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The Study of Adsorption Kinetics of Flavan-3-Ols, Dihydrochalcones and Anthocyanins onto Barley β-Glucan

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Abstract: Polyphenols can interact with dietary fibers and these interactions can affect polyphenols bioactivities. The interactions can be studied with the adsorption process, and adsorptions of flavan-3-ols (procyanidin B1, procyanidin B2), dihydrochalcones (phloretin, phloretin-2-glucoside), and anthocyanins (cyanidin-3-glucoside, cyanidin-3-galactoside) onto *β*-D-glucan from barley were studied in this work. The intention was to reveal the kinetics of the adsorption process.

Adsorption was carried out using model solutions at room temperature. The results showed that in the flavan-3-ol group procyanidin B1 showed higher adsorption capacity than procyanidin B2. Phloretin showed a higher adsorption capacity than phloretin-2-glucoside in the dihydrochalcone group and anthocyanins showed similar adsorption capacities. Parameter k_1 for all polyphenols was in the range from 0.30 h^{-1} to 0.93 h^{-1}. Adsorption capacity q_e for all polyphenols ranged from 2.90 mmol g^{-1} to 9.76 mmol g^{-1}, parameter k_2 was in the range 70–225 g mol^{-1} h^{-1}, and adsorption capacities q_e ranged from 3.70 mmol g^{-1} to 9.90 mmol g^{-1}.

Keywords: flavan-3-ol, dihydrochalcone, anthocyanin, *β*-D-glucan, kinetic models.

INTRODUCTION

POLYPHENOLS are a group of organic compounds that naturally occur in plants. They can be classified into phenolic acids, flavonoids, lignans, and stilbenes.[1] Many potential bioactivities of polyphenols have been reported among which we highlight interactions between polyphenols and food constituents such as dietary fibers. These interactions can affect polyphenols' accessibility for absorption (bioaccessibility) in the digestive tract as well as the amount of polyphenols that can be absorbed and reach various organs (bioavailability).[2]

β-glucan is a dietary fiber that can be found in various foods and food supplements.[3] It has multiple positive activities on human organism.[4–6] However, *β*-glucan is one of the fibers that can interact with polyphenols.[7,8]

A better understanding of interactions between polyphenols and dietary fibers can be achieved by exploring the adsorption process and testing the suitability of different kinetics models. The most commonly used models are pseudo-first and pseudo-second order models.[9–11] The kinetic study is widely used in different applications such as the adsorption of catechin onto cellulose,[12] the adsorption of tea polyphenols on starch,[13] or the adsorption of various adsorbates from aqueous solution on different adsorbents.[14,15] Furthermore, the adsorption of polyphenols on different adsorbents can be investigated using the various kinetic models.

The aim of this research was to study kinetics of adsorption of various polyphenols onto *β*-D-glucan. The selected polyphenols (Figure 1) belong to the flavan-3-ols (procyanidin B1 and procyanidin B2), dihydrochalcones (phloretin, phloretin-2-glucoside), and anthocyanins (cyanidin-3-glucoside and cyanidin-3-galactoside). The experimentally obtained results were fitted by non-linear pseudo-first order and non-linear pseudo-second order

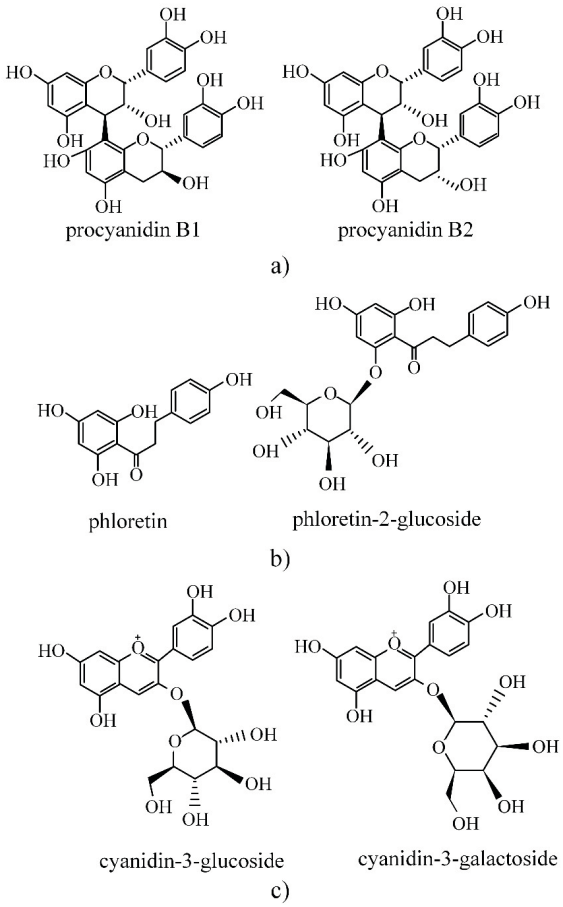

Figure 1. Chemical structures of tested flavan-3-ols (a), dihydrochalcones (b), and anthocyanins (c).

model in order to understand the adsorption kinetics of polyphenols onto *β*-D-glucan. To the best of our knowledge, only few papers dealt with modeling of adsorption kinetics of polyphenols, especially if adsorbent was *β*-D-glucan[9,16] Also, there are no papers of kinetic study with the selected polyphenols like the ones selected for our study, and *β*-D-glucan. Therefore, this work will help in better understanding the adsorption kinetics of flavan-3-ols, dihydrochalcones and anthocyanins on *β*-D-glucan and give useful data about the interactions between polyphenols and *β*-D-glucan.

MODELING

Models of adsorption kinetics can be classified into diffusion models and adsorption models. Diffusion models are considering the diffusion as the slowest step of the process which limits the rate of the entire process. The diffusion can be related to the mass transfer through the liquid film which surrounds particles of the adsorbent or to the mass transfer through the liquid that fills the adsorbent pores. Adsorption models are considering adsorption at the surface of the adsorbent as the slowest step of the process.[17] The most widely used adsorption kinetic models are pseudo-first and pseudo-second order model.[10,11,18]

Kinetics of pseudo-first order reaction is following [Eq. (1)] while [Eq. (2)] describes pseudo-second order behaviour [19].

$$q_t = q_e\left[1 - e^{-k_1 t}\right] \quad (1)$$

$$q_t = \frac{q_e^2 k_2 t}{q_e k_2 t + 1} \quad (2)$$

In [Eq. (1)] and [Eq. (2)], q_t and q_e represent amounts (mol) of an adsorbate adsorbed per mass (g) of adsorbent at reaction time t and at the equilibrium, respectively. Each equation has reaction rate constant, k, included. In order to facilitate later discussion, we marked pseudo-first-order rate constant as k_1 and the pseudo-second order one as k_2.

Pseudo-first order equation can be linearized [Eq. (3)]

$$\log(q_e - q_t) = -\frac{k_1}{2{,}303} t + \log(q_e) \quad (3)$$

Pseudo-second-order model can also be linearized [Eq. (4)]

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 q_e^2} \quad (4)$$

Two kinetics models: pseudo-first [Eq. (1)] and pseudo-second order model [Eq. (2)], were applied in this study in order to investigate the adsorption kinetic. The parameters of the models: q_e, k_1, and k_2, were obtained by non-linear regression using tool Solver in MS Excel (Microsoft Corporation, Redmond, USA).

EXPERIMENTAL

Reagents and Solutions

Methanol of HPLC grade from J. T. Baker (Deventer, Netherlands) and hydrochloric acid (37 %) from Avantor (Arnhem, Netherlands) were used during the experiments. Sodium carbonate and potassium chloride were purchased from Gram-mol (Zagreb, Croatia), while Folin–Ciocalteu reagents, sodium acetate trihydrate, sodium phosphate dodecahydrate, and sodium dihydrogen phosphate dihydrate were from Kemika (Zagreb, Croatia).

Stock solutions of standards procyanidin B1, procyanidin B2, phloretin, and phloretin-2-glucoside were prepared in concentrations of 160 mg L^{-1}, 450 mg L^{-1}, 1000 mg L^{-1} and 1000 mg L^{-1}, respectively, by dissolving appropriate amounts of the solid polyphenols in distilled water. Stock solutions of cyanidin-3-glucoside and cyanidin-3-galactoside were prepared in concentrations of 480 mg L^{-1} and 485 mg L^{-1}, respectively, by dissolving appropriate amounts of the solid polyphenols in 0.1 % solution of HCl in methanol. All solid polyphenols (procyanidin B1 and procyanidin B2 ≥ 90 %, phloretin and phloretin-2-glucoside ≥ 99 %, cyanidin-3-glucoside ≥ 96 %, cyanidin-3-galactoside ≥ 97 %) were purchased from Extrasynthese (Genay, France). Solutions were stored at -18 °C.

Solid *β*-D-glucan (95 %) obtained from barley was purchased from Sigma-Aldrich (St. Louis, USA). The stock solution was prepared in distilled water at a concentration of 190 mg L^{-1}. The solution was heated for 15 min at 80 °C and afterward stored in the refrigerator at 4 °C.

In order to retain the constant pH value of the solutions, a phosphate buffer of pH 5.5 was applied. Phosphate buffer was prepared with 0.1 M sodium phosphate dodecahydrate and 0.1 M sodium dihydrogen phosphate dihydrate. For the determination of total anthocyanins, solutions of pH 1.0 and pH 4.5 were used. pH 1.0 was 0.025 M potassium chloride, while the second one was 0.4 M sodium acetate trihydrate.

Performing the Adsorption Experiments

Adsorption of two flavan-3-ols (procyanidin B1 and procyanidin B2), two dihydrochalcones (phloretin and phloretin-2-glucoside), and two anthocyanins (cyanidin-3-glucoside and cyanidin-3-galactoside), was performed onto *β*-D-glucan. Total volumes of model solutions were 500 µL. Solutions consisted of *β*-D-glucan in the concentration of 5 mg L^{-1} and related polyphenol in the concentration of 100 mg L^{-1} ($c_{initial}$, mg L^{-1}); the rest was the buffer solution of pH 5.5. All solutions were homogenized on vortex mixer and put in an incubator for 1, 2, 5, 8, and 16 hours at room temperature. At the end of the adsorption experiment, the solutions were filtered on Eppendorf Minispin centrifuge (Eppendorf, Hamburg, Germany) by using 100–500 µL Vivaspin 500 centrifugal concentrators with polyethersulfon membrane (Sartorius, Goettingen, Germany). Afterwards, the content of unadsorbed polyphenols was analyzed (c, mg L^{-1}). Flavan-3-ols and dihydrochalcones were determined by Folin-Ciocalteu method for the determination of total phenolic content, while anthocyanins were analyzed by using the method for total anthocyanins.[20] Blank experiments considered experiments under the same conditions but without *β*-D-glucan, were conducted as well. Dihydrochalcones, flavan-3-ols and anthocyanins passed through the membrane in the blank experiment and they were determined by the use of spectrophotometric Folin-Ciocalteu method and by method for determination of total anthocyanins (c_o, mg L^{-1}). The concentration of adsorbed dihydrochalcones, flavan-3-ols and anthocyanins ($c_{adsorbed}$, mg L^{-1}) was calculated as:

$$c_{adsorbed} = c_0 - c \tag{5}$$

The concentration of unadsorbed dihydrochalcones, flavan-3-ols and anthocyanins at equilibrium (c_e, mg L^{-1}) was calculated as:

$$c_e = c_{initial} - c_{adsorbed} \tag{6}$$

The amount of adsorbed dihydrochalcones, flavan-3-ols and anthocyanins in millimoles per gram of *β*-D-glucan, q, was calculated according to [Eq. (7)].

$$q = \frac{c_{adsorbed} V_m}{\gamma_a V_a} \tag{7}$$

where V_m is the total volume of the model solution (L), γ_a is the mass concentration of *β*-D-glucan (g L^{-1}) and V_a is the volume of *β*-D-glucan (L).

Determination of Flavan-3-ols and Dihydrochalcones

Solutions for the spectrophotometric determination of flavan-3-ol and dihydrochalcone contents by the Folin-Ciocalteu method were prepared in a glass tube by adding 1580 µL of distilled water, 20 µL of sample (polyphenol) solution after adsorption, 100 µL of Folin-Ciocalteu reagent, and 300 µL of 200 g L^{-1} solution Na_2CO_3. Solutions were mixed on a vortex mixer (Grant Bio, Cambridgeshire, England) and incubated 30 minutes at 40 °C. Afterwards, the solutions were analyzed on spectrophotometer UV-2005 (Selecta, Barcelona, Spain). The absorbance was measured at 765 nm against the blank solution.[20] Calibration curves were constructed for each polyphenol in concentration range 1-1000 mg L^{-1} for dihydrochalcones, 1–600 mg L^{-1} for procyanidin B1, and 1–300 mg L^{-1} for procyanidin B2 using the same procedure. Two replicate samples were prepared and analyzed three times for each polyphenol concentration.

Determination of Total Anthocyanins

For the determination of anthocyanin content after the adsorption, two solutions were prepared, each containing 500 µL of the solution after adsorption supplemented with

1500 µL of solution with different pH. The pH value of the first solution was 1.0 (0.025 M potassium chloride), while the second one had a pH value of 4.5 (0.4 M sodium acetate trihydrate). Both solutions were incubated for 15 min at a dark place. Afterwards, the absorbance was measured at 510 nm and 700 nm with a UV-Vis spectrophotometer against the blank solution. The true absorbance of anthocyanin (A) was calculated according to [Eq. (8)], where A_{510} and A_{700} were absorbances of prepared solutions measured at 510 and 700 nm, respectively.

$$A = (A_{510} - A_{700})_{\text{pH 1.0}} - (A_{510} - A_{700})_{\text{pH 4.5}} \quad (8)$$

The calibration curves were constructed for each anthocyanin in the concentration range 1–200 mg L^{-1} using the same procedure. Two replicate samples were prepared and analyzed three times for each polyphenol concentration.

RESULTS AND DISCUSSION

During the adsorption processes, polyphenols were adsorbing onto the surface of β-D-glucan. The adsorption process was monitored at different times in order to reveal the kinetics of the adsorption.

Different behavior in the adsorption process between flavan-3-ols, dihydrochalcones and anthocyanins onto β-D-glucan can be seen (Figures 2–4). Comparing flavan-3-ols, procyanidin B1 showed higher adsorption capacity (Figure 2). Phloretin showed higher adsorption capacity among the tested dihydrochalcones (Figure 3). The tested anthocyanins showed similar adsorption capacities (Figure 4). Different adsorption capacities of polyphenols can be related to the chemical structures of polyphenols.[21] It is possible that the special arrangement of OH groups in the case of flavan-3-ols affected the adsorption capacity.

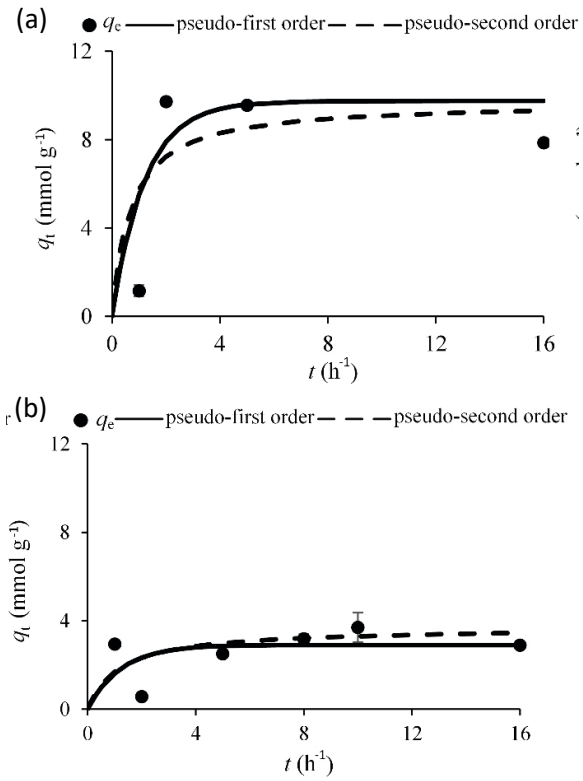

Figure 2. Experimentally obtained adsorption capacity in time (q_t) and fitted non-linear kinetic models of pseudo-first and pseudo-second order for the adsorption of flavan-3-ol onto β-glucan: (a) procyanidin B1; (b) procyanidin B2.

Furthermore, glycosylation was less favored in the case of dihydrochalcones. In the case of anthocyanins, adsorption was similar.

Adsorption is a complex process[22] and for a better understanding, different kinetic models should be applied. Kinetic study can provide the information about the

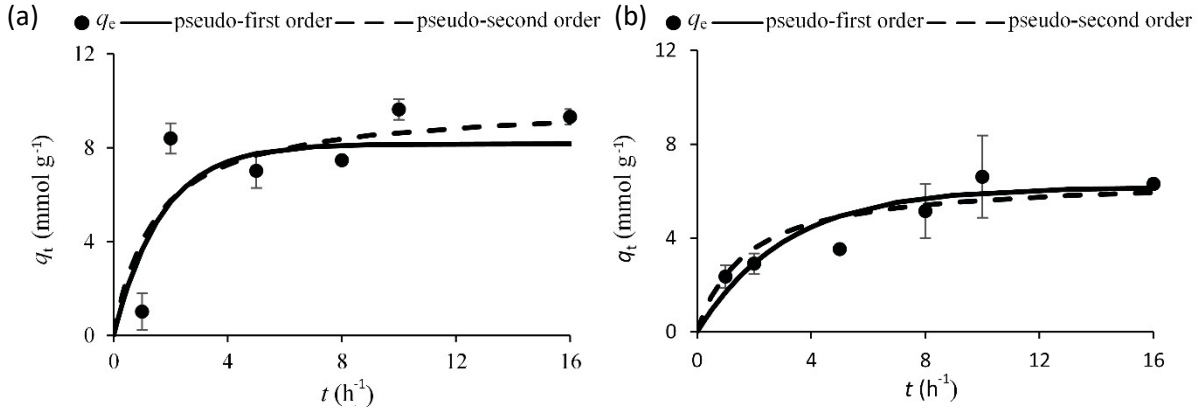

Figure 3. Experimentally obtained adsorption capacity in time (q_t) and fitted non-linear kinetic models of pseudo-first and pseudo-second order for the adsorption of dihydrochalcones onto β-glucan: (a) phloretin; (b) phloretin-2-glucoside.

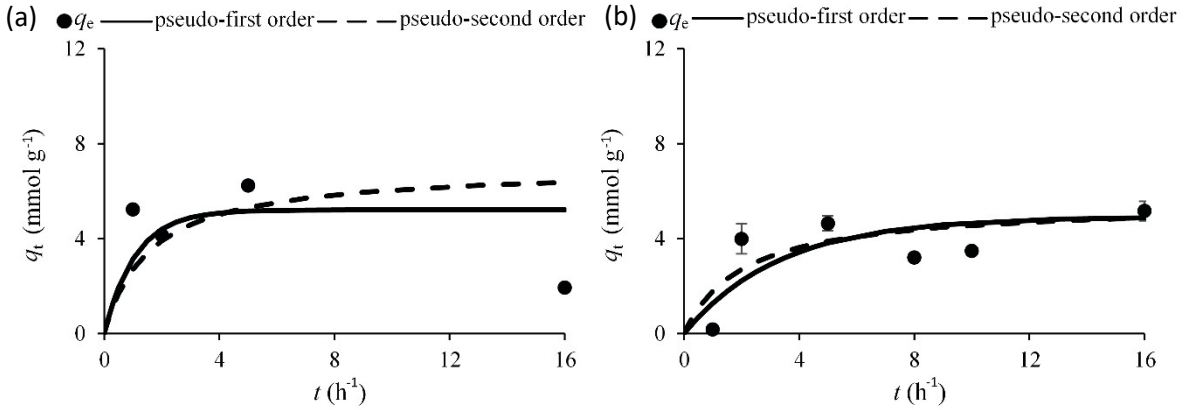

Figure 4 Experimentally obtained adsorption capacity in time (q_t) and fitted non-linear kinetic models of pseudo-first and pseudo-second order for the adsorption of anthocyanin onto *β*-glucan: (a) cyanidin-3-glucoside; (b) cyanidin-3-galactoside.

reaction pathways and the mechanism of the adsorption reactions.[23] Pseudo-first and pseudo-second order models have been widely used to describe the kinetics of the adsorption process,[9,17,24] especially kinetic model of pseudo-first order for the description of the adsorption process of solute from the liquid.[10] The pseudo-first order model is one of the probably earliest kinetic models for the

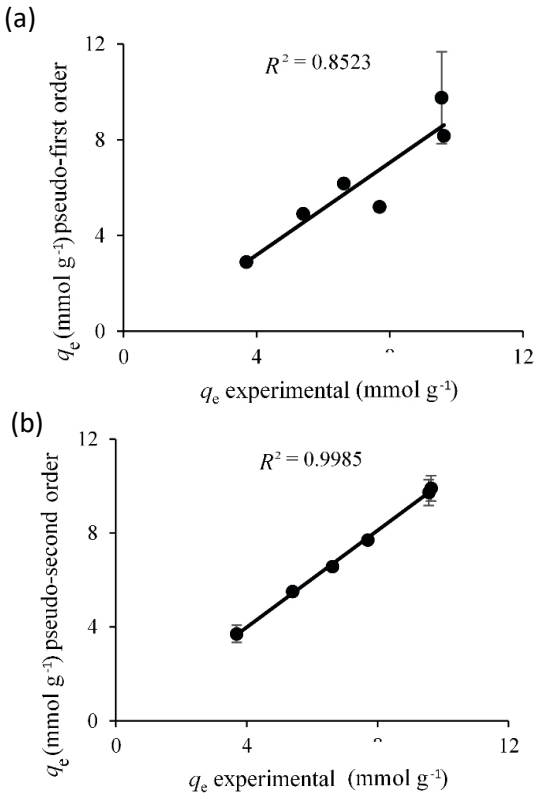

Figure 5. The correlation between adsorption capacities (q_e) determined experimentally and from kinetics models of: a) pseudo-first order; b) pseudo-second order reactions.

adsorption process. Pseudo-second order model assumes that the rate of adsorption or desorption process controls the overall kinetics. Pseudo-first and pseudo-second order models were also used in our study. Generally, linear or non-linear forms of these models can be applied.[17,19,25,26] However, the linear forms of the kinetic models can lead to erroneous results due to the modelling error. Also, parameters obtained from non-linear and linear models sometimes do not show good agreement.[19] Therefore, we decided to apply non-linear form of the models using non-linear regression with tool Solver. Figures 2–4 present the non-linear pseudo-first and pseudo-second order models for the adsorption of the tested flavan-3-ols, dihydrochalcones, and anthocyanins, respectively. The models were obtained by regression analysis. The analysis provided values of the model parameters (Table 1). Parameters k_1 and q_e obtained with pseudo-first order models were in the range from 0.30 h^{-1} to 0.93 h^{-1}, and from 2.90 mmol g^{-1} to 9.76 mmol g^{-1}, respectively. Parameter k_2 and q_e obtained with pseudo-second order model were from 70 g mol^{-1} h^{-1} to 225 g mol^{-1} h^{-1}, and from 3.70 mmol g^{-1} to 9.90 mmol g^{-1}, respectively. Adsorption capacities obtained from kinetic models for flavan-3-ol group was higher for procyanidin B1, then for phloretin in dihydrochalcones group and anthocyanins showed similar adsorption capacities. This is in accordance with experimentally obtained adsorption capacities (Figures 2–4).

In order to see how the adsorption capacities of polyphenols obtained from kinetic models agree with experimental adsorption capacities, they were put in the correlation (Figure 5). We assumed that the adsorption equilibrium was reached after 16 hours for all tested polyphenols and, accordingly, took experimental and model adsorption capacities after 16 h into correlation. Due to the determination of the coefficient R^2, pseudo-second order model showed better agreement with experimental

Table 1. Parameters of pseudo-first and pseudo-second order models describing adsorption kinetics of six polyphenols onto *β*-glucan. Mark *S* represents standard error.

Standard	Pseudo-first order			Pseudo-second order		
	k_1 / h^{-1}	q_e / mmol g^{-1}	S / 10^{-4}	k_2 /g mol^{-1} h^{-1}	q_e /mmol g^{-1}	S / 10^{-4}
Flavan-3-ols						
procyanidin B1	0.83 ± 0.08	9.76 ± 1.91	24	150 ± 2	9.72 ± 0.55	27
procyanidin B2	0.82 ± 0.17	2.90 ± 0.12	9	225 ± 5	3.70 ± 0.36	9
Dihydrochalcones						
phloretin	0.60 ± 0.00	8.16 ± 0.14	16	70 ± 1	9.90 ± 0.53	17
phloretin-2-glucoside	0.32 ± 0.00	6.17 ± 0.01	6	90 ± 1	6.57 ± 0.02	6
Anthocyanins						
cyanidin-3-glucoside	0.93 ± 0.01	5.20 ± 0.11	12	90 ± 1	7.70 ± 0.02	14
cyanidin-3-galactoside	0.30 ± 0.00	4.91 ± 0.09	12	87 ± 1	5.51 ± 0.07	9

adsorption capacities (R^2 0.9985) than pseudo-first order model (R^2 0.8523). The reaction half-time was calculated for the pseudo-first and pseudo-second order model (Table 2). Half-time was different for each polyphenol substance. Since pseudo-second order model showed better agreement with experimental capacities, the half-time of the adsorption process was calculated also for the pseudo-second order model and was from 1.51 h to 10.94 h.

Overall, the analysis of data obtained from fitted pseudo-first and pseudo-second order models showed that the adsorption capacities obtain by pseudo-second order kinetic model were closer to the values of the experimental adsorption capacities. In earlier studies kinetic was studied for the catechin adsorption onto cellulose[12] and polyphenols from vegetable extract onto tannery shavings.[9] Kinetic study of polyphenols adsorption onto tannery shavings showed better correlation between data obtained with pseudo-second order model and experimental dana.[9] Further studies on the adsorption kinetics are necessary to understand the kinetic of the polyphenol adsorption onto *β*-D-glucan.

Table 2. Half-reaction time for pseudo-first and pseudo-second order model for adsorption of six polyphenols onto *β*-glucan.

Standard	Pseudo-first order	Pseudo-second order
	$t_{1/2}$ / h	$t_{1/2}$ / h
Flavan-3-ols		
procyanidin B1	0.83 ± 0.07	5.73 ± 1.54
procyanidin B2	0.85 ± 0.24	1.51 ± 0.26
	Dihydrochalcones	
phloretin	1.16 ± 0.00	2.73 ± 0.07
phloretin-2-glucoside	2.17 ± 0.00	6.42 ± 0.71
	Anthocyanins	
cyanidin-3-glucoside	0.75 ± 0.00	10.94 ± 0.03
cyanidin-3-galactoside	2.31 ± 0.01	4.86 ± 0.46

CONCLUSION

In this study, the adsorption kinetic of six polyphenols onto *β*-D-glucan was studied. The polyphenols where selected among flavan-3-ols (procyanidin B1, procyanidin B2), dihydrochalcones (phloretin, phloretin-2-glucoside) and anthocyanins (cyanidin-3-glucoside, cyanidin-3-galactoside). During the adsorption process, polyphenols adsorbed onto the *β*-D-glucan surface. Procyanidin B1 showed higher adsorption capacity than procyanidin B2, phloretin showed higher adsorption capacity than phloretin-2-glucoside, while the tested anthocyanins showed similar adsorption capacities. Pseudo-second order kinetic model showed better correlation with the experimentally obtained values of adsorption capacity. Additional studies are necessary to better understand the kinetics of polyphenols adsorption onto *β*-D-glucan.

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