the values of polarization resistance (Rp) for a metal in the solution without and with inhibitor, respectively. The dependency of η_{inh} from the concentration of of red corn pigments is given in Fig. 4. It can be noted that the inhibiting effect increases with increase in red corn pigments concentration and the determined corrosion inhibition efficiency ranged from 30 to 70%. According to the literature finding corn silk extracts exibit inhibitive effect in the range of 66-95% [13], while surfactants obtained from corn oil show inhibitive effect ranged from 80 to 99% [14] both in acidic media for mild steel. In regard to this results, the investgated red corn has low to moderate inhibiting effect.

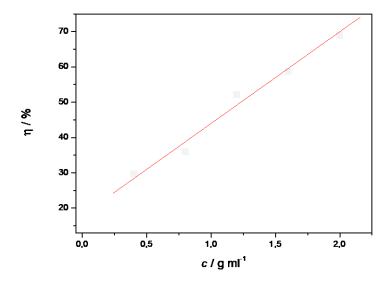


Figure. 4. The dependency of corrosion inhibition efficiency from concentration on of dark red corn seeds on mild steel in $0.1 \text{ M H}_2\text{SO}_4$

Conclusion

Electrochemical properties of dark red corn grains were investigated from the aspect of antiradical and anti-corrosion capacity. CV measurements were presented by two peaks, both in forward and the backward scan, indicating that the electrochemical oxidation of tested compounds was quasi-reversible process typical for the oxidation of polyphenols. The obtained antioxidant activity of polyphenolics was accompanied with the corrosion inhibiting examination. The linear polarization resistance measurements on mild steel were performed in order to test the corrosion inhibitive behavior in acidic solution at pH value at which the highest activity of investigated pigments is obtained. The corrosion inhibiting effect of dark red corn grains was established resulting the corrosion inhibition efficiency up to 70%.

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