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ADSORPTION KINETICS OF ANTHOCYANINS FROM ELDERBERRY EXTRACTS ON BENTONITE

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Abstract. *Adsorption kinetics of anthocyanins from aqueous extracts of elderberries on bentonite at various concentrations of anthocyanins, mass of bentonite, and temperature was investigated in this work. It was found that the equilibrium adsorption capacities and correlation coefficients for pseudo-second order model are much more reasonable than that of the pseudo-first order model.*

Keywords: *adsorption kinetics, anthocynians, bentonite, pseudo-first order, pseudo-second order*

Introduction. In recent years there is an increasing interest in anthocyanins as natural food colorants [1] and as substances with strong therapeutic effects (anti-inflammatory, anti-cardiovascular, anti-diabetic, anti-cancer) [2]. Anthocyanins are widely distributed in berries, flowers, fruits, vegetables, leaves, and roots. Among all fruits and vegetables, especially berries of dark red or dark blue colours have a very high content of anthocyanins. For example, total anthocyanin content in elderberries is between 2000-15600 mg/kg [3]. This makes the elderberries suitable raw material for extraction of anthocyanins on industrial scale.

Adsorption is one of the most effective methods of concentration, removal and purification of anthocyanins from plant extracts. However, data of anthocyanin adsorption on cheap adsorbents (for example, natural clay minerals) are extremely rare [4, 5].

The aim of this study was to get the kinetic curves of adsorption of anthocyanins from elderberry aqueous extracts using bentonite at various initial concentrations of anthocyanins, mass of bentonite, and temperature of extracts, in order to evaluate the capacity of bentonite to efficiently adsorb the anthocyanins and carry out mathematical modeling of adsorption using kinetic equations of pseudo-first and pseudo-second order.

Experimental. Fully ripe elderberries were harvested in Zhmerynka district of Vinnitsa region (Ukraine) in 2015. Berries were immediately frozen and kept at almost 20^{o}C prior to tests.

Extraction was carried out by adding the berries in 0.1M HCl (as 1:2=w:v) for 24 hours at 20^{o}C in the dark. Then the extracts of berries were separated from the berries by filtration through filter paper. Extracts of the berries were stored at 4^{o}C.

Bentonite ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O$) was employed as the adsorbent obtained from Dashukovsky deposit (Ukraine). Before adsorption studies bentonite was pounded in a porcelain mortar and mixed with distilled water at 20°C. The resulting suspension of bentonite was maintained for 2 hours, and then the top layer of suspension was separated by decanting. The washed precipitate was then dried at 95°C.

Adsorption of anthocyanins was carried out in static conditions, shaking mixtures of anthocyanin extracts with bentonite at a agitation speed of 150 rpm. After adsorption, these mixtures were filtered out and total anthocyanin concentrations in extracts were determined by pH-differential method as mg cyanidin-3-glucoside per litre extract.

Results and discussion. The adsorption kinetics of anthocyanins from elderberry extracts on bentonite is shown in Fig.1. The equilibrium time of adsorption was approximately obtained at 150 min. The rates of adsorption removal of anthocyanins increased rapidly in the first 100 min, and then slowly increased, finally reaching equilibrium after 150 min.

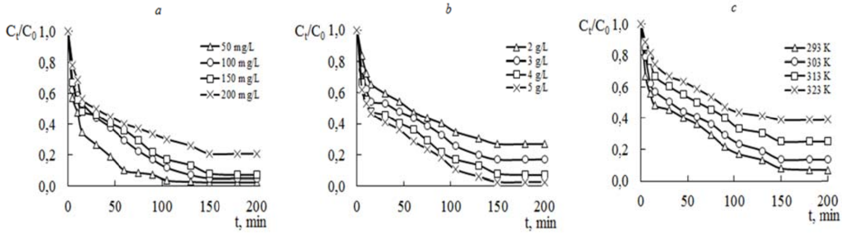

Fig.1. *Kinetic Adsorption Curves of Anthocyanines on Bentonite at Various: a - Initial Concentrations of Anthocyanins; b - Mass of Adsorbent; c - Temperature.*

Adsorption removal of anthocyanins decreased with increasing of temperature in the interval of 293–323 K as well as with increasing the initial dye concentration increases from 50 to 200 mg/L (Figs.1a and c). The adsorption at the all temperatures studied usually completed when the surface of clay is covered with a monolayer of anthocynians. After the equilibrium, the decrease in anthocyanin removal in the interval 293–323 K indicates the exothermic nature of adsorption. The adsorption capacity decreases with increasing temperature indicates that the adsorption process occurs through physical interactions. As seen from Fig.1b, removal of anthocyanins increased with increasing adsorbent mass from 2 to 5 g/L . This imply that the number of active sites of the adsorbent increase as parallel to increasing adsorbent mass.

It is known that bentonite carries a negative charge arising from isomorphous substitutions of certain atoms in their structure for other atoms of a different valence. For example, in the tetrahedral sheet, Si(IV) may be replaced by trivalent cations, or divalent cations may replace with Al(III) in the octahedral sheet. The negative potential of the adsorbent is compensated by the adsorption of anthocynian cations on its surface.

Two commonly well-known kinetic models (pseudo-first and pseudo-second order) were applied to the experimental kinetics data in order to investigate the behavior of elderberry anthocyanins on bentonite. According to the results, the theoretical values of equilibrium adsorption capacities of anthocyanins on bentonite calculated using pseudo-second order kinetic model were found to be the closest to the experimentally found values of equilibrium adsorption capacities (Table 1). The data shows that the regression coefficients for the linear plots of the pseudo-second order equation were higher than 0.98. It is clear that the equilibrium adsorption capacities and correlation coefficients for the pseudo-second order model are much more reasonable when compared with experimental results than that of the first pseudo-order model.

Table 1. Kinetic Parameters of Anthocyanin Adsorption from Elderberry Extracts on Bentonite

Parameter	A_p^{exp}, mg/g	Pseudo-first order model			Pseudo-second order model			
		A_p^{theor} mg/g	$k_1 \cdot 10^2$, min^{-1}	R^2	A_p^{theor}, mg/g	$k_2 \cdot 10^3$, $\frac{g}{mg \cdot \min}$	V_0, $\frac{мг}{г \cdot хв}$	R^2
C, mg/L								
50	12.2	8.8	3.61	0.9722	12.9	8.33	1.3	0.9994
100	23.8	19.9	2.36	0.9496	26.4	1.77	1.2	0.9908
150	34.9	23.8	2.26	0.8506	38.9	1.09	1.6	0.9848
200	39.7	27.0	1.68	0.9825	43.5	1.07	2.1	0.9933
q, g/L								
2.0	55.9	39.5	1.64	0.9754	61.0	0.68	2.6	0.9872
3.0	41.5	33.5	1.97	0.9021	46.3	0.86	1.9	0.9809
4.0	34.9	23.8	1.64	0.9676	38.2	1.17	1.6	0.9848
5.0	29.2	35.8	3.34	0.7325	32.1	1.52	1.5	0.9887
T, K								
293	34.9	30,1	2.26	0.8506	38.2	1.17	1.5	0.9848
313	32.5	24.5	1.69	0.9696	36.3	1.04	1.3	0.9859
323	28.1	23.2	1.67	0.9575	32.8	0.89	0.9	0.9864
333	22.9	21.7	2.20	0.9529	27.0	1.11	0.8	0.9904

Conclusions. According to the results, bentonite is a suitable adsorbent for the removal of anthocyanins from elderberry acid aqueous extract. It was shown that rates of adsorption removal of anthocyanins increased rapidly in the first 100 min, and then slowly increased, finally, reaching equilibrium after 150 min. It was found that the pseudo-second order model appeared to be more promising than the pseudo-first order in describing the adsorption kinetics of anthocyanins from elderberry extracst on bentonite at various conditions.

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КІНЕТИКА АДСОРБЦІЇ АНТОЦІАНІВ З ЕКСТРАКТІВ БУЗИНИ НА БЕНТОНІТІ

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Резюме. *Досліджена кінетика адсорбції антоціанів з водних екстрактів бузини на бентоніті при різних умовах проведення експерименту (при зміні концентрації антоціанів, маси бентоніту, температури). Встановлено, що рівняння псевдо другого порядку краще описує експериментальні кінетичні криві адсорбції антоціанів на бентоніті, ніж рівняння псевдо першого порядку.*

Ключові слова: *кінетика адсорбції, антоціани, бентоніт, псевдо перший порядок, псевдо другий порядок*