Activated bio-carbons prepared by physical activation of residues after supercritical extraction of raw plants

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Abstract: A series of activated bio-carbons has been obtained by physical activation of residues after supercritical extraction of blackberries, raspberries and blackcurrants. The effects of different temperatures of activation and different starting materials on the physicochemical and sorption properties of the bio-carbon samples obtained were evaluated. The physicochemical properties of the activated bio-carbons were characterized by elementary analysis, low-temperature nitrogen sorption and Boehm titration. All materials were tested as adsorbents of pollutants from gas (nitrogen dioxide) and liquid (iodine, methylene blue) phase. The sorption properties of the activated bio-carbons were tested at 23°C. The materials obtained were activated bio-carbons of surface area ranging between 303 and 442 m²/g and showing basic character of the surface. The content of elemental carbon in the obtained samples was in the range of 73.4 - 82.1 wt. %. The maximum adsorption capacities of the materials towards nitrogen dioxide were 65 mg/g, methylene blue - 207 mg/g, and iodine 1001 mg/g. According to the adsorption tests towards nitrogen dioxide, the sorption capacities of the adsorbents studied were increased if a mixture of nitrogen dioxide and air had a humidity of 70 %. The mechanism of methylene blue adsorption involved the formation of adsorptive multilayer. The most effective adsorbent of organic and inorganic pollutants proved to be the activated bio-carbon obtained from the residues after supercritical extraction of blackcurrants.

Keywords: bio-sorbents, physical activation, toxic gas removal, adsorption from liquid phase, Langmuir and Freundlich isotherm

1. Introduction

In the few last decades, increasing use of all kinds of chemicals in everyday life, along with their use in industry, has resulted in significant pollution and damage of the natural environment. The soil and groundwater have been contaminated with chemical fertilizers, pesticides, dyes or different surfactants. Some of these inorganic and organic chemicals are toxic, some show mutagenic or cancerogenic properties, so that their presence can affect living organisms (Kuramochi et al., 2012). The atmosphere is also polluted and the main pollutants are nitrogen and sulfur compounds, carbon oxide and particulates (Landau et al., 2015). Realization of the state of the natural environment has prompted the search for new and more effective methods of its cleaning. An effective method of cleaning is adsorption of pollutants for which increasingly often activated carbons, being efficient adsorbents from the liquid and gas phases, are used (Pietrzak and Bandosz, 2007; González, 2018; Bazan-Wozniak et al., 2019; Jiang et al., 2019). Growing demand for activated carbon and depletion of the non-renewable natural resources have stimulated the search for new sources of carbon and new methods of their production (Marsh and Rodrigues-Reinoso, 2006; Karadirek and Okkay, 2018). An attractive group of precursors of activated carbon are the residues from supercritical extraction of raw plants (Bazan-Wozniak et al., 2017). The process of extraction with a liquid in supercritical state is in full agreement with the rules and regulations of the so-called *Green Chemistry* aimed at minimization of waste and maximization of protection of the natural environment by development of new environmentally friendly technologies

and alternative chemical syntheses (Anastas and Warner, 1998). Extraction with a liquid in supercritical state permits extraction of bioactive substances and their separation from pollutants (Millao and Uquiche, 2016). For example, breweries increasingly often uses hog extracts obtained on industrial scale by supercritical extraction (Capuzzo and Maffei, 2013). Another example of the process application is production of vegetable oil from berry plant seeds (del Valle, 2015). Unfortunately, increasing use of supercritical extraction means increasing waste left after the process, which needs to be utilized. One of the effective and economically sound methods for utilization of such waste is its use for production of carbon adsorbents, in particular activated carbons.

The study we have undertaken was aimed at obtaining activated bio-carbons by physical activation of residues of supercritical extraction of seeds of blackberries, raspberries and blackcurrants and their comprehensive characterization. The obtained carbon adsorbents were tested in the process of removal of gas pollutant (nitrogen(IV) oxide) and model organic and inorganic liquid pollutants (methylene blue and iodine).

2.   Materials and methods

2.1.   Precursors and activated bio-carbons preparation

The precursors of the activated bio-carbons were residues after supercritical extraction of blackberries (B) raspberries (R) and blackcurrant (C) in the form of powder with grain size range of 0.15-0.85 mm. At first the precursors were washed with distilled water and then dried to constant mass at 70°C.

Then the precursors were subjected to carbonization (C) at 500°C. The process was performed in a tube furnace in nitrogen atmosphere blown at the rate of 150 cm^3/min. The precursors were heated from room temperature to the final temperature of pyrolysis at the rate of 5°C/min. After reaching the desired temperature, the samples were thermostated for 60 minutes. The bio-chars were then subjected to physical activation (A) with CO_2 blown at the rate of 250 cm^3/min in the same tube furnace. Two activation temperatures were applied, 700 or 800°C (A7 and A8), the samples were thermostated for 45 minutes. Next, the activated bio-carbon washed at first with a 5 % solution of HCl and then with distilled water. Finally, the samples were dried to constant mass at 110°C.

2.2.   Analytical procedures

The elemental analysis of the activated bio-carbons was performed by using elemental analyzer Vario EL III. The standard test methods for ash was performed according to the ASTM D2866-94 Standard (2004).

The porous structure of the obtained materials was characterized on the basis of low temperature nitrogen adsorption-desorption isotherms measured on AutosorbiQ at -196 °C. The surface area of the activated bio-carbons was calculated by Brunauer-Emmett-Teller method. The micropore volume and micropore area were determined using the t-plot method.

The pH of the activated bio-carbons was measured using the following procedure: 0.2 g of each sample was added to 10 cm^3 of distilled water and the suspension was stirred overnight to reach equilibrium. After that pH of the suspension was measured. The content of surface oxygen functional groups was determined according to the Boehm method (Boehm, 1994). A portion of 0.25 g of activated bio-carbon was placed in 25 cm^3 of 0.1 mol/dm^3 solutions of either sodium hydroxide or hydrochloric acid. The vials were sealed and shaken for 24 h and then 10 cm^3 of each filtrate was pipetted and the excess of base or acid was titrated with 0.1 mol/dm^3 HCl or NaOH, as required. The numbers of acidic sites of various types were calculated assuming that NaOH neutralizes all acidic groups and HCl reacts with all basic groups. All experiments were made twice.

For evaluation of NO_2 sorption capacity the materials in the form of granules (0.10-0.65 mm in diameter) were packed into a glass column (length 300 mm internal diameter, 9 mm bed volume 3 cm^3). The samples were tested in dry (D) and wet (W) conditions. Dry or wet air (70 % humidity) with 0.1 % of NO_2 was passed through the bed of the adsorbent at 0.450 dm^3/min. The concentration of NO_2 was monitored using Multi-Gas Monitor Q-RAE PLUS PGM-2000/2020. The tests were stopped at the breakthrough concentration of 20 ppm because of the electrochemical sensor limits. The capacities of each sorbent in terms of milligram of NO_2 per gram of adsorbent were calculated by integration of the

area above the breakthrough curves and NO_2 concentration in the inlet gas, flow rate, breakthrough time and mass of the adsorbent (Nowicki et al., 2012).

The iodine sorption ability of the activated bio-carbons was determined according to the following procedure. Portions of 0.1 g of the samples sieved to a particle size below 0.09 mm were placed in 150 cm³ flasks and 2 cm³ of 5 % HCl was added. Then 20 cm³ of stock 0.1 mol/dm³ iodine solution was added to it and the mixture was shaken for 5 min in a shaker. All the samples were filtered through filter paper and then washed with 30 cm³ of water. The resulting solution was titrated with 0.1 mol/dm³ sodium thiosulfate until became colorless.

The dye studied was methylene blue. Samples of 20 mg of the prepared activated bio-carbons with the particle size of 0.09 mm were added to 50 cm³ of dye solution with initial concentrations in the range from 10 to 90 mg/dm³ and the suspension was stirred to reach equilibrium for 24 h. After the adsorption equilibrium has been achieved, the solution was separated from the sorbent by centrifugation at 8000 rpm, for 5 min. The concentration of dye solution was determined using double beam UV–Vis spectrophotometer; model Carry Bio 100 (Varian). The amount of adsorbed dye was calculated using the following formula:

$$q_e = \frac{C_0 - C_e}{m} \times V \tag{1}$$

where C_0 is the initial dye concentration (mg/dm³), C_e is the equilibrium dye concentration (mg/dm³), m is the weight of the activated carbon (g) and V is the volume of the solution (dm³).

For interpretation of the methylene blue adsorption on the activated bio-carbons, the linear forms of Langmuir and Freundlich equations were used (Langmuir, 1918; Freundlich, 1906). The Langmuir equation assumes that the surface of adsorbent has a certain number of energetically uniform active centers or adsorption sites capable of adsorption of only one molecule of the adsorbate. The Langmuir isotherm is described by the following linear equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L \times q_{max}} + \frac{C_e}{q_{max}} \tag{2}$$

where q_e is the equilibrium amount of adsorbed dye (mg/g), K_L is the Langmuir adsorption equilibrium constant (dm³/mg) and q_{max} is the maximum adsorption capacity of the adsorbent (mg/g).

According to the Freundlich model, the number of adsorbed molecules cannot be greater than the number of active sites, and the layer formed on the adsorbent surface permits formation of subsequent layers. The model is described by the following equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{3}$$

where K_F is the Freundlich equilibrium constant (dm³/mg) and 1/n is the intensity of adsorption constant.

3.   Results and discussion

3.1. Characterization of the activated bio-carbons

Table 1 presents results of elemental analysis of the obtained activated bio-carbons. They imply that the content of mineral substance and elemental composition of the products of physical activation insignificantly depend on the type of initial material. The ash content in the activated bio-carbons varied from 6.8 to 9.2 wt. %. These values are much lower than those obtained in our earlier studies (Bazan et al., 2016), which is most probably related to the additional stage of washing the activated bio-carbons with a 5 % HCl solution and distilled water. Another conclusion drawn from the data from Table 1 is that with increasing activation temperature the content of mineral substance in the obtained bio-carbons increases.

The elemental compositions of the activated bio-carbons are very similar: the content of C^{daf} varies from 70.3 % for RCA7 to 82.1 wt. % for CCA8 and increases with increasing activation temperature. In contrast, the contents of hydrogen, nitrogen and oxygen decrease with growing temperature. Interesting is the high content of N^{daf} in the samples obtained, except for bio-carbon CCA8, which suggests that the initial materials used contain thermally stable connections of this heteroatom, which is in agreement with earlier studies (Kaźmierczak-Raźna et al., 2019). The content of sulfur in the

samples obtained is very low, it does not exceed 0.2 wt. %, which is attractive both from ecological and technological points of view.

According to the results collected in Table 2, the physical activation with CO_2 of the residues of supercritical extraction of blackberries, raspberries and blackcurrants does not permit effective development of surface area and porous structure of the bio-carbons obtained.

Their surface areas vary from 303 to 442 m²/g. The best developed surface area and microporous structure was found to have sample CCA8, the only one whose S_{BET} exceeds 400 m²/g. The contribution of micropores in this sample reaches 81 % of all pores.

Table 1. Elemental analysis of the activated bio-carbons obtained and the yield of activation processes (wt. %)

Sample	Ash	C^{daf}	H^{daf}	N^{daf}	S^{daf}	O^{daf}	Yield
BCA7	8.7	73.4	2.3	4.3	0.1	19.9	71
BCA8	9.2	79.1	1.8	3.2	0.1	15.8	52
RCA7	6.8	70.3	2.9	5.5	0.1	21.2	69
RCA8	7.5	77.0	2.5	3.9	0.1	16.5	60
CCA7	7.2	74.3	2.8	4.9	0.2	17.8	73
CCA8	7.8	82.1	1.9	1.7	0.1	14.2	58

daf- dry-ash-free basis, *- determined by difference

Table 2. Textural parameters of the activated bio-carbons

Sample	Surface area (m²/g)	Micropore area (m²/g)	Total pore volume (cm³/g)	Micropore volume (%)	Average pore diameter (nm)
BCA7	303	279	0.33	60	4.25
BCA8	323	305	0.25	71	4.23
RCA7	335	312	0.42	76	3.98
RCA8	369	333	0.38	79	3.77
CCA7	396	346	0.27	70	3.96
CCA8	442	404	0.44	81	3.68

The poorest textural parameters were found for the samples obtained by physical activation of residues of supercritical extraction of blackberries. The surface areas of the bio-sorbents obtained were observed to increase with increasing activation temperature. In general, analysis of the textural parameters of the bio-carbons studied revealed no significant impact of the type of precursor on their surface area and porous structure.

The average pore diameter measured for the bio-carbon samples varied from 3.68 to 4.25 nm, which means that the second most abundant type of pores – are small mesopores. As follows from Table 2 data, the activation at 800°C results in obtaining samples of slightly greater contribution of micropores and smaller mean pore diameter.

Figure 1 presents the pH values (Fig. 1A) of water extracts from the activated bio-carbons and the content of surface oxygen functional groups of acidic or basic character, determined by the Boehm method (1B).

According to these data, the bio-carbon adsorbents obtained have surfaces of basic character as none of them has surface functional groups of acidic nature. The pH values of water extracts from the samples varies from 9.8 to 11.2. Strongly basic character of the bio-carbons activated by carbon(IV) oxide is most probably related to the fact that this type of activator at the high temperatures applied favors the generation of basic groups (Bansal and Goyal, 2005). Moreover, analysis of Fig. 1B data shows that the number of basic groups depends on the activation temperature; the samples activated at 800°C show a higher content of basic groups than those activated at 700°C.

3.2. Adsorption of nitrogen(IV) oxide

The main aim of the study was to evaluate the sorption abilities of the adsorbents obtained towards nitrogen(IV) oxide. The results calculated on the basis of the NO_2 breakthrough capacities are collected

in Table 3. To compare the sorption capacities obtained, adsorption tests for two commercial carbons were also carried out: CWZ-22 and NORIT SX2 (Table 3). Analysing the data presented in Table 3 it can be concluded that the activated bio-carbons obtained by us show comparable and even better sorption capacities towards NO_2. The effectiveness of nitrogen(IV) oxide removal depends first of all on the conditions of the adsorption test, while to a smaller degree on the activation temperature and type of initial material.

The sorption properties of all activated bio-carbons studied were improved when the process of adsorption was carried out at 70 % air humidity. During the adsorption in the presence of steam, nitrogen(IV) oxide reacts with water molecules, leading to formation of a mixture of nitric(III) and nitric(V) acids (Bazan-Wozniak et al., 2017), so finally the amount of the adsorbed toxic gas increases.
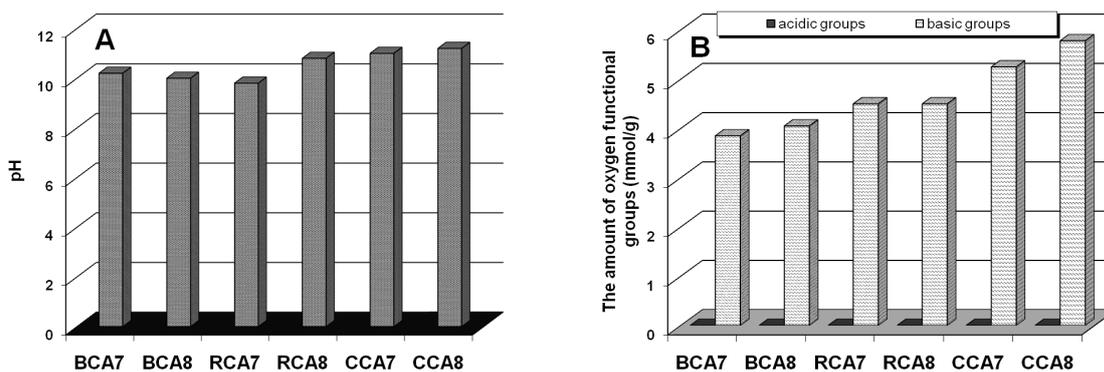
Fig. 1. The value of pH (A) and surface oxygen functional groups (B) on the activated bio-carbons

Table 3. NO_2 breakthrough capacities of the activated bio-carbons obtained

Sample	NO_2 breakthrough capacities (mg/g)	
	dry	wet
BCA7	5.9	19.1
BCA8	11.0	27.4
RCA7	6.7	24.0
RCA8	12.7	33.9
CCA7	10.5	43.8
CCA8	18.2	65.0
CWZ-22	7.9	21.0
NORIT SX2	5.0	32.9

The most pronounced effect of the presence of steam was noted for sample CCA8, obtained by physical activation of the residue of supercritical extraction of blackcurrants. The sorption capacity of this sample in high humidity was over three times higher than in dry conditions. As follows from Table 3 data, the sorption properties of the activated bio-carbons studied also depended on the activation temperature. The samples activated at 800°C showed higher sorption capacity towards nitrogen(IV) oxide than the samples activated at 700°C. The above relation holds for all samples, irrespective of the conditions of the test. The increase in the sorption capacity towards NO_2 was particularly pronounced if the process was carried out in the presence of steam. The smallest increase was noted for the samples obtained from the residues of supercritical extraction of blackberries (BCA7 and BCA8), which can be related to somewhat poorer developed microporous structure of these bio-sorbents.

The type of initial material also had an impact on the sorption capacity towards NO_2. The samples obtained from the initial material of blackcurrants showed higher effectiveness in removal of NO_2, irrespectively of the conditions of the process. The least effective were the adsorbents obtained from the initial material of blackberries.

In order to make a deeper characterization of the course of processes taking place in the activated bio-carbons during adsorption in dry and wet conditions, the curves illustrating changes in NO_2 concentration, were analyzed (Fig. 2).
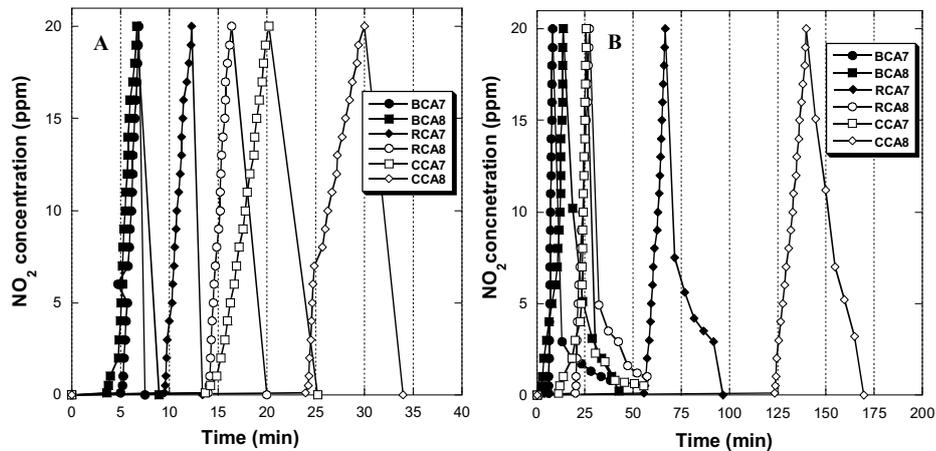
Fig. 2. NO_2 breakthrough curves for the activated bio-carbons studied in dry (A) and wet (B) conditions

As follows from the NO_2 adsorption/desorption curves, the longer time period, through which the concentration of nitrogen(IV) oxide was close to zero, was observed for the processes carried out in the presence of steam. The above relation is particularly well seen for sample CCA8 obtained from the residue of supercritical extraction of blackcurrants. After breakthrough of the bio-carbon adsorbent bed for all samples a rapid increase in the concentration of NO_2 to 20 ppm takes place. When the gas inflow to the adsorbent bed was stopped, for all samples a decrease in the NO_2 concentration to 0 ppm was observed, which suggests that most of the adsorbed nitrogen(IV) oxide had been strongly bound in the porous structure or chemisorbed (Bashkova and Bandosz, 2009).

After NO_2 adsorption on the surface of the bio-sorbents studied, their acid-base character was determined again on the basis of identification of functional groups by the Boehm method and pH values of water extracts. Fig. 3 presents the changes in concentration of surface oxygen functional
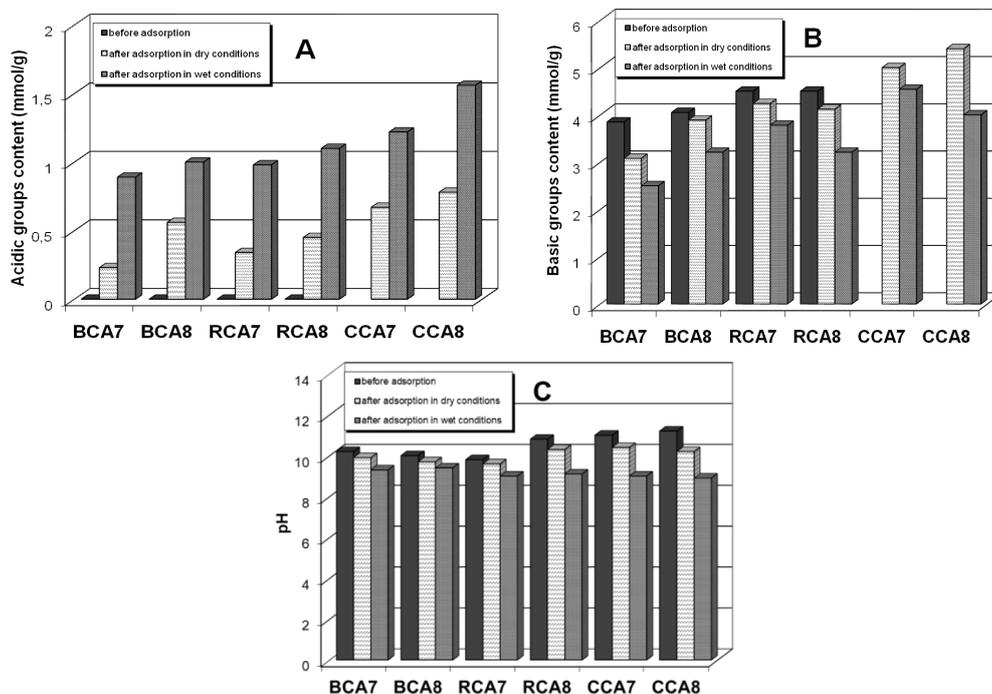
Fig. 3. Acidic (A) and basic (B) groups of the activated bio-carbons before and after NO_2 adsorption in dry and wet conditions and surface pH values for the initial and exhausted samples (C)

groups of acidic and basic character, that took place as a result of NO_2 adsorption. Prior to the NO_2 adsorption there were no functional groups of acidic character on the surface of all obtained bio-carbon samples, but according to the results collected in Fig. 3, after the NO_2 adsorption some such groups appeared. A bit higher content of acidic surface functional groups was observed when the adsorption of this toxic gas was performed in wet conditions. The results presented in Fig. 3B indicate that the content of surface functional groups of basic character on all samples after the process of NO_2adsorption significantly decreased. In addition, the above changes confirm the pH values of water extracts after the adsorption process.

3.3. Adsorption of iodine and methylene blue

The obtained activated bio-carbons were also tested as adsorbents of organic and inorganic pollutants: methylene blue and iodine, from liquid phase. The determined sorption capacities of the samples are shown in Table 4. In addition, Table 4 also shows the sorption capacities of the commercial carbons (Bazan-Wozniak et al., 2017).

According to these data, the most effective adsorbent of the two model pollutants was the activated bio-carbon obtained from the residue of supercritical extraction of blackcurrants, activated at 800°C. This sample was capable of adsorbing 1001 mg of iodine and 207 mg of methylene blue. The least efficient adsorbent was the sample obtained from the residues of supercritical extraction of blackberries, activated at 700°C. The sorption capacity of BCA7 towards iodine was 650 mg/g and towards methylene blue - 142 mg/g. Moreover, it was evidenced that with increasing temperature of activation the sorption capacity towards iodine and methylene blue increased.

In order to determine the mechanism of methylene blue adsorption on the surface of activated bio-carbons, two models were applied, the Langmuir and Freundlich ones. The results of the fit are presented in Table 5.

Table 4. Adsorption capacities of adsorbents for iodine and methylene blue

Sample	Amount adsorbed (mg/g)	
	iodine	methylene blue
BCA7	650	142
BCA8	804	181
RCA7	701	134
RCA8	839	195
CCA7	769	161
CCA8	1001	207
CWZ-22	min. 750	130
NORIT SX2	min. 800	150

Table 5. Langmuir and Freundlich parameters of the adsorption isotherms of methylene blue
onto activated bio-carbons

Sample	q_e (mg/g)	Langmuir			Freundlich		
		R^2	q_{max} (mg/g)	K_L (dm³/mg)	R^2	K_F (dm³/mg)	$1/n$
BCA7	142	0.899	143	0.008	0.911	43.75	0.504
BCA8	181	0.919	200	0.013	0.968	105.68	0.025
RCA7	134	0.853	143	0.049	0.985	21.43	0.760
RCA8	195	0.954	200	0.008	0.983	95.28	0.279
CCA7	161	0.941	167	0.012	0.983	74.13	0.403
CCA8	207	0.966	208	0.011	0.972	105.46	0.301

Analysis of the correlation coefficient values R^2 shows that closer to one was the value obtained for the fit to the Freundlich isotherm, which suggests that this model of adsorption better describes the

adsorption of the dye studied on the surface of the adsorbents obtained. The fit to the Freundlich isotherm was described by R^2 values varied from 0.911 to 0.983 and were higher than for the fit to the Langmuir isotherm (0.853-0.966). The more accurate fit to the Freundlich model indicates the multilayer adsorption of methylene blue on the surface of the activated bio-carbons studied.

4.   Conclusions

The paper presents results of a study of adsorption of gas and liquid pollutants on activated bio-carbons obtained from the residues of supercritical extraction of seeds from blackberries, raspberries and blackcurrants. As follows from analysis of physicochemical properties, as a result of physical activation of these residues the activated carbon materials of rather poorly developed surface and basic surface character were obtained. As proved by the adsorption tests towards selected gas and liquid pollutants, the poorly-developed surface area and porous structure did not eliminate these materials as potential cheap adsorbents. The most effective adsorbents were the activated bio-carbons obtained from the residues of supercritical extraction of blackcurrants.

The sorption capacity of the adsorbents studied towards NO_2 varied in the range of 5.9 – 65.0 mg. Moreover, all bio-carbons were characterized by higher effectiveness in removal of NO_2 when the adsorption process was performed in the presence of steam. The sorption capacities of the adsorbents obtained towards methylene blue and iodine varied from 142 to 207 mg/g and from 650 to 1001 mg/g, respectively. It has been shown that the mechanism of methylene blue adsorption involves the formation of multiple layers.

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