Life Science Informatics Publications

Research Journal of Life Sciences, Bioinformatics, Pharmaceutical and Chemical Sciences

Journal Home page http://www.rjlbpcs.com/

RJLBPCS ISSN 2454-6348

Original Research Article **DOI: 10.26479/2022.0804.04**

VITAMIN C INTERACTION WITH ACTIVATED CARBONS: ISOTHERMS, THERMODYNAMICS, THERMAL INVESTIGATION

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ABSTRACT: The adsorption of vitamin C on commercial Granucol-type activated carbons and new carbon AC-C was studied at 25 and 35 °C. At both temperatures, the sorption isotherms are better described by the Langmuir model than by the Freundlich sorption model. Vitamin C adsorption at 25 °C is higher than at 35 °C and can reach 433 mg/g. The adsorption capacity of AC-C coal is almost the same as that of Granukol coals. In the process of adsorption, the pH of the system changes slightly in the case of Granukol coals and significantly in the case of AC-C coal. The change in the standard Gibbs energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) was also calculated. The thermogravimetric analysis allowed to highlight the adsorption of vitamin C on the different types of activated carbon and to identify the conditions for their regeneration.

Keywords: adsorption, activated carbon, isotherm, thermal investigation, thermodynamics.

Article History: Received: July 14, 2022; Revised: August 04, 2022; Accepted: August 20, 2022.

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1. INTRODUCTION

It is well known the importance of vitamin C (L-ascorbic acid) for the normal development and vital functions of living organisms. Vitamin C has a strong antioxidant function and neutralizes free radicals in cells and protects against oxidative stress. It is a coenzyme of many metabolic processes. It participates in the formation of collagen, in the biosynthesis of carnitine and in the absorption of iron, in the conversion of dopamine into norepinephrine. In addition, ascorbic acid is needed for wound healing and tissue growth, for the implementation of adrenal function, the secretion of hormones and interferons, and the metabolism of folic acid, tyrosine and phenylalanine. Increases iron absorption, lowers blood cholesterol and helps lower blood pressure [1]. Caused by insufficient food intake, impaired absorption of the digestive system, increased need or excessive secretion, deficiency most often occurs in the elderly, alcoholics suffering from chronic malabsorption or feeding with infusions that do not contain vitamin C. This leads to fatigue and anemia, osteoarticular pain, gingivitis and tooth loss, bleeding, low immunity. There would be much more sub-deficiency conditions, and the question is currently being asked about a possible link between a lack of vitamin C intake and various diseases such as cancer, cataracts, and cardiovascular diseases [2]. In addition, vitamin C is used for the preparation of many materials in the pharmaceutical and food industries [3-6]. The human body cannot synthesize vitamin C. People get vitamin C from food. The main sources of vitamin C are plant foods. Juices from fruits, berries, vegetables, as well as wines and beer are also sources of vitamins. In the food industry, various processes are used to stabilize and improve the quality of production. Often these processes are carried out using a variety of clays, especially bentonite and activated carbons [7]. For example, commercial activated carbons of the Granucol-type are used to stabilize, cleaning and restore a commercial appearance to wines, juices, beer and strong alcoholic beverages [8-10]. Activated carbon Granucol GE is used for sorption of undesired off-taste and off-smell in beer, juice, wine and spirits. Granucol FA and Granucol BI are used for reduction of tannins and polyphenols and for the elimination of high-color due to browning reactions in juice and wine [10]. But in addition to purifying food liquids, activated carbon interacts with various components of the system, including vitamins. These uncontrolled processes are not sufficiently investigated. The purpose of this article is to investigate the interaction of vitamin C with activated carbons in different conditions.

2. MATERIALS AND METHODS

Vitamin C (L-ascorbic acid, Sigma Aldrich) was used for investigation. Commercial activated carbons Granucol BI, Granucol GE, Granucol FA and AC-C activated carbon was obtained from apricot kernels in the laboratory of the Institute of Chemistry of the Academy of Sciences of Moldova [11] were also used. The activated carbons used are predominantly mesoporous (about 70 % mesoporous) with a specific surface area of about 1360 m^2/g (Granucol) and 1385 m^2/g (AC-C) [11]. It should be noted that the Granukol coals used in the research contain up to 15% bentonite [12]. In the experiments, carbon samples with a mass of approximately 0.05 g were contacted with 50 mL of vitamin C solution for 6 h. After the expiration of the contact period, the solution was filtered, the pH measured with an accuracy of ± 0.1 pH units and subjected to quantitative analysis. Analysis of the solution was performed using UV-Vis spectroscopy at 264 nm. The experiments were performed at 25 and 35 ^oC on the water bath with the accuracy of $\pm$ 0.2 ^oC. The thermogravimetric analysis for different types of activated carbon, mixture of activated carbon and vitamin C and activated carbon, on which the adsorption of vitamin C was performed, was carried out using Mettler Toledo 851e equipment in air atmosphere, with a speed of 10 °C/min in the range temperature 25-700 °C. The mass of the sample to be analyzed was between 2.8 and 5.2 mg. The evaluation of the thermogravimetric (TG), derived thermogravimetric (DTG) and differential thermal (DTA) curves was performed with $STAR^e$ version 9.10 software.

3. RESULTS AND DISCUSSION

3.1. Sorption isotherms

In order to determine the maximum absorption capacity of activated carbon during contact with vitamin C solution, sorption isotherms at 25 and 35 °C were obtained. The amount of vitamin C retained by activated carbons at equilibrium was calculated using Equation (1):

$$S = \frac{(Co-Ce)V}{m} \qquad (1)$$

where *S* is the vitamin C adsorption at the equilibrium (mmol/g), *Co* and *Ce* are the initial and equilibrium concentration of vitamin C in the solution (mmol/L) respectively, *V* is the volume of the solution in contact with carbon (L), *m* is the mass of the carbon (g).

The experimentally obtained isotherms were calculated using the Langmuir [13] and Freundlich [14] adsorption models. When calculating isotherms using the nonlinear Langmuir model, Eq.(2) was used:

$$S = S_L \frac{K_L C_e}{1+K_L C_e} \qquad (2)$$

where *S* is the vitamin C adsorption value at equilibrium (mmol/g); S_L is the maximum capacity of the sorbent (mmol/g); K_L is the Langmuir isotherm constant (L/mmol), *C*e is the vitamin C concentration at sorption equilibrium (mmol/L).

The Langmuir isotherm constants were calculated using a linear isotherm plot (Eq.(3)):

$$\frac{C_e}{S} = \frac{1}{S_L K_L} + \frac{C_e}{S_L} \qquad (3)$$

Isotherms were also calculated using the Freundlich sorption model (Eq. (4)):

$$S = K_F\, C^{1/n} \qquad (4)$$

where *S* is the same as in Eq. (2), K_F is the Freundlich isotherm constant.

The $1/n$ is a measure of the nature and strength of the adsorption process and of the distribution of active centers. If $1/n > 1$, bond energy increases with the surface density; if $1/n < 1$, bond energy decreases with the surface density; and when $1/n = 1$, all surface sites are equivalent. The constants $1/n$ and K_F were calculated by the graph of the linear Freundlich isotherm (Eq. (5):

$$\ln S = \ln K_F + (1/n) \ln C \qquad (5)$$

The results of the study of the adsorption isotherms of vitamin C at 25 and 35 °C on activated carbon Granucol FA, Granucol BI, Granucol GE and local carbon AC-C are graphically presented in Figures 1-4.

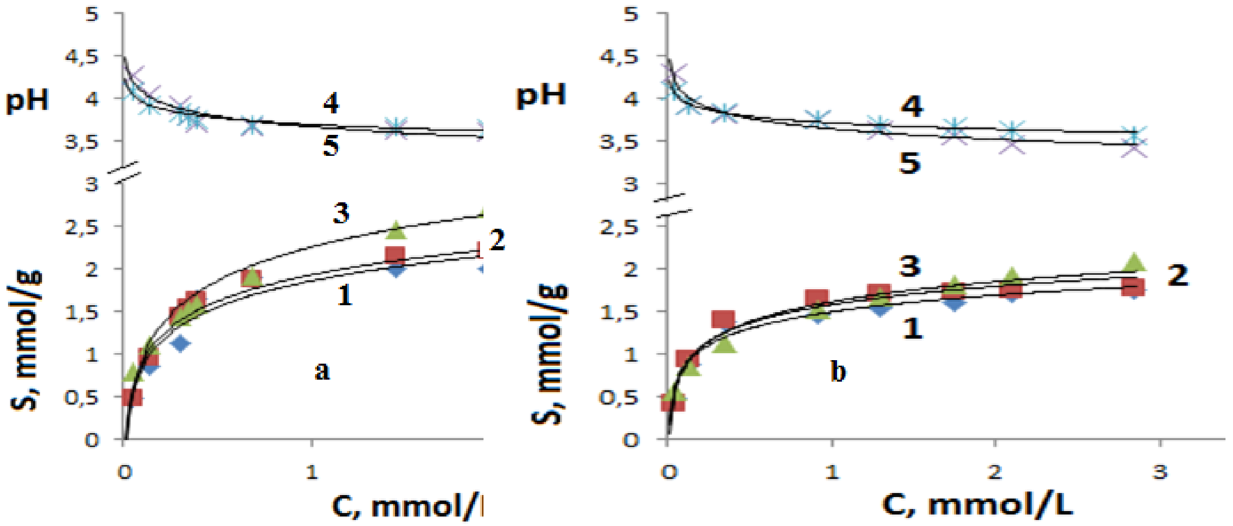


Figure 1. Vitanine C sorption isotherms on Granucol FA activated carbon at 25 (a) and 35 °C (b) obtained experimental (1), calculated with the Langmuir model (2), calculated with the Freundlich model (3), pHo up to contact with coal (4) and pHe at sorption equilibrium (5).

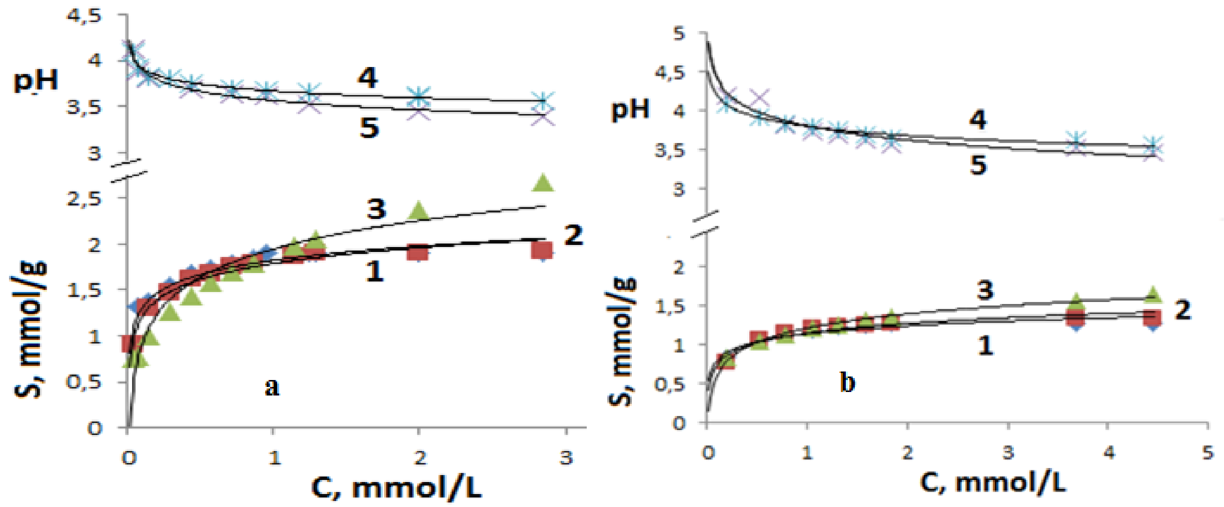


Figure 2. Vitanine C sorption isotherms on Granucol BI activated carbon at 25 (a) and 35 °C (b) obtained experimental (1), calculated with the Langmuir model (2), calculated with the Freundlich model (3), pHo up to contact with coal (4) and pHe at sorption equilibrium (5).

Figures 1-4 show that the adsorption of vitamin C on activated carbons at 25 °C is higher than at 35 °C. Thus, the adsorption of vitamin C on the studied carbons is a physical process caused by van der Waals forces. Considering that the surface of the coals is predominantly non-polar, but the vitamin C molecules are quite large and contain C, H and O atoms, we can say that the sorbent-sorbate interactions are mainly due to dispersion forces.

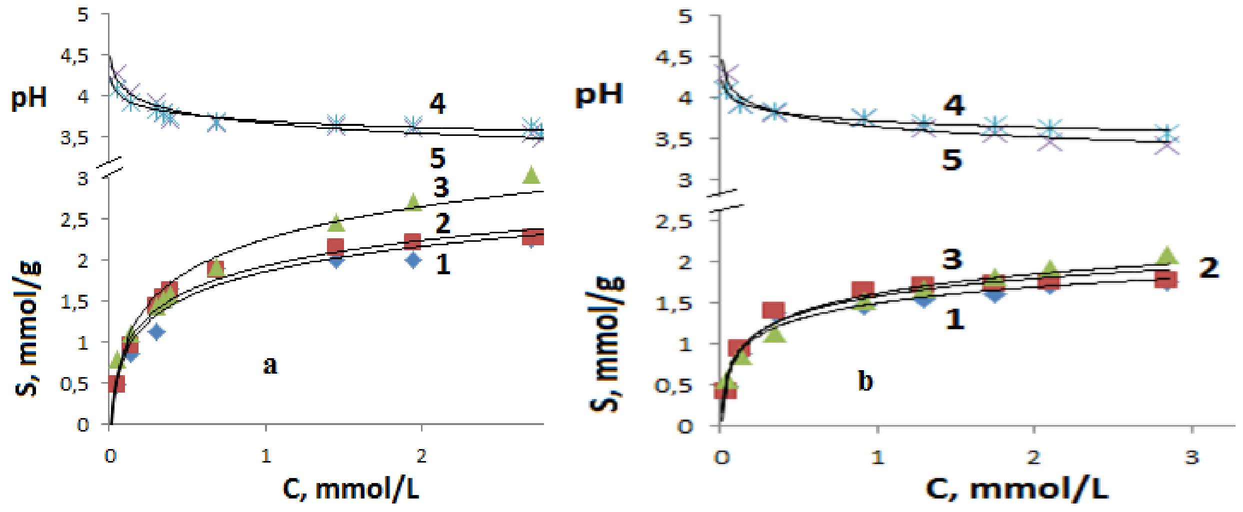


Figure 3. Vitanine C sorption isotherms on Granucol GE activated carbon at 25 (a) and 35 °C (b) obtained experimental (1), calculated with the Langmuir model (2), calculated with the Freundlich model (3), pHo up to contact with coal (4) and pHe at sorption equilibrium (5).

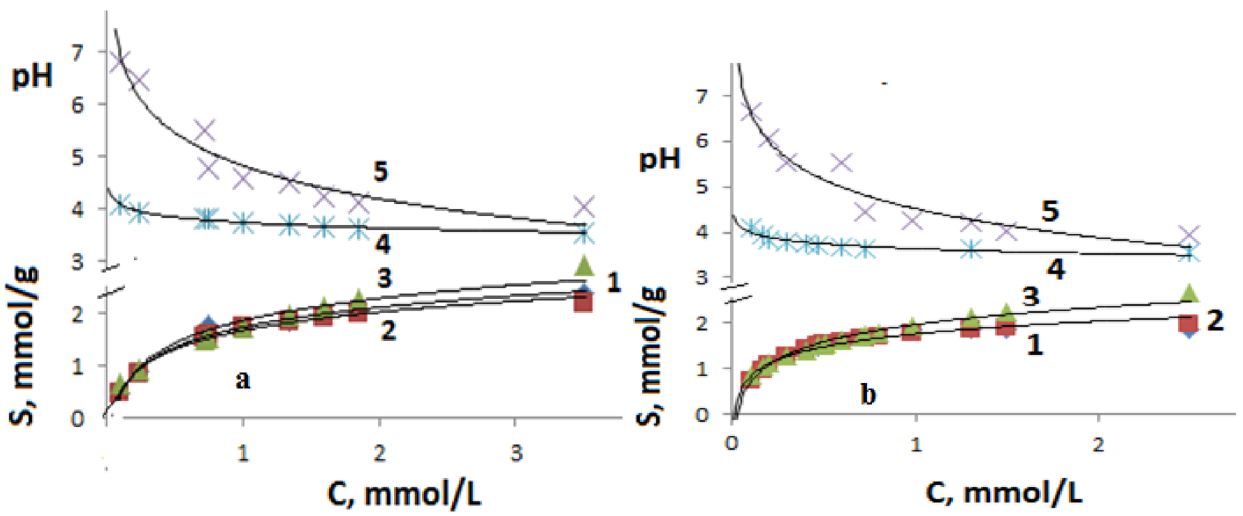


Figure 4. Vitanine C sorption isotherms on AC-C activated carbon at 25 (a) and 35 °C (b) obtained experimental (1), calculated with the Langmuir model (2), calculated with the Freundlich model (3), pHo up to contact with coal (4) and pHe at sorption equilibrium (5).

Figures 1-3 show that the pH of the solution decreases slightly during the absorption of vitamin C on Granucol coals compared to the pH of the solution before it comes into contact with the coals. In the case of the adsorption of vitamin C on AC-C coal, the pH of the solution changes significantly. Unlike Granucol-type coals, the pH of the vitamin C solution after sorption on AC-C is higher than the pH of the solution before contact with the coal (Fig. 4). The following experiments were performed in order to understand the case of the change in the pH of the vitamin C solution upon contact with the coals. It was found that when storing the solution of 1 mmol/L vitamin C at 25 °C for 6 hours the pH practically does not change, being 3.87. Upon contact of 0.055 g of Granucol BI with 50 mL of distilled water at 25 and 45 ° C for 6 hours, the pH was changed from 5.75 to 4.5 and 4.53, respectively. The decrease in pH is explained by the fact that vitamin C is an acid (L-ascorbic acid). Upon contact with 0.054 g of AC-C coal with 50 mL of distilled water for 6 hours, the pH was changed from 5.75 to 8.47 at 25 ° C and 9.6 to 45 °C. Therefore, Granucol lowers the pH of the vitamin C solution (Figs.1-3), but AC-C leads to a significant increase in pH (Fig.4). It can be seen that Granucol coal does not significantly change the state of the processed liquids, while AC-C coal changes it more strongly. As mentioned earlier, the isotherms of vitamin C adsorption on activated carbon were calculated with the Langmuir and Freundlich sorption models. The characteristics of the isotherms are shown in Table 1. Possibility of adsorption in a specific concentration range vitamin C can be expressed by a dimensionless parameter R_L, which is called the separation constant coefficient or equilibrium parameter. This parameter was calculated using the Eq.6 [15]:

$$R_L = \frac{1}{1+K_L C_0} \qquad (6)$$

where K_L is the Langmuir adsorption constant (L/mmol), and Co is the initial concentration of vitamin C (mmol/L).

According to the values of R_L, the adsorption is: unfavorable when $R_L > 1$; linear when $R_L = 1$; favorable when $0 < R_L < 1$; irreversible when $R_L = 0$.

In addition to the correlation coefficient of determination (R^2), statistical analysis of errors was carried out using nonlinear Chi-square (χ2) test (Eq.(7)) [16]:

$$\chi^2 = \sum \frac{(S_{exp.} - S_{calc.})2}{S_{calc.}} \qquad (7)$$

where *Sexp*. is the value of the sorption at equilibrium, obtained experimentally (mmol/g), *Scalc*. is the sorption value (mmol/g) calculated according to Langmuir or Freundlich sorption models.

The lower the value of χ2, the smaller the error. The values of R_L, R^2 and χ2 are shown in Table 1. According to the data in Table 1, in the range of the initial concentrations of vitamin C the R_L values fall in the range $0 < R_L < 1$. So sorption is a favorable process.The data in Table 1 also show that for almost all coals, the calculation error for the Langmuir model is less than that for the Freundlich model. Analysis of Figures 1 - 4 and the data in Table 1 shows that the specific capacity of coal during the adsorption of vitamin C is quite high. Increased absorption capacity may be caused by partial oxidation of vitamin C during adsorption. It is also seen that the Langmuir model better describes the sorption process than the Freundlich model.

Table 1. Parameters of vitamin C sorption isotherms on activated carbons

Activated carbon	Langmuir model		Freundlich model	
	25 ºC	35 ºC	25 ºC	35 ºC
Granucol FA	S_L = 1.728 mmol/g S_L = 303.43 mg/g k_L = 4.868 L/g R_L = 0.71 – 0.06 R^2 = 0.9602 χ^2 = 0.222	S_L 1.176 mmol/g S_L = 206,98 mg/g k_L = 5.669 L/g R_L = 0.261- 0.0286 R^2 = 0.9566 χ^2 = 0.1664	k_F = 1.408 1/n = 0.275 R^2 = 0.9759 χ^2 = 1.4746	k_F = 1.597 1/n = 0.488 R^2 = 0.9403 χ^2 = 1.4746
Granucol BI	S_L =1.916 mmol/g S_L = 337.41 mg/g k_L = 4.44L/g R_L = 0.362-0.0274 R^2 = 0.9332 χ^2 = 0.0518	S_L = 1.395 mmol/g S_L = 245,66 mg/g k_L = 6.098 L/g R_L = 0.247-0.033 R^2 = 0.9023 χ^2 = 0.013	k_F = 1.899 1/n = 0.329 R^2 =0.9567 χ^2 = 0.5518	k_F = 1.19 1/n = 0.216 R^2 = 0.987 χ^2 = 0.073
Granucol GE	S_L = 2.449 mmol/g S_L = 431.27 mg/g k_L = 4.8247 L/g R_L = 0.802 – 0.071 R^2 = 0.9757 χ^2 = 0.1586	S_L = 1.856 mmol/g S_L = 326.84 mg/g k_L = 8.741 L/g R_L = 0.97 – 0.0386 R^2 = 0.9628 χ^2 = 0.1546	k_F = 2.1736 1/n = 0.3376 R^2 = 0.9605 χ^2 = 0.7088	k_F = 1.556 1/n = 0.278 R^2 = 0.9759 χ^2 = 0.1789
AC-C	S_L = 2.46 mmol/g S_L = 433.20 mg/g k_L = 2.3546 L/g R_L = 0.81 – 0.11 R^2 = 0.9889 χ^2 = 0.057	S_L = 2.12 mmol/g S_L = 373.33 mg/g k_L = 5.112 L/g R_L = 0.28 – 0.005 R^2 = 0.9662 χ^2 = 0.0126	k_F = 1.745 1/n = 0.4204 R^2 =0.9462 χ^2 = 0.2355	k_F = 1.935 1/n =0.35 R^2 = 0.969 χ^2 = 0.332

3.2. Thermodynamic functions of the adsorption process

The fact that the Langmuir model adequately describes the process of vitamin C adsorption on coals made it possible to calculate the change in the standard Gibbs energy (ΔG^o), enthalpy (ΔH^o), and entropy (ΔS^o). The $\Delta G°$ values were calculated using the Eq.(8):

$$\Delta G^o = - RT \ln K_L \qquad (8)$$

The enthalpy variation (ΔH^o) was calculated with Eq.(9), considering that in the temperature range 25 - 35 ºC the caloric capacity of the system is constant:

$$H^o = R\ \frac{T_1 T_2\ \left(ln\frac{K_2}{K_1}\right)}{T_2 - T_1} \qquad (9)$$

where T_1 = 298 K, T_2 = 308 K, K_1 is K_L at 298 K, K_2 is K_L at 308 K and R = 8.314 J/mol K.

The entropy change was calculated using Eq.(10):

$$\Delta S^o = \frac{\Delta H^o - \Delta G^o}{T} \qquad (10)$$

The results obtained when calculating the thermodynamic functions for the adsorption process of vitamin C on activated carbons are presented in Table 2.

According to the data in Table 2, ($\Delta Go < 0$), the sorption of vitamin C on activated carbons is a spontaneous process. The ΔG^o values are almost the same for all coals, being slightly higher at 35 ^{o}C than at 25 ^{o}C.

Table 2. Thermodinamic functions of vitamin C adsorption on activated carbons

Activated carbon	T, ^{o}C	ΔG^o, kJ mol^{-1}	ΔH^o, kJ mol^{-1}	ΔS^o, J K^{-1}
Granucol FA	25	- 3.92	11.60	52.08
	35	- 4.44		52.08
Granucol BI	25	- 3.69	24.19	93.56
	35	- 4.63		93.57
Granucol GE	25	- 3.90	43.33	165.20
	35	- 5.55		165,19
AC-C	25	- 2.13	59.14	205,57
	35	- 4.18		205,58

The fact that $\Delta H^o > 0$ denotes that the sorption process is endothermic. Sorption processes are usually exothermic. The endothermic effect is probably caused by processes of restructuring (breaking of chemical bonds) of vitamin C molecules on the surface of coal. This is demonstrated by the IR spectra (Fig.5). It is known that the Granukol coals used contain up to 15 % bentonite, a complex mineral whose composition is determined by the clay content of montmorillonite which has the formula $Si_8Al_4O_{20}(OH)_4 \times nH_2O$ [17] In the used coals also were detected traces of Fe (III).

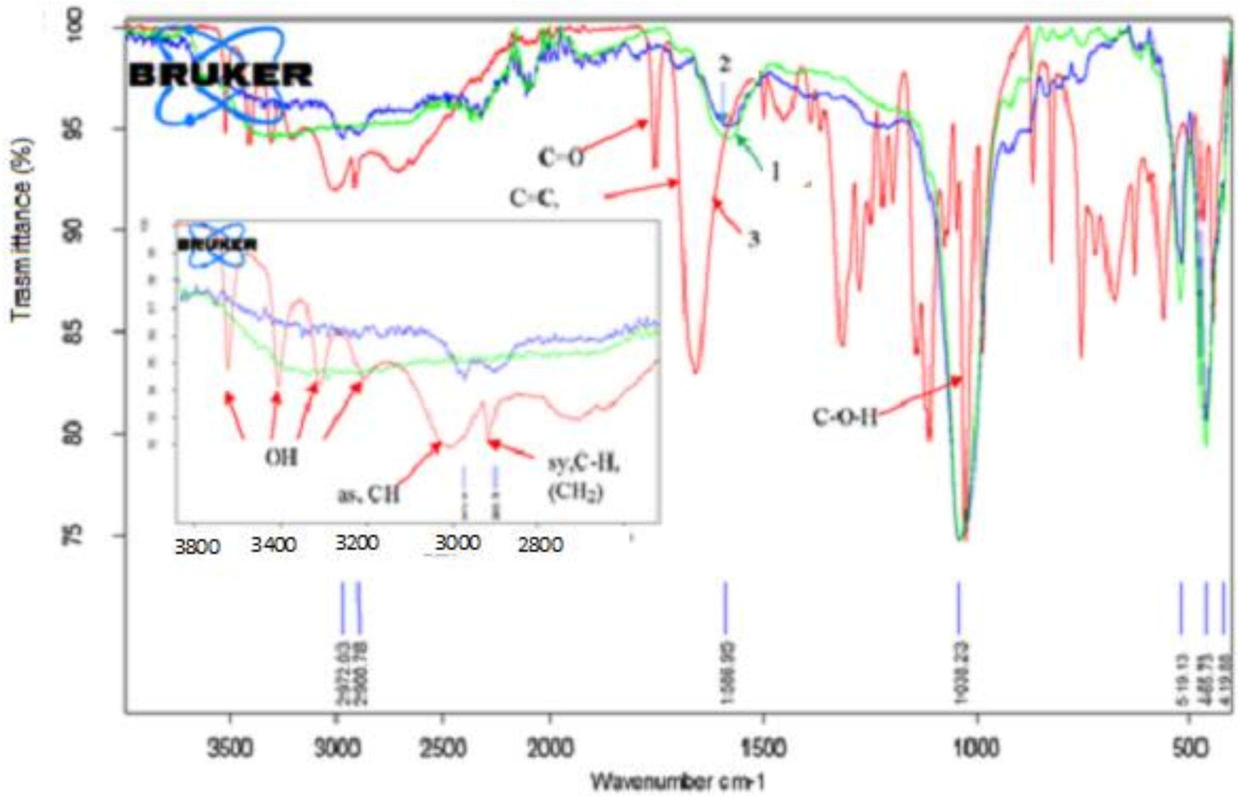
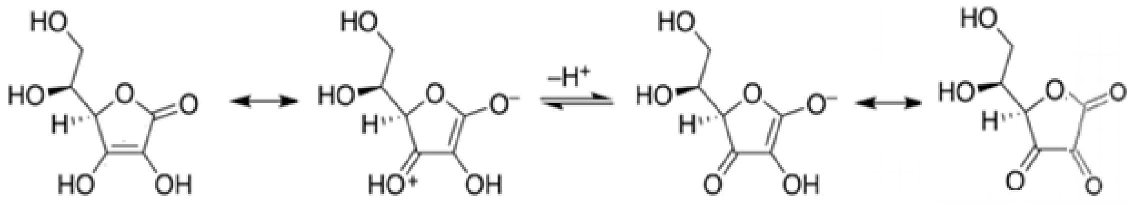


Figure 5. IR spectra of Granucol BI coal samples before (1) and after adsorption (2) and of vitamin C (3).

Spectrum 1 in Figure 5 [18] confirms the existence of bentonite in coals: the bands at 1034 cm^{-1}, 520 cm^{-1} and 465 cm^{-1} are attributed to Si-O stretching for Si-O-Al bending [19]. Absorption in the range 2500-3500 cm^{-1} refers to the OH groups of both bentonite and water compounds. The bands in spectrum 3 (Figure 5) at 2972 cm^{-1} and 2900 cm^{-1} are attributed to the C-H groups of vitamin C which was retained by coal. The intensive band at 1658 cm^{-1} (spectrum 3, Figure 5) is attributed to the stretching vibrations of C = C in lactone ring. And the bands at 1139, 1111 1075 1043 cm^{-1} are attributed to C-O-C stretch [20]. If we compare spectra 2 and 3 in Figure 5, the band at 1658 cm^{-1} disappears (spectrum 2). This indicates that one of the chemical bonds in C = C breaks. So in the phase of activated carbon the ascorbic acid oxidizes, turning into dehydroascorbic acid according to Scheme [21, 22]. The change in entropy depends on the nature of carbon and is minimal for sorption on Granucol FA (51.54 J/K) and maximum for AC-C (200.6 J/K).



Scheme of the conversion of vitamin C to dehydroascorbic acid.

The increase in entropy also confirms the possibility of a change in the structure of vitamin C molecules on carbon. The entropy of the sorption process for each coal practically does not depend on the temperature.

3,3. Thermogravimetric analysis

The thermogravimetric (TG), derived thermogravimetric (DTG) and differential thermal analysis (DTA) is a simple but highly precise and reproducible technique, which requires small amounts of sample and a short time to record and interpret the results. This technique is frequently used to characterize different types of activated carbon [23-27], but can also be used to highlight the characteristics of adsorption processes [28-30] and to identify the conditions for regeneration of adsorbent materials [31, 32]. In this study, TG, DTG and DTA analyses were used to characterize adsorbents, evaluate the sorption of vitamin C and obtain information on the possibility of heat treatment for regeneration of activated carbon.

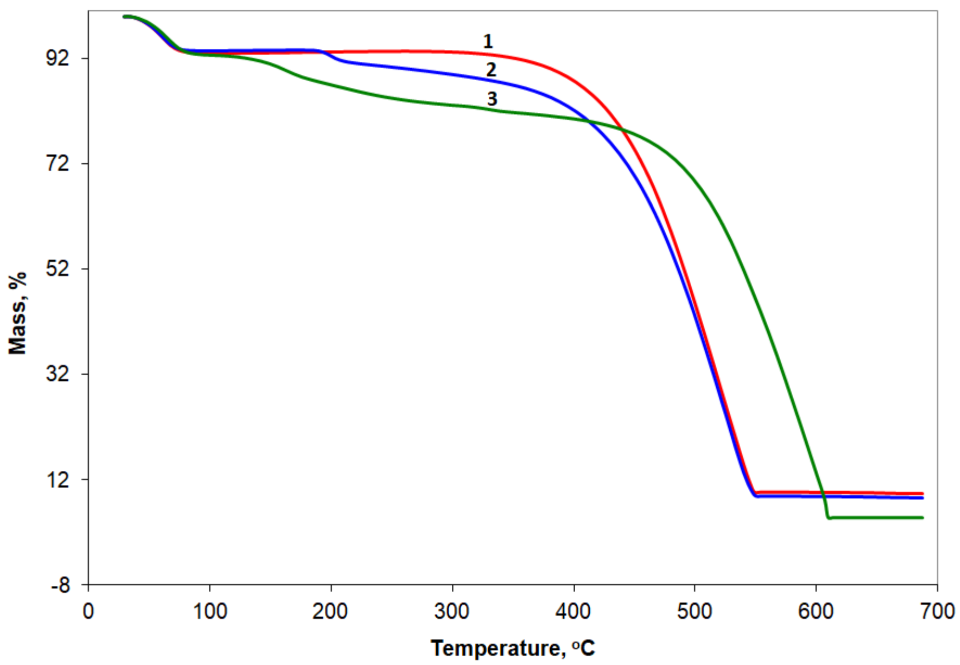


Figure 6. The TG curves of AC-C coal without vitamin C (1), mixed with vitamin C (2) and of coal that retained vitamin C from solution (3), obtained in the range of 25-700 °C

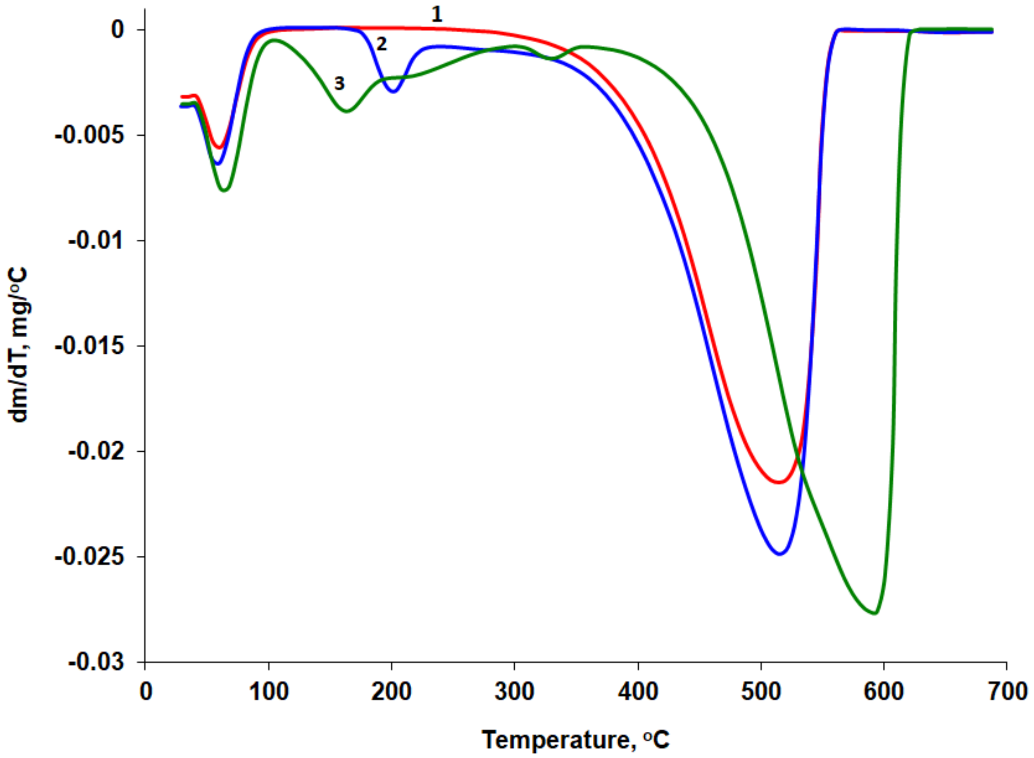
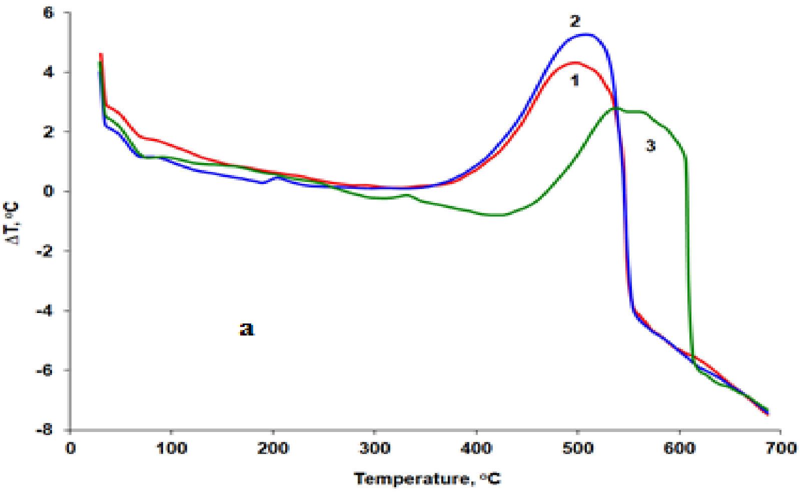


Figure 7. The DTG curves of AC-C coal without vitamin C (1), mixed with vitamin C (2) and of coal that retained vitamin C from solution (3), obtained in the range of 25-700 °C

Figures 6- 14 presents TG, DTG and DTA curves obtained for different types of activated carbon, mixture of activated carbon with vitamin C and activated carbon on which the sorption of vitamin C was performed in a comparative manner. Their evaluation using the STAR[e] version 9.10 software allowed the establishment of the main thermogravimetric characteristics presented in Table 3.



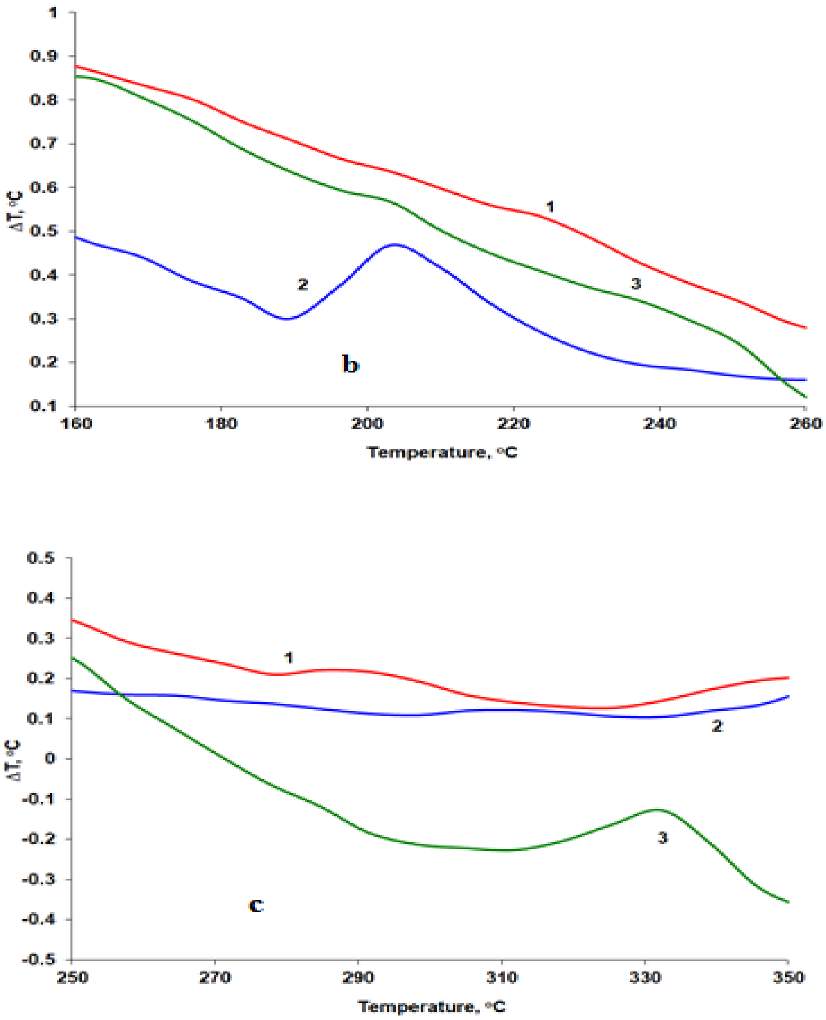


Figure 8. The DTA curves of AC-C coal without vitamin C (1), mixed with vitamin C (2) and of coal that retained vitamin C from solution (3), obtained in the range of 25-700 °C (a), 160-260 °C (b) and 250-350 °C (c).

Table 2. The main thermogravimetric characteristics

Activated carbon	Sample preparation	Stage	T_{onset}[a], °C	T_{peak}[b], °C	T_{endse}[c], °C	W^d, %	Residue %	DTA characteristics
Granucol FA	without vitamin C	I	55	73	89	14.43	18.82	endo
		II	454	540	589	66.75		exo
	adsorbed vitamin C	I	50	70	90	12.64	17.61	endo
		II	135	149	252	1.43		endo
		III	443	537	584	68.32		exo
	without vitamin C	I	54	77	99	15.43	16.39	endo
		II	463	548	599	68.18		exo

Granucol BI	mixed with vitamin	I	55	75	92	11.43	14.98	endo
		II	195	208	223	13.42		endo/exo
		III	448	544	595	60.17		exo
	adsorbed vitamin C	I	52	69	87	11.86	17.57	endo
		II	135	146	239	1.33		endo
		III	451	542	589	69.24		exo
Granucol GE	without vitamin C	I	54	78	93	17.83	14.84	endo
		II	460	549	599	67.33		exo
	adsorbed vitamin C	I	53	75	91	14.85	13.86	endo
		II	136	151	248	2.12		endo
		III	468	546	591	69.17		exo
AC - C	without vitamin C	I	46	59	73	6.97	8.53	endo
		II	414	516	547	84.50		exo
	mixed with vitamin	I	45	58	72	6.47	8.16	endo
		II	192	201	225	5.07		endo/exo
		III	416	517	547	80.30		exo
	adsorbed vitamin C	I	51	64	80	7.39	4.69	endo
		II	138	161	258	9.48		endo
		III	315	329	346	2.14		exo
		IV	476	596	610	76.30		exo

[a]The temperature at which the thermal decomposition begins; [b]the temperature at which the degradation rate is maximum; [c]the temperatureat which the thermal decomposition process ends; [d]mass losses percentage in each stage;

According to the results presented, there are two to four stages of percentage weight loss. In the case of AC-C coal without vitamin C, there is a mass loss of 6.97 % in the first stage, corresponding to the removal of moisture. The process of coal combustion takes place in the temperature range 414-547 °C. This is a strong exothermic process as shown in Figure 8 and is accompanied by a mass loss of 84.50 %. At the end of the recording of the thermogravimetric curves, an amount of residue of 8.53 % . In addition to the steps presented above, for the AC-C mixed with vitamin C test there is also a stage of thermal decomposition in the temperature range 192-225 °C, which can be associated, according to the literature [33-35], with the degradation of vitamin C. From the figure 8 (b) we find that an endothermic effect occurs, closely followed by an exothermic process. Jelić et al. [36] associated this endothermic process with the melting of vitamin C excipients. The temperature at which the decomposition rate is maximum in the second stage for coals mixed with vitamin C is 201 °C and is identical to that reported by Jelić et al. [36] at the same heating rate and working atmosphere. According to studies by Jelić et al. [36], the amount of residue for the decomposition in air of vitamin C at the rate of 10°C/min, at a temperature of 700 °C, is 0.61 %. By applying the EGA IAMS (Evolved Gas Analysis Ion Attachment Mass Spectrometry) technique, Juhász and others [35] established that the main decomposition product of vitamin C is dehydro-L-ascorbic acid. In the case of the AC-C coal sample that retained vitamin C from the solution, four stages of thermal decomposition are highlighted. Stages II and III correspond to the degradation of vitamin C retained on AC-C coals. According to the study presented by Jelić et al. [36], the figure 8 (c) in this study is identified from the DTA curve, the temperature of 332 °C, which corresponds to the carbonization process. Coal combustion takes place at a higher temperature than in the case of AC-C coal without vitamin C, and AC-C mixed with vitamin C and is accompanied by a strong exothermic effect. We also find a much lower amount of residue compared to the original activated carbon and the sample in which the coal was mixed with vitamin C. This behavior is not highlighted in the case of other type of activated carbon on which vitamin C was retained from the solution. The shift to higher temperatures by about 70 °C of the last degradation stage and the decrease in the amount of residue obtained confirms the possibility of structural modification of vitamin C molecules adsorbed on this type of activated carbon. This aspect was highlighted in the previous sections of this study by increasing the entropy and increasing the pH of the vitamin C solution. In the case of Granucol BI coal mixed with vitamin C (Figures 9 and 10, Table 3), the second stage, in which a mass loss of 13.42% occurs, may be associated with the breakdown of vitamin C. For Granucol BI coal on which vitamin C was retained, in the temperature range 135-239 °C, there appears a small loss of mass that can also be associated with the degradation of vitamin C.

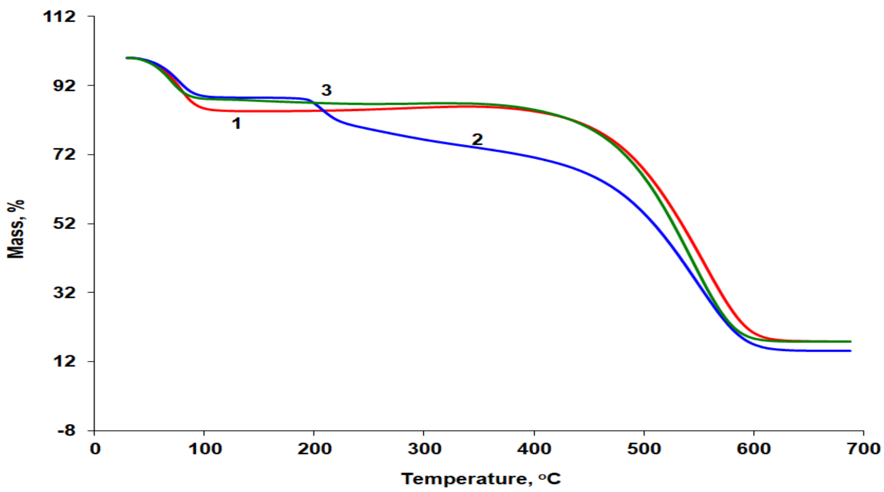


Figure 9. The TG curves of Granucol BI coal without vitamin C (1), mixed with vitamin C (2) and of coal that retained vitamin C from solution (3), obtained in the range of 25-700 ºC.

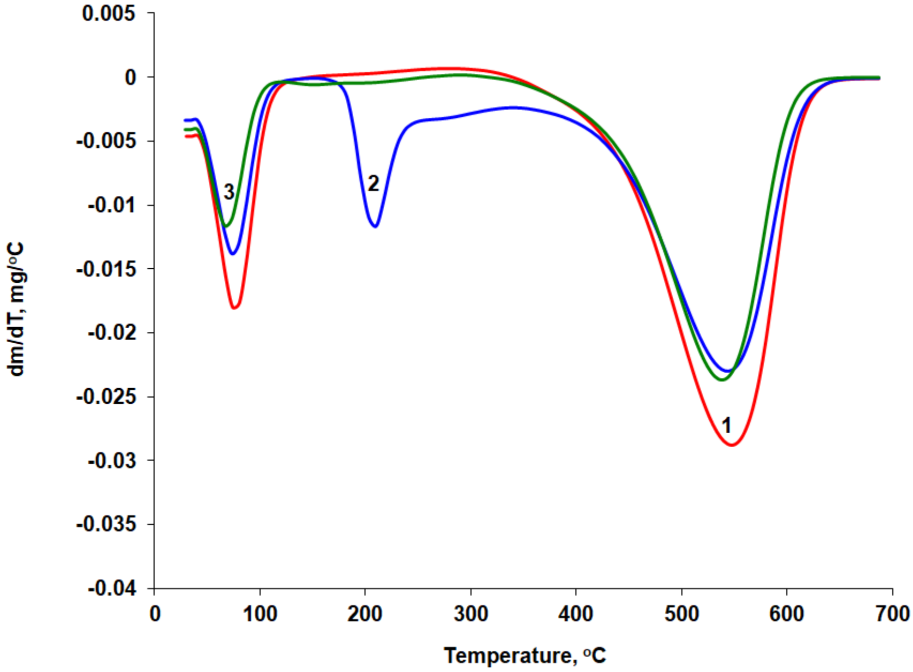
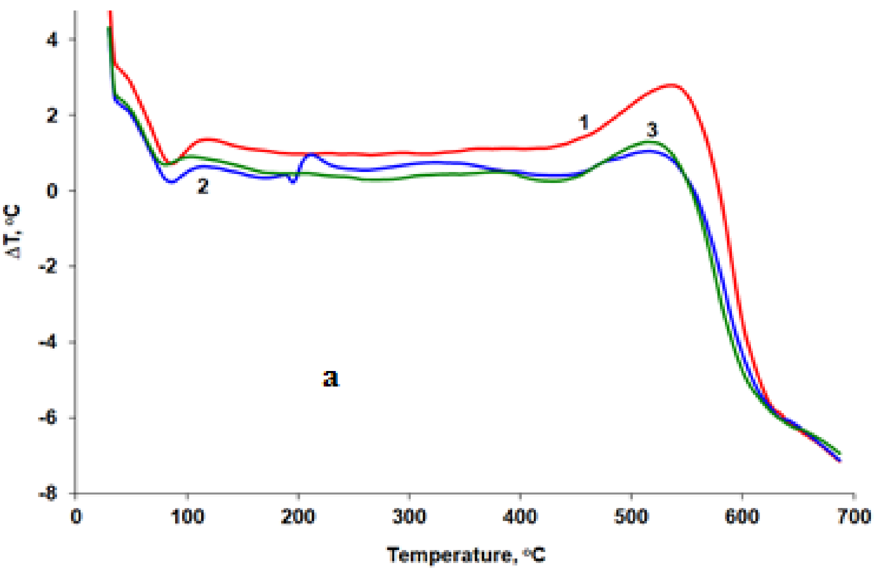


Figure 10. The DTG curves of Granucol BI coal without vitamin C (1), mixed with vitamin C (2) and of coal that retained vitamin C from solution (3), obtained in the range of 25-700 °C



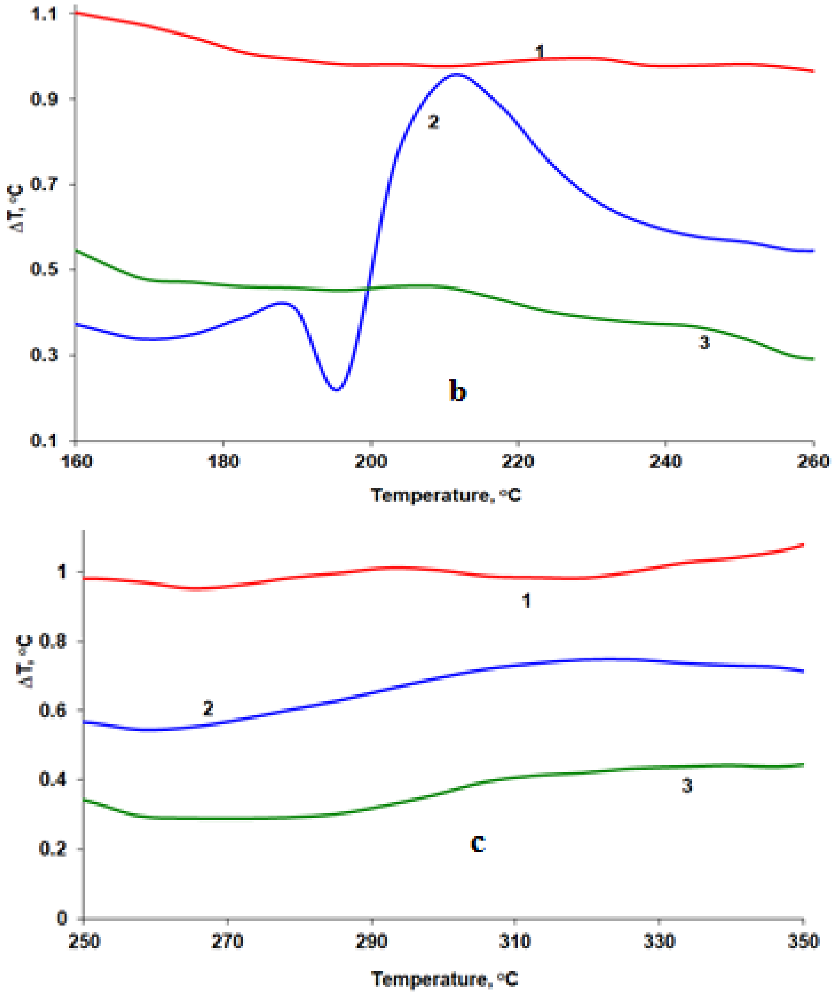


Figure 11. The DTA curves of Granucol BI coal without vitamin C (1), mixed with vitamin C (2) and of coal that retained vitamin C from solution (3), obtained in the range of 25-700 ºC (a), 160-260 ºC (b) and 250-350 ºC (c).

The amount of vitamin C retained on this type of coal is lower and we find that there is no evidence of weight loss in the temperature range 300-350°C, as encountered in the case of the AC-C coal on which vitamin C was retained. Only a small exothermic peak is observed in the DTA (curve c) shown in Figure 11. The same observations can be found for GE and FA coals on which vitamin C was retained. For Granucol GE coal on which vitamin C was retained, the mass loss in the range 136-248 °C is 2.48 %, and for Granucol FA coals is 1.43 % in the range 135-252 °C. Figures 12-14 and Table 3).

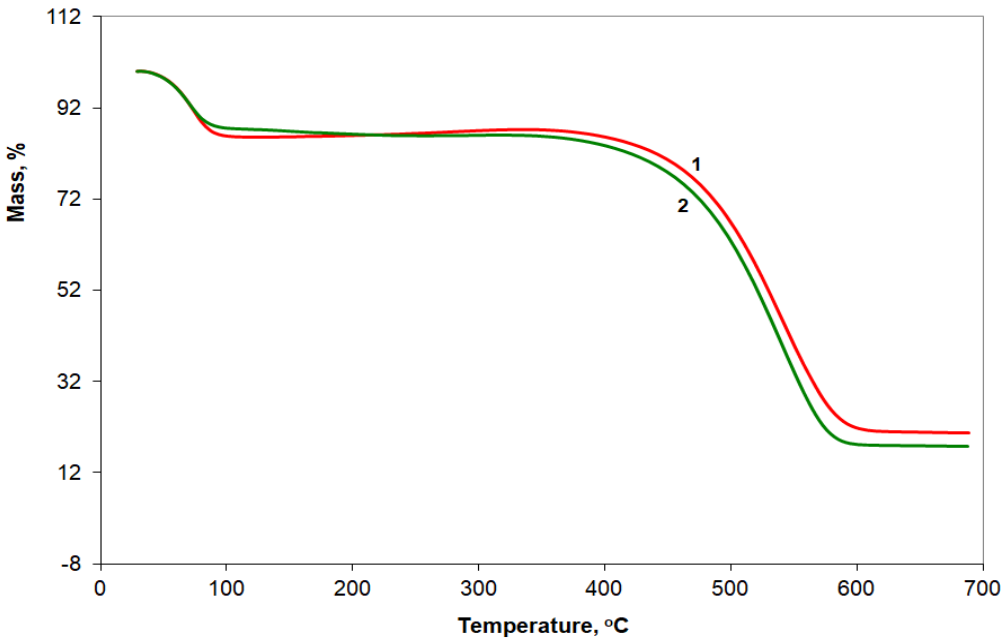


Figure 12. Comparative TG curves for Granucol FA coals before (1) and after sorption vitamin C (2).

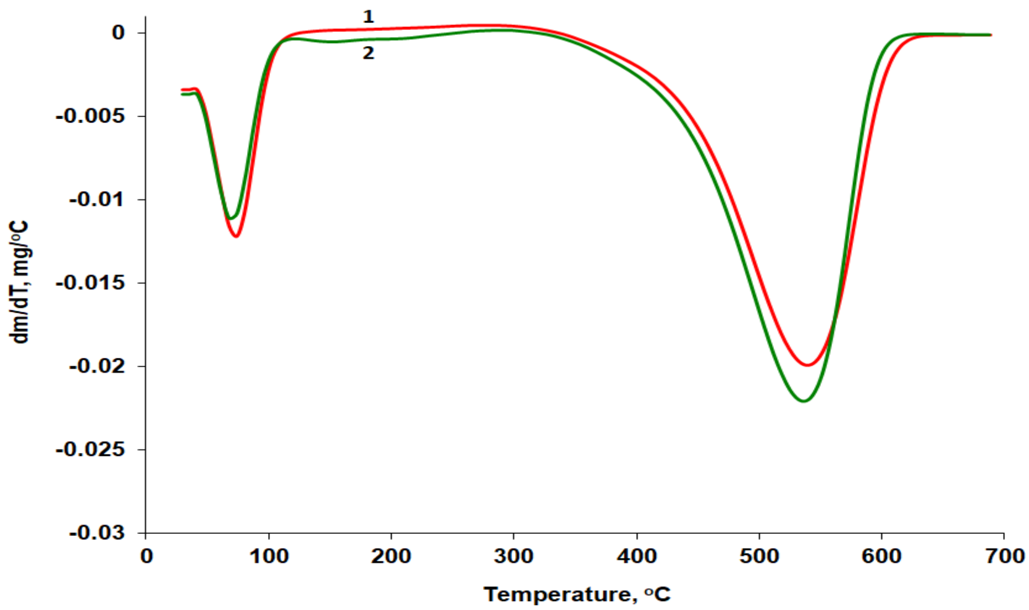


Figure 13. The DTG curves of Granucol FA coal without vitamin C (1), and of coal that retained vitamin C from solution (2), obtained in the range of 25-700 °C

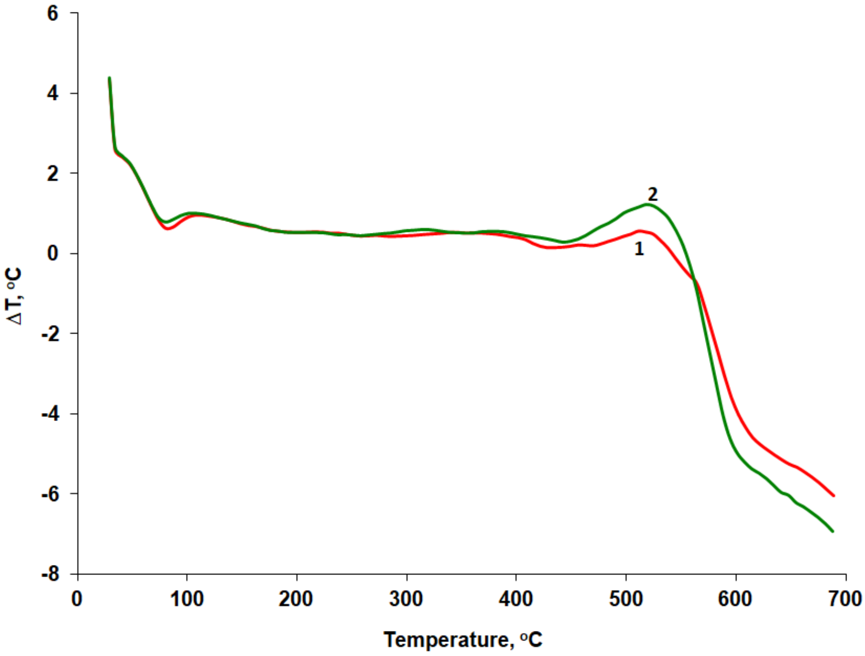


Figure 14. The DTA curves of Granucol FA coal without vitamin C (1) and of coal that retained vitamin C from solution (2).

The TG, DTG and DTA curves for Granucol GE coal are similar to those of Granucol FA. The results obtained are consistent with the values of the specific adsorption capacities obtained for the different types of activated carbon analyzed. The thermogravimetric curves recorded for the activated carbon samples on which vitamin C was retained indicate that the regeneration of the adsorbent materials can be achieved by calcination at a temperature of 350 °C.

4. CONCLUSION

The sorption of vitamin C on the activated commercial carbons Granucol BI, Granucol GE, Granucol FA and the carbon obtained in the laboratory of the Institute of Chemistry of the Academy of Sciences of Moldova, AC-C were investigated. Sorption at 25 °C is higher than at 35 °C, which indicates that adsorption is a physical process determined predominantly by dispersion forces. The sorption capacity of the coals is quite high, reaching up to 433.2 mg/g for AC-C at 25 ^{o}C. Increased absorption capacity may be caused by partial transformation (oxidation) of vitamin C into dehydroascorbic acid during contact of the solution with coal. During the sorption, the pH changes, especially in the case of AC-C coal. Vitamin C sorption isotherms obtained at 25 and 35 ^{o}C are better described by the Langmuir model than by the Freundlich sorption model. The change in thermodynamic functions shows that sorption is a spontaneous and endothermic process. The thermogravimetric analysis indicates the best adsorption capacity for AC-C coals. It has been established that by applying this method of analysis, the regeneration of adsorbent materials can be achieved by calcination at a temperature of 350 °C.

ETHICS APPROVAL AND CONSENT TO PARTICIPATE

Not applicable.

HUMAN AND ANIMAL RIGHTS

No Animals/Humans were used for studies that are base of this research.

CONSENT FOR PUBLICATION

Not applicable.

AVAILABILITY OF DATA AND MATERIALS

The author confirms that the data supporting the findings of this research are available within the article.

FUNDING

This research was carried out with the financial support of the National Agency for Research and Development, Chisinau, Moldova. (Grant number 20.80009.7007.21).

ACKNOWLEDGEMENT

The authors are grateful to Dr. Oleg Petuhov for the coals.

CONFLICT OF INTEREST

The authors have no conflict of interest.

REFERENCES

1. Kasper DL, Braunwald E, Hauser Stephen, Longo Dan, Fauci AS. Harrison's Principles of Internal Medicine. 16th ed. NY: McGraw-Hill, 2005.
2. Lîsîi L. Medical Biochemistry. Nicolae Testemiţeanu University of Medicine and Pharmacy, Chisinau, 2007 (In Romanian).
3. Al-Achi A, Greenwood R, Nzazi. G. Pharmaceutical profile of vitamin C tablets and capsules. Int J Pharm Compd. 2000 Sep-Oct; 4(5):400-3.
4. Gęgotek A, Ambrożewicz E, Jastrząb A, Jarocka-Karpowicz I, Skrzydlewska E. Rutin and ascorbic acid aooperation in antioxidant and antiapoptotic effect on human skin keratinocytes and fibroblasts exposed to UVA and UVB radiation. Arch Dermatol Res. 2019 Apr; 311(3):203-219.
5. Yasir Mehmood, Hammad Yousaf, Irfan Bashir. Formulation and evaluation of chewable modified-release tablet containing sodium fluoride and vitamin C. Int J Pure App Biosci. 2015 March - Apr; 3:95-104.
6. Jurkovič P, Šentjurc M, Kristl J, Pečar S, Gašperlin M. Comparison of two ascorbic acid derivatives effectiveness for scavenging ultraviolet-induced free radicals in the skin. J Drug Del Sci Tech. 2004 Dec; 14: 229-233.
7. Mateus A, Torres J, Marimon-Bolivar W, Pulgarín L. Implementation of magnetic bentonite in food industry wastewater treatment for reuse in agricultural irrigation. Water Resource Industry. 2021 Dec; 100154.

8. Pryadikhina A, Rozhnov A, Tretyak L, Kenijz N, Denisov D. Prevention of non-enzymatic browning of white grape wines by activated carbons Granucol. 2021 IOP Conf. Ser.: Earth Environ. Sci. 848 012012.
9. Shkolnikova MN, Rozhnov ED, Pryadikhina AA. Effects of Granucol activated carbons on sensory properties of sea-buckthorn (Hippophae rhamnoides L.) wines. Foods Raw Mater. 2019 Jun; 7: 67-73.
10. https://erbsloeh.com/fileadmin/user_upload/pdf/Wine/technical_data_sheet/GB/granucol_bi_fa_ge-wine-juice-beer-technical_data_sheet-english-erbsloeh.pdf. (24.03.202).
11. Petuhov O, Timbaliuc N, Mustuc M, Lupascu T. Kinetic and thermodynamic study on adsorption of vitamins B1 and B3 by activated carbons, Ukrainian conference with international participation «Chemistry, physics and technology of surface». May 26-27, 2021, Kyiv, Ukraine.
12. https://borkezeles.hu/site/download?id=585
13. Langmuir I. The adsorption of gases on plane surfaces of glass, mica and platinum. J Am Chem Soc., 1918; 40:1361–1403.
14. Freundlich HMF. Over the adsorption in solution. J Phys Chem. 1906; 57:385–471.
15. Hall K, Eagleton LC, Acrivos A, Vermeulen. T. Pore and solid diffusion kinetics in
16. fixed bed adsorption under constant pattern conditions. Ind En. Chem Fundam. 1966; 5: 212–223.
17. Ho YS. Review of second-order models for adsorption systems. J Hazard Mater. 2006 Aug; 136: 681–689.
18. Sodikova ShA, Makhkamova DN, Usmonova ZT. Universum: Tekh. Nauki: Elektron. Nauchn. Zh., 2019, no. 6. https://universum.com/ ru/tech/archive/item/7515. Accessed March 14, 2022.
19. Gutsanu B, Baerle N. Interaction of L-Ascorbic Acid with Activated Carbon: Kinetic Studies and the Effect of pH. Colloid J. 2022 Apr; 84: 353-363.
20. Benguella B, Yacouta-Nour A. Adsorption of bezanyl red and nylomine green from aqueous solutions by natural and acid-activated bentonite . Desalination. 2009 Jan; 235: 276-292.
21. Yohannan Panicker C, Hema Tresa Varghese, Daizy Philip. FT-IR, FT-Raman and SERS spectra of vitamin C. Spectrochimica Acta Part A. 2006 Aug;. 65: 802-804.
22. Shabbar Abbas, Chang Da Wei , Khizar Hayat, Zhang Xiaoming. Ascorbic acid: microencapsulation techniques and trends—A Review. Food Rev. International. 2012 Oct; 28(4): 343-374
23. Gerald F, Combs Jr, McClung JP. The vitamins. Fundamental aspects in nutrition and health. Chapter 10 - Vitamin C. Fifth Edition, Elsevier. 2017.
24. Arroyo-Gómez JJ, Villarroel-Rocha D, de Freitas-Araújo KC, Martínez-Huitle CA, Sapag K. Applicability of activated carbon obtained from peach stone as an electrochemical sensor for detecting caffeine. J Electroanal Chem. 2018 Aug; 822: 171–176.

25. Arias-Niquepa RA, Prías-Barragán JJ, Ariza-Calderón H, Rodríguez-García ME. Activated carbon obtained from bamboo: Synthesis, morphological, vibrational, and electrical properties and possible temperature sensor. Phys Status Solidi A. 2019 Feb; 216: 1800422.
26. Wazir AH, Wazir IU, Wazir AM. Preparation and characterization of rice husk based physical activated carbon. Energy Sources A. 2020 Jan; 42: 1-11.
27. Daiem MA, Alotaibi AA, Alosime EM, Zaidi B, Said N. Structural-property relationship in activated carbon synthesized from rice straw for electronic application. Pol J Environ Stud. 2020 Jun; 29: 3535-3547.
28. Bazan A, Nowicki P, Połrolniczak P, Pietrzak R, Thermal analysis of activated carbon obtained from residue after supercritical extraction of hops. J Therm Anal Calorim. 2016 Apr; 125: 1199–1204.
29. Velasco LF, Ania CO. Understanding phenol adsorption mechanisms on activated carbons. Adsorption. 2011 Feb; 17: 247–254.
30. Dittmann D, Eisentraut P, Goedecke C, Wiesner Y, Jekel M. et al. Specific adsorption sites and conditions derived by thermal decomposition of activated carbons and adsorbed carbamazepine. Scientific Reports. 2020 Apr; 10:6695
31. Krahnstover T, Plattner J, Wintgens T. Quantitative detection of powdered activated carbon in wastewater treatment plant effluent by thermogravimetric analysis (TGA), Water Research. 2016 Sept; 101: 510 -518.
32. Tancredi N, Medero N, Möller F, Píriz J, Plada C, at al. Phenol adsorption onto powdered and granular activated carbon, prepared from *Eucalyptus* wood. J Colloid Interface Sci. 2004 Nov; 279: 357–363.
33. Ozsoy DH, Van Leeuwen J. Removal of color from fruit candy waste by activated carbon adsorption. J Food Eng. 2010 Jun; 101: 106–112
34. Márta Juhász, Yuki Kitahara, Seiji Takahashi, Toshihiro Fujii. Thermal stability of vitamin C: Thermogravimetric analysis and use of total ion monitoring chromatograms. J Pharmaceut Biomed Analysis. 2012 Febr; 59: 190– 193.
35. Shi Jingyan, Liu Yuwenb, Wang Zhiyong, Wang Cunxin. Investigation of thermal decomposition of ascorbic acid by TG-FTIR and thermal kinetics analysis. J Pharmaceut Biomed Analysis. 2013 Apr; 77: 116– 119.
36. Márta Juhász, Yuki Kitahara, Toshihiro Fujii, Thermal decomposition of vitamin C: An evolved gas analysis_ion attachment mass spectrometry study. Food Chemistry. 2011 Nov; 129: 546–550.
37. Jelić D, Dukić-drvar A. Non-isothermal degradation of vitamin C by simultaneous thermogravimetric and differential thermal analysis. Quality life. 2014; 5(3-4):98-106.