Croatian Journal of Food Science and Technology

An equilibrium and kinetic study of phenolic acids adsorption onto β-glucan

[iD] **PETRA MATIĆ[*1], LIDIJA JAKOBEK[1], ŠIME UKIĆ[2]**

[1]*Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Department of Applied Chemistry and Ecology, Franje Kuhača 20, 31000 Osijek, Croatia*
[2]*University of Zagreb, Faculty of Chemical Engineering and Technology, Department of Analytical Chemistry, Marulićev trg 19, 10000 Zagreb, Croatia*

ABSTRACT

Phenolic acids belong to the group of natural polyphenols, which are secondary plant metabolites. Polyphenols show many positive bioactivities, which are not completely investigated. One of these bioactivities is the polyphenol interaction with food compounds, such as lipids, proteins, and dietary fibres. The information about the interactions between polyphenols and dietary fibres can be obtained through the parameters of adsorption equilibrium models, like Freundlich, Langmuir, Dubinin-Radushkevich, and others. Also, the reaction order and the kinetic constants can be obtained through kinetic models, like pseudo-first and pseudo-second order models. The objective of this study was to obtain information about the interactions between phenolic acids, like, *p*-coumaric and caffeic acid, and β-glucan as a natural dietary fibre, through non-linear adsorption models and kinetic models of the pseudo-first and pseudo-second order. The adsorption was carried out at 25 °C for 16 h, in a model solution which contained polyphenol, β-glucan and phosphate buffer pH 5.5. Kinetics was conducted at 25 °C during 1, 2, 5, 10, and 16 h. After reaching the adsorption equilibrium, the un-adsorbed polyphenols were separated from the adsorbed ones by ultrafiltration. The non-linear adsorption equilibrium models and kinetic models were determined. Adsorption process of phenolic acids and β-glucan was favored and chemical, and was best described by the pseudo-second order model.

Introduction

Polyphenols are secondary plant metabolites that can be classified on the basis of their chemical structure as phenolic acids, flavonoids, stilbens and lignans (Bravo, 1998). Earlier studies found numerous potentially positive bioactivities of polyphenols in human organism (Camouse et al., 2005; Kampa et al., 2007; Pandey et al., 2009; Scalbert et al., 2005). Furthermore, polyphenols showed that they can interact with food constituents like proteins, carbohydrates, dietary fibre, and lipids in digestive tract (Jakobek, 2015; Le Bourvellec and Renard, 2012). This bioactivity is not completely investigated. Interactions between polyphenols and dietary fibre are particularly interesting because dietary fibres are resistant to digestion and absorption in the human small intestine, with complete or partial fermentation in the large intestine (Quirós-Sauceda et al., 2014). Because of that, dietary fibres can "carry" polyphenols to the lower parts of digestive tract. These interactions can have influences on polyphenol accessibility for absorption in the human organism, and therefore their bioavailability and potentially beneficial bioactivities in the lower parts of the digestive tract (Jakobek, 2015; Palafox-Carlos et al., 2011; Quirós-Sauceda et al., 2014; Velderrain-Rodríguez et al., 2016).

To obtain more information about interactions between polyphenols and dietary fibre, adsorption processes can be studied through adsorption isotherms. Adsorption isotherms graphically present the amount of polyphenols adsorbed onto the adsorbent as a function of a concentration that

---

[*]Corresponding author E-mail:
petra.matic@ptfos.hr

remained un-adsorbed. Adsorption isotherms can be classified according to Giles et al. (1974) as L, H, C and S type. The experimental results of the adsorption can be analysed by using adsorption isotherm models like Freundlich, Langmuir and Dubinin-Radushkevich (Foo et al., 2010; Soto et al., 2011). From the constants of these models the information about adsorption can be obtained, whether the adsorption is a physical or chemical process, whether the adsorption is favoured, if the process is a single layer or a multiple layer adsorption or what is the maximum theoretical adsorption capacity (Foo et al., 2010; Soto et al., 2011). Also, the experimental results of the adsorption can be analysed by using kinetic models for pseudo-first and pseudo-second order reactions. These models can give kinetic constants of pseudo-first and pseudo-second order reactions (Marsal et al., 2012).

The aim of this work was to conduct the adsorption experiment between phenolic acids such as *p*-coumaric acid and caffeic acid and β-glucan. *p*-coumaric acid and caffeic acid belong to the group of phenolic acids, compounds with a relatively simple structure and a low molecular weight (Bravo, 1998). β-glucan is one of the water soluble natural dietary fibre which can be found in cereals, mushrooms, seaweed and yeast (Laroche and Michaud, 2007) and it showed it can interact with polyphenols (Wang et al., 2013). To obtain the information about adsorption process, the non-linear adsorption models like Freundlich, Langmuir and Dubinin-Radushkevich and kinetic models of pseudo-first and pseudo-second order were applied.

Materials and methods

Chemicals

Methanol (HPLC grade) was purchased from J.T. Baker (Netherlands). β-D-glucan from barley (G6513, ≥ 95%), *p*-coumaric acid (*trans*-4-hydroxycinnamic acid - C9008 ≥ 98%), and caffeic acid (3,4-dihydroxycinnamic acid - C0625, ≥ 98%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Folin–Ciocalteu reagent, sodium hydrogen phosphate dodecahydrate and sodium dihydrogen phosphate dihydrate were purchased from Kemika (Zagreb, Croatia). Sodium carbonate was purchased from Gram-mol (Zagreb, Croatia).

Standard preparation

Stock solutions of *p*-coumaric acid and caffeic acid were prepared in methanol in concentration of 1000 mg/L. Calibration curves were obtained by preparing different concentrations of standards from stock solution. Dilutions for *p*-coumaric acid and caffeic acid were 1, 10, 50, 100, 200 and 500 mg/L. β-glucan stock solution was prepared in concentration of 190 mg/L in distilled water, heated for 15 min at 80 °C and stored in the refrigerator at 4 °C.

Spectrophotometric Folin - Ciocalteu method for total polyphenols

Total polyphenols were monitored in adsorption study by Folin-Ciocaletu method (Singleton et al., 1999). For total polyphenol determination, 20 μL of polyphenol standard, 1580 μL of distilled water, 100 μL of Folin-Ciocalteu reagent and 300 μL of Na_2CO_3 (200 g/L) were added into a glass tube. These solutions were mixed in the vortex (Grant Bio, Cambridgeshire, England) and incubated at 40 °C for 30 min in the incubator (Memmert IN 30, Schwabach, Germany). The absorbance of a solution was measured at 765 nm against the blank solution (which contained 20 μL distilled water instead of prepared solution) with a UV-Vis spectrophotometer (Selecta, UV 2005, Barcelona, Spain).

The study of adsorption between phenolic acids and β-glucan

The adsorption experiment was carried out in a model solution in plastic cuvettes, which contained β-glucan as an adsorbent, *p*-coumaric acid or caffeic acid and a phosphate buffer solution (pH 5.5) (Wu et al., 2011). Concentrations of *p*-coumaric acid and caffeic acid were as follows: 15, 25, 50, 75, 100 and 150 mg/L, and a concentration of β-glucan was 5 mg/L. The rest of the volume was phosphate buffer. The total volume of model solution was 500 μL. The adsorption was performed at 25 °C in the incubator (IN 30, Memmert, Schwabach, Germany). After reaching the equilibrium (16 h) (Wang et al., 2013), model solutions were centrifuged (Eppendorf minispin centrifuge, Hamburg, Germany) through polyethersulfon membrane (Sartorius, Vivaspin 500, 100 - 500 μL). Adsorbed polyphenols retained on the membrane, while un-adsorbed passed through the membrane (polyphenol concentration at equilibrium, c_e). After the adsorption experiment, the non-linear Freundlich, Langmuir and Dubinin-Radushkevich models were applied. For the kinetic study, the procedure was the same as for the adsorption study, except one modification; a concentration in the model solution for *p*-coumaric acid and caffeic acid was 100 mg/L. Phenolic acid concentrations were monitored during the 1, 2, 5, 8, 10 and 16 h. After the kinetic experiment, the pseudo-first and pseudo-second order models were applied.

Adsorption isotherms

The adsorption capacity in equilibrium q_e (the phenolic acid amount (mol) adsorbed per g of β-glucan (mol/g)) was calculated with Eq. 1:

$$q_e = \frac{(c_o - c_e) \cdot V_m}{\gamma_a \cdot V_a} \qquad (1)$$

where c_o is the polyphenol initial concentration in the reaction solution (mol/L), c_e is the phenolic acid concentration in equilibrium after 16 h (mol/L), V_m is the total volume of reaction solution (L), V_a is the volume of β-glucan in the reaction solution (L) and γ_a is the β-glucan concentration in the reaction solution (g/L).

Freundlich, Langmuir and Dubinin-Radushkevich adsorption isotherm models were applied on q_e and c_e data. Parameters of Freundlich model (K_F and $1/n$) were calculated according to Eq. 2, parameters of Langmuir model (K_L and q_m) according to Eq. 3 and parameters of Dubinin-Radushkevich model (q_s and β) according to Eq. 4 (Babaeivelni et al, 2013; Foo and Hameed, 2010; Marsal et al., 2012; Soto et al., 2011):

$$q_e = K_F \, c_e^{1/n} \qquad (2)$$

$$q_e = \frac{q_m \, K_L \, c_e}{1 + K_L \, c_e} \qquad (3)$$

$$q_e = q_s \, exp \, (-\beta \, \varepsilon^2) \qquad (4)$$

where q_e is the amount of phenolic acid adsorbed per g of β-glucan at equilibrium (mol/g), c_e is the phenolic acid concentration in the solution at equilibrium (mol/L), K_F is the Freundlich constant indicative of relative adsorption capacity of β-glucan ((mol/g) (L/mol)$^{1/n}$), $1/n$ is the intensity of adsorption, K_L is the Langmuir equilibrium constant of adsorption (L/mol) or apparent affinity constant, q_m is the theoretical maximum adsorption capacity of β-glucan (mol/g), q_s is theoretical saturation capacity (mol/g), β is constant related to the adsorption capacity (mol^2/J^2) and ε is Polanyi potential (J/mol).

From Dubinin-Radushkevich, the adsorption mean free energy E (kJ/mol) can be calculated with Eq. 5, and the type of adsorption like physical adsorption (E value is up to 8 kJ/mol) and chemical adsorption (if E exceed 8 kJ/mol) can be estimated (Babaeivelni et al, 2013; Marsal et al., 2012):

$$E = \frac{1}{\sqrt{2\beta}} \qquad (5)$$

Polanyi potential ε (J/mol) or adsorption potential can be calculated according to Eq. 6 (Foo and Hameed, 2010):

$$\varepsilon = RTln \left(1 + \frac{1}{c_e} \right) \qquad (6)$$

where R is gas constant (8.314 J/mol K), T is temperature (K) and c_e is the polyphenol concentration in the solution at equilibrium (mol/L).

Kinetic study

For kinetic study, the pseudo-first and pseudo-second order models were applied in order to obtain the parameters of models (k_1, k_2, q_e).

The linear form of pseudo-first order model is given by Eq. 7 (Marsal et al., 2012):

$$\log (q_e - q_t) = - \left(\frac{k_1}{2,303} \right) t + \log (q_e) \qquad (7)$$

where q_e is the amount of phenolic acid adsorbed per g of β-glucan at equilibrium (mol/g), q_t is the amount of phenolic acid adsorbed per g of β-glucan at time t (mol/g), t is time (h) and k_1 is rate constant of pseudo-first order reaction (h^{-1}). The liner plot of t versus [log $(q_e$-$q_t)$] yield a straight line with a slope [-(k_1/2.303)] and intercept [log (q_e)] (Marsal et al., 2012).

The linear form of pseudo-second order model is given by Eq. 8 (Marsal et al., 2012):

$$\frac{t}{q_t} = \frac{1}{q_e} t + \frac{1}{k_2 \, q_e^2} \qquad (8)$$

where q_e is the amount of phenolic acid adsorbed per g of β-glucan at equilibrium (mol/g), q_t is the amount of phenolic acid adsorbed per g of β-glucan at time t (mol/g), t is time (h) and k_2 is rate constant of pseudo-second order (g/mol h). The liner plot of t versus (t/q_t) yields a straight line with a slope ($1/q_e$) and intercept ($1/k_2 \, q_e^2$) (Marsal et al., 2012).

Statistical analysis

MS Excel (Redmond, USA) was used for the data analysis. Phenolic acid standards were prepared in two replicate samples for each concentration level. Each was measured twice with Folin-Ciocalteu method (n=4) and results were used for the calibration curve. Linear regression function was used to obtain linear equations and corresponding determination coefficient R^2.

Adsorption studies were based on measuring six different concentration levels of phenolic acids, each measured three times (n=3), before and after the adsorption with Folin-Ciocalteu method. Means were calculated. For obtaining isotherm parameters, non-linear models were applied on data means with Solver in MS Excel. Solver minimized the sum of squares of errors of the data. Additionally, the root mean square error (rmse) of non-linear least square regression model was calculated according to the Eq. 9, where $c_{e,i}$ and $q_{e,i}$ are the ith measured (or mean) c_e and q_e values and f (c_e, a, b) is the non-linear model function with generic parameters a and b, and *n* is number of data points for each concentration.

$$rmse = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(q_{e,i} - f(c_{e,i}, a, b)\right)^2)} \qquad (9)$$

In kinetic studies, measurements were done three times (n=3) with Folin-Ciocalteu method.

Results and discussion

Studying adsorption processes can give useful information about interactions between polyphenols and β-glucan (Marsal et al., 2012). Various models of adsorption isotherms can then be used to analyze the adsorption data and to describe the adsorption processes. Commonly used models are Freundlich, Langmuir and Dubinin-Radushkevich (Marsal et al., 2012) which were used in this study too.

Figure 1 presents Freundlich, Langmuir and Dubinin-Radushkevich models of adsorption isotherms fitted with non-linear regression for the adsorption of *p*-coumaric acid onto β-glucan. All three models are well matched with the experimental data and curve shapes are similar. From the four types of isotherm curves (C, L, H, S), adsorption of *p*-coumaric acid onto β-glucan is best described by L type isotherm, where β-glucan has a restricted adsorption capacity for *p*-coumaric acid (Limousin et al., 2007). Figure 2 presents Freundlich, Langmuir and Dubinin-

Radushkevich models of adsorption isotherms fitted with non-linear regression for the adsorption of caffeic acid onto β-glucan. Again, all three models matched well with the experimental data and have similar curve shapes. From the isotherm curve types, the adsorption of caffeic acid onto β-glucan is best described by L type isotherm. Table 1 presents the parameters of non-linear Freundlich, Langmuir and Dubinin-Radushkevich models. Root mean square error (rmse) shows the error of each model that was applied on the experimental data. For *p*-coumaric acid, Freundlich and Dubinin-Radushkevich models matched better to experimental data since rmse was smaller. For caffeic acid, Langmuir model had lower rmse and matched better to experimental data.

Table 1 reports the parameters of all models. Due to the constant called intensity of adsorption *1/n*, it can be said that the intensity was similar and favoured for both *p*-coumaric and caffeic acid. Furthermore, several constants can be connected to the adsorption capacity of β-glucan for phenolic acids. Those are Freundlich constant K_F (the relative adsorption capacity of adsorbent), Langmuir constant q_m (the apparent maximum theoretical adsorption capacity), and Dubinin-Radushkevih constant q_s (the theoretical saturation capacity of β-glucan). According to some constants, the adsorption capacity of β-glucan was similar for both phenolic acids (similar q_m), or a little higher for *p*-coumaric acid (higher q_s and K_F). According to the Langmuir equilibrium constant of adsorption, apparent affinity constant K_L, affinity was higher for the caffeic acid. Furthermore, the adsorption for both, *p*-coumaric acid and caffeic acid, could be a chemical process (*E* was larger than 8 kJ/mol). The literature shows that the polyphenols can interact with β-glucan through non-covalent bonds (like hydrogen bonds and van der Waals interactions) and hydrophobic interactions (Gao et al., 2012; Simonsen et al., 2009; Veverka et al., 2014; Wu et al., 2011). On the other hand, the adsorption of polyphenols onto tannery shavings was described as a chemical process (Marsal et al., 2012) similar to this study.

Table 1. Parameters of non-linear adsorption models for the phenolic acids adsorption onto β-glucan.

Standard	Freundlich			Langmuir			Dubinin-Radushkevich		
	1/n	K_F (mol/g) (L/mol)$^{1/n}$	rmse	q_m (mol/g)	K_L (L/mol)	rmse	q_s (mol/g)	E (kJ/mol)	rmse
Phenolic acid									
p-coumaric acid	0.2788	0.2318	0.0027	0.0305	17990.75	0.0034	0.0708	13.79	0.0027
caffeic acid	0.2224	0.1573	0.0033	0.0307	26682.81	0.0027	0.0611	15.43	0.0031

1/n is the intensity of adsorption, K_F is the Freundlich constant indicative of relative adsorption capacity of β-glucan ((mol/g) (L/mol)$^{1/n}$),
K_L is the Langmuir equilibrium constant of adsorption (L/mol), apparent affinity constant, q_m is the theoretical maximum adsorption capacity of β-glucan (mol/g), q_s is theoretical saturation capacity of β-glucan (mol/g), E is adsorption mean free energy which indicates the physical adsorption (*E* is less than 8 kJ/mol) or chemical adsorption (*E* is larger than 8 kJ/mol), rmse is the root mean square error.
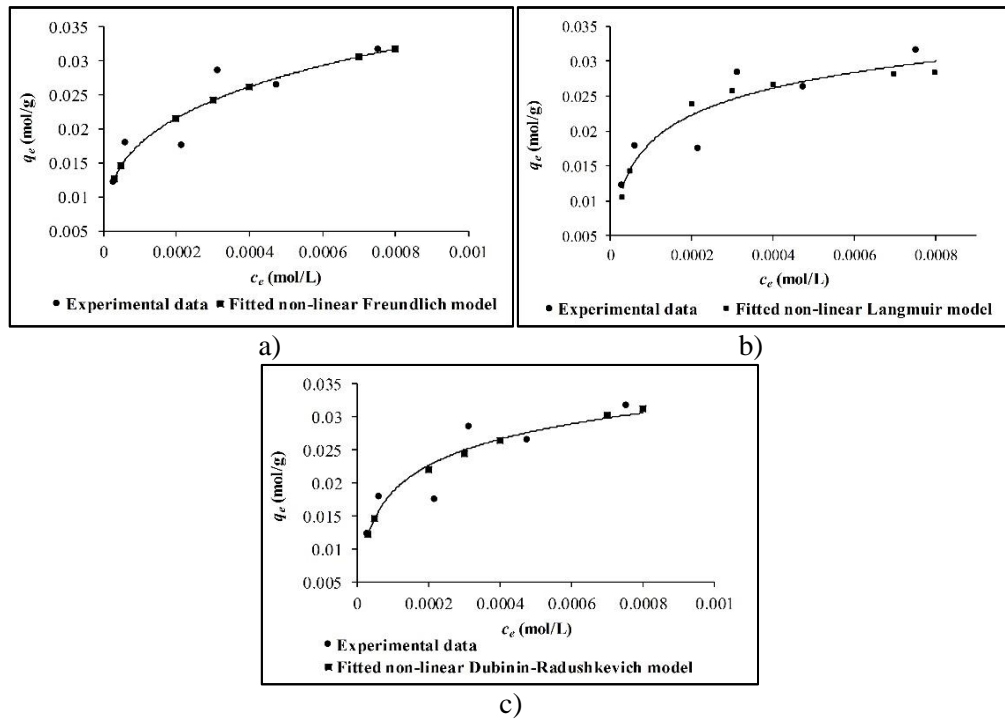
Fig. 1. Experimental equilibrium data and non-linear models for *p*-coumaric acids adsorption onto β-glucan. a) Freundlich model; b) Langmuir model; c) Dubinin-Radushkevich model (c_e is equilibrium concentration of *p*-coumaric acid in solution in mol/L, q_e is equilibrium adsorption capacity of *p*-coumaric acid onto β-glucan in mol/g).
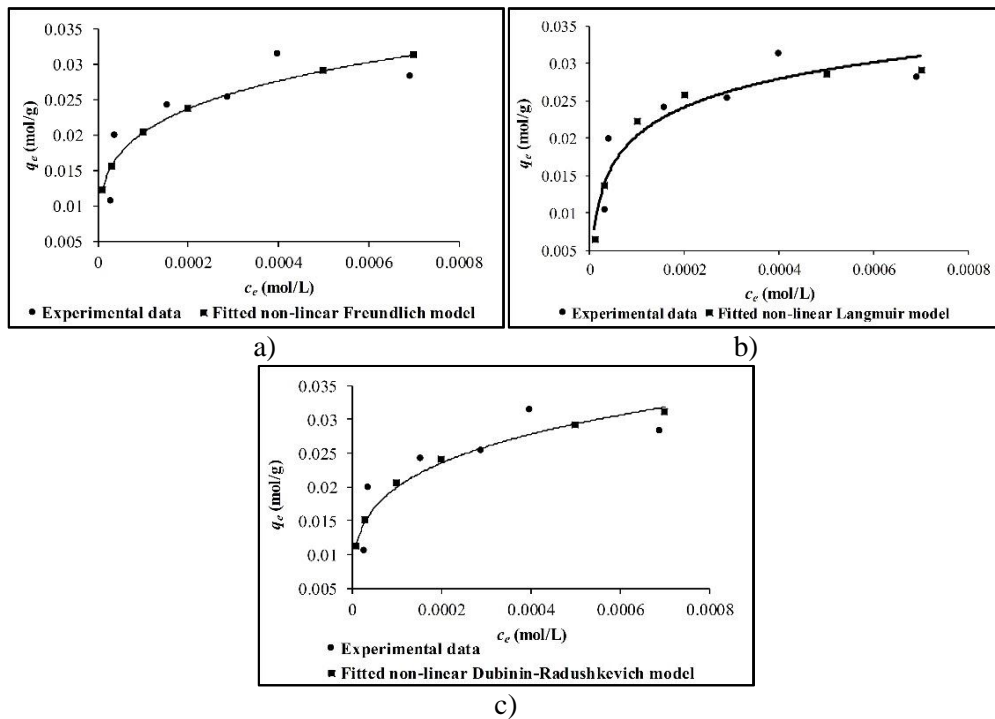

Fig. 2. Experimental equilibrium data and non-linear models for caffeic acids adsorption onto β-glucan. a) Freundlich model; b) Langmuir model; c) Dubinin-Radushkevich model (c_e is equilibrium concentration of caffeic acid in solution in mol/L, q_e is equilibrium adsorption capacity of caffeic acid onto β-glucan in mol/g).

Figure 3 presents the kinetic plots of pseudo-first and pseudo-second order models for *p*-coumaric and caffeic acid adsorption onto β-glucan, and Table 2 the parameters of these models. Due to the coefficient of determination R^2, the pseudo-first order does not match experimental results well (R^2 0.582 and 0.0095), while pseudo-second order does (R^2 0.8687 and 0.973). Calculated root mean square error (rmse) (Table 2) was also lower for pseudo-second order model which confirms that pseudo second order matched experimental results better. Also equilibrium adsorption capacity q_e obtained by pseudo-second order model (0.0235 mol/g for *p*-coumaric acid and 0.0318 mol/g for caffeic acid) is in agreement with equilibrium adsorption capacity obtained experimentally q_{exp} (0.0264 mol/g for *p*-coumaric acid and 0.0313 mol/g for caffeic acid). It was found that the adsorption of polyphenols onto tannery shavings was also pseudo-second order (Marsal et al., 2012) which is similar to our results. The rate constant of pseudo-second order model for *p*-coumaric acid was 61.2925 g/mol h and for caffeic acid -40.3022 g/mol h.
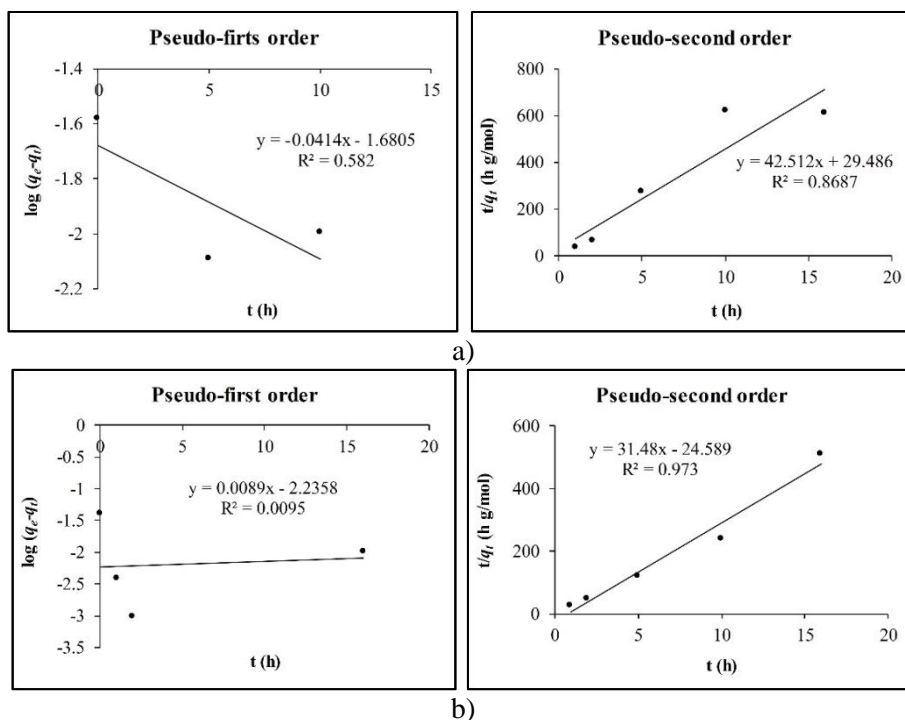

a)

b)

Fig. 3. Pseudo-firts and pseudo-second kinetic plots for phenolic acid adsorption onto β-glucan. a) *p*-coumaric acid; b) caffeic acid (t is time of adsorption process in h, q_e is equilibrium adsorption capacity of β-glucan, in mol of polyphenols per g of β-glucan (mol/g), q_t is adsorption capacity of β-glucan during the time, in mol of polyphenols per g of β-glucan (mol/g)).

Table 2. Parameters of kinetic models for adsorption of phenolic acids onto β-glucan.

Standard	Pseudo-first order			Pseudo-second order			q_{exp} (mol/g)
	k_1 (h^{-1})	q_e (mol/g)	rmse	k_2 (g/mol h)	q_e (mol/g)	rmse	
Phenolic acid							
p-coumaric acid	0.0953	0.0209	0.0055	61.2925	0.0235	0.0028	0.0264
caffeic acid	-0.0205	0.0058	0.0358	-40.3022	0.0318	0.0099	0.0313

k_1 is the rate constant of pseudo-first order (h^{-1}), k_2 is the rate constant of pseudo-second order (g/mol h), q_e is the amount of phenolic acids adsorbed per g of β-glucan at equilibrium (mol/g) obtained by model, q_{exp} is the amount of phenolic acids adsorbed per g of β-glucan at equilibrium (mol/g) obtained experimentally, rmse is the root mean square error.
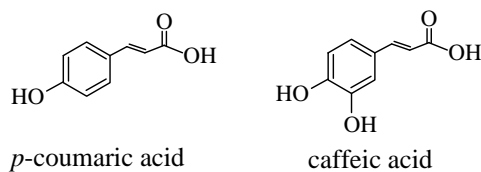

p-coumaric acid   caffeic acid

Fig. 4. Chemical structure of phenolic acids.

Figure 4 presents the chemical structure of *p*-coumaric acid and caffeic acid. The difference in the chemical structure between *p*-coumaric acid and caffeic acid is the number of hydroxyl groups. Namely, *p*-coumaric acid contains one hydroxyl group on the benzene ring, while caffeic acid contains two. The differences in the adsorption capacity could be connected to the differences in the chemical structure since it has been shown in literature that adsorption between polyphenols and β-glucan depends on the polyphenol structure (Wang et al., 2013). The adsorption capacity was higher for *p*-coumaric acid (Table 1), the phenolic acid with less OH groups. This is similar to study of Wang et al. (2013) where the adsorption was favoured for flavonoids with three or fewer hydroxyl groups (Wang et al., 2013).

Conclusions

Non-linear adsorption isotherm models (Freundlich, Langmuir and Dubinin-Radushkevich models) and kinetic models (of pseudo-first and pseudo second order reactions) were applied on the data obtained in experiments of adsorption of *p*-coumaric acid and caffeic acid onto β-glucan. Adsorption of both, *p*-coumaric acid and caffeic acid, could be described the best by the L type isotherm. For *p*-coumaric acid, Freundlich and Dubinin-Radushkevich models matched better to experimental data than Langmuir model and for caffeic acid, Langmuir model matched better to experimental data. The maximum theoretical adsorption capacity was very similar for both *p*-coumaric acid and caffeic acid, but it was higher for caffeic acid. Kinetic of the reaction was best described by pseudo-second order model for both *p*-coumaric acid and caffeic acid.

References

Babaeivelni, K., Khodadoust, A.P. (2013): Adsorption of fluoride onto crystalline titanium dioxide: effect of pH, ionic strength, and co-existing ions. *J. Colloid Interface Sci.* 394, 419-427. https://doi.org/10.1016/j.jcis.2012.11.063.

Bravo, L. (1998): Polyphenols: chemistry, dietary sources, metabolism, and nutritional significance. *Nutr. Rev.* 56, 317-333. https://doi.org/10.1111/j.1753-4887.1998.tb01670.x.

Camouse, M.M., Hanneman, K.K., Conrad, E.P., Baron, E.D. (2005): Protective effects of tea polyphenols and caffeine. *Expert Rev. Anticancer Ther.* 5, 1061-1068. https://doi.org/10.1586/14737140.5.6.1061.

Foo, K.Y., Hameed, B.H. (2010): Insight into the modeling of adsorption isotherm systems. *Chem. Eng. J.* 156 (1), 2-10. https://doi.org/10.1016/j.cej.2009.09.013.

Gao, R., Liu, H., Peng, Z., Wu, Z., Wang, Y., Zhao, G. (2012): Adsorption of (-)-epigallocatechin-3-gallate (EGCG) onto oat β-glucan. *Food Chem.* 132, 1936-1943. https://doi.org/10.1016/j.foodchem.2011.12.029.

Giles, C.H., Smith, D., Huitson, A. (1974): A general treatment and classification of the solute adsorption isotherm. I. Theoretical. *J. Colloid Interface Sci.* 47, 755-765. https://doi.org/10.1016/0021-9797(74)90252-5.

Jakobek, L. (2015): Interactions of polyphenols with carbohydrates, lipids and proteins. *Food Chem.* 175, 556-567. https://doi.org/10.1016/j.foodchem.2014.12.013.

Kampa, M., Nifli, A.P., Notas, G., Castanas, E. (2007): Polyphenols and cancer growth. *Rev. Physiol. Biochemical Pharmacology* 159, 79-113. https://doi.org/10.1007/112_2006_0702.

Laroche, C., Michaud, P. (2007): New developments and prospective applications for β (1,3) glucans. *Recent Pat. Biotechnol.* 1, 59-73. https://doi.org/10.2174/187220807779813938.

Le Bourvellec, C., Renard, C.M.G.C. (2012): Interactions between polyphenols and macromolecules: quantifications methods and mechanism. *Crit. Rev. Food Sci. Nutr.* 52, 213-248. https://doi.org/10.1080/10408398.2010.499808.

Limousin, G., Gaudet, J.P., Charlet, L., Szenknect, S., Barthès, V., Krimissa, M. (2007): Sorption isotherms: a review on physical bases, modeling and measurement. *Appl. Geochem.* 22, 249-275. https://doi.org/10.1016/j.apgeochem.2006.09.010.

Marsal, A., Maldonado F., Cuadros, S., Bautista M.E., Manich, A.M. (2012): Adsorption isotherm, thermodynamics and kinetics studies of polyphenols onto tannery shavings. *Chem. Eng. J.* 183, 21-29. https://doi.org/10.1016/j.cej.2011.12.012.

Quirós-Sauceda, A.E., Palafox-Carlos, H., Sáyago-Ayerdi, S.G., Ayala-Zavala, J.F., Bello-Perez, L.A., Álvarez-Parrilla, E., de la Rosa, L.A., González-Córdova, A.F., González-Aguilar, G.A. (2014): Dietary fiber and phenolic compounds as functional ingredients: interaction and possible effect after ingestion. *Food Funct.* 5, 1063-1072. https://doi.org/10.1039/c4fo00073k.

Palafox-Carlos, H., Ayala-Zavala, J.F., González-Aguilar, G.A. (2011): The role of dietary fiber in the bioaccessibility and bioavailability of fruit and vegetable antioxidants. *J. Food Sci.* 76, R6-R15. https://doi.org/10.1111/j.1750-3841.2010.01957.x.

Pandey, K.B., Rizvi, S.I. (2009): Plant polyphenols as dietary antioxidants in human health and diseases.

Oxid. Med. Cell Longev. 2, 270-278. https://doi.org/10.4161/oxim.2.5.9498.

Scalbert, A., Manach, C., Morand, C., Remesy, C. (2005): Dietary polyphenols and the prevention of diseases. *Crit. Rev. Food Sci. Nutr.* 45, 287-306. https://doi.org/10.1080/1040869059096.

Singleton, V.L., Orthofer, R., Lamuela-Raventós, R.M. (1999): Analysis of total phenols and other oxidation substrates and antioxidants by means of Folin-Ciocalteu reagens. *Methods Enzymol.* 299, 152-178. https://doi.org/10.1016/S0076-6879(99)99017-1.

Simonsen, H.T., Nielsen, M.S., Christensen, N.J., Christensen, U., La Cour, T.V., Motawia, M.S., Jespersen, B.P.M., Engelsen, S.B., Møller, B.L. (2009): Molecular interactions between barley and oat β-glucans and phenolic derivatives. *J. Agric. Food Chem.* 57, 2056-2064. https://doi.org/10.1021/jf802057v.

Soto, M.L., Moure, A., Domínguez, H., Parajó, J.C. (2011): Recovery, concentration and purification of phenolic compounds by adsorption: a review. *J. Food Eng.* 105, 1-27. https://doi.org/10.1016/j.jfoodeng.2011.02.010.

Veverka, M., Dubaj, T., Gallovič, J., Jorík, V., Veverková, E., Mičušík, M., Šimon, P. (2014): Beta-glucan complexes with selected nutraceuticals: synthesis, characterization, and stability. *J. Funct. Foods* 8, 309-318. https://doi.org/10.1016/j.jff.2014.03.032.

Velderrain-Rodríguez, G., Quirós-Sauceda, A., Mercado-Mercado, G., Ayala-Zavala, J.F., Astiazarán-García, H., Robles-Sánchez, R.M., Wall-Medrano, A., Sayago-Ayerdi, S., González-Aguilar, G.A. (2016): Effect of dietary fiber on the bioaccessibility of phenolic compounds of mango, papaya and pineapple fruits by an *in vitro* digestion model. *Food Sci. Technol (Campinas)* 36, 188-194. http://dx.doi.org/10.1590/1678-457X.6729.

Wu, Z., Li, H., Ming, J., Zhao, G. (2011): Optimization of adsorption of tea polyphenols onto oat β-glucan using response surface methodology. *J. Agric. Food Chem.* 59, 378-385. https://doi.org/10.1021/jf103003q.

Wang, Y., Liu, J., Chen, F., Zhao, G. (2013): Effects of molecular structure of polyphenols on their noncovalent interactions with oat β-glucan. *J. Agric. Food Chem.* 61, 4533-4538. https://doi.org/10.1021/jf400471u.