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Study of the adsorption process between the phenolic compound catechin and the dietary fiber zymosan A: The influence of pH and concentration

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Abstract: Polyphenolic compounds have shown various beneficial effects on human health as well as certain bioactivities such as interactions with dietary fiber. Factors that can influence their interactions with dietary fibers include the pH value, the polyphenolic compound concentration and compound stability. The aim of this work was to study the interactions between the polyphenolic compound catechin and the dietary fiber zymosan A from yeast through investigation of the adsorption process. The catechin stability and the influence of concentration and pH value on interactions were investigated. Catechin showed the lowest stability at pH 7.0 with degradation ratio from 6 to 15 %. The lowest adsorption capacity was at pH 7.0, then higher in water and the highest at pH 1.5. A Dubinin–Radushkevich adsorption model fit to the data and FTIR analysis indicates the presence of physical interactions between catechin and zymosan A. This study can contribute to better understanding of interactions of polyphenols and dietary fiber for possible design of functional food, or to increase bioaccessibility of polyphenols.

Keywords: catechin; zymosan A; adsorption; interactions; stability; bioavailability.

INTRODUCTION

Polyphenols are a large group of secondary plant metabolites. Based on their chemical structure, polyphenols can be classified as phenolic acids, flavonoids, stilbens and lignans. Flavonoids can be further divided to flavonols, flavones, isoflavones, flavanones, anthocyanidins and flavanols.[1] Polyphenols have shown many potentially positive bioactivities, but since their role is not completely understood they are still intensively studied.[2] Catechins are polyphenols that belong to the flavan-3-ols group. They can be found in different products such as tea, wine, fruits and cocoa products.[3] Recently, tea catechins have been studied

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due to its potentially beneficial effects on human health[4], but they have shown low absorption and poor bioaccessibility in the digestive tract.[4] One of the reasons for their poor bioaccessibility can be instability in the digestive tract which depends on pH, temperature and the presence of other substances.[5] Such environmental conditions can lead to the epimerization and oxidation of catechins.[5,6] Oxidation reactions occur in the upper small intestine. The degradation of catechins is also directly correlated to pH value.[6] Indeed, catechins are very unstable in alkaline solutions.[7] To better understand the potential beneficial effects of catechins, their behavior, stability/instability, degradation rate, or degradation products in the digestive system should be further studied. Besides environmental conditions of the gastrointestinal tract, catechins can be affected by interactions with dietary fibers. Dietary fibers have the potential to bond to polyphenols, as well as catechins, protect them from environmental conditions and "carry" them to the lower parts of the digestive tract,[8] where they can be released and show potential bioeffects. Those interactions still need additional studies. One of the insoluble dietary fibers from *Saccharomyces cerevisiae* is zymosan or *β*-(1,3)--glucan.[9] By itself, zymosan has shown several different biological activities related to inflammatory and immune responses, to protecting and delivering drugs, or to the adsorption of toxins[10–13] which have enabled its use in functional food and dietary supplement development.[9] The knowledge of its interactions with phenolic compounds, such as catechins might help to understand possible design of functional food.[14] To the best of our knowledge, the adsorption between catechin and zymosan has not been studied before. The most common and simple method for the study of the interactions between catechins and dietary fiber is the analysis of adsorption data[15,16] in which various adsorption isotherms can be applied in order to obtain information about the interactions.[17,18]

The aim of this work was to study the stability of catechin in different solvents (water, solutions of pH 1.5 and 7.0) and the interactions between catechin and the dietary fiber zymosan A, likewise in different solvents (water, solutions of pH 1.5 and 7.0). The adsorption was studied with different concentrations of catechin and Langmuir and Dubinin–Radushkevich adsorption isotherm models were used to analyze the data.

EXPERIMENTAL

Chemicals and reagents

Methanol (HPLC grade) was purchased from J.T. Baker (Deventer, Netherlands). (+)--catechin hydrate (≥ 98 %, C1251) and zymosan A from *Saccharomyces cerevisiae* (Z4250) were purchased from Sigma Aldrich (St. Louis, CA, USA). Sodium carbonate and potassium chloride were purchased from Gram-mol (Zagreb, Croatia), hydrochloric acid (37 %) from Avantor (Arnhem, Netherlands), Folin–Ciocalteu reagents from Merck (Darmstadt, Germany) and sodium hydrogen phosphate dodecahydrate and sodium dihydrogen phosphate dihydrate

from Kemika (Zagreb, Croatia). The solution of pH 1.5 was prepared by using hydrochloric acid–potassium chloride (0.1 M). The buffer of pH 7.0 was a phosphate buffer (0.1 M).

Validation of Folin–Ciocalteu method for catechin determination

Separate calibration curves to accurately determine the amounts of catechin after adsorption were prepared for catechin dissolved in each of the three different solvents (water, a solution of pH 1.5 and a solution of pH 7.0). In short, dilutions of catechin were prepared (1, 10, 50, 150, 250, 450, 550 and 700 mg L^{-1}) in water, in solutions of pH 1.5 and in solutions of pH 7 from stock solutions of catechin/1000 mg L^{-1} prepared in the same solvents. All dilutions of catechin were measured according to Folin–Ciocalteu procedure. In particular, 30 μL of catechin dilution, 2370 μL of distilled water, 150 μL of Folin–Ciocalteu reagent and 450 μL of Na_2CO_3/ /200 g L^{-1} were added in a glass tube. The solution was mixed in a vortex (Grant Bio, Cambridgeshire, England) and incubated at 40 °C for 30 min in an incubator (Memert, IN 30, Schwabach, Germany). The absorbance was measured at 765 nm against a blank solution with a UV–Vis spectrophotometer (Shimadzu, UV-1280, Kyoto, Japan). The linearity, the limit of detection (*LOD*), the limit of quatification (*LOQ*) and the accuracy were determined. The same Folin–Ciocalteu procedure was used to determine the amount of un-adsorbed catechin after the experiment of adsorption with these newly created calibration curves.

Stability/degradation of catechin in different solvents

The degradation of catechin in water and in solvents of pH 1.5 and 7.0 was studied. Dilutions of catechin ($\gamma_{initial}$, 50, 100, 150, 200, 250, 300 and 500 mg L^{-1}) were prepared in water, solvents of pH 1.5 and 7.0. They were incubated at 37 °C in the incubator for 180 min. The amount of catechin after 180 min was determined with the Folin–Ciocalteu method, representing the amount that was not degraded and remained in the solvent after 180 min ($\gamma_{remaining}$, mg L^{-1}). The concentration of degraded catechin was calculated according to the Eq. (1):

$$\gamma_{degraded} = \gamma_{initial} - \gamma_{remaining} \quad (1)$$

The degradation ratio was determined according to Eq. (2):

$$\text{Degradation} = 100\left(\frac{\gamma_{degraded}}{\gamma_{initial}}\right) \quad (2)$$

In addition, dilutions of catechin (100 mg L^{-1}) were prepared in water, pH 1.5 and 7.0. Those dilutions were put in the incubator at 37 °C for 180 min. After that, they were filtrated through a PTFE syringe filter 0.2 μm and analyzed with RP-HPLC method to see if there are additional peaks that would be the evidence of the degradation of catechin. RP-HPLC method was performed with 1260 Infinity II HPLC system (Agilent Technology, Santa Clara, CA, USA) with a quaternary pump, a photodiode array (PDA) detector, a vial sampler and Poroshell 120 EC C-18 column (4.6 mm×100 mm, 2.7 mm). The mobile phase A was 0.1 vol. % H_3PO_4 and mobile phase B 100 % methanol and following gradient: a gradient 0 min 5 % B, 5 min 25 % B, 14 min 34 % B, 25 min 37 % B, 28 min 80 % B, 30 min 80 % B, 32 min 5 % B min, 34 min 5 % B min. Each sample was injected in 10 μl. The flow rate was set to 0.5 mL min^{-1}.

Adsorption of catechin and zymosan A in different solvents

The adsorption between catechin and zymosan A was studied at 37 °C, in three different solvents (water, solutions of pH 1.5 and 7.0), with varying concentrations of catechin (50, 100, 150, 200, 250, 300 and 500 mg L^{-1}). Stock solutions of catechin were prepared in concentration of 1000 mg L^{-1} in different solvents and appropriate volume was added into tubes to achieve

these concentrations in final volume of 2 mL. Zymosan A was weighed directly into tubes to achieve concentration of 500 mg L^{-1} and appropriate solvents were added (water, solvents of pH 1.5 or 7.0) to reach the final volume of 2 mL. Solutions were put in rotator (Grant-bio PTR--35, Oxon, England) and at 37 °C in the incubator for 180 min, then centrifuged (Eppendorf, Hamburg, Germany) and aliquot of 700 μL was taken. Un-adsorbed catechin γ_e (mg L^{-1}) was quantified with the Folin–Ciocalteu method using the new calibration curves. The amount of catechin adsorbed onto zymosan A $m_{adsorbed}$ / mg was calculated according to the Eq. (3):

$$m_{adsorbed} = \left(\gamma_{remaining} - \gamma_e\right) V_m \tag{3}$$

where V_m (L) is the total volume of a model solution.

Adsorption capacity q_e (the adsorbed amount of catechin (mg) onto g of zymosan A at specific equilibrium concentration) in water, pH 1.5 and 7.0 was calculated with the following Eq. (4) where m_a (g) is the mass of zymosan A in the solution:

$$q_e = \frac{m_{adsorbed}}{m_a} \tag{4}$$

Adsorption isotherm models

The experimentally determined data of q_e (mg g^{-1}) (adsorption capacity) and γ_e (mg L^{-1}) (un-adsorbed catechin) were fitted by non-linear forms of Langmuir and Dubinin–Radushkevich adsorption isotherms (Eqs. (5) and (6)). A value γ_e corresponds to a value c_e in the adsorption isotherms. Parameters K_L (L mg^{-1}, Langmuir equilibrium constant of adsorption), q_m (mg g^{-1}, theoretical maximum adsorption capacity of zymosan A) from the Langmuir isotherm (Eq. (5)), as well as β (mol^2 J^{-2}, Dubinin–Radushkevich constant related to the adsorption capacity) and q_s (mg g^{-1}, the theoretical saturation capacity) and c_s (mg L^{-1}, the saturation concentration) from the Dubinin–Radushkevich isotherm (Eq. (6)) were determined. Since a theoretical c_s value could be a higher concentration for which our experiment was not designed, suitable c_s values were predetermined according to the largest observed data value for c_e and only the parameters β and q_s were obtained from fitting the Dubinin–Radushkevich isotherm. R and T / K in Eq. (6) represent the gas constant (8.314 J K^{-1} mol^{-1}) and the absolute temperature, respectively:

$$q_e = \frac{q_m K_L c_e}{1 + K_L c_e} \tag{5}$$

$$q_e = q_s \exp\left(-\beta R^2 T^2 \left(\ln \frac{c_s}{c_e}\right)^2\right) \tag{6}$$

The mean free energy of adsorption, E, was calculated according to Eq. (7):

$$E = \frac{1}{\sqrt{2\beta}} \tag{7}$$

FTIR analysis

Pure catechin, pure zymosan A and catechin–zymosan A binding samples were recorded in the range of 450–4000 cm^{-1} with scanning resolution of 4 cm^{-1} by FTIR (PerkinElmer UATR, MA, USA). The catechin–zymosan A binding samples were prepared with concentration of 500 mg L^{-1} catechin and 300 mg L^{-1} zymosan A in 10 mL water, then pH 1.5 and pH 7.0. Samples were putted in incubator at 37 °C for 180 min and then filtrated through

vacuum filtration unit with filters (LLG membrane filters MCE, 0.22 μm). Catechin–zymosan A binding samples retained on the filters. Samples were dried and put to FTIR analysis.

Statistical analysis

MS Excel (Redmond, Washington, USA) software was used for data analysis. The accuracy of the Folin–Ciocalteu method was determined by performing a regression analysis in MS Excel 2013 using the Data Analysis tool, with a confidence interval of 95 %. All adsorption experiments were conducted in two parallels, each concentration measured three times (n_{TOTAL} = 6). Non-linear regression analysis was performed in the MS Excel tool Solver. The sum of squared errors (*SSE*) was calculated according to the Eq. (8), where m is the number of initial concentrations used in the adsorption experiments, $c_{e,i}$ and $q_{e,i}$ are the means of the measured c_e and q_e values for the i^{th} initial concentration, $f(c_e,a,b)$ is the non-linear model function with generic parameters a and b and n_i is number of data points for the i^{th} initial concentration. The standard error, S, of nonlinear regression was calculated according to Eq. (9), where N is the total number of initial concentration cases and k = 1 or 2 is the number of parameters to be determined:

$$SSE = \sum_{i=1}^{m} n_i \left[q_{e,i} - f\left(c_{e,i}, a, b\right) \right]^2 \quad (8)$$

$$S = \sqrt{\frac{SSE}{N-k}} \quad (9)$$

RESULTS AND DISCUSSION

Validation of Folin–Ciocateu method for catechin determination

The results for the linearity (R^2), limit of detection (*LOD*), limit of quantification (*LOQ*) and accuracy for the catechin determination in different solvents (ultrapure water, pH 1.5 and pH 7.0) are presented in Table I.

TABLE I. Validation parameters (linearity (R^2), limit of detection (*LOD*), limit of quantification (*LOQ*), accuracy) of spectrophotometric method for the determination of catechin in different solvent; results are based on two replicate samples of each standard concentration, each measured twice; accuracy was determined by performing a regression analysis with a confidence interval of 95 %, catechin solutions were incubated for 180 min in different solutions to enable degradation and calibration according to the actual presence of catechins in different environments; range: 1–700 mg L^{-1}

Validation parameter	Ultrapure water	pH 1.5	pH 7.0
	Calibration curve		
Calibration equation	$y = 0.0011x + 0.0104$	$y = 0.0011x + 0.0108$	$y = 0.0012x + 0.0104$
R^2	0.9994	0.9950	0.9990
LOD / mg L^{-1}	0.85	0.85	0.19
LOQ / mg L^{-1}	2.57	2.57	0.59
	Accuracy		
Slope	1.0164	0.9920	1.0411
95 % Confidence interval	0.9994–1.0334	0.9518–1.0322	0.9795–1.0195
Intercept	0.5018	1.3745	0.3197
95 % Confidence interval	–4.9923–5.9958	–13.4753–16.224	–6.5074–7.1468

Catechin showed linear calibration curves in all solvents (R^2 from 0.9950–0.9994), with reasonably low *LOD* and *LOQ*. The method was accurate according to the analysis with 95 % reliability, which rejected the existence of a systematic error (the confidence interval for the slope of the calibration curve includes a value 1 and for the intercept includes a value 0). Validated Folin–Ciocalteu method demonstrated to be suitable for the determination of the concentration of catechin after the adsorption process in water, pH 1.5 and 7.0.

Degradation of catechin in different solvents

The degradation of catechin was studied for initial concentrations of catechin 50, 100, 150, 200, 250, 300 and 500 mg L^{-1} which were diluted in water, solvents of pH 1.5 and 7.0. Dilutions were incubated for 180 min and 37 °C. After that period the concentration of catechin was determined with the Folin–Ciocalteu method to see the concentration of remaining non-degraded catechin. Catechin was stable in water and pH 1.5 and it did not degrade (data not shown). An earlier study also reported the stability of catechins from green tea around pH 4.[19] However, catechin did degrade at pH 7.0 (Fig. 1a). The concentrations of

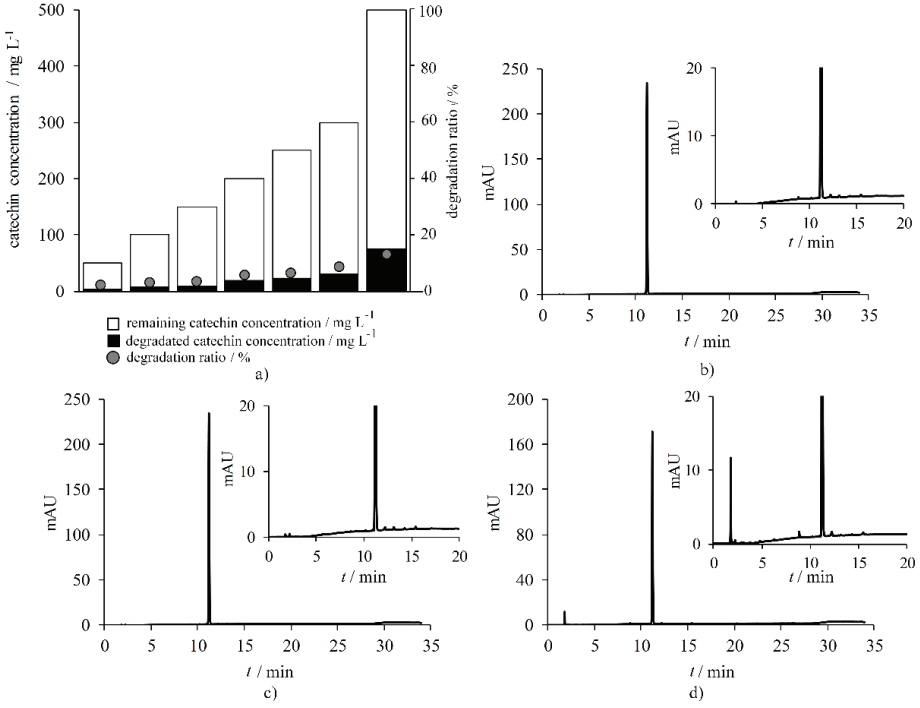

Fig. 1. Degradation of catechin for different initial catechin concentrations (50, 100, 150, 200, 250, 300 and 500 mg/L) at: a) pH 7.0 after 180 min incubation determined with Folin–Ciocalteu method, b) chromatograms of catechin (100 mg L^{-1}) at 280 nm, after the incubation for 180 min in ultrapure water and c) pH 1.5 and d) pH 7.0.

remaining catechin after 180 min were lower than the initial concentrations which suggested the degradation of catechin due to elevated pH. The degradation degree was from 6 to 15 %. Furthermore, the degradation percentage increased with the increasing initial concentration of catechin. This agrees with earlier study that reported the degradation of catechin at pH from 5.0 to 9.0.[20] Different factors like pH, temperature, concentration or the presence of other substances can influence the stability of catechin, which can lead to epimerization or degradation of catechin.[5,19,21,22] The degradation (or stability) of catechin in different solvents was investigated with the HPLC method in order to see any additional peaks on chromatograms. The HPLC chromatograms of catechin in different solvents after the incubation for 180 min at 37 °C are shown in Fig. 1. Catechin showed stability in water and at pH 1.5, but less stability at pH 7.0. Additional peaks appeared on the chromatogram at pH 7.0 (Fig. 1d) This agrees with our results obtained with the Folin–Ciocalteu method which indicated that catechin degraded at pH 7 into different products which need further identification. An earlier study found different semiquinones and dimerization products at near-neutral or greater pH.[6] The degradation of catechin can influence the adsorption capacity since the degraded catechin might be calculated into the amount that actually adsorb onto zymosan A. That is why we used the concentration of non-degraded catechin in the calculation of adsorption capacity after the adsorption experiment (Eq. (1)).

Adsorption of catechin onto zymosan A in different solvents

The adsorption capacities between catechin and zymosan A in different solvents are shown in Fig. 2. The adsorption capacities in the solvent of pH 7 reported here are values corrected for the degradation of catechin at this pH according to Eqs. (3) and (4). Catechin adsorbed onto zymosan A in amounts from 5 to 61 mg g^{-1} depending on the initial of catechin and the pH of the surrounding. Since the adsorption capacity depends on various factors such as the properties of the adsorbent, the properties of the adsorbate, the properties of the solution, or the type of experiment,[23] it is difficult to compare the results with the literature. The adsorption capacity of standards of polyphenols from tea adsorbed onto oat *β*-glucan in the amount of 156 to 405 mg g^{-1} (at pH 5.80, then polyphenol concentration 0.7 mg mL^{-1}, at 50 °C and concentration of buffer 0.10 M),[24] then tea polyphenols at different pH values adsorbed onto *β*-glucan up to 116 mg g^{-1} (at pH 5.56, at 50 °C and concentration of buffer 0.13 M).[25]

Adsorption capacity differed depending on different pH value (Fig. 2). Catechin showed the lowest adsorption capacity in pH 7.0, higher in water and the highest at pH 1.5, depending on the catechin concentration. At different pH, catechin can be present in dissociated or non-dissociated forms. Which chemical forms of catechin exist at certain pH, can be seen in the pK_a value[17] and distri-

bution diagram of species.[26] At pH values lower than pK_a, catechin exists mostly in a non-dissociated form, while at pH values above pK_a, dissociated form dominates. According to the observed pK_a values for catechin (8.77, 9.97 and 11.99),[26] it appears that catechin exist in non-dissociated form at pH 1.5 and in water (pH 5.47). This might have caused higher amounts of catechin in non-dissociated form to bond to zymosan A at pH 1.5 and as a result show a higher adsorption capacity. At pH 7.0, catechin could be present in both non-dissociated and dissociated forms.

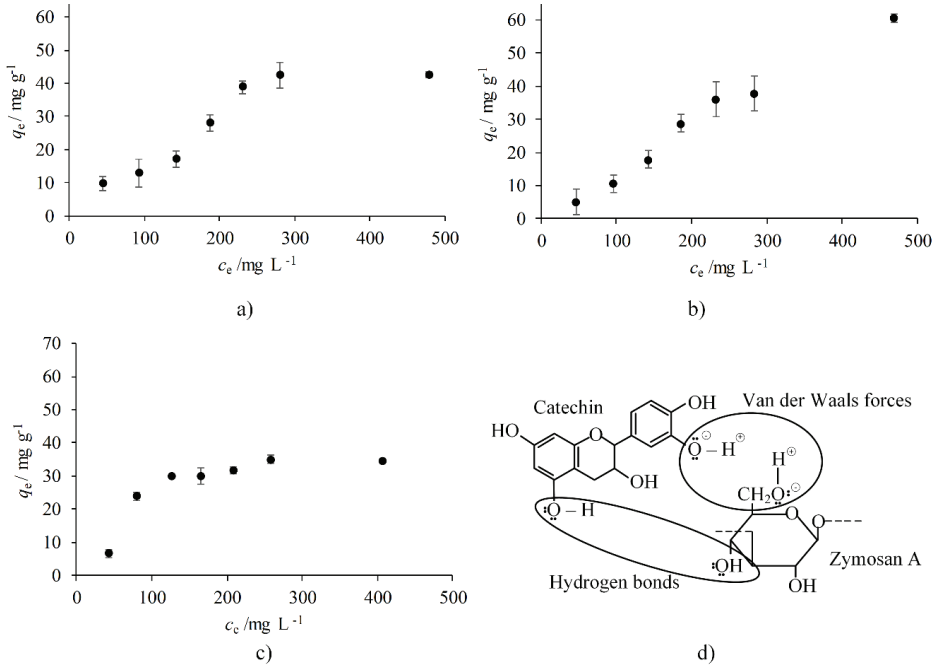

Fig. 2. Adsorption capacities q_e / mg g^{-1} of zymosan A for catechin at different concentrations of catechin: a) adsorption in water; b) pH 1.5; c) pH 7.0; d) possible interactions between catechin and zymosan A.

The ratio of dissociated/non-dissociated form increases with the increase of pH. This could explain the lower adsorption capacity of catechin at pH 7.0. Catechin dissociated and possibly degraded, which affected lower amount of catechin bonded to zymosan A at pH 7.0 and in water. Due to the higher ratio of dissociated/non-dissociated forms with higher pH, some studies have pointed to the less stability of catechin in neutral and alkaline area[27] which agrees with our results. The data after the adsorption process (the amount of catechin adsorbed on zymosan A q_e and unadsorbed catechin concentration c_e) are presented as adsorption isotherms (Fig. 2) and adsorption isotherm models were fitted in order to possibly describe the adsorption process.

Adsorption isotherm models

The obtained data in the adsorption process (c_e *vs.* q_e) can be analyzed with adsorption isotherm equations. The non-linear equations of Langmuir and Dubinin–Radushkevich were fit to the experimental data. Table II summarizes the values of the determined parameters of the isotherm models obtained with least possible error S using the add-in called Solver. The parameters q_m from the Langmuir model and the q_s from the Dubinin–Radushkevich model which represent the predicted apparent maximum adsorption capacities/saturation capacities of zymosan, were from 36 to 65 mg g^{-1} with maximal S error 3. The R^2 was between 0.8477 and 0.9697 for both Langmuir and Dubinin–Radushkevich model. Due to error S and R^2 both models fit the experimental data well, except Langmuir models for adsorption in water which fit les the experimental data (R^2 is 0.8477). The result of Langmuir fit for adsorption at pH 1.5 should be taken with caution, since the equilibrium has not been reached. The q_m and q_s values are in accordance with experimentally determined adsorption capacities (Fig. 2).

TABLE II. Theoretical parameters of Langmuir and Dubinin–Radushkevich adsorption isotherms for different solvent type and 37 °C

Solvent	Langmuir				Dubinin–Radushkevich			
	q_m / mg g^{-1}	K_L / L mg^{-1}	S	R^2	q_s / mg g^{-1}	E / J mol^{-1}	S	R^2
Water	44	0.01	3	0.8477	47	2384	2	0.9326
pH 1.5	62	0.005	3	0.9231	65	2047	3	0.9638
pH 7.0	37	0.01	2	0.9665	36	2805	3	0.9697

All determined free energies of adsorption (E) were lower than 8,000 J mol^{-1}, which indicates the presence of physical interactions between catechin and zymosan A, like the formation of H-bonds, hydrophobic interactions or van der Waals forces (Fig. 2d). The bonds between catechin and zymosan A could be through oxygen atoms and OH–groups on the zymosan A molecule and OH--groups on catechin molecule. This agrees with earlier studies.[25,28] It has been shown that the bonds between polyphenols and dietary fiber like β-glucan can be hydrophobic interactions, hydrogen bonds and van der Waals interactions.[25,29,30] Also, a mechanism of interaction between polyphenols ((–)-epigallocatechin-3--gallate)) and β-glucan[24] was proposed through oxygen atoms and OH-groups on the β-glucan molecule and OH-groups on polyphenols. The formation of hydrogen bonds reduces the distance between the aromatic rings of polyphenols and β--glucans, which enables van der Waals interactions.[24] The OH–groups of catechin on benzene rings might be the main functional groups which bind to zymosan A in the adsorption process (Fig. 2d). It can be suggested that the studied adsorption models reasonably fit the data and these models can be suitable for the

adsorption studies in this work. In an earlier study, the Langmuir model was also suitable for describing the catechin adsorption onto cellulose.[17]

FTIR spectrum

FTIR analysis can be used to identify functional groups in the adsorption process.[17] Fig. 3 shows the FTIR spectra of pure catechin and zymosan A and a sample of zymosan A with bonded catehin, all in three different solvents (water, pH 1.5 and 7). Catechin peaks were compared with those found in the literature.[31,32] The catechin molecule poses five OH groups on benzene rings (Fig. 2d). The OH–groups on ring A showed peaks 3276 (O–H group stretching) and 1142 cm^{-1} (C–O–H stretching).[31] The OH–groups on ring B show peaks 1354 cm^{-1}

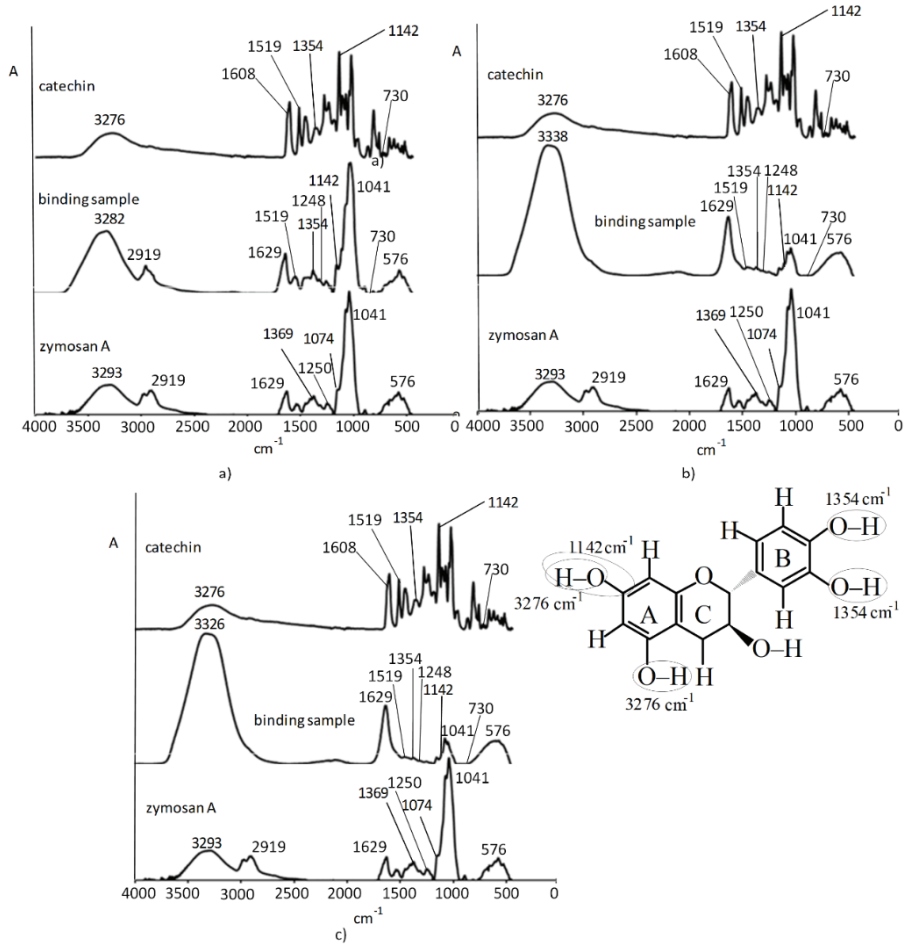

Fig. 3. FTIR spectrum of catechin, catechin–zymosan A binding sample and zymosan A: a) at water; b) at pH 1.5 and c) at pH 7.0.

(O–H in plane bending)[31]. Catechin showed other peaks like 1608 cm^{-1} (ring A deformation), 1519 (ring B deformation) and 730 (C–H out of plane bending).[33]

The FTIR spectra of catechin agree with those published in the literature.[31,32] The pure zymosan A showed characteristic peaks at 3293 (OH stretching groups), 2919 (C–H stretching), 1369 (C–H bond), 1250 (CH_2OH stretch) and 1041 cm^{-1} (C–O–C stretch). The FTIR spectra of zymosan A agree with those published in the literature.[9] Comparing the FTIR spectra of pure zymosan and pure catechin molecule with FTIR spectra of binding samples, the formation of complex can be confirmed.[33] Similar peaks to the peaks for the catechin molecule were observed in the characteristic peaks of catechin–zymosan A binding sample (Fig. 3, 1519, 1354, 1142 and 730 cm^{-1}). Furthermore, the peaks of zymosan A were found in all binding samples (1629, 1041 and 576 cm^{-1} in water, pH 1.5 and 7 and additional 2919 cm^{-1} in water). The appearance of catechin and zymosan peaks in the binding samples indicates possible catechin and zymosan A interactions. Differences in the FTIR spectrum for all the binding samples can be seen (Fig. 3). The decrease in intensity of peaks (around 1100–1600 cm^{-1}) for binding samples at pH 1.5 and 7 was stronger than for peaks at water. Also, the peak of OH groups of the binding samples at water (3282 cm^{-1}) were not so strong and less broad then peaks at pH 1.5 (3338 cm^{-1}) and at pH 7.0 (3326 cm^{-1}). The decrease in intensity could indicate intermolecular interactions such as hydrogen bonding. In earlier work, disappearance of peaks of hydrogen groups in phospholipid complex of naringenin and naringin PLGA nanosphere complex[33] also indicated such intramolecular bonding. These results have significance for the behavior in the digestive system, for carrying catechins with dietary fibers through the digestive system. Due to the fact that catechin degrade in intestinal tract, one way to improve its bioaccessibility can be the delivery system with dietary fiber[4] like zymosan A. This offers an additional chance for pharmaceutical industry to create some other dietary supplements based on zymosan A and phenolic compounds together. More studies should be carried out before that.

CONCLUSION

The stability/degradation of catechin and catechin adsorption onto zymosan A in different solvents (water, pH 1.5 and 7.0) was studied. The stability of catechin was pH dependent. After incubation in water, pH 1.5 and 7.0 for 180 min at 37 °C, catechin was stable in water and at pH 1.5. However, it degraded up to 15 % at pH 7.0. HPLC analysis revealed additional peaks of the degradation product. Catechin did adsorb onto zymosan A in water, pH 1.5 and 7.0. The lowest adsorption capacity was found to be at pH 7.0, higher at water and the highest at pH 1.5. Different ratios of non-dissociated/dissociated forms of catechin affected the higher adsorption at pH 1.5 and lower at pH 7.0 and in water. Langmuir and Dubinin–Radushkevich models gave additional information on the

adsorption process. The Dubinin–Radushkevich model indicated the presence of physical interactions between catechin and zymosan A. FTIR analysis showed that catechin could bond on zymosan A through OH–groups on benzene rings of catechin. This study can contribute to better understanding of interactions between catechin and zymosan A and possible design of functional food.

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И З В О Д

ИСПИТИВАЊЕ ПРОЦЕСА АДСОРПЦИЈЕ ПОЛИФЕНОЛНОГ ЈЕДИЊЕЊА КАТЕХИНА И ДИЈЕТЕТСКОГ ВЛАКНА ЗИМОСАН А: УТИЦАЈ pH И КОНЦЕНТРАЦИЈЕ

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Полифенолна једињења показују различите ефекте корисне за људско здравље као и одређене биоактивности као што су интеракције са дијететским влакнима. Фактори који утичу на њихове интеракције са дијететским влакнима укључују pH вредност, стабилност полифенолних једињења и концентрацију. Циљ овог рада је испитивање интеракција између полифенолног једињења катехина и дијететског влакна зимосан А из квасца праћењем процеса адсорпције. Испитивана је стабилност катехина и утицај концентрације и pH вредности на интеракције. Катехин је показао најнижу стабилност на pH 7,0 са процентом деградације од 6 до 15 %. Најнижи капацитет адсорпције је постигнут на pH 7,0, затим виши у води и највиши на pH 1,5. Дубинин–Радушкевич адсорпциони модел примењен на добијене податке и FTIR спектроскопска анализа указују на постојање физичких интеракција између катехина и зимосана А. Ово испитивање може допринети бољем разумевању интеракција између полифенола и дијететских влакана за потенцијални дизајн фунционалне хране, као и повећању биодоступности полифенола.

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REFERENCES

1. F. Truzzi, C. Tibaldi, Y. Zhang, G. Dinelli, E. D'Amen, *Int. J. Mol. Sci.* **2** (2021) 5541 (https://doi.org/10.3390/ijms22115514)
2. L. Jakobek, P. Matić, *Trends Food Sci. Technol*. **83** (2019) 235 (https://doi.org/10.1016/j.tifs.2018.11.024)
3. S. Ho, Y. Y. Thoo, D. J. Young, L. F. Siow, *Food Chem*. **275** (2019) 594 (https://doi.org/10.1016/j.foodchem.2018.09.117)
4. Z. Y. Cai, X. M. Li, J. P. Liang, L. P. Xiang, K. R. Wang, Y. L. Shi, R. Yang, M. Shi, J. H. Ye, J. L. Lu, X. Q. Zheng, Y. R. Liang, *Molecules* **23** (2018) 2346 (https://doi.org/10.3390/molecules23092346)
5. V. K. Ananingshig, A. Sharma, W. Zhou, *Food Res. Int.* **50** (2013), 469 (https://doi.org/10.1016/j.foodres.2011.03.004)
6. A. P. Neilson, A. S. Hopf, B. R. Cooper, M. A. Pereira, J. A. Bomser, M. G. Ferruzzi, *J. Agric. Food Chem.* **55** (2007) 8941 (https://doi.org/10.1021/jf071645m)
7. Q. V. Vuong, C. E. Stathopoulos, M. H. Nguyen, J. B. Golding, P. D. Roach, *Food Rev. Int.* **27** (2011) 227 (https://doi.org/10.1080/87559129.2011.563397)

8. A. E. Quirós-Sauceda, H. Palafox-Carlos, S. G. Sáyago-Ayerdi, J. F. Ayala-Zavala, L. A. Bello-Perez, E. Álvarez-Parrilla, L. A. de la Rosa, F. A. González-Córdova, G. A. González-Aguilar, *Food Funct*. **5** (2014) 1063 (https://doi.org/10.1039/C4FO00073K)
9. G. Venkatachalam, A. Senthilkumar, M. Doble, *ACS Omega* **5** (2020), 15973 (https://doi.org/10.1021/acsomega.0c01243)
10. T. Miura, N. Ohno, N. N. Miura, Y. Adachi, S. Shimada, T. Yadomae, *FEMS Microbiol. Immunol.* **24** (1999) 131 (https://doi.org/10.1111/j.1574-695X.1999.tb01274.x)
11. M. Salgado, S. Rodríguez-Rojo, R. L. Reis, M. José Cocero, A. R. C. Duarte, *J. Supercrit. Fluids* **127** (2017) 158 (https://doi.org/10.1016/j.supflu.2017.04.006)
12. A. Yiannikouris, J. Francois, L. Poughon, C.-G. Dussap, G. Bertin, G. Jeminet, J.-P. Jouany, *J. Agric. Food Chem*. **52** (2004) 3666 (https://doi.org/10.1021/jf035127x)
13. A. Yiannikouris, G. Andre, A. Poughon, J. Francois, C.-G. Dussap, G. Jeminet, G. Bertin, J.-P. Jouany, *Biomacromolecules* **7** (2006) 1147, (https://doi.org/10.1021/bm050968t)
14. T.R. Falcão, C. A. O. Rodrigues, A. A. de Araújo, C. A. A. X. de Medeiros, L. A. L. Soares, M. R. A. Ferreira, R. C. Vasconcelos, R. F. de Araújo Júnior, M. L. D. de Sousa Lopes, G. C. B. Guerra, *BMC Complement Altern. Med*. **19** (2019) 1 (https://doi.org/10.1186/s12906-019-2454-3)
15. P. Matić, Š. Ukić, L. Jakobek, *Chem. Biochem. Eng. Q*. **35** (2021) 177 (https://doi.org/10.15255/CABEQ.2020.1902)
16. A. Siemińska-Kuczer, M. Szymańska-Chargot, A. Zdunek, *Food Chem*. **373** (2022) 131487 (https://doi.org/10.1016/j.foodchem.2021.131487)
17. Y. Liu, D. Yiang, L. Sanguansri, Y. Cai, X. Le, *Food Res. Int.* **112** (2018) 225 (https://doi.org/10.1016/j.foodres.2018.06.044)
18. Y. Liu, D. Yiang, L. Sanguansri, M. A. Augustin, *Food Chem*. **271** (2019) 733 (https://doi.org/10.1016/j.foodchem.2018.08.005)
19. N. Li, L. S. Taylor, M. G. Ferruzzi, L. J. Mauer, *J. Agric. Food Chem*. **60** (2012) 12531 (https://doi.org/10.1021/jf304116s)
20. Y. Narita, K. Inouye, *J. Agric. Food Chem.* **61** (2013) 966 (https://doi.org/10.1021/jf304105w)
21. M. Shi, Y. Nie, X. Q. Zheng, J. L. Lu, Y. R. Liang, J. H. Ye, *Molecules* **21** (2016) 1345 (https://doi.org/10.3390/molecules21101345)
22. Z. Xu, L. Wei, Z. Ge, W. Zhu, *Eur. Food Res. Technol*. **240** (2015) 707 (https://doi.org/10.1007/s00217-014-2375-9)
23. M. L. Soto, A. Moure, H. Domínguez, J. C. Parajó, *J. Food Eng*. **105** (2011) 1 (https://doi.org/10.1016/j.jfoodeng.2011.02.010)
24. R. Gao, H. Liu, Z. Peng, Z. Wu, Y. Wang, G. Zhao, *Food Chem., B* **132** (2012) 1936 (https://doi.org/10.1016/j.foodchem.2011.12.029)
25. Z. Wu, H. Li, J. Ming, G. Zhao, *J. Agric. Food Chem.* **59** (2011) 378 (https://doi.org/10.1021/jf103003q)
26. J. Herrero-Martínez, M. Sanmartin, M. Rosés, E. Bosch, C. Ràfols, *Electrophor.* **26** (2005) 1886 (https://doi.org/10.1002/elps.200410258)
27. T. Raab, D. Barron, F. A. Vera, V. Crespy, M. Oliveira, G. Williamson, *J. Agric. Food Chem*. **58** (2010) 2138 (https://doi.org/10.1021/jf9034095)
28. Y. Gao, R. Yiang, J. Qie, J. Chen, D. Xu, W. Liu, Q. Gao, *Carbohydr. Polym., A* **90** (2012) 1411 (https://doi.org/10.1016/j.carbpol.2012.05.096)
29. H. T. Simonsen, M. S. Nielsen, N. J. Christensen, U. Christensen, T. V. La Cour, M. S. Motawia, B. P. M. Jespersen, S. B. Engelsen, B. L. Møller, *J. Agric. Food Chem*. **57** (2009) 2056 (https://doi.org/10.1021/jf802057v)

30. M. Veverka, T. Dubaj, J. Gallovič, V. Jorík, E. Veverková, M. Mičušík, P. Šimon, *J. Funct. Foods* **8** (2014) 309 (https://doi.org/10.1016/j.jff.2014.03.032)
31. A. M. Mendoza-Wilson, D. Glossman-Mitnik, *J. Mol. Struct*. **761** (2006) 97 (https://doi.org/10.1016/j.theochem.2006.01.001)
32. M. Krysa, M. Szymańska-Chargot, A. Zdunek, *Food Chem*. **393** (2022) 133430 (https://doi.org/10.1016/j.foodchem.2022.133430)
33. A. Semalty, M. Semalty, D. Sing, M. S. M. Rawat, *J. Incl. Phenom. Macrocycl. Chem.* **67** (2010) 253 (https://doi.org/10.1007/s10847-009-9705-8).