

Removal of methylene blue from aqueous solutions via adsorption on activated biocarbon obtained from post-extraction residue

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Abstract: This paper deals with adsorption of a cationic dye – methylene blue – on the activated biocarbon obtained via chemical activation of horsetail herb post-extraction residue. The effects of initial dye concentration, temperature, solution pH, as well as the phase contact time on the adsorption effectiveness have been tested. The adsorbent prepared was characterized based on the results of elementary analysis, surface area measurements, thermal analysis as well as determination of the acid-base nature of its surface. It has been shown that micro/mesoporous horsetail herb-based activated biocarbon exhibits a significantly higher ability to methylene blue uptake than the commercial activated carbon prepared from peat. It has been also found that the adsorption capacity increases with the increasing initial dye concentration in the solution and the phase contact time. The maximum adsorption toward methylene blue was found at pH=12 and at temperature of 40 °C. A better fit to the experimental data was obtained with a Langmuir isotherm than Freundlich one, whereas better fit of the kinetic data was achieved using the pseudo-second order model.

Keywords: post-extraction residue, chemical activation, activated biocarbon, methylene blue, adsorption

1. Introduction

Dynamic development of various branches of industry as well as continuously increasing consumption of various types of food and industrial products have led to a significant increase in the level of the natural environment pollution. A huge part of these pollutants are organic compounds and heavy metals discharged into industrial and municipal wastewater as well as into surface waters (Çeçen and Aktaş, 2011, Bandosz, 2006). A serious threat to soils and waters are mainly surfactants, sewage from the textile, chemical and tanning industries, as well as artificial fertilizers and pesticides. One of the main problems of wastewater treatment is the removal of dyes and heavy metals (Yagub et al., 2014). It can be realised via osmosis or coagulation processes, but the most effective and relatively cheap method is adsorption on porous sorbents, due to the high efficiency of the process and the possibility of recovering many of the removed contaminants, for example metal ions (Wiśniewska et al., 2020; Wawrzekiewicz et al., 2019; Rafati et al., 2016; Peruchi et al., 2015; Saleh and Gupta, 2012; Huang and Chen, 2009). Activated carbons are the most often used materials for this purpose. What is important, they can be applied not only as adsorbents, but also as catalyst supports, catalysts or reducing agents (Grzybek et al., 2008; Bottani and Tascón, 2008; Mei et al., 2019; Rechnia-Gorący et al., 2020, Szewczuk-Karpisz et al., 2020).

Recently, the use of activated carbons has been regularly increasing, which is why new precursors for their production are constantly being sought. The use of biomass offers a wide range of possibilities in this respect. Every year, in the literature on the subject, there are many new reports on the use of plant waste for the production of carbonaceous adsorbents. Such precursors include, among others, fruit stones, nut shells, waste resulting from the processing of sugar cane, sunflower seeds, corn cobs as

well as various types of wood (Mazurek et al., 2021; Wiśniewska and Nowicki 2019; Wu et al., 2018; Tuomikoski et al., 2019; Nowicki et al., 2016; Kazmierczak-Razna et al., 2015;). An interesting group of the activated carbon precursors is also solid waste generated in the extraction of raw plants in the solid - liquid and/or solid - supercritical gas system, e.g. hop cones, chamomile or calendula flowers (Bazan-Wozniak et al., 2021; Bazan-Wozniak and Pietrzak, 2020).

One of the plant raw materials that is increasingly often subjected to extraction processes is the horsetail herb, which is widely used in the production of dietary supplements, herbal products and a wide range of cosmetic products intended for acne skin, hair or nails care. Each year, the extraction of this herb produces a significant amount of solid waste that requires management. Therefore, the main objective of the research presented in this study was to assess the usefulness of the horsetail herb post-extraction residue as an activated biocarbon precursor and to investigate the physicochemical and sorption properties of the carbonaceous material obtained in this way. From the ecological point of view, the use of this type of precursor for the carbonaceous adsorbents production can be an excellent alternative to commercial products obtained from peat, wood or fossil coals. Moreover, it is an attractive way to dispose of waste materials, which currently are most often landfilled or incinerated.

2. Experimental

2.1. Materials

The precursor of the activated biocarbon was solid residue (R) generated in the solvent extraction of horsetail herb, a popular weed containing significant amounts of saponin, flavonoids, silica and alkaloids. One-step chemical activation was applied in order to prepare carbonaceous adsorbent characterized by well-developed surface area and porous structure as well as intermediate acid-base character of the surface. The activation parameters and procedure of heating were selected based on our previous research on the production of activated carbons from the residue of supercritical extraction of plants, citrus fruit skins and pistachio nutshells (Nowicki et al., 2016; Bazan-Wozniak et al., 2017, Bazan-Wozniak et al., 2018). At the beginning, the starting material (dried and cut into 0.5 cm long pieces) was impregnated with potassium carbonate at the precursor/alkali weight ratio of 1:2. The impregnation step was carried out for 12 h at room temperature, with occasional stirring. After that, the mixture was dried to complete evaporation of water at 110 °C, placed into a quartz boat and subjected to thermal treatment in a laboratory resistance furnace, equipped with a quartz tubular reactor.

The impregnated sample was heated (10 °C/min) from room temperature to the final activation temperature of 800 °C and annealed at that temperature for 45 min, under nitrogen atmosphere (flow rate of 250 mL/min). After that, the product of chemical activation (denoted as P) was cooled down to room temperature in an inert gas flow and subjected to two-stages washing procedure – firstly with a boiling 5 % solution of HCl and then with hot demineralized water on a vacuum filtration funnel with a glass sintered disc, until free of chloride ions. Finally, the activated biocarbon prepared was dried to a constant mass at 110 °C and ground in an agate mortar to a grain size of 0.1 mm. For comparison purpose a commercial powder activated carbon - Norit® SX2 (denoted as N) was applied. It is a commonly known, steam activated and acid washed carbon, obtained from peat (a detailed characterization is given in our earlier work, Nowicki et al., 2015).

2.2. Methods

The elemental analysis of the starting post-extraction residue and activated biocarbon prepared, was performed on an Elementar Analysensysteme GmbH instrument – model Vario EL III CHNS. The analysis consisted in the catalytic combustion of the samples at 1200 °C, the separation of exhausted gases on adsorption columns and their detection based on the difference in thermal conductivity. The total ash content was determined by burning the carbon materials in a microwave muffle furnace (Phoenix, CEM Corp.) at 815 °C for 60 min (according to the DNS ISO 1171:2002).

The porous structure of activated biocarbon sample was characterized on the basis of low-temperature nitrogen adsorption/desorption measured at -196 °C by Autosorb iQ analyser, provided by Quantachrome Instruments. Prior to the analysis, the activated biocarbon sample was degassed under vacuum at temperature of 300 °C, for 12 h, in order to remove all pre-adsorbed species. The

surface area of the material was found on the basis of the multilayer adsorption BET (Brunauer–Emmett–Teller) theory. The pore size distribution and total pore volume were determined based on the BJH (Barrett–Joyner–Halenda) model. Moreover, the micropore volume and surface area were calculated by the t-plot method.

To determine the content of surface oxygen functional groups of acidic and basic character, the Boehm method was applied (Boehm, 1994; Boehm et al., 1964). Volumetric standards of 0.1 mol/L sodium hydroxide and 0.1 mol/L hydrochloric acid were used as the titrants.

The pH values of water extract of the precursor as well as the product of activation were measured by means of pH meter manufactured by Metrohm Ion Analysis, equipped with a combined glass electrode – Unitrode Pt1000, calibrated with standards solutions of pH 3, 7 and 10. Measurements were performed according to the following procedure: a portion of 1 g of the carbonaceous material was mixed with 50 mL of doubly distilled water and stirred magnetically overnight to reach equilibrium. After that, the pH of the suspension was measured upon continuous stirring.

Thermal analysis was carried out on a STA 449 Jupiter F1 (Netzsch, Germany) under the following operational conditions: heating rate 10 °C/min, the dynamic atmosphere of helium (50 mL/min) and air (40 mL/min) in the temperature range of 0–1000 °C, sample mass of about 5 mg, sensor thermocouple type P TG-DSC. As a reference, empty Al₂O₃ crucible was used.

2.3. Batch adsorption measurements

Methylene blue (MB) was obtained from Avantor Performance Materials Poland S.A. and used without further purification. A stock solution (1000 mg/L) was prepared by dissolving the required amount of dye powder in distilled water. All working solutions of desired concentrations were prepared by diluting the stock solution.

Adsorption of methylene blue from aqueous solution was performed using the following procedure. Samples of the prepared activated biocarbon in the same portions of 0.025 g (particle size of 0.1 mm) were added to 50 mL of the dye solution with the initial concentrations in the range from 10 to 200 mg/L and the suspensions were stirred magnetically (200 rpm) for 12 h, at temperature of 22 ± 1 °C. After the adsorption equilibrium state had been achieved, the solutions were separated from the carbonaceous materials by centrifugation at 3000 rpm, for 5 min. The methylene blue concentration was established spectrophotometrically using a double beam Cary 100 Bio UV–Vis spectrophotometer (provided by Varian) at the wavelength of 665 nm.

The equilibrium adsorbed amount of methylene blue (q_e , mg/g) was calculated according to the following formula:

$$q_e = \frac{c_{ads} \cdot V_{MB}}{m_{ABC}} \quad (1)$$

where c_{ads} (mg/L) is the difference in the MB concentration in the system before and after its adsorption, V_{MB} (L) is the volume of the dye solution, and m_{ABC} (g) is the mass of activated biocarbon used, respectively.

The pH effect on methylene blue removal efficiency was studied according to the following procedure: A portion of 0.025 g of the biocarbon sample was shaken with 50 mL solution of MB in the concentration of 100 mg/L for 8h, at pH from the range 2.0–10.0. After shaking, the suspension was centrifuged and the final concentration of dye was determined as described above. The solution pH before the experiments was adjusted by adding appropriate amounts of 0.1M HCl or 0.1M NaOH.

The influence of the temperature on MB adsorption efficiency was investigated at 20, 30 and 40 °C. A portion of 0.025 g of the biocarbon sample was stirred magnetically (200 rpm) with 50 mL solution of MB in the concentration of 170 mg/L for 8h, at pH 8.

The procedure for the kinetic experiments was similar to this applied for the equilibrium tests. The experiment was carried out by 50 mL of 100 mg/L methylene blue solution with 0.015 mg of the activated biocarbon, at pH 8. The suspension was stirred magnetically (200 rpm) for 6 h, at temperature of 22 ± 1 °C. Samples of the solution were collected at the intervals of 15 minutes and subjected to MB concentration measurements. The amount of MB adsorbed at time t (q_t , mg/g), was calculated according to the following formula:

$$q_t = \frac{(c_{init} - c_t) \cdot V_{MB}}{m_{ABC}} \quad (2)$$

where C_{init} and C_t (mg/L) are the liquid-phase concentrations of MB at the initial moment and at time t , respectively. V_{MB} is the volume of the dye solution (L) and m_{ABC} is the mass of dry activated biocarbon used (g).

For comparison purpose, similar adsorption experiments were performed for commercial activated carbon Norit® SX2 (N). The mechanism of methylene blue adsorption on both carbonaceous materials was analysed by the Langmuir and Freundlich models, whereas the kinetic of adsorption was investigated using the pseudo first order equation (PFO) proposed by Lagergren and the pseudo second order equation (PSO) proposed by Ho and McKay.

3. Results and discussion

3.1. Physicochemical properties of the activated biocarbon prepared from post-extraction residue

As follows from the data presented in Table 1, horsetail herb post-extraction residue used for the study was characterized by quite a high content of mineral substance (most probably due to the high silica content in the starting plant material) and a relatively low content of elemental carbon (a bit over 44 wt. %). In contrast, the product of its chemical activation showed more than twice higher contribution of carbon in the structure and slightly lower ash content. The increase in the content of elemental carbon was accompanied by a considerable decrease in the content of the other elements, mainly oxygen. These changes are related to the high temperature of the activation process, which is responsible for breaking of the least stable chemical bonds and the removal of significant amount of heteroatoms in the form of simple gas and liquid compounds, rich in hydrogen and oxygen. The effect of these changes is the progressive aromatization of the carbonaceous structure as well as formation of the porous system in the activation product.

Table 1. Elemental composition of the post-extraction residue (R) and activated biocarbon prepared via its chemical activation (P) [wt. %]

Sample	Ash ^d	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen
R	13.8	44.5	4.5	3.3	1.5	46.2
P	12.5	90.8	1.4	2.2	0.6	5.4

The results presented in Table 2 as well as in Fig. 1 and 2 imply that chemical activation of the starting material with K_2CO_3 leads to effective development of the surface area and porous structure. The surface area of the activated biocarbon prepared exceeds $964 \text{ m}^2/\text{g}$ (a value similar to the surface area of typical commercial activated carbons available on the market), while the total pore volume is almost $1 \text{ cm}^3/\text{g}$. The porous structure of the carbon material prepared consists of comparable amounts of micro and mesopores, as the contribution of micropores in the total pore volume is 47%. Micro/mesoporous nature of sample P is confirmed by the course of the isotherm of low-temperature nitrogen adsorption/desorption, shown in Fig. 1. In the range of low relative pressure, the isotherm is almost parallel to the x axis, indicating the presence of micropores. However, a H4 type hysteresis loop observed at relative pressures p/p_0 above 0.5 indicates the presence of mesopores, in which capillary condensation of the adsorbate takes place. The presence of micropores and small mesopores of diameter below 10 nm is also confirmed by the pore size distribution curve presented in Fig. 2.

The data characterizing the acid-base nature of the precursor and activated biocarbon studied are collected in Table 3. They clearly indicate that the surface of the post-extraction residue contains a significant amount of functional groups of basic and acidic character, with a slight predominance of the latter. A high number of basic sites on the precursor surface may be related to a high content of mineral substance in its structure. As a result of the activating agent (potassium carbonate) action as well as the high temperature applied in the activation process ($800 \text{ }^\circ\text{C}$), the number of surface functional groups (both acidic and basic one) significantly decreases (almost twice). Chemical activation of the horsetail herb post-extraction residue lead also to an increase in the value of pH of water extract, from level 5.98 to 6.75.

Table 2. Textural parameters of the activated biocarbon obtained from horsetail herb post-extraction residue

Sample	Surface area [m ² /g]	Total pore volume [cm ³ /g]	Micropore volume [cm ³ /g]	Micropore contribution [%]	Mean pore diameter [nm]
P	964	0.958	0.455	47	3.972

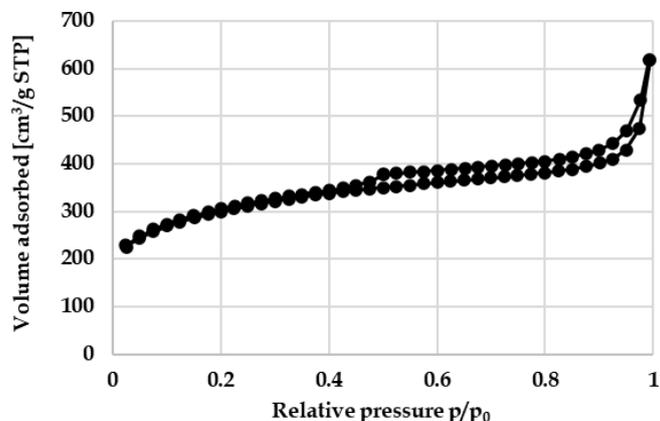


Fig. 1. Low-temperature nitrogen adsorption/desorption isotherm for the activated biocarbon prepared from post-extraction residue

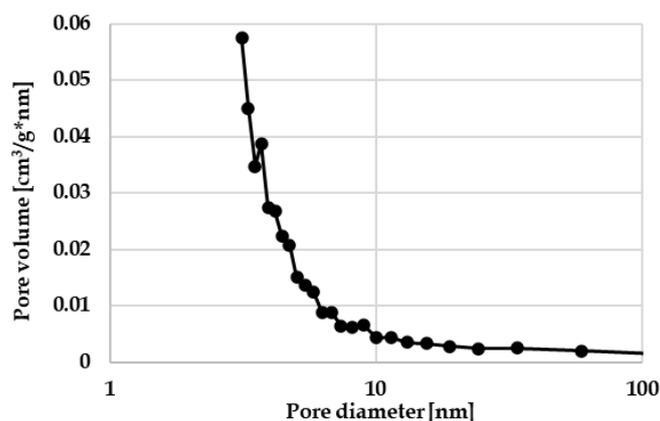


Fig. 2. Pore size distribution for the activated biocarbon prepared from post-extraction residue

Table 3. Acid-base properties of the precursor (R) and activated biocarbon prepared (P)

Sample	Acidic functional groups [mmol/g]	Basic functional groups [mmol/g]	Total content of surface groups [mmol/g]	pH of water extracts
R	1.69	1.48	3.17	5.98
P	0.94	0.78	1.72	6.75

3.2. Sorption abilities of the activated biocarbon toward methylene blue

The first stage of adsorption study was to check the effect of the initial methylene blue (MB) concentration on the amount of dye adsorbed from water solutions. The experiments were performed until reaching equilibrium between the adsorbent and MB molecules remaining in solution. The results presented in Fig. 3 and Table 4 are the evidence that activated biocarbon tested is characterized by very good sorption abilities towards methylene blue, which is most probably a consequence of its well-developed surface area and the micro/mesoporous nature of the structure.

The sorption capacity of the adsorbent studied towards MB significantly depends on the initial concentration of this organic dye, which suggests that at lower concentrations, MB molecules can bind

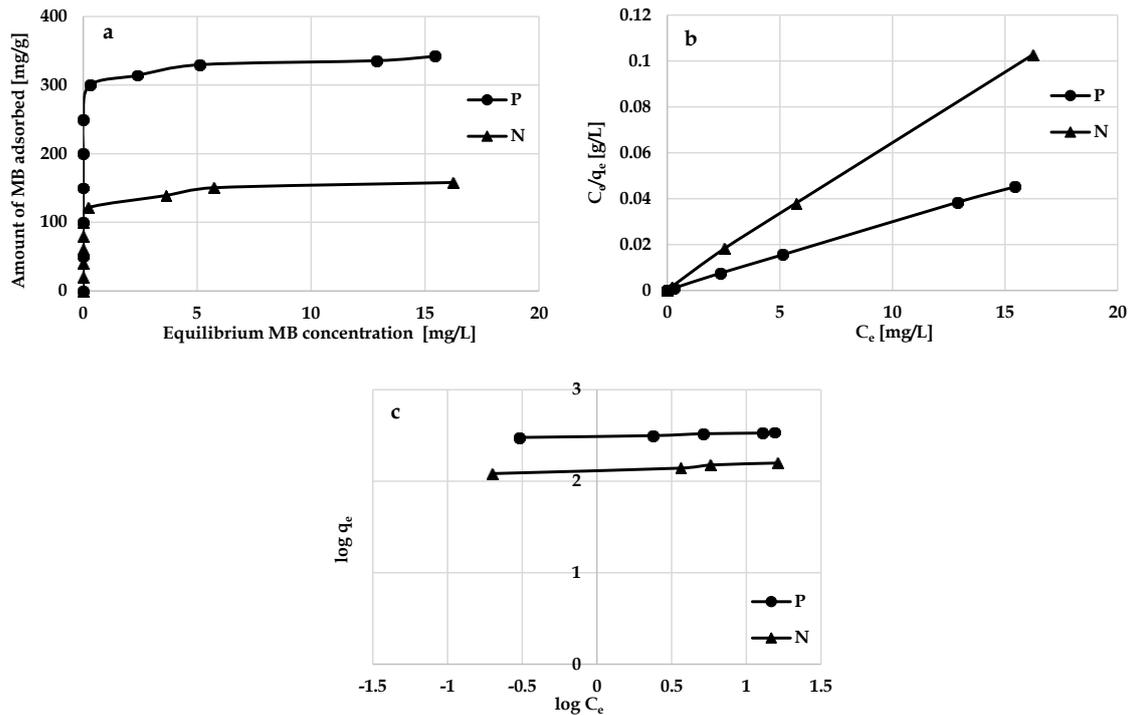


Fig. 3. Adsorption of methylene blue on activated biocarbon prepared from post-extraction residue (P) and commercial activated carbon (N): (a) equilibrium adsorption of MB, (b) Langmuir isotherm plots, and (c) Freundlich isotherm plots

Table 4. Langmuir and Freundlich parameters of the isotherms of MB adsorption on activated biocarbon prepared from post-extraction residue (P) and commercial activated carbon (N)

Sample	Langmuir model			Freundlich model		
	q_{\max}	R^2	K_L	$1/n$	R^2	K_F
P	334.4	0.9993	4.98	0.017	0.9011	317.02
N	161.3	0.9999	15.50	0.037	0.7384	143.35

q_{\max} - the maximum adsorption capacity (mg/g), K_L - the Langmuir adsorption equilibrium constant (L/mg), K_F - the Freundlich equilibrium constant [mg/g (mg/L) $^{1/n}$], $1/n$ - the intensity of adsorption, R^2 - correlation coefficients.

to any available active centres on the biocarbon surface or there is an excess of active centres on the adsorbent surface. At higher methylene blue concentrations, a completely different situation takes place, because most or even all the available active centres are occupied by the organic dye molecules (a state of the complete saturation of the activated biocarbon surface is achieved). The shape of the MB adsorption isotherm recorded for sample P is smooth and single, which indicates that we are dealing with a monolayer coating of the adsorbent surface with the dye particles.

Analysis of the results presented in Fig. 3 and Table 4 implies also that the sorption capacity of the activated biocarbon prepared (334.4 mg/g) exceeds twice the result obtained for the commercial micro/mesoporous activated carbon Norit® SX 2 - a multi-purpose adsorbent, dedicated inter alia to water purification. For both adsorbents tested (P and N) the Langmuir model fits the experimental data more accurately than the Freundlich isotherm, as evidenced by significantly higher value (close to 1) of the correlation coefficient. Moreover, the value of $1/n$ parameter - a measure of surface heterogeneity/adsorption intensity is very low (especially for sample P), which suggests that adsorption conditions are favourable, which means that dye molecules has an easy access to porous system of the adsorbent. It indicates also a very high heterogeneity of both carbonaceous adsorbents surfaces.

According to the data presented in Fig. 4, the effect of pH solution on the efficiency of methylene blue adsorption is significant for both materials under investigation. For the activated biocarbon

prepared from horsetail herb post-extraction residue the difference in sorption capacity recorded at pH 2 and 12 is over 41 mg/g. For sample N the increase in sorption capacity is much less pronounced and does not exceed 14 mg. In strongly acidic solutions, oxygen functional groups present at the adsorbent surface are protonated and the excess of H^+ ions can compete with the MB molecules for the active sites, which considerably restricts the adsorption of methylene blue. At higher pH, the concentration of hydrogen ions in the solution significantly decreases as a result of surface groups deprotonation and negative charge appears at the adsorbent surface, which enhances the electrostatic attraction between the dye cations and the negatively charged carbon surface and, thus, has a beneficial effect on sorption effectiveness.

Another parameter that influences the efficiency of organic pollutants removal from aqueous solutions is temperature. According to the results of the adsorption tests carried out at 20, 30 and 40 °C (presented in Fig. 5) the maximum sorption capacity was observed at 40 °C. However, it should be emphasized that the beneficial effect of temperature is significantly less pronounced than that of pH of the solution. The observed increase in the sorption capacity of the tested activated carbons at a higher temperature is most likely a consequence of the increase in the diffusion rate of adsorbate molecules through the outer boundary layer as well as easier penetration of the porous structure by the more mobile at higher temperature dye molecules.

The knowledge of the kinetics of the reaction is also an important parameter from the adsorptive point of view. Therefore, two commonly known kinetic models – pseudo first and pseudo second order ones were used to determine the kinetics of MB sorption on activated biocarbon prepared. According to the data presented in Table 5 obtained both for the prepared by us as well as commercial activated carbon are better described by the kinetic equation of pseudo 2nd order. It is evidenced by the fact that

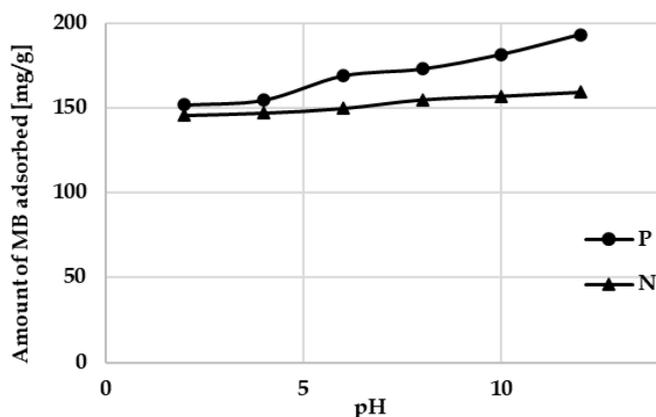


Fig. 4. The effect of pH on the adsorption of methylene blue on activated biocarbon prepared from post-extraction residue (P) and commercial activated carbon (N)

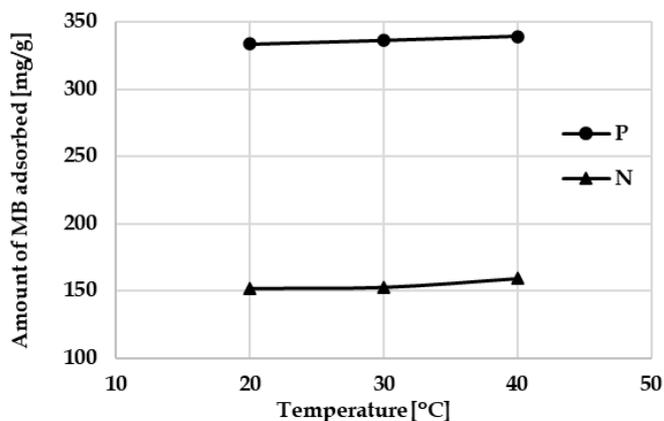


Fig. 5. The effect of temperature on the adsorption of methylene blue on the activated biocarbon prepared from post-extraction residue (P) and commercial activated carbon (N)

correlation coefficients of the linear regression for this type of kinetics were 0.9999 and 0.9998, respectively, so significantly higher than the R^2 value obtained for pseudo 1st order kinetic. It can be also supposed that the methylene blue molecules undergo chemisorption on the surface of the tested adsorbents.

Table 5. Kinetic parameters for MB adsorption on the activated biocarbon prepared from post-extraction residue (P) and commercial activated carbon (N)

Sample	PFO			PSO		
	q_{cal}	R^2	k_1	q_{cal}	R^2	k_2
P	25.85	0.6786	0.00292	277.78	0.9999	0.00173
N	15.54	0.8759	0.00852	158.73	0.9998	0.00171

q_{cal} - the calculated adsorption capacity (mg/g), k_1 - the pseudo first order adsorption rate constant (1/min), k_2 - the pseudo second order adsorption rate constant (g/(mg·min)), R^2 - correlation coefficients

3.3. TG/DTG analysis of the activated carbons before and after methylene adsorption

The last stage of the experimental study was thermal analysis of the obtained activated biocarbon and the commercial product, as well as selected samples after methylene blue adsorption on these materials. For this purpose, two series of samples were prepared. The first one included: P - activated biocarbon prepared from horsetail herb post-extraction residue, P_1 - sample obtained via MB adsorption at 40 °C, at pH 12, $c_{init} = 320$ mg/L (complete discoloration of the aqueous solution); P_2 - sample obtained via MB adsorption at 40 °C, at pH 12, $c_{init} = 340$ mg/L (incomplete discoloration of the solution); P_3 - sample obtained via MB adsorption at 40 °C, at pH 6, $c_{init} = 260$ mg/L (complete discoloration of the solution). The second series consisted of analogous samples N, N_1 , N_2 , N_3 obtained during the adsorption of MB on commercial activated carbon. Thermal stabilities and degradation behaviour of the samples were studied by means of thermogravimetry in air and helium atmosphere. For each material, the beginnings of the individual mass loss stages (T1, T2, T3, T4) were determined. Moreover, additional factors: the initial temperature of decomposition (ITD) and the residual mass of sample (RM) were defined.

The curves obtained from the TG and DTG analysis for all "N" series samples are presented in Fig. 6 and the values of these measurements collected in Table 6. Comparing the course of the TG and DTG curves for the "N" series, similarities at high temperature can be noticed. On the other hand, the stages

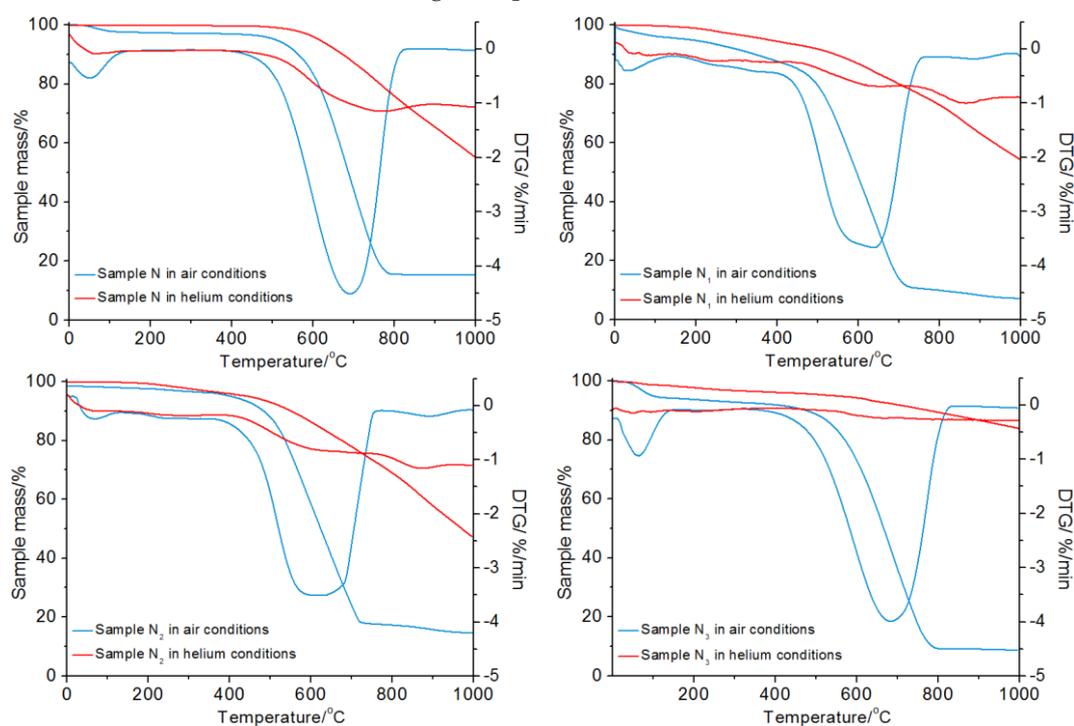


Fig. 6. The TG and DTG curves of the "N" series samples analyzed in air and helium conditions

of thermal degradation (and their number) were recorded at different temperature values. The initial decomposition temperatures of the analysed materials in air atmosphere, range from 346.2 °C (for sample N₃) to 394.0 °C (for sample N₁). On the DTG curves two additional decomposition stages appear: the first one in the range: 19.6 – 28.7 °C and the second one from 138.3 to 174.3 °C for samples after methylene blue adsorption.

By analysing the TG and DTG curves recorded in helium atmosphere one can see that the beginning of the initial decomposition stage varies between 371.6 °C (sample N) and 433.2 °C (sample N₃). The first decomposition stage on DTG curves was recorded in range: 17.9 – 28.7 °C. For all the samples after methylene blue adsorption (N₁, N₂, and N₃) the start of the second mass loss stage can be observed in the range of 136.1 - 148.0 °C. For samples N₁ and N₂ one more decomposition stage (at the temperature of 743.4 and 744.5 °C, respectively) was observed.

The residual mass values (RM) of samples in helium conditions assessed at the final temperature of the experiment (1000 °C) were in the range from 47.4% to 83.9% and they are considerably higher than those for the analogous materials analysed in air atmosphere (range RM: 7.22% - 15.42%).

The results obtained from the TG analysis for "P" series samples are presented in Table 7. The Fig. 7 shows the course of TG and DTG curves in air and helium conditions. For "P" samples initial thermal degradation (ITD) in air atmosphere start from 319.5 °C for P sample to 392.3 °C for P₁ sample. For all the samples after methylene blue adsorption (P₁, P₂ and P₃) two additional thermal degradation stages were recorded. The first is observed from 22.1 °C to 31.7 °C, whereas the second decomposition stage appears in the range: 132.6 - 162.2 °C.

Table 6. Results of the TG/DTG analysis of the "N" series samples in the air and helium conditions

Thermal analysis in air atmosphere				
Sample	N	N ₁	N ₂	N ₃
T ₁ /°C	24.0	25.9	28.7	19.6
T ₂ /°C	-	150.9	138.3	174.3
T ₃ (ITD)/°C	375.3	394.0	388.2	346.2
RM (%)	15.42	7.22	14.57	8.75
Thermal analysis in helium atmosphere				
Sample	N	N ₁	N ₂	N ₃
T ₁ /°C	27.3	17.9	28.7	23.6
T ₂ /°C	-	148.0	136.1	138.7
T ₃ (ITD)/°C	371.6	423.2	380.0	433.2
T ₄ /°C	-	743.4	744.5	-
RM (%)	55.3	54.3	47.4	83.9

Table 7. Results of the TG/DTG analysis of the "P" series samples in the air and helium conditions

Thermal analysis in air atmosphere				
Sample	P	P ₁	P ₂	P ₃
T ₁ /°C	29.5	22.1	31.7	26.6
T ₂ /°C	-	149.4	132.6	162.2
T ₃ (ITD)/°C	319.5	392.3	348.4	378.9
RM (%)	20.5	14.5	30.6	16.5
Thermal analysis in helium atmosphere				
Sample	P	P ₁	P ₂	P ₃
T ₁ /°C	29.5	27.3	26.6	27.2
T ₂ /°C	-	155.3	152.5	156.3
T ₃ (ITD)/°C	377.1	432.1	443.8	505.5
T ₄ /°C	-	708.8	703.8	-
RM (%)	54.4	55.7	59.9	71.1

Based on the data obtained in helium atmosphere, the first decomposition stage occurs in the range from 6.6 °C to 29.5 °C, while the second stage - in the range 152.5 - 156.3 °C. The beginning of the initial decomposition of "P" series samples can be found on the DTG curves between 377.1 (sample P) to 505.5 °C (for sample P₃). For samples P₁ and P₂ one additional stage of mass loss is observed. For sample P₁ the beginning of this stage appears at 708.8 °C, whereas for sample P₂ - at 703.8 °C. The residual mass (at 1000 °C) of the studied materials in the air ranges from 14.5 to 30.6%, while for the materials analysed in helium atmosphere it varies between 54.4 and 71.1%.

The first mass loss, noticeable both for the samples analysed in the air and those analysed in helium, is most likely related to the evaporation of water molecules physically bound to the samples surface. The second stage of mass loss, also for both series, is observed only for the samples obtained after methylene blue adsorption. That is why this step is supposed to be related to the thermal decomposition of the dye (Fig. 8). The temperature of this stage seems not to depend on the sample preparation and conditions of analysis. The initial decomposition temperature is slightly shifted towards higher temperatures for the samples made in helium atmosphere. The ITD values for the dye treated samples are significantly higher compared to the analogous values for samples N and P. It can be also concluded that the samples P₁, P₂ and P₃ have adsorbed more dye than analogous "N" series samples, as evidenced by a much higher residual mass for the former samples.

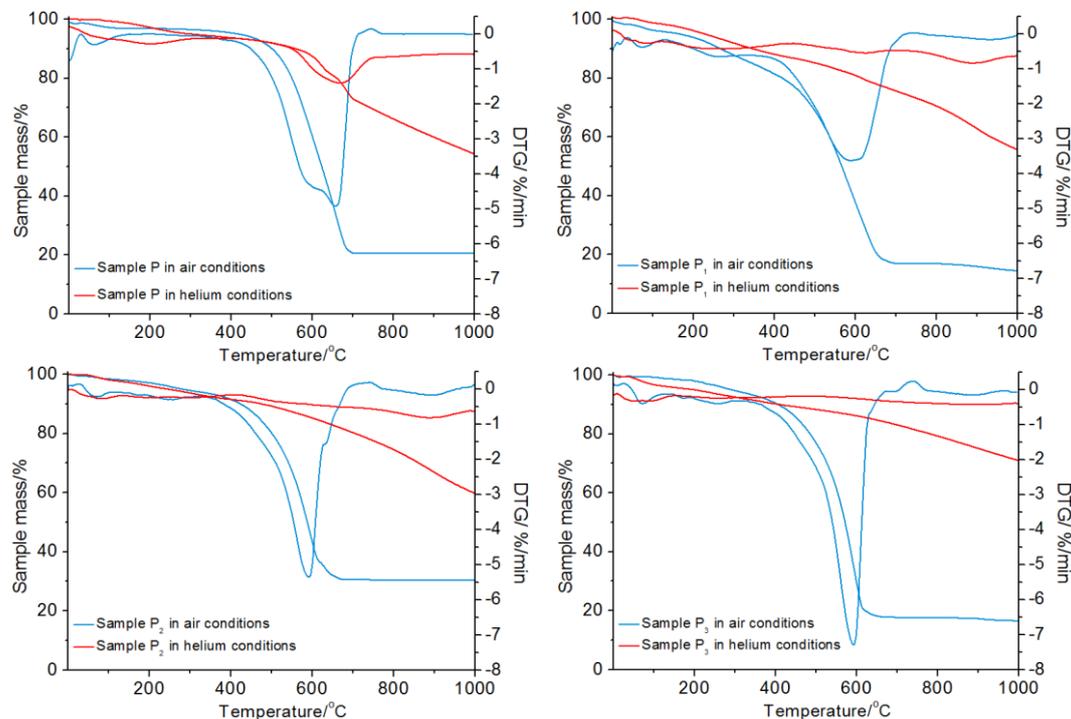


Fig. 7. The TG and DTG curves of the "P" series samples analyzed in air and helium atmosphere

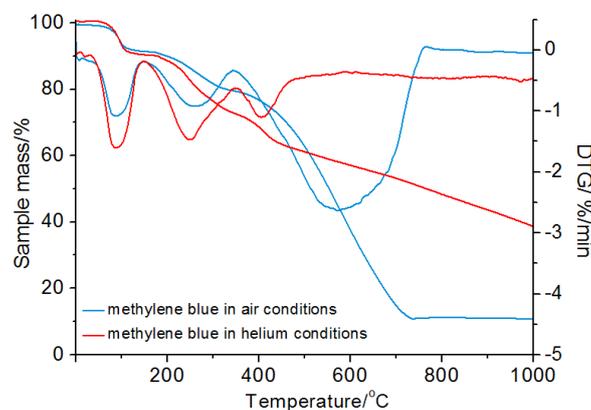


Fig. 8. The TG and DTG curves of methylene blue

4. Conclusions

The above presented and discussed results have clearly shown that the residues of solvent extraction of horsetail herb can be successfully applied for production of carbonaceous adsorbents, characterized by high effectiveness in removal of organic dyes from water solutions. Chemical activation of the aforementioned precursor with K_2CO_3 allows obtaining activated biocarbon with a well-developed specific surface area and a micro/mesoporous structure, which favours the adsorption of pollutants with large particle sizes, e.g. organic dyes.

The results obtained have shown that the choice of adsorption parameters is very important for evaluation of sorption abilities of the carbon material prepared. The adsorption capacity of the activated biocarbon sample studied increases with increasing initial concentration of methylene blue in the solution, which suggests that at low MB concentrations its adsorption has random character, whereas at higher concentrations the active centres present on the adsorbents surface are all occupied and the adsorbent structure is fully saturated. What is more, with increasing alkalinity of the solution as well as the temperature of the system, the effectiveness of the dye adsorption on the activated biocarbon prepared from post-extraction residue significantly increases. The optimal results were obtained at pH 12 and at temperature of 40 °C. The adsorption of methylene blue is characterized by the Langmuir isotherm model, which indicates the formation of an adsorbate monolayer on the porous surface of the activated biocarbon prepared. As far as the kinetics of the adsorption is concerned, it was found to be best described by the pseudo-second order model.

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