Activated biocarbons obtained from post-fermentation residue as potential adsorbents of organic pollutants from the liquid phase

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Abstract: A series of new synthetic carbonaceous adsorbents has been prepared via physical and chemical activation of residue of alcoholic fermentation of corn starch. Two different variants of thermal treatment procedure - microwave and conventional heating have been applied for preparing of the activated biocarbons. All the samples under investigation were characterised by elementary analysis, surface area measurements as well as determination of the number of surface functional groups. The electrokinetic properties of examined materials were studied using potentiometric titration and electrophoresis methods, which enabled determination of the surface charge density and zeta potential of activated biocarbon particles. Moreover, sorption properties of the carbonaceous materials towards two organic dyes - methylene blue and malachite green were tested. The final products were activated biocarbons of medium developed surface area ranging from 21 to 879 m²/g, showing acidic character of the surface and various content of surface functional groups. More favourable textural parameters as well as sorption properties toward both organic dyes were revealed by chemically activated samples. The obtained results indicated also considerable effect of adsorbed dye molecules on the structure of electrical double layer formed at the solid/liquid interface.

Keywords: post-fermentation residue, activated carbons, organic dyes adsorption, electrokinetic properties, zeta potential, surface charge density

1. Introduction

Activated carbons are materials characterized by a highly developed surface area, a polydisperse porous structure and a high degree of surface reactivity, which makes them very effective and universal adsorbents (Bottani and Tascón, 2008; Marsh and Rodríguez-Reinoso, 2006). Currently, it is difficult to find any branch of modern industry in which they would not be applied. Carbonaceous adsorbents play an important role in the food, pharmaceutical and cosmetic industries, in the treatment of drinking water and wastewater as well as in the treatment of industrial waste gases or gas storage (Bandosz, 2006; Bazan-Wozniak et al., 2017; Çeçen and Aktaş, 2011; Wróbel-Iwaniec et al., 2015). Carbon materials can be also applied as catalysts or catalysts supports as well as electrode materials for electrochemical capacitors and lithium-ion batteries (Kazmierczak-Razna et al., 2021; Malaika et al., 2019; Rechnia-Gorący et al., 2020). Such a wide range of the use of activated carbons means that their global production increases every year, which justifies the study on the searching for new precursors for their production and the optimization of their physicochemical properties for specific applications.

The industrial production of activated carbons is mainly based on the physical or chemical activation of coconut shell, wood, peat and fossil coals (Marsh and Rodríguez-Reinoso, 2006; Nowicki et al., 2008). Recently, various types of waste materials (e.g. agricultural waste, residue of supercritical extraction, discarded plastics or cardboard, sawdust, sewage sludge, etc.) have also been applied as precursors of this type of adsorbents (Bazan and Pietrzak, 2020; Bouhamed et al., 2016; Isshakov et al., 2021; Kazmierczak-Razna et al., 2019; Kołodyńska et al., 2017; Szewczuk-Karpisz et al., 2020; Wiśniewska et

al., 2021; Wu et al., 2018). Regardless of the type of the starting material and activating agent used, the activated carbons production procedure is based on the use of conventional heating, which has many drawbacks. The most important of them are non-uniform heating of the material during pyrolysis and/or activation stage, the necessity of using high temperatures as well as very long period of samples annealing at the final process temperature. A good solution to this problem may be the use of microwave heating in the production of activated carbons. As is well known, microwave heating is based on direct conversion of electromagnetic energy into heat, as a result of which thermal treatment of carbonaceous materials can be carried out at a lower temperature or for a shorter period of time, when compared to the conventional method. What is more, this method allows to uniform heating of the whole volume of carbon sample during pyrolysis or activation step.

Considering the above, the main purpose of the present study was to obtain a series of new synthetic activated biocarbons by way of physical (thermal) and chemical activation of the solid residue generated in the process of alcoholic fermentation of corn starch as well as to compare the influence of conventional and microwave method of heating on the physicochemical parameters and sorption abilities of the materials prepared. In addition, electrokinetic studies were carried out in order to determine the adsorption mechanism at the solid/liquid interface. The parameters obtained in their course, such as the solid surface charge density and zeta potential, allows to characterize the structure of electrical double layer in the presence of the examined adsorbate (Ostolska and Wiśniewska 2014, 2015). Analysis of their sign and value enables the specification of the arrangement of organic compound molecules in the adsorption layer. In such a way the adsorbate functional groups responsible both for binding to the solid surface and for solid particles stability can be selected. Additionally, the electrostatic conditions occurring in the system during the adsorption process can be defined. Such information are extremely important for not only effective removal of undesired organic compounds from aqueous solution, but also for successful separation of the solid with adsorbed pollutants from liquid phase.

2. Experimental

2.1. Materials

The precursor of the activated biocarbons was solid waste (undecomposed monosacharides) generated during alcohol fermentation of corn starch. At the beginning the starting material was dried at 110 °C to constant mass, then ground with a cutting mill Culatti (Kleinfeld) and finally sieved to a uniform size range of 1.0-2.0 mm. Such prepared precursor was divided into two parts and subjected to direct physical (PA) or chemical (CA) activation. During the activation the samples were heated in two variants – in a conventional laboratory resistance furnace ($_c$) or in microwave muffle furnace ($_m$).

One part of the precursor was impregnated with potassium carbonate solution (weight ratio of 2:1) at room temperature for 24h and then dried to constant mass at 110 °C. After drying, the impregnated sample was placed in a porcelain crucible and subjected to heat treatment under a stream of nitrogen blown with the rate of 20 L/h. The sample was heated (10 °C /min) from room temperature to the final activation temperature of 700 °C in microwave furnace (CA_m) or conventional furnace (CA_c), annealed at the final activation temperature for a period of 15 or 30 min respectively, and then cooled down in nitrogen flow. The prepared biocarbons were next subjected to two-stages washing procedure: firstly with hot 5% solution of hydrochloric acid (under reflux, for 15 min) and later with 10 L of hot demineralized water on vacuum filtration funnel with glass sintered disc and finally dried at 110 °C to constant mass.

The remaining part of the precursor was subjected to direct physical activation with carbon dioxide. This process was carried out at 700 °C, under a stream of CO_2 with the flow rate of 15 L/h, for 15 min in case of microwave-assisted activation (PA_m) or 30 min for conventional activation (PA_c). The products of physical activation were washed with 5 L of hot demineralised water to remove side products of activation and dried to constant mass at 110 °C.

2.2. Methods

The total ash (mineral matter) content for all materials under investigation was determined according to the ISO 1171:2002 standard: samples in a form of dry powder were burned at temperature 815ºC, for

60 min in microwave muffle furnace. Elemental composition of the starting post-fermentation residue as well as the products of its activation was determined using the elemental analyser CHNS Vario EL III, provided by Elementar Analysensysteme GmbH.

The textural characterization of the activated biocarbons was based on nitrogen adsorption-desorption isotherms measured at -196 °C on Autosorb iQ surface area analyzer provided by Quantachrome Instruments. Prior to analysis the carbon samples were degassed under vacuum for 12 h, at temperature of 300 °C. On the grounds of results of these measurements the BET surface area (S_{BET}), total pore volume (V_t) and mean pore diameter (D) were determined. Moreover, micropore volume (V_{mic}) was calculated using the t-plot method.

The content of surface oxygen functional groups were determined according to the Boehm back titration method (Boehm, 1994), using 0.1 M NaOH and HCl volumetric standards as the titrants and methyl orange as the indicator. The pH of water suspensions of each material was determined using the following procedure: a portion of 0.5 g of the carbonaceous material was mixed with 25 ml of distilled water and stirred for 24h to reach equilibrium. After that time, pH of the suspension was measured by means of CP-401 pH-meter (Elmetron) equipped with EPS-1 glass electrode.

The activated biocarbons obtained were subjected to sorption studies towards two organic dyes – malachite green (MG) and methylene blue (MB). The adsorption tests were performed at room temperature, according to the following procedure. Samples of the prepared materials in the same portions of 0.025 g with the particle size ≤ 0.1 mm were added to 0.05 L of malachite green or methylene blue solution with initial concentrations in the range from 0 to 250 mg/L and the suspensions were stirred to reach equilibrium for 12 h. After the adsorption equilibrium had been achieved, the solutions were separated from the carbonaceous materials by centrifugation. The dyes concentrations in the solution before and after adsorption were determined using a double beam UV–Vis spectrophotometer (Cary 100 Bio, Varian) at a wavelength of 617 nm in case of MG and 665 nm for MB. All experiments were made in triplicate. The equilibrium adsorption amounts (mg/g) were calculated according to the following formula:

$$q_e = \frac{(c_{init} - c_{fin}) \cdot V_D}{m_{AcB}} \tag{1}$$

where c_{init} and c_{fin} (mg/L) are the initial and final concentration of the malachite green or methylene blue, V_D (L) is the volume of the dyes solution, and m_{AcB} (g) is the mass of activated biocarbons used, respectively. The equilibrium data were analysed according to Langmuir and Freundlich models.

The electrokinetic studies included determination of the surface charge density and zeta potential of activated biocarbon particles. The solid surface charge density as a function of solution pH was obtained using the potentiometric titration method (Janusz, 1994; Skwarek et al., 2014), whereas the zeta potential dependence on solution pH - applying microelectrophoresis method. The potentiometric titration was performed automatically, using a set consisting of: thermostated Teflon vessel, glass and calomel electrodes (Beckman Instruments), PHM 240 pH-meter (Radiometer), laboratory stirrer, RE 204 thermostat (Lauda), automatic Dosimat 765 microburette (Metrohm) and computer with the "Titr_v3" program. The zeta potential was determined based on the electrophoretic mobility measurements using the Zetasizer Nano-ZS (Malvern Instruments). The adjusted pH of examined suspensions (with accuracy ±0.1) was measured using the pH-meter produced by Beckman Instruments, whereas they were sonicated using the Misonix XL-2020 device. The electrokinetic measurements were performed for solid suspensions without and in the presence of dye.

Potentiometric titrations (within pH range 3-10) were performed in the systems containing 50 mL of appropriate solution (without and containing examined dyes with concentrations corresponding with those used in adsorption measurements). The initial solution pH value was about 3.5. After addition of appropriate weight of the solid, the suspensions were titrated with NaOH solution (concentration 0.1 mol/L). The solid mass was determined taking into account the fact that the solid surface area available for titration should be equal to 20 m² – and so 0.023 g for CA_c and CA_m, 0.24 g for PA_c and 0.12 g for PA_m.

The zeta potential of activated biocarbon particles was determined from the elctrophoretic mobility data using the Henry's equation (Hunter, 1981; Ohshima, 1994). The samples were prepared adding 0.023 g of CA_c and CA_m, as well as 0.1 g of PA_c and PA_m to 100 mL of water or aqueous dye solution (dyes concentrations corresponding with those used in adsorption measurements). After 2 minutes of

sonication the suspension was divided into 8 parts. In each of them the appropriate pH value was determined, i.e. 3, 4, 5, 6, 7, 8, 9 and 10. The electrophoretic mobility of all samples was then successively measured using dip cell system.

3.　Results and discussion

3.1.　Physicochemical parameters of the activated biocarbons prepared

According to the data presented in Table 1 the raw post-fermentation residue is characterized by moderate content of elemental carbon (50.8 wt.%) in the structure. The low carbonization degree of the starting material is also indicated by the very high oxygen content (41.7% by weight). In the structure of the precursor, there is also a significant amount of mineral matter (ash) and nitrogen, while the remaining part are small amounts of hydrogen and sulphur.

Table 1. Elemental composition of the post-fermentation residue and materials obtained via its activation [wt. %]

Sample	Ash^d	Carbon	Hydrogen	Nitrogen	Sulphur	Oxygen
Precursor	5.5	50.8	1.6	5.3	0.6	41.7
CA$_c$	4.3	73.9	2.7	3.0	0.1	20.3
CA$_m$	7.1	68.4	2.6	3.9	0.2	24.9
PA$_c$	11.2	80.6	2.1	5.7	0.4	11.2
PA$_m$	10.4	77.2	1.9	6.8	0.7	13.4

Activation of the starting material leads to significant changes in the elemental composition. The content of individual elements in the structure of the activated biocarbons is significantly influenced by both the type of activating agent and the heating variant applied during the activation process. Each of the activated biocarbons prepared (especially samples subjected to physical activation with carbon dioxide) is characterized by a much higher content of elemental carbon than the starting material. The effect of the heating variant applied during activation step is more diverse. In case of samples activated chemically with K_2CO_3 (CA$_c$ and CA$_m$), a higher C^{daf} content was observed for the sample heated in a conventional way, whereas for analogous materials activated with CO_2 (PA$_c$ and PA$_m$) the opposite relationship is observed. The obtained data have also shown that thermal treatment in a microwave furnace (most probably due to its shorter duration) allows for the preservation of larger amounts of heteroatoms (nitrogen, sulphur and oxygen) in the carbonaceous structure. Only in case of hydrogen, the content was slightly higher for the samples activated in a traditional laboratory resistance furnace.

From the adsorptive point of view, the size of the specific surface area and the type of porous structure generated during activation process are of particular importance. Therefore, in the next stage of the research, the basic textural parameters of the obtained activated carbons (e.g. BET surface area, total pore volume, micropore contribution in the porous structure as well as average pore diameter) were characterized,. The results of these studies are presented in Table 2.

Table 2. Textural parameters of the activated biocarbons obtained from post-fermentation residue

Sample	BET surface area [m²/g]	Total pore volume [cm³/g]	Micropore volume [cm³/g]	Micropore contribution [%]	Mean pore diameter [nm]
CA$_c$	861	0.61	0.45	74	2.81
CA$_m$	879	0.62	0.44	71	2.84
PA$_c$	21	0.06	-	-	12.27
PA$_m$	41	0.04	0.02	49	3.95

The data collected in Table 2 indicate that activated carbons prepared exhibit very different textural parameters. Only chemical activation with potassium carbonate permit effective development of the surface area and pore structure formation. The S_{BET} surface area of these samples varies from 861 m²/g to 879 m²/g, while the total pore volume from 0.61 to 0.62 cm³/g. For both analogous materials obtained

by means of direct physical activation, the textural parameters are so disadvantageous (S_{BET} of 21 and 14 m^2/g respectively), that it would be more appropriate to use the term biochars to define them. However, in order to avoid unnecessary confusion, the term activated biocarbons were consistently used in the following parts of the work.

As follows from further analysis of the data presented in Table 2, in case of chemically activated samples, the influence of the heating mode on the development of the porous structure is insignificant. It is evidenced by the fact, that surface area of CA_c sample is only 18 m^2 g lower than for analogous product of microwave-assisted activation CA_m. What is more, both variants of chemical activation lead to the effective development of the microporous structure. The contribution of micropores in the total pore volume for CA_c and CA_m biocarbons is equal to 74 and 71% respectively, and the average pore diameter does not exceed 2.85 nm.

The situation is completely different for physically activated materials. The PA_c sample obtained in a conventional furnace shows significantly less favourable textural parameters than the analogous carbon PA_m heated by means of microwaves. Surface area of PA_C sample is twice as small as that of microwave-heated sample and its structure contains only large pores, as indicated by the mean pore diameter exceeding 12 nm as well as the complete absence of micropores in the structure. In turn, the analogous biocarbon sample prepared in microwave muffle furnace shows intermediate micro-/mesoporous character of the structure (V_{mic}/V_t = 49 %, average pore diameter = 3.95 nm).

In order to characterize the chemical nature of the surface of the activated biocarbons prepared the contents of the surface functional groups of acidic and basic character as well as pH of water extracts were measured. The data presented in Table 3 imply that the acidic-basic character of the surface depends first of all on the method of activation. The second factor influencing the chemical nature of carbonaceous materials prepared (however to a lesser extent) is the variant of sample heating applied during activation process.

Table 3. Acid-base properties of the activated biocarbons prepared from post-fermentation residue

Sample	Acidic functional groups [mmol/g]	Basic functional groups [mmol/g]	Total content of surface groups [mmol/g]	pH of water extracts
CA_c	1.46	0.31	1.77	6.26
CA_m	1.39	0.19	1.58	5.84
PA_c	0.71	0.06	0.77	3.86
PA_m	1.11	0.16	1.27	3.77

The direct physical activation products show a clearly acidic character of the surface, as evidenced by the low pH value of their aqueous extracts (~ 3.8) and the distinct predominance of acidic moieties, especially in case of PA_c biocarbon. In case of analogous samples obtained by chemical activation with potassium carbonate, the amount of both acidic and basic surface functional groups is much higher. The pH of the water extracts of these activated biocarbons is also higher (5.84 and 6.26, respectively), which suggests that on their surface is covered by acidic groups of lower strength than in case of CO_2 activated carbons. The greatest amount of the functional species (1.77 mmol/g) was found on the surface of sample CA_c obtained via chemical activation conducted in a conventional laboratory furnace, while the lowest (approximately 0.8 mmol/g) on analogous sample activated with CO_2. According to the data presented in Table 3, the amount of surface functional groups depends also to some extent on the heating method applied during activation stage. However, it should be emphasized that this impact is different for each of the activation methods used. In case of samples activated with carbon dioxide, significantly more functional groups of acidic and basic nature contain product of microwave-assisted activation, whereas for chemically activated biocarbons, the exact opposite relationship is observed.

3.2. Sorption abilities of the activated biocarbons toward organic dyes

In the next stage of the research, the usefulness of the obtained activated biocarbons for the removal of organic impurities from aqueous solutions was assessed. Two organic dyes of different molecule size -

methylene blue (MB) and malachite green (MG) were used as model pollutants. The Langmuir and Freundlich adsorption models were used to analyse the experimental results.

The shape of the adsorption isotherms recorded at room temperature both in case of methylene blue (Fig. 1) and malachite green (Fig. 2) clearly shows that the amount of dye absorbed by individual activated biocarbons increases significantly with the increase of the initial concentration of the dyes solutions, striving to achieve a state of full saturation. This phenomena is especially well seen for biocarbons obtained via chemical activation.
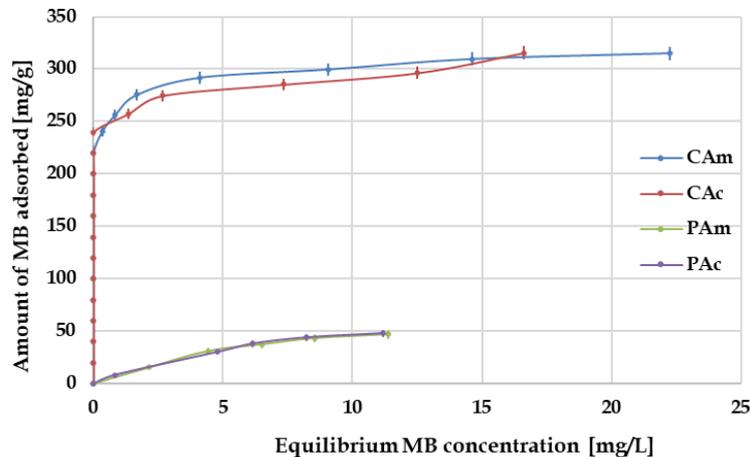
Fig. 1. The equilibrium adsorption isotherms of methylene blue onto activated biocarbons prepared by chemical and direct physical activation.
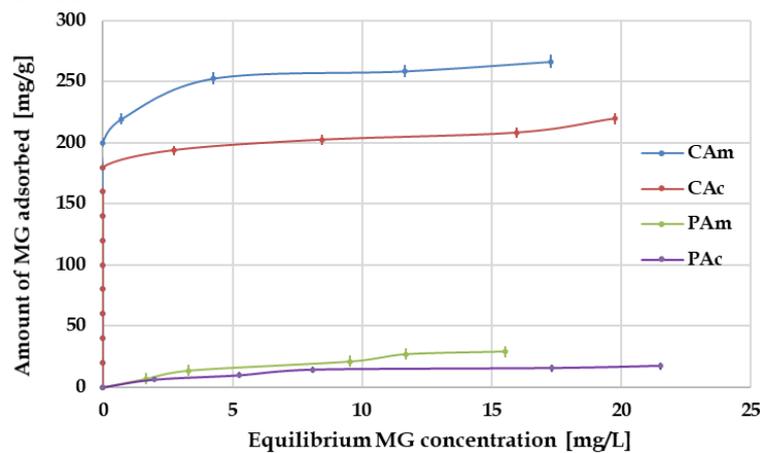
Fig. 2. The equilibrium adsorption isotherms of malachite green onto activated biocarbons prepared by chemical and direct physical activation.

This type of relationship may indicate that at low pollutants concentrations, the adsorption of dyes selected for research takes place in a completely random way, which is caused by the availability of many free active sites on the surface of carbonaceous adsorbents. In turn, at the higher dyes concentrations in an aqueous solution all the available active centres are occupied by methylene blue or malachite green molecules and consequently the complete saturation of the surface/porous structure of the tested carbon materials is achieved. As the shape of the majority of isotherms is smooth and single, it may be also supposed that we observe a monolayer coverage of the activated biocarbons surface with the methylene blue and malachite green molecules.

Analysis of the data displayed in Tables 4-5 makes it clear that method of thermochemical treatment of the precursor during the activation stage significantly influences the adsorption capacity toward organic dyes. The most effective adsorbent (both for methylene blue and malachite green) proved to be CA_m sample, obtained via microwave-assisted chemical activation. Its sorption capacity toward MB (312.5 mg/g) is almost twice as high as for commercial activated carbon Norit® SX2 (161.3 mg/g). In case of MG the difference between CA_m and commercial product is less than 31 mg. The analogous

sample CA_c, obtained in a conventional manner shows equally favourable sorption capacity towards the dyes selected for the tests. As expected, the products of physical activation, in particular the PA_c sample, are characterized by much lower efficiency in removal of both organic dyes from aqueous solutions. The adsorption capacity of the sample activated by CO_2 in a conventional laboratory furnace is almost 4 times lower in case of methylene blue and as much as 12 times lower for malachite green, than these observed for CA_m sample. The high and comparable sorption abilities of CA_m and CA_c biocarbons are most probably a consequence of their well-developed porous structure and surface area (Table 2). The textural parameters of the physically activated materials (especially PAC) are much less attractive, which is significantly reflected in the effectiveness of removal of both organic dyes. Changing the heating method from conventional to microwave one resulted in an increase in adsorption capacity, however the values of 90.6 mg/g (for MB) and 44.8 mg/g (in case of MG) recorded for PA_m sample are still significantly lower than for commercial activated carbon.

Table 4. Langmuir and Freundlich parameters of the adsorption isotherms of MB onto activated bioarbons

Sample	Langmuir model			Freundlich model		
	q_{max}	R^2	K_L	$1/n$	R^2	K_F
CA_c	301.2	0.999	20.75	0.063	0.971	254.16
CA_m	312.5	0.999	22.86	0.064	0.981	261.10
PA_c	81.0	0.984	0.08	0.705	0.990	9.66
PA_m	90.6	0.962	0.19	0.650	0.964	10.38
Norit® SX2	161.3	0.999	15.15	0.037	0.738	143.35

q_{max} - the maximum adsorption capacity of the biocarbons (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.

Table 5. Langmuir and Freundlich parameters of the adsorption isotherms of MG onto activated bioarbons

Sample	Langmuir model			Freundlich model		
	q_{max}	R^2	K_L	$1/n$	R^2	K_F
CA_c	214.1	0.999	27.47	0.055	0.868	182.01
CA_m	263.9	0.999	17.23	0.059	0.961	225.94
PA_c	20.4	0.986	0.19	0.427	0.942	4.75
PA_m	44.8	0.949	0.10	0.624	0.969	5.44
Norit® SX2	233.0	0.998	4.30	0.052	0.793	179.3

q_{max} - the maximum adsorption capacity of the biocarbons (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.

As follows from the data included in Tables 4 and 5 the adsorption of both dyes onto activated carbons obtained as a result of chemical activation is most likely according to the assumptions of the Langmuir model, i.e. with the formation of an adsorption monolayer on the surface of carbonaceous materials. This is indicated by the values of the correlation coefficient R^2 for this model, which are very close to the unity. In case of physically activated carbons the situation is more varied. During the adsorption of methylene blue the Freundlich model (assuming that the adsorbent can be covered with several layers of the adsorbate) turned out to be a better fit for the experimental data. The same is also true for the adsorption of malachite green on PA_m sample. On the other hand, in case of PA_c sample, a higher R^2 value was recorded for the Langmuir model. However, it should be emphasized, that the value of the correlation coefficients for both models differs significantly from the value of 1, which suggest that the mechanism of adsorption is more complicated.

3.3. Electrokinetic studies

The analysis of curves of the surface charge density (σ_0) of both examined activated biocarbons as a function of solution pH presented in Fig. 3 indicates that the pH values corresponding with point of

zero charge (pzc) are equal to 5.8, 5.0, 3.8 and 3.6 for CA_c, CA_m, PA_c and PA_m, respectively (Table 6). It means that activated biocarbons obtained through physical activation procedure have more acidic character than those obtained through chemical activation. Within the pH range higher than pH_{pzc}, the solid surface is negatively charged, which favours binding of dye molecules with cationic character (presence of electrostatic attraction).

The adsorption of MB and MG dyes causes significant changes in solid surface charge density – σ_0 are lowered and assumes more negative values almost in the whole examined pH range. The consequence of this is shift of pH_{pzc} of systems containing dye towards the lower pH values in comparison to suspensions without organic substance (Table 6). Moreover, such effect observed for MG is considerably greater than that of MB.
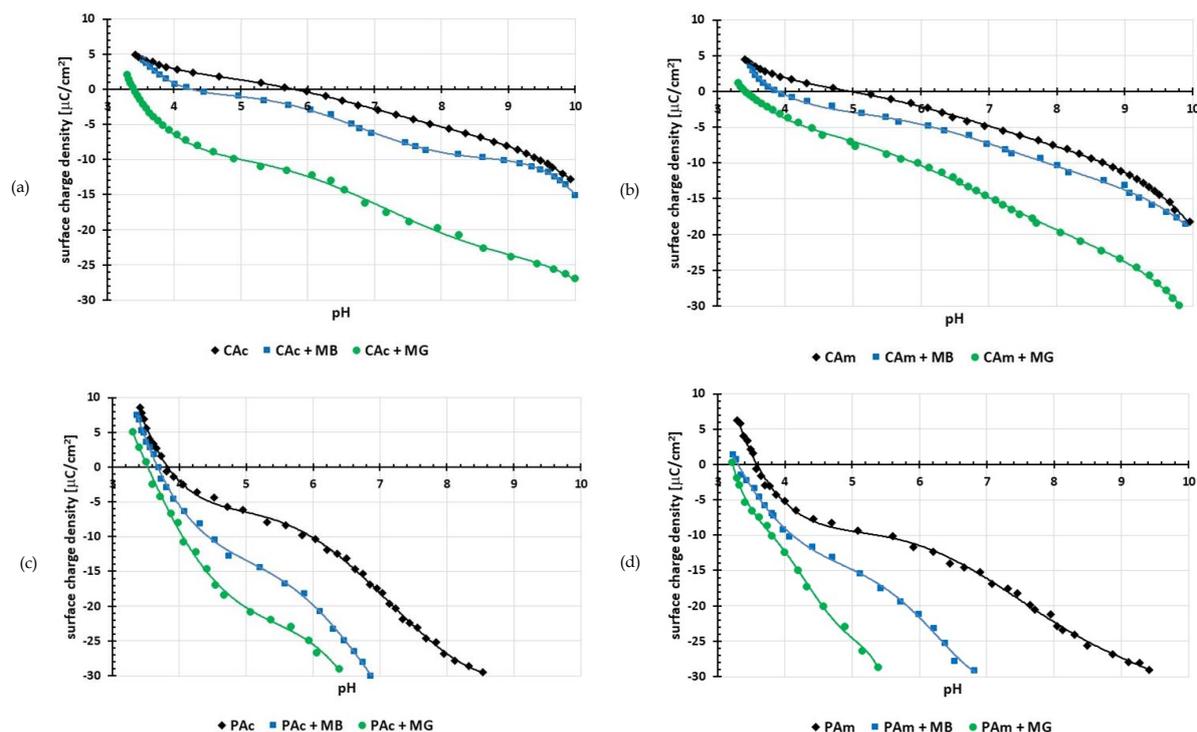
Fig. 3. Surface charge density of activated biocarbons: (a) CA_c, (b) CA_m, (c) PA_c and (d) PA_m without and with adsorbed MB or MG dyes as a function of solution pH

Table 6. Points of zero charge (pH_{pzc}) of examined activated biocarbons without and with adsorbed MB or MG dyes

Activated biocarbon without dye	pH_{pzc}	Activated biocarbon with MB dye	pH_{pzc}	Activated biocarbon with MG dye	pH_{pzc}
CA_c	5.8	CA_c + MB	4.3	CA_c + MG	3.4
CA_m	5.0	CA_m + MB	3.9	CA_m + MG	3.4
PA_c	3.8	PA_c + MB	3.7	PA_c + MG	3.5
PA_m	3.6	PA_m + MB	3.2	PA_m + MG	3.2

The adsorption of cationic molecules causes the creation of additional number of negatively charged surface groups on the activated biocarbon surface, and thus the absolute value of the solid negative charge increases. Due to the specific structure of the MG molecule and the possibility of a positive charge displacement between the amine groups and the central carbon of dye molecule (due to the shift of the mobile hydrogen ion - proton) (Fig. 4(b), Stiepanow 1980), the effect of the σ_0 change observed for malachite green is significantly greater. Such proton migration between amine groups and sulfur atom in MB molecule is also possible, but linear structure of MB molecule (Fig. 4(a), Stiepanow 1980) makes that changes in its position in the formed adsorption layer are significantly limited. Moreover greater

adsorption of MB on the examined activated biocarbon surfaces suggest their rather perpendicular arrangement in the adsorption layer (parallel - flat arrangement of MB molecules would result in lower adsorption due to blockage of surface sites).

(a)

(b)
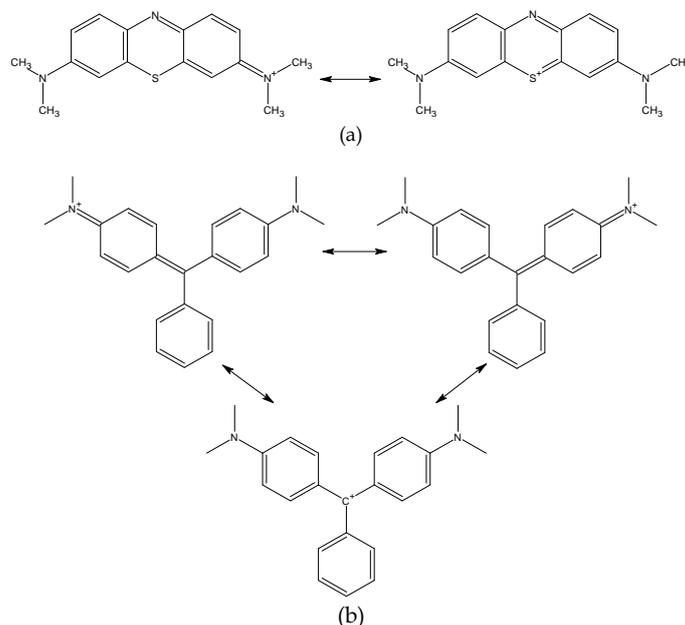
Fig. 4. Structure of (a) MB and (b) MG molecules (Stiepanow 1980)

The analogous behaviour was noted in the systems containing ionic dye and other solids, namely simple and mixed oxides (Wawrzkiewicz et al. 2017, 2019; Wiśniewska et al. 2008, 2020). For these suspensions the adsorption of anionic dye resulted in the solid surface charge density increase, whereas the adsorption of cationic dye caused its decrease (due to the creation of additional surface groups oppositely charged in relation to the adsorbate molecules).

Some changes in the surface properties of the solid in the dye presence can be also caused by the formation of hydrogen and chemical bonds between the nitrogen and sulfur atoms with free electron pairs and activated biocarbon surface groups, mainly of acidic character (Wiśniewska et al. 2020).

The cationic dyes adsorption influences considerably the zeta potential and isoelectric point (iep) position of examined carbon materials. The respective data are presented in Fig. 5 and in Table 7. In a few cases the position of iep was determined by the obtained curves extrapolation to the value $\zeta=0$. The electrokinetic potential zeta (ζ) describes the charges composition located in the slipping plane area formed around the solid particles within the electrical double layer (edl). As can be seen in Fig. 5 and in Table 2 the pH_{iep} values obtained for the solid suspensions without dyes differ from the corresponding pH_{pzc} values, especially in the activated biocarbon samples obtained through chemical activation (they are about 2.5 units smaller). Such difference is result of permeation of the edl formed on the opposite pore walls of the adsorbent, which leads to a change in the ionic composition of the slipping plane area. Due to the fact, that chemically activated biocarbons are characterized by considerably developed microporous structure, this phenomenon is of great importance in their case (Hunter, 1981; Janusz and Skwarek 2021).

Table 7. Isoelectric points (pH_{iep}) of examined activated biocarbons without and with adsorbed MB or MG dyes.

Activated biocarbon without dye	pH_{iep}	Activated biocarbon with MB dye	pH_{iep}	Activated biocarbon with MG dye	pH_{iep}
CA_c	3.3	CA_c + MB	11.1	CA_c + MG	10.4
CA_m	2.6	CA_m + MB	11.8	CA_m + MG	9.4
PA_c	2.5	PA_c + MB	10.7	PA_c + MG	8.0
PA_m	2.2	PA_m + MB	10.0	PA_m + MG	7.1
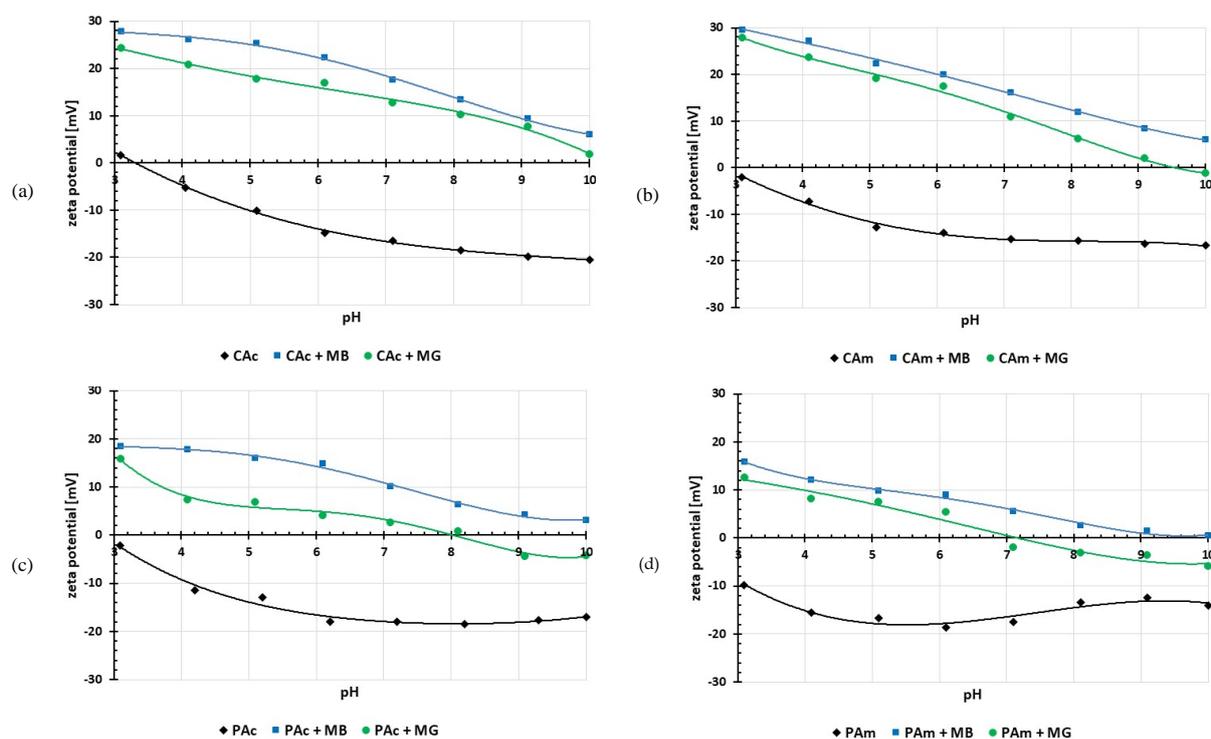
Fig. 5. Zeta potential of activated biocarbons: (a) CA$_c$, (b) CA$_m$, (c) PA$_c$ and (d) PA$_m$ without and with adsorbed MB or MG dyes as a function of solution pH

For all examined activated biocarbons the zeta potential assumes negative values within almost whole studied pH range. The addition of cationic dyes causes significant increase of ζ potential and change of its charge to positive. It results mainly from the cationic nature of the dyes, as well as from their specific arrangement at the solid-solution interface. The cationic groups of adsorbed dye molecules directed towards the solution and located in the slipping plane area are responsible for positive values of zeta potential. As a result, the pH$_{iep}$ point for the suspensions with dyes assume high values within basic range of solution pH (Table 7). Methylene blue turned out to be more effective in the increase of zeta potential of solid particles, which confirms the perpendicular arrangement of its linear molecules in the adsorption layer and the exposure of positive nitrogen containing groups towards the slipping plane area.

4. Conclusions

The above presented and discussed results have shown that the waste materials such as residue of alcoholic fermentation of corn starch can be used for production of activated biocarbons characterized by high effectiveness in removal of organic dyes from water solutions. The adsorption properties of the carbon materials studied are comparable or even better than those of the commercial adsorbents. It has been also proved, that application of microwave and conventional heating in preparation of carbonaceous adsorbents allows producing a wide gamut of materials with very different physicochemical properties. The results have also indicated that the presence of cationic dyes influences significantly the structure of electrical double layer formed at the activated biocarbon/aqueous solution interface. This is manifested by marked changes in the surface charge density and zeta potential of the examined solids, as well as position of pH$_{pzc}$ and pH$_{iep}$ points. The adsorption of MB and MG dyes causes decrease of the surface charge density and the increase of the zeta potential of carbon materials. This is caused by the cationic groups of dye molecules, which can be formed in different places within one dye molecule as a result of displacement of the mobile hydrogen cation. In such a way these groups are present in the surface and diffusion part of electrical double layer influencing σ$_0$ and ζ values of the activated biocarbon particles dispersed in aqueous solution.

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