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The Application Of Adsorption Isotherms With Proper Fitting To Interpret Polyphenol Bioaccessibility *In Vitro*

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INTRODUCTION

Bioaccessibility of polyphenols describes their accessibility for absorption in the digestive tract. Dietary fibers, together with some other food components, can affect bioaccessibility since they can interact with polyphenols. One of the ways of studying these complex reactions *in vitro* is to study the adsorption of polyphenols onto dietary fiber. The experimental results (the amount of polyphenols adsorbed onto dietary fiber q_e, and the amount non-adsorbed c_e) can be modelled with adsorption isotherm equations. Parameters obtained from these equations can help in the attempt to interpret the adsorption process and by that to interpret bioaccessibility *in vitro*. But, adsorption isotherms require proper fitting to lower the error of models and to obtained correct parameters of adsorption equations.

The aim of this work was to study the adsorption between apple polyphenols and β-glucan, to model the experimental data with Langmuir, Dubinin-Radushkevich, and Hill adsorption isotherms with improved fitting, and to use corrected parameters from adsorption isotherms to interpret the adsorption process.

MATERIALS AND METHODS

Polyphenols were extracted from the flesh and peel of apples and adsorbed onto β-glucan (until the adsorption reached equilibrium). The amount of total free polyphenols before and after adsorption were determined by using the Folin-Ciocalteu method. The q_e (adsorption capacity, mg g^{-1}) and c_e (polyphenol concentration in equilibrium, mg l^{-1}) were modelled with equations of adsorption isotherms. Experimental data fitting (q_e and c_e) was conducted by using improved minimization of the sum of squares errors.

Langmuir isotherm

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

Dubinin-Radushkevich isotherm

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

$$\varepsilon = RT \ln\left(\frac{c_s}{c_e}\right)$$

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

Hill isotherm

$$q_e = \frac{q_m c_e^{n_H}}{K_D + c_e^{n_H}}$$

q_m - the apparent maximum adsorption capacity of β-glucan (Langmuir and Hill)
K_L -the Langmuir equilibration constant of adsorption or apparent affinity constant
q_s – the theoretical isotherm saturation capacity
β - constant related to the adsorption capacity
ε – Polany potential
C_s – concentration of saturation according to Dubinin-Radushkevich
E – the mean free energy of adsorption
n_H - the Hill coefficient describing cooperativity (n_H>1 positively cooperative bonding,
n_H<1 negatively cooperative bonding, n_H=1 noncooperative (independent) binding)
K_D – apparent disocciation constant
SSE – sumn of square errors

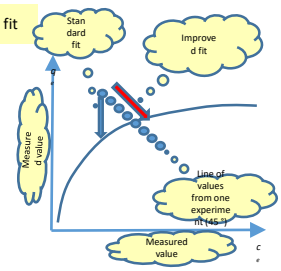
Standard fit | **Improved fit**

Summ of square errors (SSE)

$$sse = \sum_{i=1}^{n} \left(q_{e,measured} - q_{e,calculated}\right)^2$$

Standard error (S)

$$S^2 = \sum_{i=1}^{n} \frac{\left(q_{e,measured} - q_{e,calculated}\right)^2}{n-3}$$



RESULTS AND DISCUSSION

Adsorption isotherms (examples, Figure 1 to 4) fitted according to the new, improved fitting, showed lower standard error (Table 1) and can be considered more accurate and precise for the interpretation of adsorption. According to the new parameters (Table 1), peel polyphenols showed higher theoretical, maximal adsorption capacity (q_m) and theoretical capacity of saturation (q_s). Parameter n_H points to the positively cooperative bonding for wild apple polyphenols and negatively cooperative in bonding for all other polyphenols. Parameters describing energy of adsorption showed that the bonds between peel polyphenols and β-glucan might be physical, and between flesh polyphenols and β-glucan, it might be chemical.

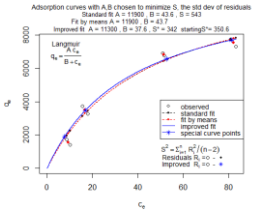


Figure 1. Langmuir adsorption isotherm of wild apple peel polyphenols adsorbed onto β-glucan

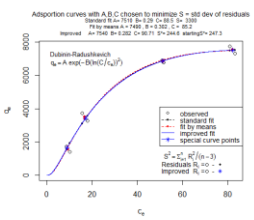
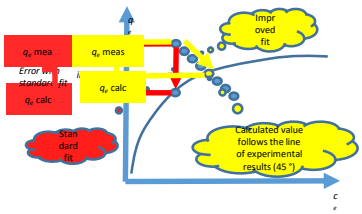


Figure 2. Dubinin-Radushkevich adsorption isotherm of wild apple peel polyphenols adsorbed onto β-glucan

Improved Fit:

q_e on curve where it crosses the line that corresponds to the initial concentration



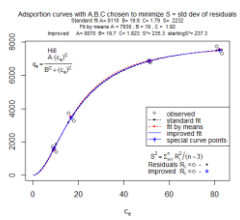


Figure 3. Hill adsorption isotherm of wild apple peel polyphenols adsorbed onto β-glucan

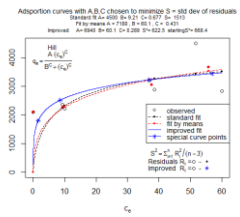


Figure 4. Hill adsorption isotherm of wild apple flesh polyphenols adsorbed onto β-glucan

Table 1. Coefficients of Langmuir, Dubinin-Radushkevich and Hill adsorption isotherms obtained with standard fit and improved fit

Adsorption isotherm			Apple varieties							
			Wild apple peel		Wild apple flesh		Slavonska srčika peel		Slavonska srčika flesh	
			Standard fit	Improved fit	Standard fit	Improved fit	Standard fit	Improved fit	Standard fit	Improved fit
Langmuir	q_m	mg g^{-1}	11900	11300	3870	3540	8350	8470	5850	2690
	K_L	l mg^{-1}	0.0229	0.0266	0.149	0.341	0.018	0.017	0.0457	132.98
	SSE		543	342	1340	637.3	643	569.8	1530	465.4
Dubinin Radushkevich	q_s	mg g^{-1}	7510	7540	3640	3690	6700	6760	5000	2770
	β	mol^2 J^{-2}	4.727 10^{-8}	4.596 10^{-8}	1.1 10^{-8}	0.4 10^{-8}	2.5 10^{-8}	2.64 10^{-8}	1.49 10^{-8}	0.11 10^{-8}
	C_s	mg l^{-1}	88.5	90.7	134	300	300	300	300	300
	E	J mol^{-1}	3252.4	3298.2	6732.8	10338	4463.2	4351.9	5799.8	21859.5
	SSE		3300	247.3	1481	646.9	2419	653.9	167	495
Hill	q_m	mg g^{-1}	8110	8070	4500	6940	13600	12000		
	n_H		1.79	1.82	0.68	0.289	0.613	0.6697		
	K_D		211.3	228.99	4.496	3.27	27.4	28.92		
	SSE		2232	237.3	1513	622.5	1667	607.5		

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CONCLUSION

New, more accurate fitting allows more reliable insight into the bonding between polyphenols and dietary fibers and accordingly into the bioaccessibility explanation, *in vitro*.