

COMPARATIVE STUDY OF THE LOCAL VEGETABLE ACTIVATED CARBON WITH COMMERCIAL ONES FOR ADSORPTION OF METHYLENE BLUE

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Abstract. Activated carbons have great applicability in the conditioning of wines: discoloration, removal of foreign taste and smell, correction of organoleptic parameters, etc. The purpose of this work was to compare the structural and sorption characteristics of local vegetal activated carbon obtained from apricot stones (AC-C, Republic of Moldova) with that of commercial activated carbons (Granucol[®] BI/GE/FA, Germany). The physico-chemical characteristics of studied activated carbons have been evaluated by standard methods (nitrogen sorption isotherms, IR spectroscopy, pH value of activated carbons suspension etc.) and the adsorption capacity by using methylene blue dye as a reference substance. Experimental data were analysed by theoretical models: Langmuir and Equilibrium isotherm models, and pseudo-first-order, and pseudo-second-order kinetic models. The adsorption capacity of the local activated carbon (AC-C, 690 mg/g) is higher by 30% than that of activated carbons from Granucol[®] series (approx. 535 mg/g).

Keywords: activated carbon, adsorption, isotherm model, kinetic model, methylene blue.

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Introduction

Activated carbons due to their distinct qualities like high specific surface area, high porosity, and desired surface functionalization have considerable applications in adsorption/separation, pollution removal, water treatment, food and beverages processing, etc. [1,2].

During the production of wines, among the important processes are the technological treatments with adjuvant materials, these being administered with the aim of facilitating the clarification and stabilization of the wine. Today there is a complex of adjuvant substances that are used in the wine industry, differing according to their nature and specific properties. Most of them adsorb macromolecular compounds on their surface or facilitate the formation of conglomerates, which leads to sedimentation and clarification of the wine [3]. Among the adjuvant substances used in winemaking, there are activated carbons, in a wide variety; these act by surface tension (adsorption) and serve not only for clarification, but more often for decolorization and removal of unpleasant odours and tastes from wine. In general, the activated carbons used in

winemaking should meet certain quality criteria, among them are: the brightening power of methylene blue should be 70-75%, ash content 6%, iron content no more than 2% [3].

In winemaking, commercially available activated carbons of Granucol[®] type (FA, BI, GE) (ERBSLÖH, Germany), which are of vegetable origin and contain up to 20% of bentonite in the mixture, have gained a wide spread [4-8]. The activated carbons of Granucol[®] type are especially recommended to decolorize wines and to remove mold, yeast and barrel odours, as well as the extremely offensive mouse odour. Depending on treatment, the activated carbons of Granucol[®] type are applied as follow [4]: Granucol[®] FA – for the elimination of reddish off-colours due to browning reactions; Granucol[®] BI – for the reduction of tannins and polyphenols and for the elimination of brownish high-colour; Granucol[®] GE – for the off-taste and off-odours adsorption.

The practice of using different organic substances as reference materials for testing adsorbents and evaluating their adsorption capacity is quite widespread. Among others methods, the methylene blue test has become

popular because it is easily applicable, needs no special equipment and yield accurate results. Methylene blue is a basic dye belonging to the group of quinone imine dyes, containing a phenothiazine ring. In aqueous solutions, methylene blue is in the form of a cation with aligned bonds and has an affinity for materials of amphoteric nature [9]. Methylene blue dye has been used for determining surface specific area of various materials for several decades [9].

The present work aimed to compare the adsorption properties of a local vegetal activated carbon obtained from apricot stones (AC-C, Republic of Moldova) with that of commercial activated carbons (Granucol[®] BI/GE/FA, Germany) used in winemaking by using methylene blue as model compound. Here are presented the preliminary results.

Experimental

Materials

Commercially available activated carbons (AC) used in winemaking of Granucol[®] type (FA, BI, GE) (ERBSLÖH, Germany) and a sample of activated carbon obtained in the laboratory from apricot stones by physico-chemical method with water vapours on a fluidized bed reactor (AC-C) (Laboratory of Ecological Chemistry, Institute of Chemistry [10]) were used for the research. The activated carbons from the Granucol[®] series have the following granulometric composition: >125 μm (0%); 90÷125 μm (cca. 14%); 56÷90 μm (cca. 27%); 45÷56 μm (cca. 46%); <45 μm (cca. 13%). In the experiments, the Granucol[®] series activated carbons (FA, BI, GE) were used in their initial form, and the activated carbon obtained in the laboratory, AC-C, was crushed and the working fraction between 45÷125 μm was selected.

Methylene blue (MB) dye was purchased from Fluka. MB is a cationic dye with a molecular mass of $M = 319.85 \text{ g/mol}$ and molecule size of $1.69 \times 0.74 \times 0.38 \text{ nm}$, it is stable and often used as a standard dye/sorbate for determining the sorption characteristics of adsorbents towards organic molecules or dyes (Figure 1) [9].

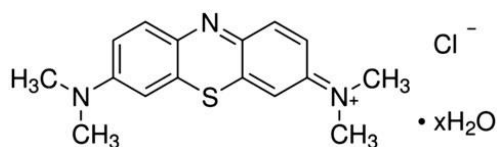


Figure 1. The structural formula of methylene blue [9].

Methods

Some physico-chemical characteristics of the activated carbons (humidity, ash content and pH value of the activated carbon suspension) were determined by standard methods [11]. In brief, the activated carbon *humidity* (U, %) was determined by drying the samples in an oven at a temperature of 110°C until the constant mass; the *ash* (A, %) content was determined by calcination of the activated carbon samples in an oven at 850°C until the constant mass; the *pH value of the activated carbon suspension* was determined by equilibrating 0.1 g of activated carbon with 100 mL double-distilled water (solid:liquid ratio 1:1000) and recording the pH value of the suspension after 24 h of contacting-stirring.

Textural parameters of the activated carbons were determined from the adsorption isotherms of nitrogen at 77 K by means of the AUTOSORB-1MP equipment (Quantachrome) [12]. The specific surface area (S_{BET}) was determined using the Brunauer–Emmett–Teller (BET) equation. The total pore volume (V_{total}) was determined from the amount of nitrogen gas adsorbed at the relative pressure of 0.99. In order to determine the volume of the micropores (V_{micro}) the *t*-method was used, while the volume of mesopores (V_{meso}) was calculated from the difference between the total volume and the volume of micropores. The NLDFT (Non-Linear Density Function Theory) equilibrium model was employed for evaluating the effective (predominant) radius of the pores and the distribution of the pores volumes as a function of the pores radii.

Infrared (FTIR) spectra of activated carbons were recorded on the FT-IR Spectrometer Spectrum 100 (PerkinElmer, USA) in ATR mode.

Adsorption of methylene blue. MB stock solution was prepared by dissolving a weighed quantity of $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$ in distilled water and MB solutions in range of 50–1000 mg/L were obtained by diluting the stock solution.

The adsorption process of methylene blue was studied under static conditions; the adsorption isotherms were determined from aqueous solutions at room temperature by contacting the dry activated carbon samples with a solution of the methylene blue of different concentrations (in ascending order) at the same solid: liquid ratio (1:1000), under stirring for a reasonable period of time in order to reach the adsorption equilibrium. Temperature was controlled by a thermostatic bath and monitored throughout each experiment (temperature meter WTW 538). The equilibrium concentrations of methylene blue were

determined with the JENWAY 6505 UV-Vis spectrophotometer at $\lambda = 665$ nm (after separation of phases by filtration), and the adsorption value, expressed in mg/g, was calculated from Eq.(1).

$$a = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

where, C_0 is the initial concentration of MB (mg/L);
 C_e the equilibrium concentration of the MB (mg/L);
 V is the volume of contact solution (L);
 m the mass of the dry activated carbon (g).

The kinetic and equilibrium experimental data of methylene blue on activated carbons were correlated by using the pseudo-first-order kinetic model (Lagergren) [13], pseudo-second-order kinetic model (Ho and McKay) [14], Langmuir isotherm [15] and Freundlich isotherm [16]. The general expressions of the theoretical models are presented in Eqs.(2)-(6) (Table 1).

The evaluation of *specific surface area* (S_{MB} , m^2/g) of adsorbents can be performed by determining the maximal adsorption of methylene blue on the adsorbent surface, using the Eq.(7).

$$S_{MB} = \frac{a_{max} * N_A * A_{MB}}{M_{MB}} \quad (7)$$

where, $a_{max} = Q_0$ which is the methylene blue adsorption capacity in the monolayer

(mg/g) at 25°C, determined from Langmuir isotherm;

A_{MB} is the area occupied by one methylene blue molecule (m^2 per molecule);

N_A is the Avogadro number ($6.02 \cdot 10^{23}$ molecules per mol);

M_{MB} is the methylene blue molar mass (319.85 g/mol).

Results and discussion

Characterization of activated carbon samples

The activated carbon samples from the Granucol® series (FA, BI, GE) have a low moisture content, 2-3%, ash content of 16-20%, and the surface of the activated carbons is slightly acidic, being in accordance with the values presented in the technical passport of these carbons (Table 2) [4]. Unlike the activated carbon samples from Granucol® series, the local activated carbon (AC-C) has a low ash content (approx. 6%), and the surface is weakly basic (Table 2). The characteristics of the porous structure (S_{BET} , V_{micro} , V_{meso} , V_{total}) determined from the nitrogen sorption-desorption isotherms reveal that the activated carbon sample obtained from apricot stones, under laboratory conditions, are very close to those of the activated carbons from the Granucol® series, the specific surface is between the values 1220-1385 m^2/g , the total volume of the pores 0.95-1.2 cm^3/g , and the share of mesopores is approx. 65-70% of the total pore volume (Table 3, Figures S1-S4).

Table 1

Descriptions of applied mathematical models.

Theoretical model	Mathematical expression	Description	Eq. no.	Ref.
Pseudo-first-order kinetic model (Lagergren)	$\frac{dq_t}{dt} = k_1(q_e - q_t)$	q_t and q_e are the amount of adsorbate sorbed per mass of sorbent (mg/g) at any time and equilibrium, respectively; k_1 is the rate constant (min^{-1}).	(2)	[13]
Pseudo-second-order kinetic model (Ho and McKay)	$\frac{dq_t}{dt} = k_2(q_e - q_t)^2$	k_2 is the rate constant, q_t is the adsorbate uptake capacity at any time t .	(3)	[14]
Langmuir	$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e}$	q_e is the adsorption capacity (mg/g); C_e is the adsorbate concentration at equilibrium (mg/L); K_L is the Langmuir constant of the sorption equilibrium (L/mg); Q_0 is the monolayer formation capacity (mg/g).	(4)	[15]
	Separation factor: $R_L = \frac{1}{1 + K_L C_0}$	C_0 is the initial concentration (mg/L); K_L is Langmuir constant (L/mg).	(5)	
Freundlich	$q_e = K_F C_e^{1/n}$	K_F is the empirical constant that provides information about the adsorption capacity of the sorbent; n is the empirical constant indicating the intensity of the sorption process.	(6)	[16]

The surface chemistry characteristics of studied activated carbons (of Granucol[®] type and AC-C) was analysed by IR spectroscopy. Generally, the IR spectra present characteristic absorptions to activated carbons (Figure S5) [17-19]: (i) the absorptions at approx. 800 cm⁻¹ are attributed to the out-of-plane vibration of the C-H bond [17,19-22]; (ii) the bands in the 1000-1200 cm⁻¹ region are difficult to interpret because these are an overlap of broad bands and can be attributed to the C-O bond in phenols/ethers/esters [17,20,21]; (iii) bands in the range of 1500-1600 cm⁻¹ are attributed to aromatic rings (C=C bonds in the activated carbon skeleton) coupled with strongly conjugated carbonyl (C=O) groups [17-20]; (iv) the absorption (shoulder) at 1700 cm⁻¹ in the spectrum of Granucol[®] FA activated carbon is often attributed to C=O bond vibrations from carboxylic groups, ketones and aldehydes [17,18,22]; (v) the absorptions of low intensity, present in the range 2800-3000 cm⁻¹, are frequently attributed to the CH bond from aliphatic groups CH, CH₂ and CH₃ [19]; (vi) the absorptions in the range 3300-3700 cm⁻¹ are attributed to the OH group from alcohols, phenols and carboxylic acids [17,19,21,22].

Adsorption of methylene blue

Kinetics and adsorption isotherms of methylene blue at different temperatures on activated carbons of Granucol[®] type (FA, BI, GE) are presented in Figures 2-7 and for local activated carbon AC-C in Figures 8 and 9. The concentration of methylene blue decreases rapidly during the first 5–10 min of phase contact, after which the speed of the methylene blue adsorption decreases until a relatively constant value is reached. After 10 minutes of phase contact (at the initial concentration of methylene blue of 500 mg/L) activated carbon Granucol[®] FA adsorbs approximately 80% of MB from the solution, Granucol[®] Bi approximately 50%, Granucol[®] Ge approximately 65%, and activated carbon AC-C adsorbs the most, 90% of methylene blue molecules. As seen from the kinetic curves, the adsorption equilibrium of methylene blue on activated carbons Granucol[®] FA, Granucol[®] GE and AC-C is established after approx. 100 min (Figures 2, 6 and 8), but for Granucol[®] BI the equilibrium is established after approx. 250 min

(Figure 4). The kinetic adsorption curves represent dependencies that are linear at small contact times between phases, and then become curved. According to the literature, this indicates that diffusion within the sorbent grain controls the overall process rate [23].

Table 2

Characterization of activated carbon samples.			
Sample	U*, %	A**, %	pH of AC suspension
Granucol [®] FA	2.23	19.95	4.3
Granucol [®] BI	3.39	19.21	3.8
Granucol [®] GE	1.65	16.76	3.8
AC-C	3.67	5.82	8.8

*U- humidity; **A- ash content

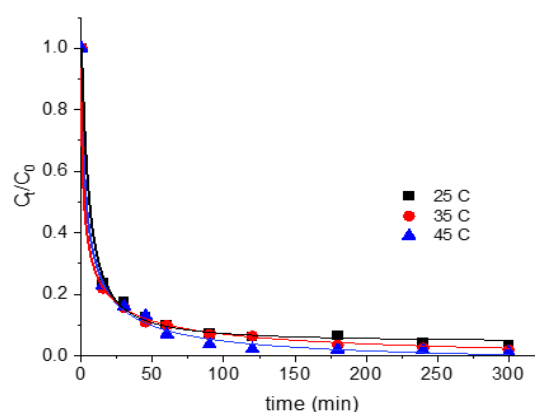


Figure 2. Kinetics of methylene blue adsorption on activated carbon Granucol[®] FA at different temperatures. Solid:liquid ratio - 1:1000.

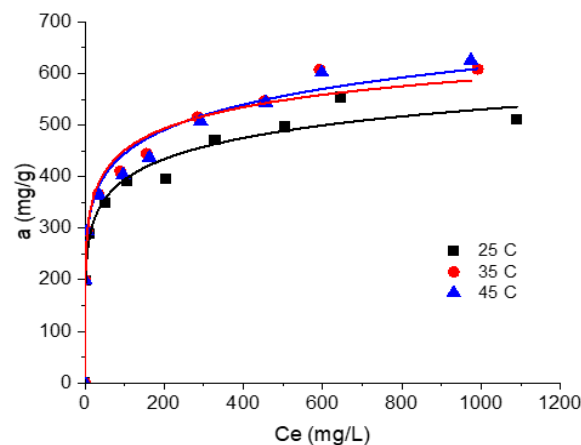


Figure 3. Adsorption isotherms of methylene blue on activated carbon Granucol[®] FA at different temperatures. Solid:liquid ratio - 1:1000; contacting time 5 h.

Table 3

Activated carbons textural parameters determined from nitrogen sorption isotherms.					
Sample	S _{BET} , m ² /g	V _{micro} , m ³ /g	V _{meso} , cm ³ /g	V _{total} , cm ³ /g	V _{meso} , %
Granucol [®] FA	1360	0.347	0.846	1.193	71.0
Granucol [®] BI	1221	0.310	0.693	1.003	69.1
Granucol [®] GE	1384	0.364	0.721	1.085	66.4
AC-C	1385	0.335	0.608	0.943	64.5

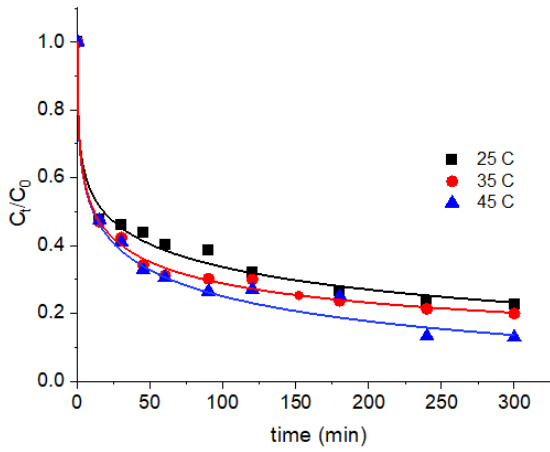


Figure 4. Kinetics of methylene blue adsorption on activated carbon Granuacol® BI at different temperatures. Solid:liquid ratio - 1:1000.

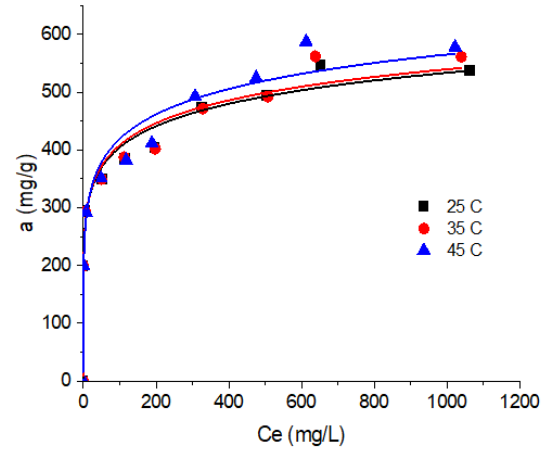


Figure 5. Adsorption isotherms of methylene blue on activated carbon Granuacol® BI at different temperatures. Solid:liquid ratio - 1:1000; contacting time 5 h.

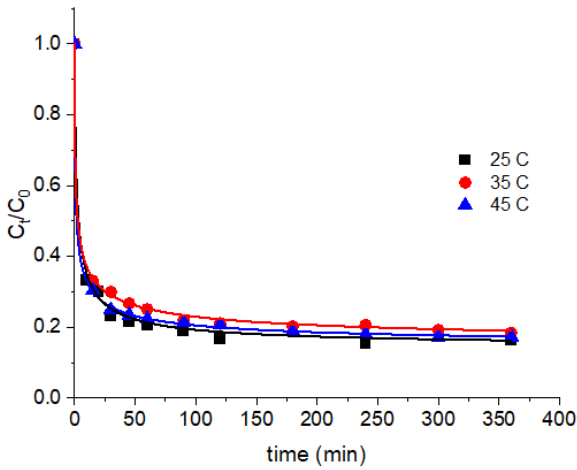


Figure 6. Kinetics of methylene blue adsorption on activated carbon Granuacol® GE at different temperatures. Solid:liquid ratio - 1:1000.

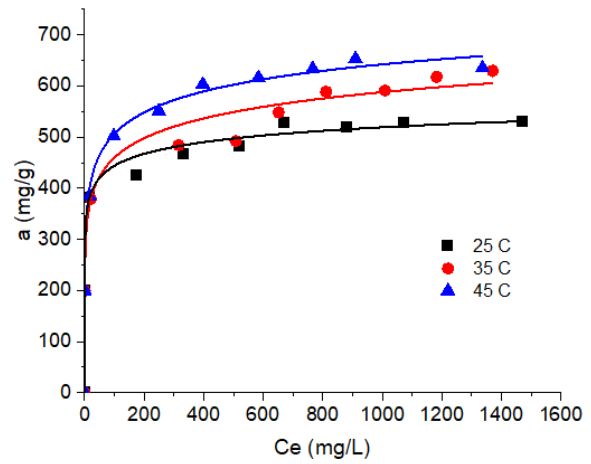


Figure 7. Adsorption isotherms of methylene blue on activated carbon Granuacol® GE at different temperatures. Solid:liquid ratio - 1:1000; contacting time 5 h.

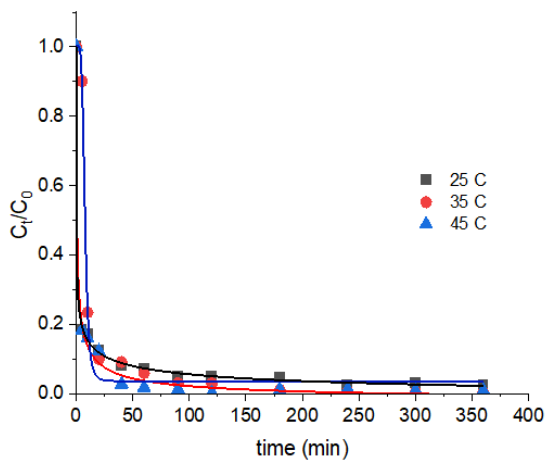


Figure 8. Kinetics of methylene blue adsorption on activated carbon AC-C at different temperatures. Solid:liquid ratio - 1:1000.

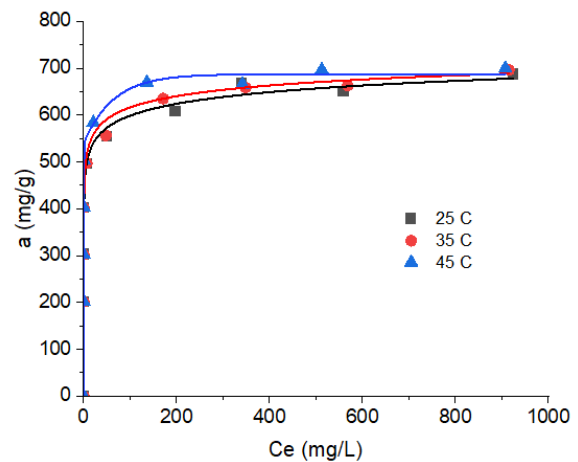


Figure 9. Adsorption isotherms of methylene blue on activated carbon AC-C at different temperatures. Solid:liquid ratio - 1:1000; contacting time 5 h.

The experimental data of methylene blue adsorption on studied activated carbons (Granucol[®] type and AC-C) are very well described by the pseudo-second-order kinetic model, since the calculated adsorption values are close to the experimental ones, and the value of the correlation coefficient (R^2) is close to 1 compared to the adsorption values and R^2 obtained for the pseudo-first-order kinetic model (<0.894) (Tables 4 and 5). According to some authors, the adsorption process of MB on Granucol[®] type activated carbons proceeds in two stages, the first of which is mentioned physical adsorption [24]. Results regarding the adsorption of MB on activated carbons from hazelnut shells and walnut shells indicate that the adsorption process occurs through both physical and chemical adsorption [25,26].

The adsorption isotherms of methylene blue on activated carbons of Granucol[®] series (FA, GE, BI) at temperatures of 25, 35 and 45°C are presented in Figures 3, 5 and 7. The experimental adsorption isotherms for local activated carbon AC-C are presented in Figure 9. According to the results, the adsorption capacity of the studied activated carbons for methylene blue increases with the temperature, but insignificantly.

Furthermore, the adsorption capacity of AC-C activated carbon at 25°C is approximately 30% higher compared to Granucol[®] activated carbons.

The adsorption process of methylene blue dye on activated carbons has been described by the Langmuir and Freundlich adsorption isotherm models, which are mathematical models that describe how the adsorbed substance interacts with the adsorbent, providing information about the nature of interactions between the adsorbate and the adsorbent. In the Langmuir adsorption isotherm model, it is assumed that the maximum adsorption corresponds to a monolayer of molecules saturated on the adsorbent surface. According to this theory, once a molecule has occupied an active site, no further sorption can take place on that site, and possible molecular interactions between active sites of the adsorbent are also excluded [15]. The Freundlich adsorption isotherm model describes non-ideal and reversible adsorption, unrestricted by the formation of a monolayer of adsorbed molecules on the adsorbent surface. The model is used to describe adsorption in heterogeneous systems, taking into account the molecular interactions between active sites as well as those between adsorbate molecules [16].

Table 4

Kinetic parameters for methylene blue adsorption on activated carbons of Granucol [®] type.								
Sample	Temp.	$a(\text{exp.})$ mg/g	Pseudo-first-order kinetic model (Lagergren)			Pseudo-second-order kinetic model (Ho and McKay)		
			$q_e(\text{cal.})$ mg/g	K_1 min^{-1}	R^2	$q_e(\text{cal.})$ mg/g	K_2 g/mg·min	R^2
FA	25°C	483	421	0.668	0.767	490	0.00699	0.983
	35°C	490	406	0.738	0.894	500	0.000875	0.915
	45°C	495	430	0.428	0.875	515	0.000175	0.937
BI	25°C	385	295	0.109	0.789	387	0.00058	0.972
	35°C	400	302	0.096	0.875	390	0.000186	0.972
	45°C	435	352	0.069	0.881	410	0.000082	0.984
GE	25°C	413	420	1.009	0.855	415	0.00285	0.972
	35°C	419	356	0.925	0.865	417	0.00175	0.977
	45°C	425	462	0.875	0.784	429	0.00105	0.995

Table 5

Kinetic parameters for methylene blue adsorption on local activated carbon AC-C.							
Temp.	$a(\text{exp.})$ mg/g	Pseudo-first-order kinetic model (Lagergren)			Pseudo-second-order kinetic model (Ho and McKay)		
		$q_e(\text{cal.})$ mg/g	K_1 min^{-1}	R^2	$q_e(\text{cal.})$ mg/g	K_2 g/mg·min	R^2
25°C	499	415	0.0656	0.879	507	0.00965	0.976
35°C	495	425	0.0996	0.855	510	0.00513	0.982
45°C	520	406	0.0959	0.819	532	0.00098	0.984

The adsorption equilibrium data for methylene blue on studied activated carbons from Granucol[®] series are best described by the Langmuir isotherm model and correlate well with literature data (Table 6) [23,25,26]. According to adsorption isotherms, at temperature of 25°C, the Granucol[®] type samples adsorb approx. 535 mg/g of methylene blue (Figures 3, 5 and 7). The maximum monolayer adsorption capacity of Granucol[®] type activated carbons (calculated according to the Langmuir model) correlates well with values of adsorption capacity obtained experimentally (Table 6). For all activated carbons from Granucol[®] series the R_L value fell within the limits of 0.001÷0.04, which means that the process of adsorption of methylene blue on the studied samples is favourable [23].

The adsorption isotherms of methylene blue dye on AC-C activated carbon were obtained under the same conditions as for the samples from in the Granucol[®] series. The adsorption capacity of the AC-C sample for methylene blue dye at all three temperatures is very close in value, being approximately 690 mg/g. Similarly, close values were obtained from theoretical calculations using the Langmuir adsorption model (Figure 9, Table 7). The separation factor R_L has values

smaller than 1, indicating that the adsorption process of methylene blue dye on AC-C activated carbon is favourable (Table 7). The adsorption capacity for methylene blue of the AC-C activated carbon (690 mg/g) is higher than that of activated carbons from Granucol[®] series (approx. 535 mg/g) by 30%.

It was interesting to evaluate how the amount of dye adsorbed on the activated carbon samples correlates with their surface area. For methylene blue adsorption in monolayer, we can deduce the surface area of activated carbon covered by the dye molecules, which is equal to the total surface area of the adsorbed methylene blue molecules, expressed by Eq.(7). The activated carbon area covered by one molecule of methylene blue may change because attachment may be done with different orientations [27].

The calculated values of the total surface area of the methylene blue molecules adsorbed compared to the S_{BET} value of the studied activated carbons, determined from the sorption-desorption isotherms of nitrogen, are presented in Table 8. The total surface area of the methylene blue molecules adsorbed on activated carbons was calculated using the Q_0 value obtained at 25°C (Tables 6 and 7).

Table 6

Langmuir and Freundlich isotherms constants for adsorption of methylene blue on activated carbons of Granucol[®] type.

Sample	Temp.	$a(exp.)$ mg/g	Langmuir			R_L	Freundlich		
			Q_0 mg/g	K_L L/mg	R^2		K_F	$1/n$	R^2
FA	25°C	535	537	0.664	0.998	0.003	251	0.117	0.989
	35°C	585	581	0.327	0.999	÷	275	0.089	0.914
	45°C	606	613	0.243	0.999	0.039	245	0.107	0.994
BI	25°C	537	533	0.966	0.999	0.001	258	0.096	0.872
	35°C	561	505	0.996	0.999	÷	244	0.105	0.972
	45°C	578	595	0.996	0.998	0.01	242	0.098	0.984
GE	25°C	531	525	1.009	0.999	0.004	247	0.132	0.972
	35°C	605	601	0.248	0.999	÷	271	0.099	0.978
	45°C	658	648	0.218	0.998	0.038	292	0.081	0.996

Table 7

Langmuir and Freundlich isotherms constants for adsorption of methylene blue on activated carbon AC-C.

Temp.	$a(exp.)$ mg/g	Langmuir			R_L	Freundlich		
		Q_0 mg/g	K_L L/mg	R^2		K_F	$1/n$	R^2
25°C	687	671	0.529	0.999	0.00008	325	0.127	0.837
35°C	696	690	0.508	0.999	÷	428	0.066	0.984
45°C	699	693	0.503	0.999	0.019	360	0.113	0.835

According to the obtained results, the (calculated) surfaces covered with methylene blue molecules differs from that the S_{BET} values. For Granucol[®] FA and Granucol[®] GE the value of S_{MB} is smaller than that of S_{BET} and can be explained as follow, due to the dimensions of the methylene blue molecule, pores with dimensions smaller than approximately 1.3 nm² will not be accessible for adsorption. Regarding the activated carbons samples for which were obtained values of S_{MB} higher than that of S_{BET} it can be assumed that methylene blue molecules were adsorbed on the activated carbons surface in more than one orientation (Table 8).

Table 8

Specific surface area calculated from adsorption isotherms of nitrogen (S_{BET}) and methylene blue (S_{MB}).

Sample	S_{BET} , m ² /g	S_{MB}^* , m ² /g			
		S_1	S_2	S_3	
Granucol [®]	FA	1360	1299	564	252
	BI	1221	1304	566	253
	GE	1384	1289	563	252
AC-C	1385	1668	724	323	

*Using for calculations the surface area covered by a molecule of methylene blue of 1.29 nm² (S_1), 0.56 nm² (S_2), and 0.25 nm² (S_3).

The results obtained regarding the adsorption of methylene blue on the studied activated carbons (Granucol[®] type and AC-C) highlight that further research is needed to elucidate the mechanism of methylene blue adsorption. However, comparing the results obtained regarding the physico-chemical characteristics and adsorption capacity of methylene blue of the AC-C activated carbon from apricot stones, obtained under laboratory conditions (Laboratory of Ecological Chemistry, Institute of Chemistry), with those of commercial activated carbons of Granucol[®] type (FA, BI, GE), it can be concluded that AC-C activated carbon can be recommended for applications in winemaking.

Conclusions

The physico-chemical characteristics of new activated carbon from apricot stones AC-C, evaluated by standard methods (nitrogen sorption-desorption isotherms, IR spectroscopy, pH value of activated carbons suspension), are comparative with that of the commercially activated carbons of Granucol[®] type. The surface area (S_{BET}) of AC-C sample is of 1385 m²/g and for activated carbons of Granucol[®] type ranges between 1220-1385 m²/g.

Adsorption studies using methylene blue dye as a reference substance revealed a higher

adsorption capacity of AC-C activated carbon (690 mg/g) by 30% than that of activated carbons from Granucol[®] series (approx. 535 mg/g). Kinetic studies showed that the kinetic data were well described by the pseudo-second-order kinetic model. The adsorption also closely fit the Langmuir isotherm rather than the Freundlich model, suggesting monolayer adsorption rather than multilayer adsorption.

According to the obtained results, the local vegetal activated carbon (AC-C) has proven to be effective compared to commercial ones (Granucol[®] series) in removing methylene blue dye from solutions and can be recommended for further research in order to be used in winemaking.

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Supplementary information

Supplementary data are available free of charge at <http://cjm.ichem.md> as PDF file.

References

- Marsh, H.; Rodriguez-Reinoso, F. Activated Carbon. Elsevier, 2006, 536 p. DOI: <https://doi.org/10.1016/B978-0-08-044463-5.X5013-4>
- Fatma, I.; Assad, H.; Kumar, A.; Hussain, C.M. Food Industry Applications of Activated Carbon. Verma, C.; Quraishi, M.A. Eds. Activated Carbon Progress and Applications. The Royal Society of Chemistry, 2023, pp. 250–267. DOI: <https://doi.org/10.1039/BK9781839169861-00250>
- Tardea, C. Chemistry and analysis of wine. Ion Ionescu de la Brad: Iasi, 2007, 1398 p. ISBN: 978-973-147-004-7 (in Romanian). <https://iuls.ro/universitate/editura-ion-ionescu-de-la-brad/>
- ERBSLÖH Geisenheim GmbH. <https://erbsloeh.com/produkt-kategorie/all-products/sector-wine/>
- Velioglu, Y.S.; Ekici, L.; Poyrazoglu, E.S. Phenolic composition of European cranberrybush (*Viburnum opulus* L.) berries and astringency removal of its commercial juice. International Journal of Food Science & Technology, 2006, 41(9), pp. 1011–1015. DOI: <https://doi.org/10.1111/j.1365-2621.2006.01142.x>
- Shkolnikova, M.N.; Rozhnov, E.D.; Pryadikhina, A.A. Effects of Granucol activated carbons on sensory properties of sea-buckthorn (*Hippophae rhamnoides* L.) wines. Foods and Raw Materials, 2019, 7(1), pp. 67–73. DOI: <http://doi.org/10.21603/2308-4057-2019-1-67-73>

7. Cibuc, M.; Obada, L.; Rusu, E.; Golenco, L.; Nemteanu, S. The influence of used adjuvants of fining grape must on extract of white wine. *Journal „Lucrări Științifice. Seria Horticultură”*, 2013, 56(2), pp. 315–320.
DOI: https://www.uaiasi.ro/revista_horti/files/Nr2_2013/copera_cuprins_Vol-56-2_2013.pdf
8. Soldatenko, E.; Taran, N.; Morari, B.; Soldatenko, O.; Stoleicova, S. Optimization of blend components for improving red sparkling wines production. *Journal of Agroalimentary Processes and Technologies*, 2014, 20(2), pp. 183–187.
DOI: <https://journal-of-agroalimentary.ro/journal-of-agroalimentary-processes-and-technologies-2014-20-2/optimization-of-blend-components-for-improving-red-sparkling-wines-production>
9. Khan, I.; Saeed, K.; Zekker, I.; Zhang, B.; Hendi, A.H.; Ahmad, A.; Ahmad, S.; Zada, N.; Ahmad, H.; Shah, L.A.; Shah, T.; Khan I. Review on methylene blue: Its properties, uses, toxicity and photodegradation. *Water*, 2022, 14(2), pp. 242–272.
DOI: <https://doi.org/10.3390/w14020242>
10. Lupascu, T.; Petuhov, O.; Timbaliuc, N.; Cibotaru, S.; Rotaru, A. Adsorption capacity of vitamin B₁₂ and creatinine on highly-mesoporous activated carbons obtained from lignocellulosic raw materials. *Molecules*, 2020, 25(3), pp. 3095–3106.
DOI: <https://doi.org/10.3390/molecules25133095>
11. STAS 5388-80. Vegetable active carbon. Test methods. Editura Tehnica: Bucuresti, 1980, 18 p. (in Romanian).
12. AUTOSORB AS-1. AS1Win. Gas Sorption System. Operation manual. Firmware: Ver 2.55. AS1Win Software: Version 2.0 and Newer; Quantachrome Instruments: Boynton Beach, FL, USA, 2008.
13. Lagergren, S. About the theory of so-called adsorption of soluble substances. *Kungliga Svenska Vetenskapsakademiens Handlingar*, 1898, 24(4), pp. 1–39.
14. Ho, Y.S.; McKay, G. Pseudo-second order model for sorption processes. *Process Biochemistry*, 1999, 34(5), pp. 451–465.
DOI: [https://doi.org/10.1016/S0032-9592\(98\)00112-5](https://doi.org/10.1016/S0032-9592(98)00112-5)
15. Langmuir, I. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of American Chemical Society*, 1918, 40(9), pp. 1361–1403.
DOI: <https://doi.org/10.1021/ja02242a004>
16. Freundlich, H.; Heller, W. The adsorption of cis- and trans-azobenzene. *Journal of American Chemical Society*, 1939, 61(8), pp. 2228–2230.
DOI: <https://doi.org/10.1021/ja01877a071>
17. Li, B. Characterization of pore structure and surface chemistry of activated carbons – A Review. Salih, S. Ed. *Fourier Transform - Materials Analysis*. InTech, 2012, pp. 165–190.
DOI: <https://doi.org/10.5772/37460>
18. Radovic, L.R. Ed. *Chemistry & Physics of Carbon*. CRC Press: Boca Raton, 2007, 30, 264 p.
DOI: <https://doi.org/10.1201/9781420042993>
19. Zawadzki, J. Infrared spectroscopy in surface chemistry of carbons. Thrower, P.A. Ed. *Chemistry and Physics of Carbon*. Marcel Dekker: New York, 1989, 21, pp. 147–380.
20. Bandosz, T.J. *Activated Carbon Surfaces in Environmental Remediation*. Academic Press: New York, 2006, 7, 588 p.
21. Akolekar, D.B.; Bhargava, S.K. Influence of thermal, hydrothermal, and acid-base treatments on structural stability and surface properties of macro-meso-, and microporous carbons. *Journal of Colloid and Interface Science*, 1999, 216(2), pp. 309–319.
DOI: <https://doi.org/10.1006/jcis.1999.6306>
22. Bohli, T.; Ouederni, A. Improvement of oxygen-containing functional groups on olive stones activated carbon by ozone and nitric acid for heavy metals removal from aqueous phase. *Environmental Science and Pollution Research*, 2016, 23, pp. 15852–15861.
DOI: <https://doi.org/10.1007/s11356-015-4330-0>
23. Murphy, O.P.; Vashishtha, M.; Palanisamy, P.; Kumar, K.V. A review on the adsorption isotherms and design calculations for the optimization of adsorbent mass and contact time. *ACS Omega*, 2023 8(20), pp. 17407–17430.
DOI: <https://doi.org/10.1021/acsomega.2c08155>
24. Gutanu, V.; Tutovan, E.; Isac-Gutul, T. Kinetics of methylene blue sorption on activated carbons. In: *Integration through research and innovation: Natural and exact sciences*. CEP USM: Chisinau, 2020, pp. 238–241. ISBN 978-9975-152-50-1. (in Romanian).
https://ibn.idsi.md/sites/default/files/imag_file/Integrare_prin_cercetare_Stiinta_naturii_2020.pdf
25. Dogan, M.; Abak, H.; Alkan, M. Adsorption of methylene blue onto hazelnut shell: kinetics, mechanism and activation parameters. *Journal of Hazardous Materials*, 2009, 164(1), pp. 172–181.
DOI: <https://doi.org/10.1016/j.jhazmat.2008.07.155>
26. Lupascu, T.; Ciobanu, M.; Culighin, E. Adsorption of methylene blue from aqueous solutions on activated coal CAN-9: kinetics and equilibrium studies. *Romanian Journal of Ecology & Environmental Chemistry*, 2022, 4(1), pp. 22–28.
DOI: <https://doi.org/10.21698/rjeec.2022.102>
27. Vilar, V.J.P.; Botelho, C.M.S.; Boaventura, R.A.R. Methylene blue adsorption by algal biomass based materials: Biosorbents characterization and process behaviour. *Journal of Hazardous Materials*, 2007, 147(1-2), pp. 120–132.
DOI: <https://doi.org/10.1016/j.jhazmat.2006.12.055>