MATHEMATICAL DESCRIPTION OF THE ADSORPTION REMOVAL OF ANTHOCYANINS FROM RED CABBAGE EXTRACTS

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Nowadays the adsorption removal of anthocyanins from water extracts of different plants is important task for food, pharmaceutical and cosmetic industry, because, on the one side, they are water-soluble natural dyes alternative to synthetic food dyes, and, on the other side, they have potential health benefits as substances with certain medicinal activities such as anti-inflammatory, anti-cardiovascular, and anti-cancer.

Among plants Red cabbage has a high content of anthocyanins and it may become one of the accessible and relatively cheap sources of those substances. Red cabbage anthocyanins were identified as cyanidin-3,5-diglucoside and cyanidin-3-sophoroside-5-glucoside [1].

The specific aim of this paper was to use adsorption kinetic models of pseudo-first-order and pseudo-second-order, adsorption models of Langmuir and Freundlich for mathematical description of the adsorption removal of anthocyanins from Red cabbage extracts onto Bentonite.

Adsorbent was Bentonite from Dashukovsky deposit (Ukraine). This is a cheaper adsorbent and it has follow chemical composition (%): SiO_2 – 49,6; Al_2O_3 – 13,5; Fe_2O_3 – 7,2.

Preparation extract Red cabbage: leaves of Red cabbage were comminuted on a grater and extracted with 0,1 M HCl (as w:v= 1:2) for 24 h at 20 ^oC in the dark. Then Red cabbage extract was filtered and centrifuged. The concentration of anthocyanins in Red cabbage extract was determined using pH-differential method.

All the adsorption experiments were carry out in static conditions under agitation at 150 rpm. Kinetic adsorption curves were obtained for different: concentration of anthocyanins in the range of 65 to 130 mg/L, adsorbent dosage in the range of 10 to 25 g/L, temperature of 20 to 50 ^0C, and pH of 2 to 4. Equilibrium isotherms of those dyes were carried out for different temperatures in the range of 20 to 40 ^0C for 2 h, when the concentration of anthocyanins in the extracts was constant.

Kinetic adsorption curves demonstrate that equilibrium adsorption time of anthocyanins of Red cabbage amounts to 90 min. The rates of anthocyanin adsorption increased rapidly in the first 10 min, and then slowly increased afterward, reaching equilibrium time. The values of correlation coefficients for the application of the pseudo-first-order model and pseudo-second-order model for all the kinetic studies indicate that pseudo-second-order model fits the experimental kinetic data more accurately than the pseudo-first-order model (Table 1).

It follows from adsorption isotherms of Red cabbage anthocyanins that adsorption capacity of Bentonite is high at low temperature, which indicates the adsorption is a thermopositive process. Values of Langmuir constants (A_∞ and β) and Freundlich constants (K_F and n) presented in Table 2. The correlation coefficients of both Langmuir and Freundlich adsorption equations are high and those equations may be use for mathematical description of the equilibrium adsorption isotherms (Table 2).

The change in standard Gibb's free energy (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o) of adsorption Red cabbage anthocyanins onto Bentonite were calculated in the range of 20 to 40 ^0C. Results revealed that the adsorption process was spontaneous ($-\Delta G^o=$ 25,1-25,5 kJ/mol) and exothermic ($\Delta H^o= -28,0$ kJ/mol). The negative values of change in standard entropy ($-\Delta S^o=$ 0,008-0,009 kJ/(mol·K)) suggest the decreased randomness at the solid/solution interface during the adsorption of Red cabbage anthocyanins onto Bentonite.

The present investigation showed that adsorption kinetic model of pseudo-second-order, adsorption models of Langmuir and Freundlich can be applied for mathematical description of the adsorption of anthocyanins from Red cabbage extracts onto Bentonite.

Table 1

Kinetic parameters for the adsorption removal of anthocyanins from Red cabbage extract by Bentonite

Parameter	A_e^{exp}, mg/g	Pseudo-first-order model $ln(A_e - A) = ln A_e - k_1 t$			Pseudo-second-order model $\frac{t}{A} = \frac{t}{k_2 A_e^2} + \frac{1}{A_e} t$		
		A_e^{calc} mg/g	$k_1 \cdot 10^2$, min^{-1}	R^2	A_e^{calc} mg/g	$k_2 \cdot 10^2$, $\frac{g}{mg \cdot min}$	R^2
C, mg/L							
65	2,99	1,03	2,8	0,8656	3,05	11,0	0,9997
75	3,17	1,03	3,3	0,7865	3,24	11,0	0,9997
85	3,20	1,03	5,1	0,9832	3,36	0,4	0,9989
130	4,15	1,02	10,9	0,9199	4,77	1,0	0,9935
q, g/L							
10	4,54	1,06	4,6	0,8866	4,64	8,0	0,9999
15	3,70	1,02	5,4	0,8116	3,74	11,6	0,9998
20	2,99	1,03	2,8	0,8656	3,05	11,0	0,9997
25	2,82	1,06	0,3	0,9630	2,88	15,0	0,9999
T, K							
293	2,99	1,03	2,8	0,8656	3,05	11,0	0,9997
303	2,36	1,04	0,4	0,8530	2,45	10,0	0,9992
313	2,25	1,05	2,9	0,9477	2,35	0,8	0,9991
323	2,04	1,03	0,9	0,8498	2,17	0,5	0,9947
pH							
2	2,99	1,03	2,8	0,8656	3,05	11,0	0,9970
3	1,96	1,05	48,0	0,9730	2,13	5,0	0,9979
4	1,43	1,04	9,0	0,9587	1,56	6,0	0,9985

Table 2

Isotherm parameters for adsorption removal of anthocyanins from Red cabbage extract by Bentonite

T, K	Model					
	Langmuir			Freundlich		
	A_∞, mg/g	$\beta \cdot 10^2$, mg/g	R^2	K_F	n	R^2
293	11,6	7,7	0,9947	1,7	0,6	0,9859
303	10,6	4,8	0,9759	1,1	0,6	0,9217
313	10,4	4,8	0,9780	1,1	0,6	0,9531

[1] Hrazdina G., Iredale H., Mattick L.R. Anthocyanin composition of Brassica oleracea cv. Red Danish/ Phytochemistry.- 1977.- 16(2).- P. 297-299.