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EQUILIBRIUM AND THERMODYNAMIC STUDIES OF ANTHOCYANIN ADSORPTION ON FIBROUS CATION EXCHANGER FIBAN K-1

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In the last decades there has been an increased interest of researchers in the obtaining anthocyanins from available and low–cost plant materials, not only as natural food dyes but also for pharmaceutical products. Among plant sources of anthocyanins chokeberries and elderberries have attracted the interest of consumers due to abundant anthocyanin contents. In this study, adsorption equilibrium and thermodynamics of anthocyanins from chokeberry and elderberry extracts by fibrous cation exchanger FIBAN K–1 were investigated. The anthocyanin extracts were obtained by macerated in 0.1 M HCl under the follow extraction parameters: solid-liquid ratio = 1:2 at 293 K for 24 h. The total anthocyanin content in the extracts was determined by pH-differential method. Adsorption experiments were carried out under static conditions, shaking mixtures of anthocyanin extracts of the berries with FIBAN K–1. The adsorption isotherms were of L-type according to the classification of Giles. The adsorption capacity of FIBAN K– 1 for the chokeberry and elderberry anthocyanins increased as the temperature increased from 293 to 313 K. The Langmuir, Freundlich, and Temkin adsorption models were used to describe the experimental adsorption isotherms. These models had a good agreement with the experimental data for adsorption of the anthocyanins, but the Langmuir model was the most favorable model for studying the adsorption equilibrium of the chokeberry and elderberry anthocyanins on FIBAN K–1. Thermodynamic parameters of the anthocyanin adsorption, such as $\Delta G°$, $\Delta H°$, *and* $\Delta S°$ *were calculated. The* $\Delta G°$ *values were negative, thus indicating that the adsorption of the chokeberry and elderberry anthocyanins on FIBAN K-1 was spontaneous and favorable process under the experimental conditions. The decrease of the* $\Delta G°$ *values with increasing temperature shows that adsorption is more favorable at high temperature. The* $\Delta H°$ *values were positive for the anthocyanins of both kind of berries, which indicates the adsorption was an endothermic reaction. The* $\Delta S°$ *values were positive, which means that the anthocyanins in the aqueous phase are more organized than those in the adsorbent-liquid interface.*

***Keywords**: anthocyanins, FIBAN K-1, adsorption, equilibrium, isotherms, thermodynamics*

INTRODUCTION

The extraction of anthocyanins from various plants and purification their extracts by adsorption has received increased attention in recent years, since anthocyanins are widely used not only as natural food dyes, but they are also perspective pharmaceutical products [1, 2]. This is connected with the fact that anthocyanins have antioxidant, hepato-, cardio-, nephro-, neuro-protective and anti-obesity activities. Hence, there is growing necessity to obtain functional active ingredients and therapeutic agents for various disease prevention and treatment.

There are a lot of plant sources rich in the anthocyanins content (fruits, vegetables, colored grains, by-products of fruit and vegetable processing). Among plant sources of anthocyanins chokeberries and elderberries have attracted the interest of consumers due to abundant anthocyanin contents. For example, total anthocyanin content is between 5–10 $g \cdot kg^{-1}$ in chokeberries, 2–10 $g \cdot kg^{-1}$ in elderberries [3].

According to the chemical nature anthocyanins are classified as polyphenols, and are glycosilate polyhydroxy or polymethoxy derivatives of 2-phenylbenzopyrilium, i.e., anthocyanins are heteroxides of an aglycone unit (anthocyanidin), which is a derivative of flavylium ion [4]. Anthocyanidins are differed in substituents, R, which can be –H, or –OH, or $-OCH_3$ groups. The carbohydrate moiety of anthocyanins most often consists of glucose but may also consist of other mono- and disaccharides, for example, rhamnose, arabinose, and galactose. The structure and electric charge of all anthocyanins depend on the pH of the medium, due to participation of their structural elements in protonation/deprotonation reactions: in an acidic medium, anthocyanins acquire a positive charge and act as cations while in alkaline conditions, they acquire a negative charge and become anions [4].

The anthocyanins in chokeberries and elderberries are a mixture of cyanidin glycosides. There arecyanidin-3-galactoside (68.9 %), cyanidin-3-arabinoside (24.5 %), cyanidin-3-xyloside (3.8 %), cyanidin-3-glucoside (2.8 %) in chokeberries and cyanidin-3-glucoside with cyanidin-3-sambubioside (83.1 %), cyanidin-3-sambubioside-5-glucoside (15.1 %), cyanidin-3-rutinoside (1.8 %) in elderberries [5].

Removal of anthocyanins from plant materials and purification by adsorption are the important premise of their application. Extraction removal of anthocyanins from plant materialsis non-selective method and anthocyanin solutions contain large amounts of various compounds such as organic acids, amino acids, sugars, and proteins which are detrimental to stability of anthocyanins [6]. Adsorption is an effective method for purification of bioactive components in a single step [7]. The right choice of adsorbents is an important condition of adsorption process efficiency. Different adsorbents such as macroporous resins [8–12], clays [13, 14], mesoporous carbons [15], amorphous silica [16], waste brewery's yeast biomass [17], chitosan films [18], chitosan and alginate beads [19] were used for the removal and purification of anthocyanins from extracts of different plants.

Our previous research showed that fibrous strongly acid cation exchanger FIBAN K–1 can be used for removal and purification of chokeberry and elderberry anthocyanins [20, 21]. At the same time, for novel adsorbents' introduction, the adsorption studies of equilibrium and thermodynamics are essential in supplying the basic information required for the design and operation of adsorption equipment.

The objective of the present work was to investigate equilibrium and thermodynamic aspects in order to evaluate anthocyanins adsorption of chokeberries and elderberries on FIBAN K–1 because these issues have not been examined yet.

EXPERIMENTAL

Chemical reagents of analytical grade (hydrochloric acid, glacial acetic acid, sodium acetate (trihydrate), potassium chloride) were purchased from Cherkassy State Chemical Plant (Ukraine).

Fresh chokeberries and elderberries were harvested in Vinnitsa region (Ukraine). The berries were immediately frozen and kept in a freezer at –18 °C, prior to use.

The thawed berries were crushed using a blender and mixed with 0.1 M water solution of HCl. The ratio of weight (g) of berries to volume (mL) of HCl was 1: 2. It was used maceratson for 24 h in the darkness at 20 °C. Hereafter the berry extracts were separated from the berries by filtration through filter paper and stored at 4 °C.

In our research [21] some characteristics were presented of the obtained berry extracts such as initial anthocyanin concentration (C_1), total soluble solids (C_2), pH-value, density (ρ), viscosity (η), Briggs coefficient ($^{o}B_x$) and they are shown in Table 1.

Table 1. Characteristics of berry extracts at 20 °C

Parameter	Chokeberry	Elderberry
C_1, mg/g	300	500
C_2, %	9.95	10.86
pH	1.05	1.55
ρ, g/cm^3	1.010	1.020
η, mPa·s	1.075	1.269
$^{o}B_x$	52	56

Total monomeric anthocyanin concentration was determined according to the pH-differential method [22]. The principle of the method is to cause the structural transformation of anthocyanins manifested by different colorations in two distinct pH values (1.0 and 4.5). The difference in absorbance of a sample is considered as proportional to anthocyanins content. The absorbance of the sample was measured using an UV-VIS spectrophotometer (SF-56, Spectral, Russia).

Content of total anthocyanins is expressed in mg of cyanidin-3-O-glucoside (Fig. 1) per L of extract [5] and calculated according to the following equation:

$$\mathrm{C} = \frac{\left[(A_{515} - A_{700})_{pH=1,0} - (A_{515} - A_{700})_{pH=4,5}\right] \cdot M \cdot DF \cdot 1000}{l \cdot \varepsilon} \quad (1)$$

where A_{515} and A_{700} are the absorbances of an extract at pH 1.0 and pH 4.5; M is the molar mass of anthocyanins (cyanidin-3-glucoside), g mol^{-1} (M = 449.2 g·mol^{-1}); DF is the dilution factor as a final volume per the initial volume; l is the path length, cm; ε is the molar extinction coefficient of cyanidin-3-glucoside), L $mol^{-1}cm^{-1}$ (26900 L $mol^{-1}cm^{-1}$); 1000 is a conversion factor from g to mg.

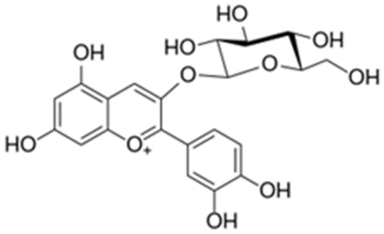

Fig. 1. Structural formula of cyanidin-3-glucoside

Calculation of total anthocyanin concentration is based on the molecular weight and the molar extinction coefficient of cyanidin-3-glucoside, the most common anthocyanin in nature [23].

The measurements of pH of the anthocyanin extracts were carried out using a pH meter (Universal ionomer EV-74, Belarus). Briggs coefficient was calculated using refractive index which was measured with a refractometer (Abbe Refractometer RL-1, Poland). The determination of density of the anthocyanin extracts was carried out by a pycnometer method. The kinematic viscosity of the anthocyanin extracts was measured using a capillary Ubbelohde viscometer. Total soluble solids were determined drying 20 mL of the anthocyanins extracts at 105 °C during 24 h and dry matter was weighted in an analytical scales and results were expressed in %.

It was used a fibrous strongly acid cation exchanger FIBAN K-1 with $–SO_3^-H^+$ functional groups as an adsorbent of the anthocyanins (Fig. 2). The adsorbent was developed and synthesized at the Institute of Physical Organic Chemistry of National Academy of Sciences of Belarus. FIBAN K–1 was obtained by direct radiochemical grafting of styrene and divinylbenzene into industrial polypropylene staple fiber and following sulfonation of the graft fiber. The diameter of the ion exchange fiber was 40 µm, water uptake 0.7 g_{H2O}/g [24].

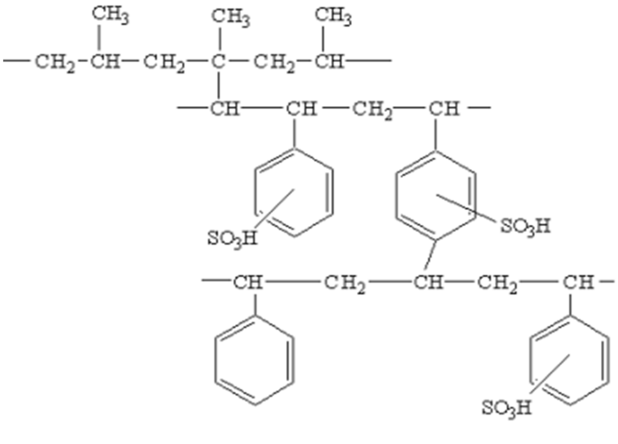

Fig. 2. The structure of representative fragment of FIBAN K–1

Adsorption experiments were carried out under static conditions, shaking mixtures of the anthocyanin extracts of the berries with FIBAN K–1 at such terms: pH = 2; concentration of anthocyanins 5-300 mg·L^{-1}; adsorbent mass 3.75 g·L^{-1}; agitation speed 150 rpm; 135 min (equilibrium time); 293, 303 and 313 K. Our kinetic studies have shown [21] that the achievement adsorption equilibrium was for 135 min at the adsorption terms indicated above.

The amount of the anthocyanins on the adsorbent at equilibrium time (q_e, mg·g^{-1}) was calculated from the difference in the anthocyanin concentration in the aqueous phase before and after adsorption, according to Equation (2):

$$q_e = \frac{C_0 - C_e}{m} V, \tag{2}$$

where C_o is the initial concentration of the anthocyanins, mg·L^{-1}; C_e is the equilibrium concentration of the anthocyanins after adsorption, mg L^{-1}; m is the mass of the adsorbent, g; and V is the volume of the dye solution, L.

In order to ensure the reproducibility of the results, all the adsorption experiments were performed in triplicate, and the average values were used in data analysis. Relative standard deviations were found to be within ±3 %.

Two-parameter models are often used to describe the adsorption isotherm, because, though quite simple, they can be easily modeled. The adsorption isotherms for adsorption removal of the anthocyanins on FIBAN K–1 were investigated using two-parameter adsorption models, viz., Langmuir (Equation (3), the Freundlich (Equation (4), and Temkin (Equation (5):

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \ , \tag{3}$$

$$ln q_e = ln K_F + \frac{1}{n} ln C_e \ , \tag{4}$$

$$q_e = \frac{RT}{b} ln K_T + \frac{RT}{b} ln C_e \ , \tag{5}$$

where C_e is the equilibrium dye concentration in solution, mg L^{-1} ; K_F is the Freundlich constant related to the adsorption capacity, mg$^{1-1/n}$ L$^{1/n}$ g^{-1}; $1/n$ is the adsorption intensity; q_m is the monolayer capacity of the adsorbent, mg g^{-1}; K_L is the Langmuir constant that relates to energy of adsorption, L mg^{-1} ; K_T is the Temkin equilibrium constant corresponding to the maximum binding energy, L g^{-1}; b is the heat of adsorption, J mol^{-1}.

The adsorption thermodynamic parameters (standard Gibbs free energy change ($\Delta G°$), standard enthalpy change ($\Delta H°$), and standard entropy change ($\Delta S°$), are used in the determination of spontaneity of the adsorption process, the nature of the adsorption process, and the adsorbent applicability. In this study the thermodynamic parameters were calculated by Equations (6) and (7):

$$\Delta G^o = -RT ln K^o, \tag{6}$$

$$ln K^o = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{R} \cdot \frac{1}{T}, \tag{7}$$

where $\Delta G°$ is the standard Gibbs free energy change, J mol^{-1}; R is the universal gas constant (R = 8314 J mol^{-1} K^{-1}); T is the absolute temperature, K; $K°$ is the dimensionless thermodynamic adsorption constant; $\Delta S°$ is the standard entropy change, J mol^{-1} K^{-1}; $\Delta H°$ is the standard enthalpy change, J mol^{-1}.

The $K°$ values (without units) were calculated from the data of K_L from the Langmuir isotherm by Equations (8) [25]:

$$K^o = K_L \cdot \gamma \cdot M \cdot 10^3 \ . \tag{8}$$

K_L is the Langmuir constant, L mg^{-1}; γ is the number of moles of pure water per liter, mol·L^{-1} (γ = 55.5 mol·L^{-1}); M – the molar mass of anthocyanins (cyanidin-3-glucoside), g·mol^{-1} (M = 449.2 g·mol^{-1}); 10^3 is the factor that allows converting g in mg.

The values of $\Delta S°$ and $\Delta H°$ were evaluated from the intercept and slope of the Van't Hoff plot of ln K^o *vs.* $1/T$, respectively [15], assuming that $\Delta H°$ and $\Delta S°$ are temperature independent from 293 to 313 K.

The applicability of the employed models for the experimental adsorption equilibrium data was confirmed by calculating the linear regression coefficient (R^2), standard error (SE) and Chi-square test (χ^2). The mathematical equations of SE and χ^2 are given below:

$$\text{SE} = \sqrt{\frac{\sum_{i=1}^{N}\left(q_{i,calc} - q_{i,exp}\right)^2}{N-2}} \ , \tag{9}$$

$$\chi^2 = \sum_{i=1}^{N} \frac{\left(q_{i,calc} - q_{i,exp}\right)^2}{q_{i,calc}} \ , \tag{10}$$

where $q_{i,calc}$ is the theoretical amount of the adsorbed anthocyanins on the adsorbent, which was calculated from one of the isotherm model equations, mg g^{-1}; $q_{i,exp}$ is the experimental amount of the adsorbed anthocyanins on the adsorbent, mg g^{-1}; N is the number of the data points.

The higher values for correlation coefficients (R^2) and the smaller values for SE and χ^2 imply more accurate estimations and were taken into account when choosing the most suitable adsorption models.

RESULTS AND DISCUSSION

Adsorption Isotherms and Equilibrium Studies. The association between the anthocyanin equilibrium concentrations in the solution and the amounts of the anthocyanins on the adsorbent at equilibrium time at a steady temperature is defined by the adsorption isotherm which plays a major role in determining the interactive behaviors between adsorbates and adsorbents. Besides, analysis of the experimental adsorption isotherms using adsorption models is important to develop an equation which accurately represents the obtained results and can be used for design purposes. Selecting the model of isotherm for the adsorption process, the following conditions must be satisfied: (i) the model of the isotherm and the determined equilibrium data must have a superlative fit, (ii) the isotherm function must be thermodynamically accurate, and (iii) in ideal situations, the calculation of concentration is from the capacity and the other way around [26].

Fig. 3 shows the experimental adsorption isotherms of the chokeberry and elderberry anthocyanins on FIBAN K–1 at different temperatures by plotting q_e in terms of C_e. As can be seen from Fig. 3, the isotherms obtained are of L-type according to the classification of Giles [27] and allows us to assume that the adsorption process of the chokeberry and elderberry anthocyanins on FIBAN K–1 could occur in monolayers.

According to Fig. 3, the adsorption capacity of FIBAN K–1 for the chokeberry and elderberry anthocyanins increased as the temperature increased from 293 to 313 K, indicating that the adsorption was an endothermic process. These results were consistent with previous reports that elevated temperatures facilitated the removal of the eggplant anthocyanins on mesoporous carbon C1 [15] and the purple potato anthocyanins on microporous resins XAD-7HP and XAD-4. However, some studies have shown that temperatures can have a negative effect on the adsorption of the mulberry anthocyanins on microporous resin XAD-7HP [9] and the muscadine grapes anthocyanins on microporous resins XAD-16N and XAD-1180 [11].

In the present study, the Langmuir, Freundlich, and Temkin two-parameter adsorption models were used to describe the experimental adsorption isotherms, because they are the most often used isotherm models, quite simple and can be easily modeled.

The Langmuir isotherm is the simplest theoretical model for describing monolayer adsorption, which assumes a uniform adsorbent surface with energetically identical adsorption sites [8]. The Freundlich adsorption isotherm is an empirical equation which predicts that the adsorbent surface is heterogeneous. This model can be used to describe the adsorption behavior of a monomolecular layer as well as that of a multimolecular layer [11]. The Temkin isotherm considers the effect of the adsorbate interaction on the adsorbent based on the uniformly distributed binding energies. It also assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbate/adsorbent interactions [17].

Calculated constants from the Langmuir, Freundlich, and Temkin adsorption isotherms of the chokeberry and elderberry anthocyanins on FIBAN K–1 at various temperatures are summarized in Table 2. In general, these models had a good agreement with the experimental data for adsorption of the anthocyanins having correlation coefficients higher than 0.8895 at all temperatures, but the Langmuir model is the most favorable one for studying the adsorption equilibrium of the chokeberry and elderberry anthocyanins on FIBAN K–1: the R^2 values are higher ($R^2 > 0.9895$) and the values of SE and χ^2 are the lowest for the Langmuir model than for the Freundlich and Temkin models. The fitness of the Langmuir model to the adsorption process connotes that the anthocyanins from solution bulk were adsorbed on specific monolayer which is homogeneous in nature.

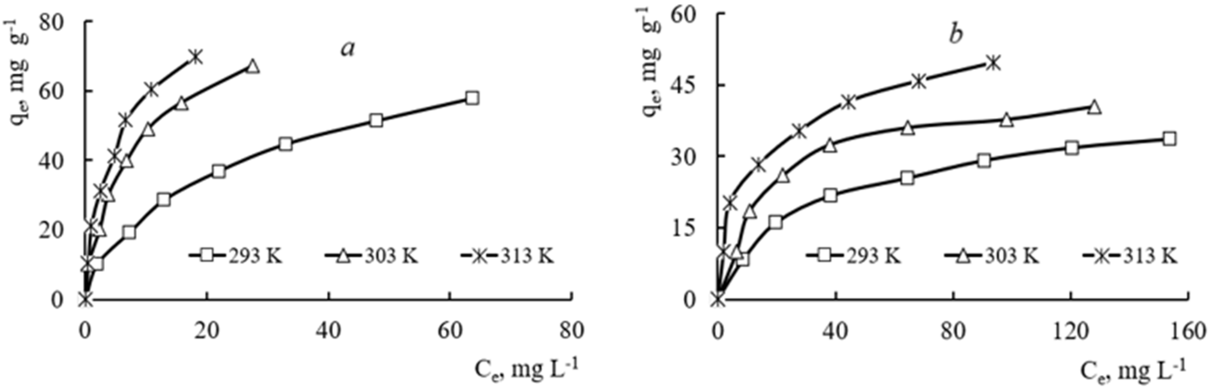

Fig. 3. Adsorption isotherms of the anthocyanins on FIBAN K–1 at different temperatures: *a* – chokeberry; *b* – elderberry

Table 2. Comparison of the isotherm models

Isotherm model	Parameter	Chokeberry			Elderberry		
		293 K	303 K	313 K	293 K	303 K	313 K
Langmuir	q_m(mg g^{-1})	71.43	80.00	82.64	40.49	45.87	53.48
	$K_L \cdot 10^2$ (L mg^{-1})	5.55	16.76	26.25	2.98	5.49	9.47
	R^2	0.9805	0.9831	0.9904	0.9975	0.9964	0.9925
	SE	2.29	2.70	2.99	0.77	1.41	3.34
	χ^2	1.72	3.00	1.58	0.14	0.57	3.00
Freundlich	$1/n$	0.51	0.52	0.51	0.46	0.42	0.38
	n	1.96	1.92	1.96	2.17	2.38	2.63
	K_F (mg$^{1-1/n}$ L$^{1/n}$ g^{-1})	7.25	14.18	18.16	3.55	5.98	9.19
	R^2	0.9951	0.9914	0.9670	0.9575	0.8895	0.9423
	SE	1.86	5.81	4.93	2.16	4.49	3.52
	χ^2	0.41	2.41	2.48	1.07	3.64	2.92
Temkin	K_T (L g^{-1})	0.73	2,49	3.09	0.30	0.56	1.51
	b (kJ mol^{-1})	0.174	0.164	0.148	0.279	0.257	0.257
	R^2	0.9594	0.9502	0.9839	0.9986	0.9732	0.9895
	SE	3.80	5.00	3.32	0.37	2.34	2.21
	χ^2	5.70	16.42	2.68	0.03	1.22	0.94

The maximum Langmuir adsorption capacity of the chokeberry anthocyanins on FIBAN K–1 increased from 71.43 mg/g at 293 K to 82.64 mg/g at 313 K, and the maximum Langmuir adsorption capacity of the elderberry anthocyanins on FIBAN K–1 increased from 40.49 mg/g at 293 K to 53.48 mg/g at 313 K (Table 2). The positive influence of temperature on the anthocyanins adsorption of the both types of berries on FIBAN K–1 can be related to the enhancement of the diffusion rate of the anthocyanins through the boundary layer "solution-adsorbent" due to decrease of solution viscosity.

The Freundlich isotherm constant n represents the strength of the adsorption process, and its value should be greater than 1 and less than 10 for favorable adsorption conditions [11]. The n values obtained from Freundlich plots were greater than 1 for all studied temperatures, indicating favorable adsorption conditions.

The Temkin constants b related to heat of adsorption decreased as the temperature increased from 293 to 313 K. The low values of b indicate an ion-exchange mechanism for the present study.

According to [17], the Langmuir, Freundlich, and Temkin adsorption models had a good agreement with the experimental data for adsorption of anthocyanins from grape pomace extracts by waste yeast having correlation coefficients higher than 0.970. The authors reported that the Temkin model was the most favorable model (R^2 = 0.996) and the linear plots for Temkin adsorption isotherms indicated that the adsorption was a chemisorption process.

Thermodynamic Studies. Changes in standard Gibbs free energy ($\Delta G°$), enthalpy ($\Delta H°$), and standard entropy ($\Delta S°$) of the chokeberry and elderberry anthocyanin adsorption on FIBAN K–1 are shown in Table 3.

Table 3. Thermodynamic parameters of adsorption of the anthocyanins on FIBAN K–1

Berry	T (K)	$K° \cdot 10^{-6}$	$-\Delta G°$ (kJ·mol^{-1})	$\Delta H°$ (kJ·mol^{-1})	$\Delta S°$ (J·K^{-1}·mol^{-1})	R^2
Chokeberry	293	1.37	34.4	59.8	322	0.9504
	303	4.19	38.4			
	313	6.53	40.8			
Elderberry	293	0.74	32.9	43.8	262	0.9997
	303	1.37	34.4			
	313	2.34	35.7			

As shown in Table 3, the $\Delta G°$ values were negative, thus indicating that the adsorption of the chokeberry and elderberry anthocyanins on FIBAN K–1 was spontaneous and favorable process under the experimental conditions. The decrease of the $\Delta G°$ values with increasing temperature from 293 to 313 K shows that adsorption is more favorable at high temperature. The $\Delta H°$ values were positive for anthocyanins of both berries, which indicates that the adsorption was an endothermic reaction, which was consistent with the decreasing values of $\Delta G°$ with the rise of temperature. The $\Delta S°$ values were positive, which means that the anthocyanins in the aqueous phase are more organized than those in the adsorbent-liquid interface.

Carvalho *et al.* [18] and Pinheiro *et al.* [19] observed the same behavior in relation to positive values of $\Delta H°$ and $\Delta S°$ of the red cabbage anthocyanins on chitosan films and grape pomace anthocyanins on chitosan and alginate beads. The authors explained positive value for standard enthalpy change due to the predominant contribution of anthocyanin desolvation (bound water present in the anthocyanins). Therefore, the energy required to overcome solvation was higher than the energy released by the bond between the adsorbent and the adsorbate.

In this experiment, the changes in standard enthalpy of chokeberry and elderberry anthocyanin adsorption on FIBAN K–1 are equal, respectively 59.8 and 43.8 $kJ \cdot mol^{-1}$. When $20\ kJ \cdot mol^{-1} < \Delta H° < 80\ kJ \cdot mol^{-1}$, the electrostatic interaction plays an important role in the adsorption process [28].

Considering the presence of hydroxo groups and benzene rings in the composition of anthocyanins and the formation of a flavylium cation in an acidic medium, the adsorption of the chokeberry and elderberry anthocyanins on FIBAN K–1 can be explained by simultaneous action of different kinds of interactions including hydrogen bonding, van der Waals, hydrophobic, and electrostatic interactions. Apparently, in the system under investigation electrostatic interactions between the fixed functional sulfogroups of FIBAN K–1 and flavylium cations, should be considered as driving force for adsorption.

CONCLUSIONS

In this paper, equilibrium and thermodynamic studies of the chokeberry and elderberry anthocyanins from their acidic aqueous extracts on fibrous cation exchanger FIBAN K–1 were carried out. Isotherm studies indicated that the Langmuir, Freundlich and Temkin models had a good agreement with the experimental data for adsorption of the anthocyanins on FIBAN K–1, but the Langmuir model fitted the experimental data better than the Freundlich and Temkin models. The adsorption equilibrium was described by the Langmuir isotherm model with maximum adsorption capacity of 82.64 $mg \cdot g^{-1}$ for the chokeberry anthocyanins and 53.48 $mg \cdot g^{-1}$ for the elderberry anthocyanins on FIBAN K–1 at 313 K. Thermodynamic calculations showed that the chokeberry and elderberry anthocyanins adsorption by FIBAN K–1 was endothermic and of spontaneous nature. The $\Delta S°$ values were positive, which means that the anthocyanins in the aqueous phase are more organized than those in the adsorbent-liquid interface.

Рівноважні та термодинамічні дослідження адсорбції антоціанів на волокнистому катіоніті ФИБАН К-1

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В останні десятиліття спостерігається підвищена зацікавленість дослідників щодо отримання антоціанів з доступної та недорогої рослинної сировини з метою їхнього застосування не тільки як природних харчових барвників, але й як фармацевтичних препаратів. Серед рослинних джерел антоціанів аронія та бузина відносяться до перспективної сировини завдяки великому вмісту антоціанів. У даній роботі досліджено адсорбційну рівновагу та термодинаміку антоціанів екстрактів аронії та бузини на волокнистому катіоніті ФИБАН К–1, який містить у своєму складі сильнокислотні SO_3H–групи, що приєднані до ароматичних кілець. Екстракти антоціанів отримували мацерацією сировини в 0.1 М HCl за наступними умовами екстракції: співвідношення сировина-рідина = 1:2 при 293 К протягом 24 год. Загальний вміст антоціанів в екстрактах визначали pH-диференціальним методом. Адсорбційні досліди проводили в статичних умовах, струшуючи суміші антоціанових екстрактів ягід з ФИБАН К–1. Отримані адсорбційні ізотерми віднесено до L-типу за класифікацією Джайлса. Адсорбційна здатність ФИБАН К–1 зростала при підвищенні температури від 293 до 313 К. Для опису експериментальних ізотерм адсорбції застосовано адсорбційні моделі Ленгмюра, Фрейндліха та Тьомкіна. Ці моделі добре узгоджувалися з експериментальними даними, але модель Ленгмюра була найбільш сприятливою для дослідження адсорбційної рівноваги антоціанів аронії та бузини на ФИБАН К–1. Розраховано термодинамічні параметри адсорбції антоціанів: $\Delta G°$, $\Delta H°$ і $\Delta S°$. Значення $\Delta G°$ були від'ємними, що свідчить про те, що адсорбція антоціанів аронії та бузини на ФИБАН К-1 була спонтанною та сприятливою в умовах експерименту. Зменшення значень $\Delta G°$ зі збільшенням температури показало, що адсорбція більш сприятлива при високій температурі. Значення $\Delta H°$ були позитивними при адсорбції антоціанів обох видів ягід, що свідчить про ендотермічний процес. Значення $\Delta S°$ були позитивними, тобто антоціани аронії та бузини у водній фазі є більш організованими системами, ніж на межі поділу адсорбент-рідина.

***Ключові слова**: антоціани, ФИБАН К–1, адсорбція, рівновага, ізотерми, термодинаміка*

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