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Impact of chemical activation on selected adsorption features of powdered activated carbon

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ABSTRACT

The use of activated carbons both in research and in the design or optimization of many industrial processes is connected with the need for continuous improvement of their quality. Improvement of their production methods, surface activation or modification plays a significant role. The aim of our study was to evaluate the effect of chemical and physical activation on the parameters of powdered activated carbon (PAC). Additionally, we wanted to identify further processes directed at stabilizing the activated carbon features. Carried out tests led to reach the final product which may be safely used in medicine to eliminate toxic micropollutants from the human gastrointestinal system. After raw charcoal material synthesis high-temperature, physical activation, as well as single and double chemical activation, has been carried out. Primary tests included only activated carbon processing. Then PAC was subjected to proper processes of combined physical and chemical activation. In order to determine the sorption efficiency, there was tested dye 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride (NCBI), as an indicator of contamination of aqueous solutions. For our experiments, we did numerous adsorptive tests including porosity, the pH of zero charge point, specific surface area and microscopy observation of the PAC surface. The features of tested dye (NCBI), Methylene Number, extinction and pH of the aqueous extract were also evaluated. The reached result has proven that short chemical activation has hardly changed features of ground and powdered raw material. Conducted research on combined physical and chemical activation with CH_3COOH showed that high temperature and acid operation change activated carbon parameters, increase porosity and NCBI adsorption. Chemical activation also significantly corrected pores size. The best adsorption of NCBI with a positive charge was achieved at neutral pH.

Keywords: Powdered activated carbon; PAC modification (activation); Dye; Adsorption

1. Introduction

Activated carbons (AC) belong to the group of micro-textured carbon materials. They are characterized by a very well-developed porous structure and specific surface area. Their skeleton consists of a network of hexagonal carbon rings arranged irregularly, being a factor that shapes their porous surface. The porous structure consists of numerous interconnected pores of varying shapes and sizes. Micropores play the most important role and their size is confronted with the size of adsorbed contaminants. The main function of mesopores, apart from the

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adsorption process itself, is to transport compounds from the surface macropores to the micropores. The macropores catch pollutant molecules from the solution due to electrochemical and Van der Waals forces [1–3].

The selection of appropriate raw materials, conditions of the production process, as well as activation or modification enable the generation of activated carbons with diversified properties and multiple applications [4]. The use of activated carbons both in research and in the design or optimization of many industrial processes is connected with the need for continuous improvement of their quality. Improvement of methods of their production plays also a significant role [1]. Activated carbon has many applications in the environment, cosmetology, medicine and industry. It is used for separation, recovery, complete removal or modification of various compounds from water, wastewater, air, medical or cosmetic solutions, body fluids, removal of hydrogen sulfide from natural gas, etc.

The surface of each activated carbon can be modified to obtain the required adsorption properties. Lu et al. [5] give different ways to activate and modify the surface of activated carbons by chemical, physical and thermal methods. Impregnation or washing of the activated carbon can also be used. Physical activation, otherwise known as thermal activation, is a process consisting of two stages. Carbonization (pyrolysis) of the basic raw material is the first stage, which is carried out at high-temperature (about 500°C–1,000°C) in an inert gas atmosphere. The second stage is the stimulation of the produced carbonization. This consists of a high-temperature activation of the material (about 800°C–1,000°C) in an oxidizing agent atmosphere, which includes water vapor (800°C–1,000°C), carbon dioxide (800°C–1,000°C), oxygen (below 800°C) or a combination of these gases. The chemical activation cycle can occur independently or in combination with a physical activation process. Additionally, it offers many possibilities during the formation of activated carbons, which have specific requirements and pore sizes [6].

Chemical activation can significantly affect the adsorption efficiency, targeting activity and applicability of a given activated carbon [7]. It involves the formation of a special coating of specific cation or anion groups on the surface of the activated carbon grain when exposed to a particular agent. Chemical activation can be carried out in both aqueous solutions and/or gaseous environments. Substances used for chemical modification of activated carbons in aqueous media can be nitric acid (V), hydrogen peroxide, a mixture of concentrated nitric acid and sulfuric acid. Among activators of an oxidizing nature, chlorine water, sodium chlorate, dichromate, potassium, a mixture of chlorate and nitric acid, and solutions of potassium permanganate and ammonium persulphate can be used [8,9]. Chemical activation in gaseous environments is carried out with oxygen from the air, ozone, water vapor, carbon dioxide and NO_x [2,10].

Besides chemical or physical activation, the impregnation of activated carbons with various inorganic or organic compounds can be used. These can be oils, waxes, macromolecular compounds. The properties of activated carbon can also be improved by the chemical binding of various ligands, deposition of nanoparticles or colloids of metals and their oxides. It is important to isolate the remaining post-production reactants as well as decomposition products and ash from the final carbon material. This allows obtaining good quality and valuable products [9].

Activation of the activated carbon surface is particularly important for materials used as medical adsorbents. These should be produced under a high purity regime. In general, activated carbon has been used for a long time as a therapeutic agent. In medicine, its applications are almost unlimited: from internal administration as oral adsorbent (in tablet or powder form) to extracorporeal applications, for example, in haemoperfusion columns. Powdered activated carbons (PAC) can enhance the therapeutic effect of dressing materials, dental fillings or antiseptic fluids [6]. They are effective in eliminating toxins from the blood. Due to their unique properties, activated carbons can be used to treat internal inflammatory conditions such as; liver and kidney failure, sepsis and rheumatic disease [10,11]. The most commonly used activated carbons in medicine support the treatment of gastrointestinal diseases. The advantage is that they act causally, adsorbing chemical compounds and bacterial toxins to their surface thus preventing the irritating effect of both microorganisms and the toxins they produce on the intestinal mucosa. Due to their large adsorption surface, they have a strong absorbing effect, preventing secondary absorption of the adsorbed substances. Activated carbons effectively adsorb selected xenobiotics including salicylates, barbiturates, clonidine, beta-blockers, phenytoin, cocaine and other stimulants, bacterial toxins and absorb gases, reducing bloating after meals [9]. They are available over-the-counter, but their effectiveness often requires high doses.

Taking mentioned above factors into account, the aim of our study was to evaluate the effect of chemical and physical activation on the parameters of powdered activated carbon. Additionally, we wanted to identify further processes directed at stabilizing the activated carbon features. The goal was to reach the final product which may be safely used in medicine to eliminate toxic micropollutants from the human gastrointestinal system.

2. Material and methods

2.1. Material

Experiments were carried out at the activated carbons production plant Grand Activated Sp. z o.o. and in the Laboratories of the Faculty of Civil Engineering and Environmental Sciences and Faculty of Mechanical Engineering of the Bialystok University of Technology. The research concerned the improvement of PAC of medical type by physical and chemical methods. The raw material for the production was waste chips of mixed hardwood of birch, oak and hornbeam. Dry distillation of wood was used for the production process. After initial carbonization and grinding, the charcoal-raw-material was exposed to physical thermal activation in rotary furnaces at a temperature of approx. 800°C. Then it was subjected to grinding in a Loesche-type mill to a powdered form. An average sample of activated carbon after this stage of production was characterized by the following properties: Methylene Number (MNo) – 41 mL, ash content (ash) – 4.88%, pH – 11.7, iodine value (IV) – 141.08 g/100 g, Phenolic Number (PNo) – 30.24%.

2.2. Synthesis of activated carbon

Fig. 1 shows the scheme for the production of pulvered activated carbons (PAC) considered in this study. The basic improvement of the charcoal structure was physical thermal activation in rotary furnaces at a temperature of approx. 800°C. Half-product washing was repeated after every operation and processing with the prepared condensate of distilled water, low in mineral content. The used solution had a constant pH value of 7.1. The prepared solution was blended in a reactor to wash out and remove mineral compounds originally contained in the charcoal-raw-material and processed charcoal after physical activation.

The raw materials for the production of medical activated carbons were charcoal dust, technical hydrochloric acid (HCl) and condensate of distilled water. Raw charcoal was in powder form with 88% of grains parts of 0.12 mm and was characterized by an iodine value of 1,300 mg/g. It included Ash of 6%. Hydrochloric acid (HCl) was prepared purely for analysis with a 31% concentration. The production of medical activated carbons was carried out in a line of scrubbers, centrifuges and dryers with a system of exhaust ventilation. Due to the highly corrosive effect of hydrochloric acid solutions, all equipment requires acid-resistant materials that do not react with HCl. The production of medical activated carbon must comply with standard requirements. For a single batch production of the scrubber charge, a 1:4 ratio of hydrochloric acid solution to the amount of coal must be used. The acid solution concentration depends on the ash content of the raw charcoal and hesitates between 4.5% and 6.0%. The activated carbon demineralization time in the scrubber was 16 h. To control the process after 8 h of demineralization, the residual acid in the reactor was determined. The demineralization process was completed when the residual concentration of hydrochloric acid was within 0.08%–0.15%. In the case of a higher residual concentration, the demineralization process is extended by 2 h. After the washing process and centrifugation, the product reached a moisture content of 50% ± 5%. Then the activated carbon was dried and homogenized in a mixer-dryer device to a moisture content of less than 5%. The drying temperature was maintained at 120°C. The total drying time was approximately 16 h. To control After 12 h of drying the moisture was controlled. Its content below 5% determined the final powdered medical activated carbon product.

2.3. Characterization of the material

Physical and chemical activation of the material was being implemented in the steps presented. The research was conducted in the order included initial preparation, then high-temperature physical activation, first stage chemical activation, second stage chemical activation, tests on activated carbon pH and 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride (NCBI) decolourization ability:

2.3.1. Basic material – preliminary tests

Primary tests included activated carbon processing. The raw material was subjected to standard physical carbonization, HCl demineralization and then trial chemical activation at the initial concentration of 1.74% acetic acid solution with an activation time of 20 h. Then the coal was fast washed and dried according to the current production technology. After the HCl reacted with the ash contained in the activated carbon, it was moved to centrifuges. During centrifugation, the acid solution was washed out of the coal with distilled water. After the elimination of the acid residue, the washing water was centrifuged and then neutralized with condensate distillate water. The coal was then dried, homogenized and sterilized at high temperature. In order to improve the parameters, the primary obtained activated carbon powder was poured into mixing reactors where a chemical activator, a solution of CH_3COOH, was injected. The extraction, washing and drying process was carried out using raw activated carbon, condensate distilled water and CH_3COOH.

2.3.2. PAC processed by combined physical and chemical activation

In order to determine the sorption efficiency, there was tested dye NCBI, as an indicator of contamination of aqueous solutions. The study was concentrated on the adsorption capacity for investigated activated carbon. Experiments included proper research based on preliminary results obtained during the previous stage. The raw material was physically activated in a rotary carbonization furnace at 800°C. Chemical activation was carried out with 0.5%, 1.5%, 3%, and 9% solution of CH_3COOH. The time of this activation was 3 h. After chemical activation, the sample was washed with distilled water on a Büchner funnel connected to a vacuum pump. Washing was completed when the concentration of acetic acid in the leachate reached approximately 0.003%. Next, the washed material was dried at 105°C–110°C for 6–8 h. Activated carbon samples were taken after completed activation and washing processes (with acetic acid for particular tested concentration ranges). The values of tested dye – 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride adsorption (NCBI), Methylene Number, extinction and pH of the aqueous extract were evaluated. Pore distribution and total porosity of activated carbon also were assessed.

2.3.3. PAC subjected to an additional chemical activation

The double-activation process was applied for the activated carbons previously carbonized and activated in a high-temperature furnace, then first stage chemical activated and washed with distilled water. An additional chemical activation process consisted of additional acidification of the activated carbon samples with 0.5% acetic acid solution. After repeated chemical activation, the PACs were dried and the adsorption capacity of 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride was tested. Methylene Number, pH and ash content were determined for the samples. Pore distribution and total porosity of activated carbon also were assessed. An extended study of the effect of activated carbon pH on the decolourization capacity of 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride followed an additional chemical activation. It was assessed by the magnitude of the filtrate extinction.

2.3.4. Studied adsorbate advanced tests

A number of spectrophotometric tests were carried out on chemical dye 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride – NCBI of 0.0012% tested solution. For this purpose, equal volumes of 1% CH_3COOH solution, distilled water and 5% NaOH solution were added successively to properly diluted samples of NCBI. The obtained solutions were mixed and their pH was determined, extinction was measured and the amount of 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride contained in 100 cm^3 of the solution was read from the calibration curve.

2.4. Adsorptive tests

2.4.1. Porous texture

Porosity texture studies were performed using the mercury porosimeter PASCAL 440. The porosimeter operates in the pressure range from 1,000 to 400 MPa, which allows for pore volume measurements in the radial range from about 1.8 to 7,500 nm, that is, from very small micropores (25–1.8 nm) to macropores (7,500–25 nm). The apparatus records the volume of mercury entering the pores of the tested material. It makes it possible to present a curve of the dependence of the open pore volume on the applied pressure and the distribution of the pore volume. Total porosity is defined as the ratio of pore volume to the external volume occupied by the sample.

2.4.2. pH of zero charge point

The pH of zero charge point (pH_{zpc}) was an indicator of the activated carbon surface charge. To determine the pH_{zpc}, the NaCl solution was added to six laboratory flasks and its initial pH was set as 2, 4, 6, 8, 10 and 12. Changes of pH were realized with a solution of HCl and a solution of NaOH. Next 0.100 g of PAC samples were added to each flask with prepared individual pH solution, then shaken for 10 min and kept for 1 d. The final pH of prepared solutions was measured using a laboratory pH meter. The pH_{zpc} value of the activated carbon samples was determined based on pH initial and pH final. The crossing point of the final pH vs. initial pH curves was pH_{zpc}.

2.4.3. Specific surface area

The specific surface area was determined by gas adsorption using the Brunauer–Emmett–Teller method.

2.4.4. Microscopy observation of activated carbon surface

Observations of the surface and cross-section of the activated and inactivated carbon grains were made using a Hitachi S-3000N (Hitachi Ltd., Mechanical Engineering Faculty BUT) scanning electron microscope with an X-ray microprobe analyzer of chemical composition energy-dispersive X-ray spectroscopy. The microscopic observations were carried out at the accelerating voltage of the microscope – 2 kV. The used observation magnification range was from 500 to 10,000 times. The obtained images were stored in PC memory for comparative analysis. Photographs of the surface of each sample were taken in randomly selected areas.

2.4.5. Determination of Methylene Number

The determination of the Methylene Number was performed according to the PN-75/C-97551 standard "Decolouring Activated Carbons" [12]. Additionally, the determination of the concentration of 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride solution was poured, which was prepared in accordance with the draft standard "Active Carbons. Determination of Methylene Number" [13]. The evaluation of the filtrate color was determined using a spectrophotometer with visible light by Carl Zeiss. In order to select optimum conditions for calorimetric measurement, an absorption (extinction) curve of the solution was prepared, which shows the course of solution absorption depending on the wavelength of light. Based on the course of the absorption curve at a constant layer thickness (1 cm), the wavelength of 660 nm for spectrophotometric measurements for 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride was determined. Then, a number of extinction measurements were carried out for the filtrate evaluated according to PN-75/C-97551 standard, as colorless. On the basis of these measurements, the extinction range of 0.07–0.085 was determined, which the examined filtrate should correspond to. The result of the determination should be the amount of cm^3 of the discolored 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride solution by the tested activated carbon, for which the extinction of the filtrate is within the adopted range of 0.07–0.085.

3. Research results and discussion

The activated carbon used in the experiments and described in this study was produced at Grand Activated Sp. z o.o. as a medical quality product. It acts in the gastrointestinal tract and is not absorbed from it. It is prepared to catch dangerous for health chemical compounds and bacterial toxins. No catalysts nor organic solvents were used in the production process, which could be released in the human body. Safe wood material was used, which was subjected firstly to physical activation at 800°C and then followed by two steps of chemical activation in order to improve its porous structure features.

3.1. Results obtained in preliminary tests

As described in the 2.3.1 section raw charcoal was processed. During the preliminary tests on an industrial scale, a technological control of the activation process with acetic acid and the effectiveness of the rinsing process was carried out. The manufacturing process was conducted under a high purity regime. In order to open pores in activated carbon, the process of HCl demineralization, rinsing and drying was carried out. These operations were carried out under real production conditions on an activated carbon production line, according to the current manufacturing technology. There was conducted trial of chemical activation with CH_3COOH solution of initial concentration of 1.74%. The process of chemical activation with acetic acid lasted about 20 h. Then the carbon powder pulp was sent for centrifugation, neutralized with condensate at pH 7.1 and dried. Activated carbon samples were taken to determine preliminary parameters and check realized processes' efficiency. The obtained results are shown in Table 2.

After the activated carbon pulp was fed into the centrifuge, the concentration of acetic acid in the leachate was controlled. It was as follows:

- after 45 min of centrifuging – 0.725%
- after 80 min of centrifuging – 0.225%
- after 100 min of centrifuging – 0.098%
- after 110 min of centrifuging – 0.012%

Centrifugation was completed when the concentration of acetic acid in the leachate was below 0.02%. After drying the activated carbon and its final preparation, an average sample of the carbon production was taken which had the following properties: Methylene Number – 36 mL, ash content – 1.29%, pH – 6.5, iodine value – 138.95 g/100 g of coal, phenol number – 30.24%.

Analyzing the results obtained in preliminary manufacturing tests, it was noted that after initial chemical activation and industrial washing, the Methylene Number of activated carbon decreases to the value of 36 mL. The results of tests carried out during trial chemical activation and washing of activated carbon, presented in Table 2, indicate the significant influence of the centrifuge washing operation on the formation of ash content and Methylene Number in the final product. The sample taken during the loading of the PAC pulp onto the centrifuge contained 3.57% of ash and its MNo was 29 mL. The 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride (NCBI) decolorization capacity of activated carbon (chemical activated but not washed) was therefore 12 mL lower compared to activated carbon before acid activation. The sample taken after 0.5 h of washing was characterized by MNo = 33 mL, while the sample after washing and laboratory drying contained only 1.29% of Ash and had MNo = 41 mL. The average activated carbon sample reached in the trial process in the production line as a final product was characterized by a Methylene Number of 36 mL, 5 mL lower than the initial sample before activation. The ash content decreased from 4.88% to 1.29%, constituting a 73% decrease from the original value. Porous structure test showed low efficiency of the reached product. Short chemical activation has hardly changed the features of powdered raw material of charcoal. The specific surface area and porosity were not developed. 20-h acetic acid activation, washing and drying helped to increase porous structure. The specific surface area and porosity reached 740 m^2/g and 0.36 cm^3/g. Activated carbons with such porous structures cannot be used as medical products. According to the available literature [14,15], effective medical-type activated carbons should have a Methylene Number above average value, that is, 39 mL. Their specific surface area and porosity should exceed 1,000 m^2/g reach a porosity of 0.7–0.8 cm^3/g to ensure good removal of toxins from the gastrointestinal tract [16]. Some gastral diseases are caused by high concentrations of dangerous substances which have to be removed from the human body as fast as possible.

For every medical PAC compulsory inter-operational laboratory tests have to be carried out based on the risk analysis. Tests need to meet the standards of the European Pharmacopoeia [16] (Table 1). According to the current

Table 1
Parameter and other required medical features of tested PAC tested as API according to European Pharmacopoeia*

No.	Parameter	Requirements
1.	Shape	Black light powder lump-free
2.	Solubility	Insoluble in any solvent
3.	Identity: Test A – combustion	When heated to redness carbon burns slowly without flame
4.	Identity: Test B – adsorption	Not less than 40 g of phenazone is absorbed by 100 g of carbon
5.	Acidity	Not more than 0.25 mL 0.02 moL/L NaOH
6.	Alkalinity	Not more than 0.75 mL 0.02 moL/L HCl
7.	Acid-soluble substances	Not more than 30 mg/1.0 g (3%)
8.	Alkali-soluble substances	Solution colour below standard GY4
9.	Substances soluble in 96% ethanol	Solution colour below standard Y6 or GY6 Residue not more than 8 mg/1.6 g (0.5%)
10.	Fluorinating substances	Fluorescence of the test solution is not more intense than that of a solution of 83 mg of quinine in 1,000 mL of 0.005 moL/L sulfuric acid
11.	Sulfides	No change in colour of the lead paper
12.	Copper	No 25 ppm
13.	Lead	Not more than 10 ppm
14.	Zinc	Not more than 25 ppm
15.	Drying loss	Not more than 15%
16.	Sulfated ash	Not more than 5%
17.	Adsorption of carbon per dried substance	Not more than 40 g of phenazone is adsorbed by 100 g activated carbon
18.	Microbiological purity	Total microorganisms – not more than 1,000 g

Own investigations based on [12,13,14];

*The requirements in Table 1 are in line with the European Pharmacopoeia set of standards – the European reference for medicines quality control. It contains official standards that provide a scientific basis for quality control throughout the product life cycle. These standards are legally binding – as laid down in the Council of Europe Convention on the development of European Pharmacopoeia and in EU and National Pharmaceutical Legislation [12,13,14].

regulations Directive, 2001/83/EC [17] the finished product of medical activated carbon after positive laboratory results can be transferred as a medicinal marketable product of active pharmaceutical ingredient (API) type.

3.2. Results conducted on combined physical and chemical activation

Before proper manufacturing of the medical activated carbon, it was essential to improve its parameters. That is why combined physical and chemical activation was undertaken to continue PAC examination. The next step of research and laboratory trials was therefore started to enhance the adsorbability of the dye of 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride (NCBI). The most important was foremost the porous structure development. The basic improvement of the processed raw charcoal structure was high-temperature physical thermal activation in rotary furnaces with the oxidizing gas CO_2 and water steam at 800°C–900°C. The result was an amorphous carbon material. Chemical activation and washing trials followed this process. In order to achieve better carbon features, a number of chemical activation were carried out under laboratory conditions. Parallel close monitoring of the operation and quality control of the activated carbons was undertaken. Before the chemical activation process, the average coal sample was characterized by a Methylene Number of 38 mL and an ash content of 5.08%. Laboratory acid activation tests were carried out using an acetic acid solution with concentrations of 0.5%, 1.5%, 3% and 9%. Individual samples labeled as follows:

- Carb/0.5 – activated carbon activated with 0.5% CH_3COOH solution,
- Carb/1.5 – activated carbon activated with 1.5% CH_3COOH solution,
- Carb/3 – activated carbon activated with 3% CH_3COOH solution,
- Carb/9 – activated carbon activated with 9% CH_3COOH solution.

Table 3 summarises the results of measurements taken during physical (sample 0) and chemical activation processes. The results are consistent with the study of Liou [19]. The reduction in ash content is mainly due to the removal of silica from the coal samples. The aim of both types of activation is always to increase the porosity and to unclog the carbon structure. Porosity and specific surface area of activated carbon are among the basic factors determining the adsorption capacity of contaminants of different sizes. According to Benaïssa [3], appropriate measures must be taken to allow the activator to penetrate pores and to increase the contact surface between the acid and the raw charcoal material. Furthermore, according to Arivoli et al. [20], impurities inside the pores can be partially dissolved and removed during the washing process. It can also result in a more porous carbon structure and assist the activating agent to enter the pores. After washing, the ash content decreased and the NCBI adsorption efficiency increased. Reduced ash content in the samples may help with subsequent unclogging of the pores. A higher ash content shows that the more volatile component needs to be removed during the activation process. The expected effect should be a larger specific surface area and larger pore volume [21,22]. Table 3 compares the values of parameters characterizing the porous structure of the materials used in the study. As can be seen from the presented data, the highest specific surface area is characteristic for washed activated carbon Carb/1.5 (880 m^2/g) and it is the form Carb/9 after chemical activation with acidic acid of 9% concentration (790 m^2/g). The smallest specific surface area (SSA) corresponds to carbon undergoing only physical activation (410 m^2/g), which is also characterized by the smallest total pore volume (0.24 cm^3/g). Similar pore volumes characterize Carb/0.5.

Product washing had a great impact on PAC structure parameters. Carb/1.5 no washed had much less SSA than Carb/1.5 washed. The difference was over 200 m^2/g. Pretty good results were obtained also for Carb/9 activated with the highest concentration of CH_3COOH. However, which is surprising, the SSA and porosity for Carb/9 and Carb/3 were similar. Taken into account previous step of test – there was found that more important is time of chemical activation than activator concentration.

From the laboratory tests on PAC activation with the use of solutions of CH_3COOH with concentrations of 0.5%, 1.5%, 3.0% and 9.0%, it has been found that the taken acid concentrations do not affect the size of the Methylene Number. For individual samples, MNo-s were obtained in the range of 38–39 mL and were about 2–3 mL lower than in the initial sample. The results show that the degree of activation affects the properties of PAC and therefore the type of activation should be applied appropriately in the production of activated carbons to achieve the highest surface area and pore volume, which is also confirmed by Karagöz et al. [23] and Nakagawa et al. [24].

The ash contents in the tested activated carbons after chemical activation and washing ranged from 1.25–1.54%. The highest ash content of 1.83% was found in the sample with 0.5% CH_3COOH solution, indicating the insufficient concentration of the used solution. The effect of the washing degree of the chemically activated PAC on the MNo and ash content was confirmed. Carb/1.5 sample single activated contained 3.11% Ash and its Methylene Number was 30 mL. The same washed sample had 1.43% ash. Compared to the unwashed sample, the amount of ash decreased by 54%. Rinsing also had a beneficial effect on the MNo, which increased from 30 to 36 mL for the Carb/1.5. Conducted research on combined physical and chemical activation with given tested CH_3COOH concentration showed that high temperature and acid operation change activated carbon parameters, increase porosity and NCBI adsorption. Nevertheless, that activation was not sufficient for medical activated carbon. Harmful toxins or heavy metals removal from the human gastrointestinal tract needs better adsorption properties.

3.3. Results obtained by double chemical activation

Samples of activated carbons reached in the previous step of examinations (3.3.) were physically and chemically activated and then washed. As written above their porous structure and adsorption features have not met good adsorbent expectations and still were lower than assumed. That is why we have made a decision about additional chemical activation. We supposed that pores volume and specific surface area are not open enough and blocked by other particles. Samples single activated with CH_3COOH were additionally activated with 0.5% acetic acid solution and dried. After these processes, they were then tested for MNo, extinction, pH, ash content, NCBI adsorption. Their porous structure also was controlled. Table 4 summarises the results of the measurements.

The tabulated data presented in Tables 2–4 show that both in the preliminary tests and in a number of laboratories activated samples, the Methylene Number after activation was lower than in PAC before chemical activation. Additional acidification of the carbon with 0.5% CH_3COOH resulted in a light decrease in MNo of 3–4 mL (Table 4) for Carb/3 and Carb/9. Carb/1.5 showed the highest difference in MNo between single and double activated samples. Its other features were also the worst. For example – double activation had also an impact on NCBI adsorption. Better adsorption was noted by neutral pH. NCBI adsorption after activation decreased from 233.6 to 184.4 mg/g. In contrast, the change in NCBI adsorption for Carb/3 and Carb/9 for the single and double activated samples was quite small and hesitated about 15 mg/g, that is, from 239.3 to 225.4 mg/g for Carb/3 and from 245.6 to 233.4 mg/g for Carb/9.

On the other hand, porosity structure tests proved better properties for double-activated products. The surface and pores space closer depended on activator operation than pH values and NCBI adsorption. Fig. 2 explains how have changed micro-, meso- macropores inside the material Carb/1.5. Used for activation CH_3COOH showed its acidic features and helped to open pores inside every examined PAC. The poorest micropores volume was observed only for physically activated carbon. Probably great influence on it have lack of washing and drying because the residues of ash and other parts still were present in material structure and blocked pores. That is why direct before chemical activation washing and drying was established. Pores sizes were bigger and the most visible improvement was observed for mesopores. Chemical activation significantly corrected pores size in every considered range: from micro- to macropores. As mentioned in 3.1., after preliminary tests and physical activation SSA was only 420 m^2/g (Table 2). Chemical surface stimulation with single and double activation significantly improved activated carbon parameters. The smallest CH_3COOH concentration increased SSA to 720 m^2/g even by single activation but double activation changed slightly this parameter. The best results were obtained for double activation of Carb/9. SSA rose to 1,080 m^2/g. A similar trend was observed for porosity. Low porosity after physical only activation has changed to 0.34 cm^3/g firstly for Carb/1.5 single activated and for Carb/9 double activated finally to 0.86 cm^3/g. This product appeared good adsorbent with high porous structure and

Table 2
Properties of the tested samples after preliminary chemical activation, centrifugation, washing, and drying

Sample	MNo (mL)	pH	Ash (mg/g)	SSA (m^2/g)	Porosity (cm^3/g)
After 1 h acetic acid activation	29	5.5	4.31	420	0.19
After 20 h acetic acid activation	29	5.0	3.57	510	0.23
After 0.5 h centrifugation	33	6.4	2.55	550	0.23
After washing and drying	40	6.5	1.29	590	0.29
After entire activation process	36	6.5	1.29	740	0.36

Own investigation

Table 3
Properties of activated carbons undergoing a single-step chemical activation process

Sample	Activation	Washing		PAC properties						
	Initial conc. CH3COOH (%)	Initial conc. (%)	Final conc. after washing (%)	Ash (%)	pH	MNo (mL)	Extinction	MB adsorption (mg/g)	SSA (m^2/g)	Porosity (cm^3/g)
Sample 0 no washed	–	–	–	5.08	10.6	41	0.075	252.3	410	0.24
Carb/0.5	0.5	0.25	0.0030	1.83	6.3	38	0.08	229.8	610	0.28
Carb/1.5	1.53	0.44	0.0035	1.54	5.6	38	0.08	239.3	720	0.34
Carb/3	3.06	0.72	0.0035	1.24	5.1	38	0.08	239.3	760	0.41
Carb/9	9.00	5.91	0.0037	1.41	4.5	39	0.08	245.6	790	0.49
Carb/1.5 no washed	1.47	–	–	3.11	4.6	30	0.08	181.4	630	0.32
Carb/1.5 washed and dried	1.47	0.42	0.0035	1.43	6.3	36	0.08	217.7	880	0.68

Own investigations

Table 4
Activated carbons parameters after double chemical activation

Sample	Ash (%)	pH	NCBI		NCBI adsorption (mg/g)	SSA (m^2/g)	Porosity (cm^3/g)
			MNo	Extinction			
Carb/1.5	1.12	6.8	38	0.075	233.6	720	0.34
Carb/1.5 double acid	1.46	5.0	30	0.075	184.4	880	0.40
Carb/3	1.25	6.7	38	0.08	239.3	760	0.41
Carb/3 double acid	1.35	4.4	34	0.07	225.4	950	0.62
Carb/9	1.41	6.7	39	0.08	245.6	790	0.49
Carb/9 double acid	1.46	4.1	35	0.085	233.4	1080	0.86

Own investigations

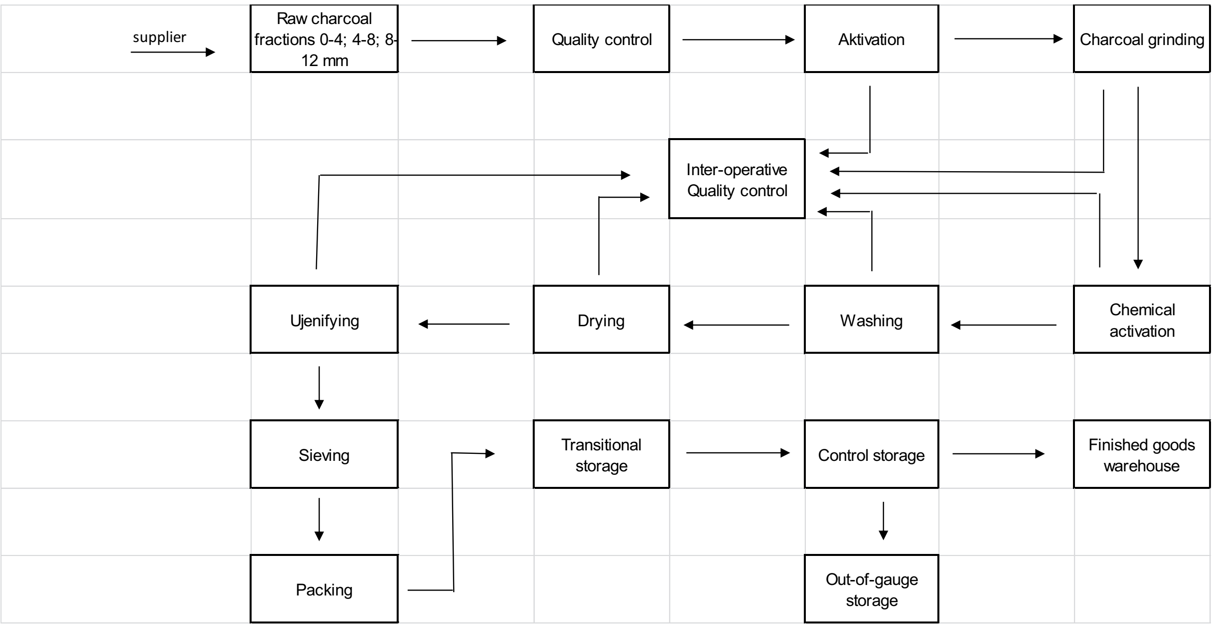


Fig. 1. Scheme for the production of pulvered activated carbons (PAC).

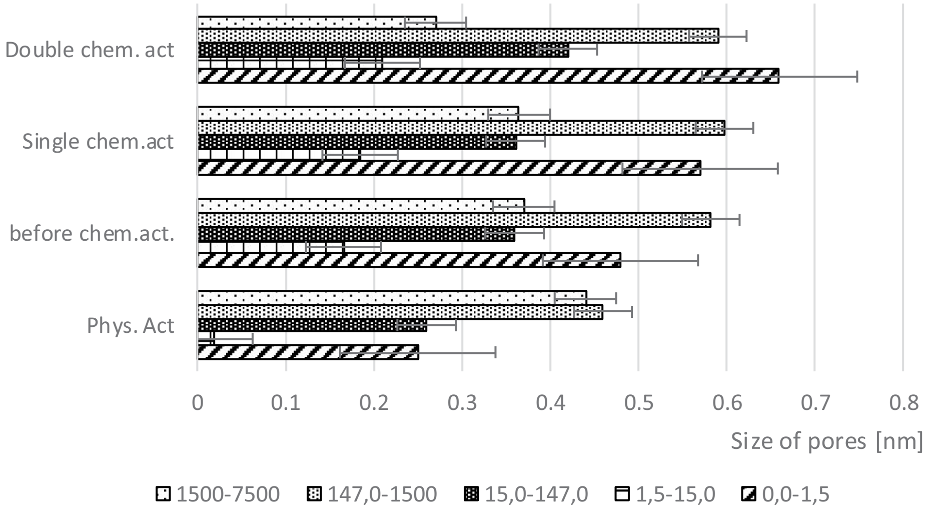


Fig. 2. Pores range for Carb/1.5 single and double activated.

adsorption properties. It may be safely used as a medical product that is able to remove toxins and other dangerous substances from the human gastrointestinal tract.

3.4. Impact of the pH on the NCBI

For samples: Carb/1.5 single and Carb/1.5 double acid activation, an extended study was performed on the impact of the activated carbon pH on the NCBI decolorization ability. The examination was assessed by the magnitude of the extinction of the filtrate with dependence on solution pH. The obtained results are presented in Table 5.

The pH of the solution has a significant influence on the adsorption process and also regulates the degree of dissociation of active sites on the adsorbent, possible ion exchange and heavy metal precipitation. In order to evaluate the effect of pH on NCBI adsorption, proper tests were carried out for pH values of 3, 4, 5, 6, 7 and 8 for Carb/1.5 single and double activated carbon. The effect of pH on the NCBI adsorption on PACs is shown in Table 5. It can be concluded that the observed adsorption changes for both carbons at the same pH are very similar. When comparing the tested activated carbons with each other, it was found that the additional acid activation, in this case, does not produce clear results. This can be explained by the fact that the similarity of the obtained results is due to the adsorption of the same compound but also the same group of activated adsorbents with CH_3COOH. When activated carbon is regularly washed by water or operates in an aqueous environment, free adsorption of H^+ and OH^- ions occurs and a hydroxylated surface is produced on the porous material. According to literature data, carboxyl or hydroxyl groups of adsorbents convert from H^+ to –COOH and –OH at higher concentrations and lower mobility of H^+ ions in solution [25]. Such a phenomenon can occur when the carbon surface is chemically activated with acids.

As mentioned, an important factor influencing the adsorption process of various pollutants on activated carbons is the pH of the solution, which affects the electrostatic interactions between the carbon surface and the adsorbed substance. The pH of the solution determines the charge on the surface of the carbon and also influences the dissociation of a particular compound located in the immediate area of the carbon. If the pH of the solution is less than pH_{pzc} (pH at which the charge on the carbon surface is zero) the total charge on the surface of activated carbon will be positive. At a higher pH of the solution, the charge will be negative. The pH of the solution also affects the dissociation of the compound. In our study, the adsorption of NCBI remained constant in a basic environment. NCBI (3,7-bis(dimethylamino)-phenothiazin-5-ium chloride) is a synthetic cationic tri-heterocyclic compound that contains a central aromatic thiazine ring system. This structure allows transferring a delocalized positive charge at neutral pH. Its increase was observed at higher pH values (>6). The experimentally determined pH_{pzc} values, allowing to determine the activated carbon surface charge, were 5.91 for Carb/1.5 single activated and 5.32 for Carb/1.5 double activated. The slightly better and relatively unchanged adsorption of NCBI in a basic environment is due to the interaction of the negatively charged activated carbon surface with the cationic tri-heterocyclic groups of dye molecules. The combination of these factors supports adsorption. The increase in adsorption efficiency in alkaline media can be explained by the interaction of the negatively charged adsorbent surface, which repels the 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride molecules. The maximum adsorption in the neutral pH range may be due to the interaction of NCBI with the negative sites on the PAC surface. In this pH range, there are lower concentrations of H^+ ions and the active sites on the coal surface are more negative, resulting in greater adsorption.

The pH_{pzc} value of activated carbon is a parameter characterizing the appropriate pH range in which the adsorbent surface is electrically neutral. As part of our own research, it was estimated that carbons after double acid activation with CH_3COOH contain more acidic functional groups on the surface compared to those subjected only to physical high-temperature activation. Similar conclusions were reached by Gupta and Nayak [26] analyzing an adsorbent made from modification of orange peels with iron oxide nanoparticles. The adsorption efficiency of NCBI rose with the pH of the solution. Cottet et al. [16] tested methylene blue dye. He has found out that the pH zero point for his activated carbon hesitated between pH 2.5 and 5.5 and the dye has basic features. On the other hand, according to Abedi et al. [25] and Aygün et al. [27], the total or external surface charges are positive at lower solution pH. Thus, poorer adsorption of NCBI occurred at the lower pH of the solution. When the pH value decreased, the activated carbon surface was more positively charged [27]. The adsorption of NCBI

Table 5
Comparison of pH influence on Carb/1.5 single and double chemically activated

	Carb/1.5 single activation pH_{pzc} = 5.91		Carb/1.5 double activation pH_{pzc} = 5.32	
pH	Extinction	NCBI adsorption (mg/g)	Extinction	NCBI adsorption (mg/g)
3	0.05	178.3	0.065	176.3
4	0.05	184.4	0.075	187.9
5	0.055	196.7	0.070	196.7
6	0.055	233.6	0.070	184.4
7	0.055	234.2	0.070	233.4
8	0.057	233.1	0.070	232.9

Own investigation

with a positive charge during their experiments may be maximally achieved by neutral pH.

3.5. Microscopic observations of the activated carbon structure

Using a Hitachi S-3000N microscope (Hitachi Ltd., Mechanical Engineering Faculty BUT), the surface of the samples was analyzed to determine changes in the surface structure of the tested PAC with the different physical and chemical activation methods. Examined material of inactivated charcoal dust samples was also observed for comparative analysis.

Fig. 3 shows a magnification of the activated and inactivated carbon surfaces. The structure of raw charcoal that was the basic material for PAC manufacturing is quite flat. The charcoal was ground but its fragmentation did not change features of typical coal. The common for such material is chipping. Preliminary physical activation has hardly changed the surface of examined carbon grains. On the other hand, some progress has already been made with preliminary chemical activation. The surface structure was not flat anymore. Visible effects of acid pitting may be observed. As mentioned in section 2.3.2. PAC was processed by combined physical and chemical activation using different CH_3COOH concentrations. By the lowest concentration of 0.5%, the Carb/0.5 structure improvement was not noticeable. The edges of the grains were smooth and the pores were not evident. Carb/1.5 after single acid activation looked similarly. The effect of single acid activation was pictured for Carb/3. The photo shows open macropores and doorway to mesopores. The surface of the PAC was modified by a double activation and surface changes were evident for every tested concentration. Nevertheless Carb/1.5 double activated still is characterized by quite sharp edges. Carb/3 double activated compared to Carb/3 single activated reached a smaller range of macropores and developed mesopores. The best structure modification was observed for Carb/9. Numerous pores are evident in its structure. High magnification shows pores of different sizes from macro- to micropores. Microscopic observation has proved the adsorption tests result present in Tables 3 and 4.

3.6. NCBI testing

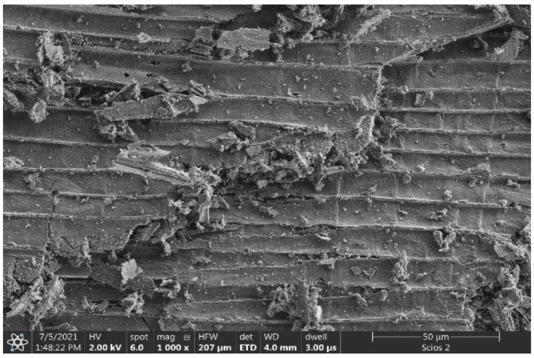
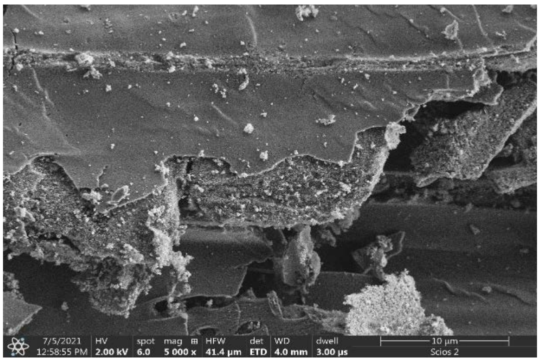
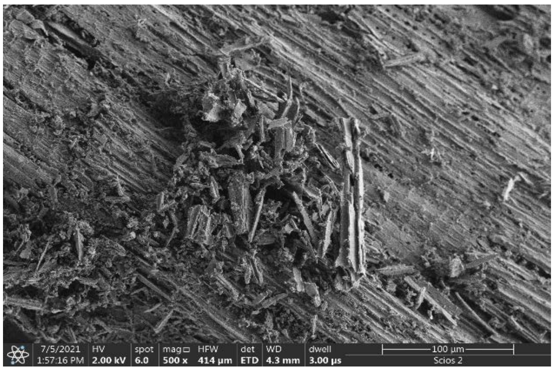
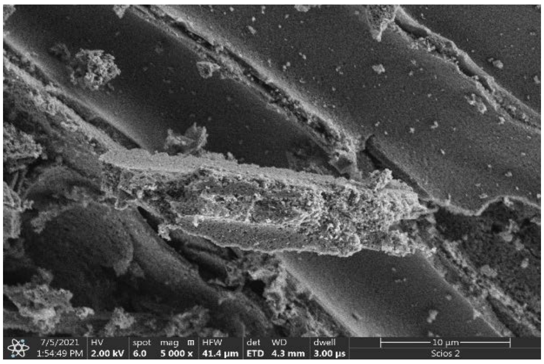
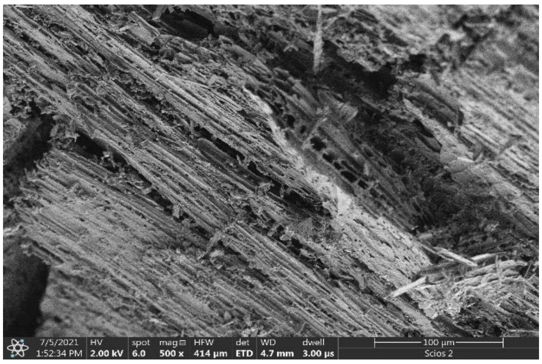
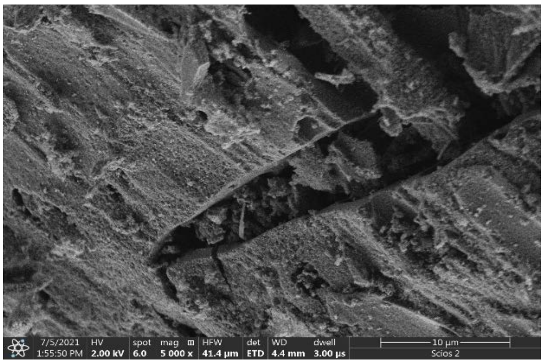
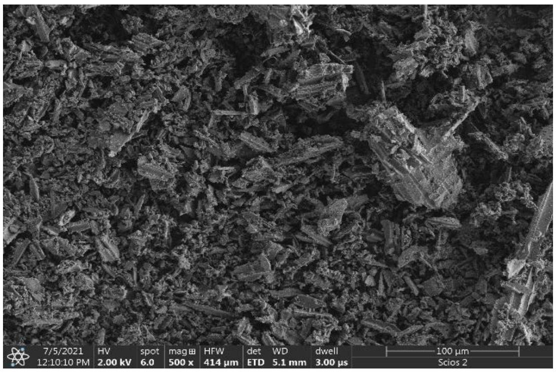
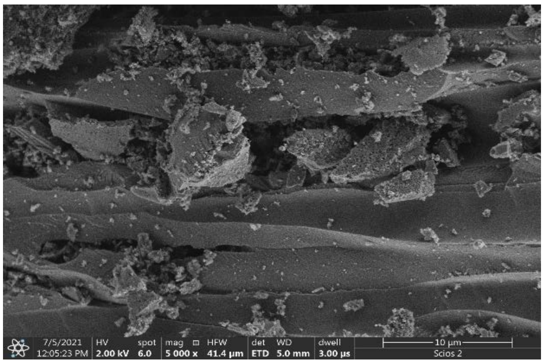
The study results presented in Table 5 and described in the 3.5 section are related to spectrophotometric tests on 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride (Table 6). This included an investigation of the scope and reasons for the change of the Methylene Number of PAC which followed the operation of partial activation with a CH_3COOH solution. The factor most influencing the efficiency of adsorption from aqueous solutions on carbon materials is the hydrophobicity of the adsorbed compound, which can be expressed by solubility [18]. Considering the structure and physicochemical properties of the NCBI dye, it can be concluded that the size of its molecule has a significant influence on the adsorption process [21]. Tested 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride had a small molecular size and it is a linear molecule.

Nevertheless, all samples of CH_3COOH activated PAC showed lower Methylene Numbers than the corresponding original samples before chemical activation. In order to clarify the reasons for this phenomenon, which was regularly observed in the practice of PAC production, complementary measurements of the 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride solution was carried out. This is important in the case of doubly activated carbon which, due to its small pore size, reduces the access of larger molecules, while the linear molecules of NCBI can more easily reach the small pores of the adsorbent [28]. For adsorbents containing larger pore sizes (only physically activated carbons and 1-time industrially activated carbons), the effect of differences in molecular size of adsorbates on adsorption efficiency is smaller [29]. This is also confirmed by the smaller difference in adsorption size for material with larger pores compared to chemically activated carbon-containing smaller pores. A high affinity for NCBI was observed here. The significantly higher adsorption capacity towards the dye for the additionally acidified activated carbon may be due to the fact that materials chemically activated have a much larger specific surface area and pore volume compared to the materials modified only physically [15,30,31].

A number of spectrophotometric tests were performed on 0.0012% NCBI solution in an acidic environment (with the addition of 1% CH_3COOH), neutral (with the addition of H_2O) and alkaline (with the addition of 5% NaOH). The prepared solutions were mixed and their pH was determined, extinction was measured and the amount of 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride (NCBI) contained in 100 cm^3 of its solution in distilled water was read. The measurement results are summarised in Table 6.

According to the available literature [27,28,30,32], carbon pH is an important parameter to evaluate the adsorption capacity. It can affect the dissociation of functional groups available on the adsorbent surface, the charge density of the adsorbent surface and its structure [32]. It can also affect the ionization degree of the adsorbate molecules and it is responsible for the higher/lower sorption capacity of the adsorbent [29]. It should be noted that the amounts of 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride introduced into the individual acidic, neutral and basic solutions differing in pH were the same and equal to 0.122 mg in 100 cm^3 of distilled water. On the other hand, the amounts of NCBI read from the standard curve on the basis of the magnitude of extinction, varied and were respectively: for pH 4.1 – the amount of dye 0.155 mg/100 cm^3, for pH 6.0–0.122 mg/100 cm^3, and for pH 10.7–0.086 mg/100 cm^3. In addition to our studies, pH was measured for the solution of 0.15% NCBI. Such concentration was adsorbed on the activated carbons investigated in preliminary test, single and double activation processes. The pH value of 0.15% NCBI was 4.5. The NCBI filtrate from PAC (compulsory for the MNo determination) for a sample before chemical activation was pH = 7.4 and the chemically activated average sample was pH about 5.0.

The trend in pH changes of the chemically activated carbon tested in our investigations was consistent with the reported literature [5,33]. Lu et al. [5] observed a decrease in the pH of nitric acid-modified carbon, from 7.72 to 2.01 for oxidized AC. The authors reported that such low pH values of these activated carbons were due to the demineralization of organic impurities and an increase in acidic surface functional groups on the surface of the activated carbon. The pH of sulfuric acid-activated carbons in the study of Borah et al. [33] were 6.4 and 3.5, respectively. The decrease in pH can also be attributed to oxidation. Tested in our examinations 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride solution in acidic medium has a green-turquoise color, while in basic medium shows a blue-violet color. The coloring of NCBI solution varies in different environments, with the highest intensity of coloring occurring in an acidic environment, and the lowest extinction found in a basic

Material	**Zoom 500/1000x**	**Zoom 5000x**
Raw charcoal dust		
Preliminary tests Physical activation		
Preliminary tests Chemical activation		
Carb/0.5		

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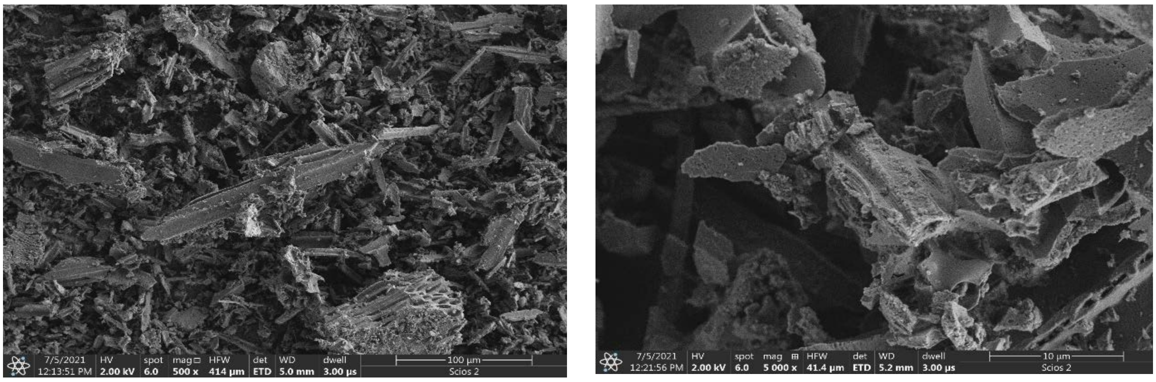
Carb/1.5 single activated



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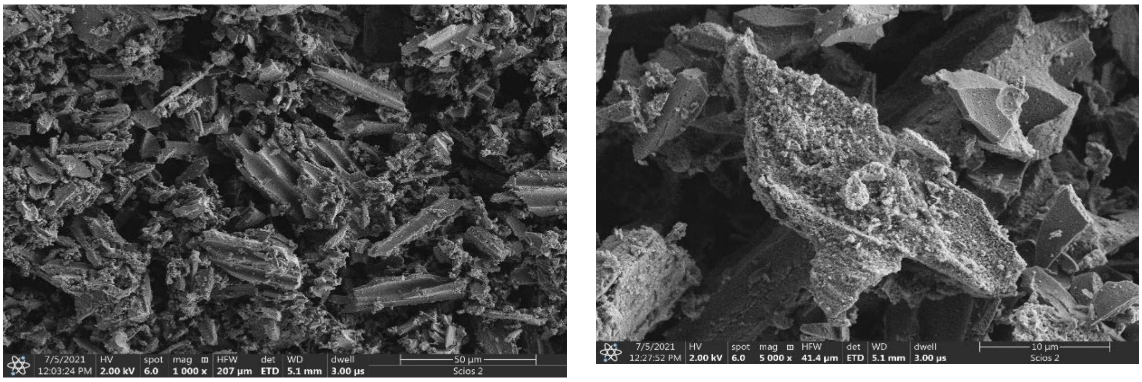
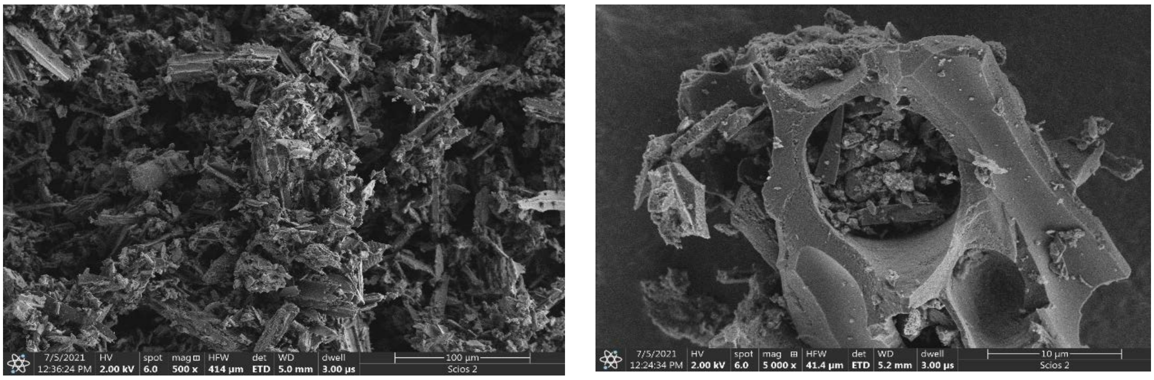
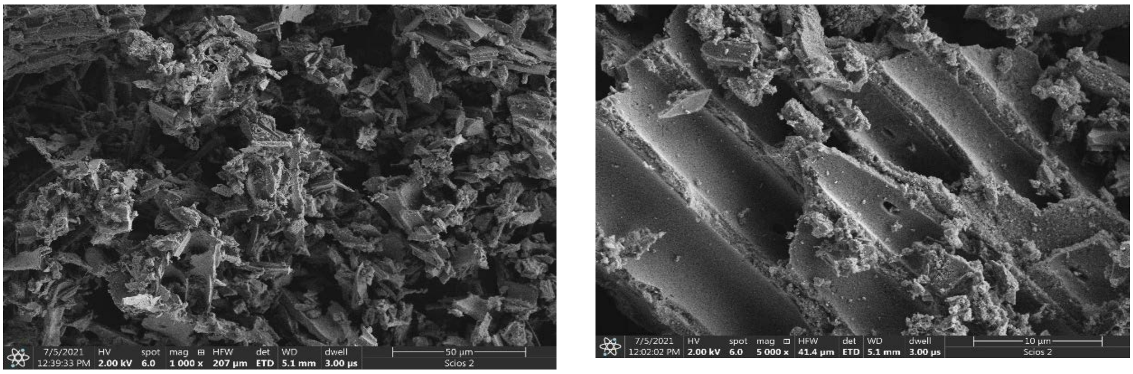


Carb/3 single activated



Carb/3 double activated



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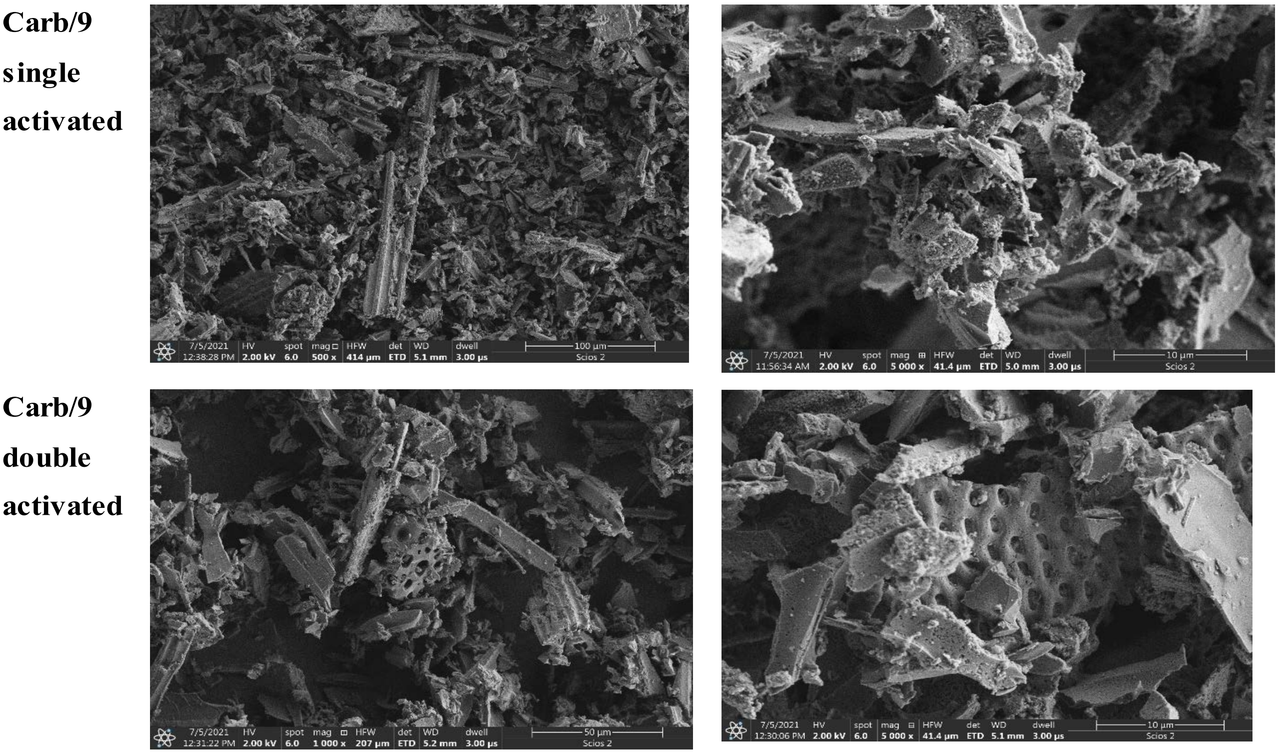

Fig. 3. Microscopic pictures of tested PAC.

Table 6
Measurement results for NCBI solution

NCBI sample	pH	Extinction	NCBI in 100 cm^3
NCBI + 1% CH_3COOH	4.1	0.315	0.155 mg
NCBI + H_2O	6.0	0.245	0.122 mg
NCBI + 5% NaOH	10.75	0.175	0.086 mg

Own investigation

environment. The NCBI solution used in the study had a pH of 4.5. On the other hand, regular and not processed activated carbon (no physical nor chemical activation), is characterized by a pH of the aqueous extract reaching pH up to 10, while medical activated carbons have a pH ranging from 6 to 7. However, the pH of the filtrate after MNo determination for physically activated PAC is usually weakly alkaline. The pH of the filtrate was slightly acidic for most tested medical PACs. It may be explained by 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride adsorption in the activated carbon which is a cationic tri-heterocyclic compound. The difference between acidic and neutral environments is 27% and between alkaline and neutral environments, it is 29.5%. With regard to the results obtained for both chemically activated and washed activated carbons, these differences in the NCBI adsorption detection should be taken into account. The correction applies only to the acidified samples tested, as the pH was then maintained at 4–5. For the "no washing" samples in a single activation, it was about 4.6. In Tables 3 and 4, it is possible to see the lower values of NCBI adsorption for these activated carbons samples. Thus, considering the detection correction, the true adsorption value should be increased by 27% and stands for Carb/1.5 double acid about 230 mg/g, for Carb/3 double acid about 280 mg/g and for Carb/9 double acid about 290 mg/g. Similarly, there were detected differences in the Methylene Number values of several milliliters are due to the different environments (pH) of activated and not chemically activated PAC. The increased MNo of double chemically activated carbons with an acid solution and carbons single activated but not washed with distilled water should also be included in the total calculation.

4. Summary and conclusions

The aim of our study was the evaluation of the effect of chemical and physical modification on the parameters of medical PAC. We also have identified further processes directed at stabilizing reached activated carbon as the final product so that it can be safely used in medicine to eliminate toxic micropollutants from the human gastrointestinal system. The research concerned the improvement of PAC of the medical type which may be prepared for the pharmaceutical market and should become effective adsorber. After raw material synthesis, high-temperature activation, as well as single and double chemical activation, has been carried out. Primary tests included activated carbon processing. The raw material was subjected to standard physical carbonization, HCl demineralization and then trial chemical activation. Then PAC was subjected to proper processes of combined physical and chemical activation. In order to determine the sorption efficiency, there was tested dye 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride (NCBI), as an indicator of contamination of aqueous solutions. According to literature data [3,14,15,20,21,29,31] when analyzing the influence of the properties of the different individual dyes on the adsorption rate, factors such as its molecular size and structure, dissociation capacity and solubility should be taken into account. For our experiments, we did numerous adsorptive tests including porosity, the pH of zero charge point, SSA and microscopy observation of the PAC surface. The values of tested dye – 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride adsorption (NCBI), Methylene Number, extinction and pH of the aqueous extract were also evaluated.

5. Conclusions

- The average activated carbon sample reached in the preliminary processes as a final product was characterized by a low Methylene Number, however, the ash content decreased significantly. Porous structure test showed low efficiency of the reached product. Short chemical activation has hardly changed the features of ground and powdered raw material. The specific surface area and porosity were not developed.
- Conducted research on combined physical and chemical activation with CH_3COOH showed that high temperature and acid operation change activated carbon parameters, increase porosity and NCBI adsorption. Product washing had a great impact on PAC structure parameters. PAC not washed had much less SSA than washed. The difference was over 200 m^2/g. Pretty good results were obtained also for PAC activated with the highest concentration of CH_3COOH. Nevertheless examined activation was not sufficient for medical activated carbon.
- Porosity structure tests proved better properties for double-activated products. The surface and pores space closer depended on activator operation than pH values and NCBI adsorption. Chemical activation significantly corrected pores size in every considered range: from micro- to macropores. The best results were obtained for double activation of Carb/9. SSA augmented reached 1,080 m^2/g. A similar trend was observed for porosity. Carb/9 appeared good adsorbent with high porous structure and adsorption properties. It may be safely used as a medical product which is able to remove toxins and other dangerous substances from the human gastrointestinal tract.
- For samples: Carb/1.5 single and double activated, an extended study was performed on the impact of the activated carbon pH on the NCBI dye decolorization. The experimentally determined pH_{pzc} values were 5.91 for Carb/1.5 single- and 5.32 for Carb/1.5 double activated. The slightly better and relatively unchanged adsorption of NCBI in a basic environment was due to the interaction of the negatively charged activated carbon surface with the cationic tri-heterocyclic groups of NCBI dye molecules. The combination of these factors supports adsorption. Poorer adsorption of NCBI occurred at the lower pH of the solution. When the pH value decreased, the activated carbon surface was more positively charged. Thus, the adsorption of NCBI with a positive charge was achieved at neutral pH.
- A number of spectrophotometric tests were performed on NCBI solution with a concentration, in acidic, neutral and alkaline environments. Tested dye of 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride in acidic solution had a green-turquoise color, while in basic showed a blue-violet color. The coloring of NCBI solution varies in different environments, with the highest intensity of coloring occurring in an acidic environment, and the lowest extinction found in a basic environment.
- Microscopic observations helped to understand the activation processes. Preliminary physical activation has hardly changed the surface of examined carbon grains. The best structure modification was observed for Carb/9. Numerous pores are evident in its structure. High magnification shows pores of different sizes from macro- to micropores. Microscopic observation has proved adsorption tests results.

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