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# The influence of the synthesis pH on the morphology and adsorption properties of carbon spheres



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# ABSTRACT

Microporous spherical carbon materials were obtained from the resorcinol–formaldehyde resin, treated in a solvothermal reactor heated with microwaves, and then subjected to carbonization. The effect of the pH on the changes in the carbon spheres' morphology and the adsorption performance was investigated. In order to improve the adsorption efficiency, carbon spheres were subjected to the activation using potassium hydroxide and their properties were compared to those of the non-activated ones. The adsorption performance of the produced materials was evaluated in detail by examining nitrogen and carbon dioxide adsorption from the gas phase, the morphology – using Scanning Electron Microscopy, and surface chemistry – using X-ray Photoelectron Spectroscopy.

#### 1. Introduction

The testing of the carbon materials properties is currently still a highly researched topic. Besides well-known activated carbons, other forms of carbon are also intensively investigated, such as graphene, carbon black, carbon fibers, carbon nanofibers, and nanotubes. These materials have many interesting properties, which means that numerous studies on their potential application are conducted [1]. Among carbon materials that enjoy considerable interest carbon spheres can be mentioned as well, used e.g. in lithium batteries [2], as lubricants [3], carbon catalyst support [4], or in biomedicine [5]. There are two different approaches to the synthesis of carbon spheres. The first one is based on the high-temperature decomposition of carbon-containing materials in an inert atmosphere and includes chemical vapor deposition, arc discharge, and laser ablation [6]. The second approach relies on the low-temperature pyrolysis and catalytic decomposition of organic compounds by the heat treatment of polymers or other materials [7,8]. In the last case usually phenol-formaldehyde [9,10,11,12] or resorcinol-formaldehyde [13,14] polymer spheres are created and then subjected to the heat treatment, often in autoclave [6]. This stage can also be performed using microwaves heated solvothermal reactors [13,14]. The final step of the preparation is carbonization. Sugars

[15,16,17,18,19] or wastes [20,21,22] can be also processed as raw materials using this method.

To improve the adsorption properties of carbon spheres physical or chemical activation processes can be performed. Physical activation occurs when carbonized materials are treated at approximately 700-900 °C in the presence of oxidizing gases, mainly steam or carbon dioxide [23,24,25]. The chemical activation involves impregnating raw materials with certain chemical agents, such as ZnCl<sub>2</sub> [26], H<sub>3</sub>PO<sub>4</sub> [27], KOH [28], K<sub>2</sub>CO<sub>3</sub> [29], K<sub>2</sub>C<sub>2</sub>O<sub>4</sub> [14], NaOH [30], which are thermally decomposed in the next preparation step. Similarly, as in the case of activated carbon [31], potassium hydroxide is widely used in the production of activated carbon spheres with a high surface area, due to its good distribution in fine size pores, low environmental pollution, low corrosiveness, and low cost [32,33,18]. Additionally, to further improve the performance of certain carbon materials, and find an optimal path for their preparation, a combination of both pathways (chemical and physical) can be used [7,23]. The material obtained in this way has excellent properties such as a very porous structure, large surface area, high micropore volume, controllable pore size distribution, high mechanical strength, smooth surface, high wear resistance, excellent durability, good fluidity, and low ash content as well as low moisture content [34].

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Taking into account the characteristics mentioned above, it is not surprising that carbon spheres are tested as adsorbents applied for both liquid and gas phases. Recently, special attention has been paid to the capture of carbon dioxide, due to the increase in the amount of this gas in the atmosphere caused by anthropological activities, e.g. energy industry, progressive urbanization, or burning of fossil fuels such as coal, oil, or gas. Wang et al. [35] prepared porous carbon spheres by direct carbonization of resorcinol-formaldehyde resin spheres with potassium salt. The prepared materials exhibited desired properties such as high CO2 capture performance up to 4.83 mmol/g, good CO2 selectivity against N2, and stable recyclability. Ludwinowicz and Jaroniec [36] studied the influence of different activating agents on the porosity of carbon spheres and their CO2 adsorption properties. It was found that KOH activation yielded the highest volume of micropores and the content of small micropores as well as the CO2 uptake for the KOH-activated sample was the highest. Dassanayake and Jaroniec [37] obtained high inherent microporosity of polypyrrole-derived carbon spheres, which was further activated using a KOH agent. The high ultramicropore volume was obtained and resulted in superior CO<sub>2</sub> uptakes under ambient pressure, reaching 7.73 mmol/g and 5.42 mmol/g at 0 °C and 25 °C, respectively. Wang et al. [38] used hemp stem hemicellulose as a precursor to prepare well-shaped carbon spheres with large surface area by an improved low-temperature hydrothermal carbonization method and KOH activation. They indicated that the plentiful micropores lead to excellent CO2 and CH4 adsorption capacities at ambient pressure and 0 °C. The above results promise satisfying prospects for future application.

This work aimed at determining the influence of the synthesis pH on the morphology and adsorption capacity of spherical carbon materials obtained by the carbonization of resorcinol–formaldehyde resin and the same materials with the pore structure improved by the activation process. The influence of pH on the spheres' morphology and porosity was determined and their adsorption performance was evaluated in detail by examining  $CO_2$  capture.

# 2. Materials and methods

# 2.1. Materials

Carbon spheres (CS) were obtained from resorcinol and formaldehyde, treated in a solvothermal reactor heated with microwaves, and then subjected to carbonization (RF). For this purpose, 2.4 g of resorcinol was dissolved in an aqueous alcohol solution composed of 240 mL distilled water and 96 mL ethanol. To adjust pH, ammonium hydroxide (25 wt%) was slowly dropped into the beaker. The materials were obtained at pH values of 7.50; 8.60; 8.85; 9.00; 9.25; 9.50 and 10.00. Then, 3.6 mL of formaldehyde (37 wt%) was slowly dropped and the whole was mixed using a magnetic stirrer at ambient conditions to facilitate a polycondensation reaction. After 24 h, the mixture was transferred into a microwave reactor (Ertec, Poland) and the treatment there was carried out for 15 min under a reaction pressure of 20 at. Next, the products were dried for 24 h at 80 °C and then carbonized in a high-temperature furnace (HST 12/400 Carbolite) (Carbolite, Derbyshire, UK) under argon atmosphere with the temperature increasing from 20  $^\circ C$  to 350  $^\circ C$ at a heating rate of 1  $^\circ$ C/min and holding time of 2 h and from 350  $^\circ$ C to 700 °C at a heating rate of 1 °C/min. After 2 h the sample was cooled to room temperature under an argon atmosphere. The final product was washed with distilled water and dried for 48 h at 80 °C in air. The obtained materials were marked as RF\_EtOH\_7.50; RF\_EtOH\_8.60; RF\_EtOH\_ 8.85; RF\_EtOH\_9.00; RF\_EtOH\_9.25; RF\_EtOH\_9.50, and RF\_EtOH\_10.00.

The selected materials (RF\_EtOH\_7.50; RF\_EtOH\_ 8.85; RF\_EtOH\_9.00, and RF\_EtOH\_10.00) were also subjected to the activation process. The activated samples were labeled ARF. 1 g of carbon spheres -RF, prepared as described above, was placed in a quartz boat and the appropriate amount of potassium hydroxide solution with a concentration of 5 mol/dm<sup>3</sup> was added to obtain the materials with an initial KOH content of 70 %. The resulting solution was mixed for 1 h and dried at 100 °C for 24 h. Next, the sample was activated in a high-temperature furnace (HST 12/400 Carbolite) (Carbolite, Derbyshire, UK) under an argon atmosphere with the temperature increasing from 20 °C to 700 °C at a heating rate of 10 °C/min, and after 5 min it was cooled to room temperature under argon atmosphere. In order to remove potassium from the sample, the final product was boiled in distilled water under reflux for 1 h, and the pH of the filtrate was checked. The boiling procedure was repeated until a neutral pH was reached. Finally, the sample was dried for 48 h at 100 °C. The obtained materials were marked as ARF\_EtOH\_7.50; ARF\_EtOH\_8.85; ARF\_EtOH\_9.00, and ARF\_EtOH\_10.00.

# 2.2. Methods

Two scanning electron microscopes were used to study and characterize the morphology of the obtained samples: the VEGA3-TESCAN (Tescan Orsay Holding a.s., Libušina, Brno – Kohoutovice, Czech Republic) device for general characterization and to generate statistics of the diameters of the obtained spheres; as well as SU8020 Ultra-high Resolution Field Emission Scanning Electron Microscope (Hitachi ltd., Chiyoda, Tokyo, Japan) for a more accurate description of the texture at higher resolution. Spheres' diameter distribution in the samples was carried out using a graphical analysis of a series of SEM images with both software measuring tools (Fiji ImageJ) and analog counting to achieve repeatable quantitative results. The wideness of distribution was compared on the basis of  $\times$  values obtained for different samples, where  $\times =$  (standard deviation)/mean.

The X-ray photoelectron spectra were acquired using Mg K $\alpha$  (hn = 1253.6 eV) radiation in a Prevac (PREVAC sp. z o.o., Rogów, Poland) system equipped with Scienta SES 2002 electron energy analyzer operating at constant transmission energy (Ep = 50 eV). The spectrometer was calibrated by using the following photoemission lines (with reference to the Fermi level): EB Cu 2p3/2 = 932.8 eV, EB Ag 3d5/2 = 368.3 eV and EB Au 4f7/2 = 84.0 eV. The instrumental resolution, as evaluated by the full-width at half maximum (FWHM) of the Ag 3d5/2 peak, was 1.0 eV. The samples were placed into a silver-lined molybdenum sample holder.

Surface properties were determined using N2 adsorption/desorption isotherms performed on a QUADRASORB evoTM Gas Sorption automatic system (Quantachrome Instruments, Boynton Beach, FL, USA) at -196 °C. Before each adsorption experiment, samples were outgassed at 250  $^\circ\text{C}$  under a vacuum of 1  $\times$  10  $^{-5}$  mbar for 12 h using a MasterPrep multi-zone flow/vacuum degasser from Quantachrome Instruments to remove adsorbed species that could intervene in the adsorption processes. The surface area (SBET) was determined in the relative pressure range of 0.05-0.30 and calculated based on Brunauer-Emmett-Teller (BET) equation. The total pore volume (TPV), was calculated from the volume of nitrogen held at the highest relative pressure (p/p0 = 0.99). The volume of micropores V<sub>m</sub> with dimensions smaller than 2 nm was calculated as a result of integrating the pore volume distribution function using the DFT method; the volume of mesopores V<sub>meso</sub> with dimensions from 2 to 50 nm was calculated from the difference of the total pore volume TPV and the volume of micropores V<sub>m</sub>.

Carbon dioxide adsorption isotherms at 0 °C and 25 °C were measured using the same Quadrasorb<sup>TM</sup> automatic system (Quantachrome Instruments, Boynton Beach, FL, USA) mentioned above in the pressure range between 0.01 and 0.98 bar. From CO<sub>2</sub> adsorption isotherms at 0 °C, pore size distribution (PSD) and the volume of ultramicropores v<sub>s</sub> with dimensions smaller than 1.0 nm (<1 nm) was determined and calculated by integrating the pore volume distribution function using the NLDFT method.

# 3. Results and discussion

SEM images of the non-activated samples are presented in Fig. 1. It was found that carbon spheres after treatment in the microwave reactor and subsequent carbonization at 700  $^{\circ}$ C according to the described temperature program, obtained in pH value up to 9.25 (Fig. 1d) had high regularity in size and spherical shape with a smooth outer surface. Generally, at lower pH spheres exist in a rather individual form, not bonded permanently with other CS, which is shown in Fig. 1a (pH 7.5),

but at higher pH (8.85) for certain regions in the sample's volume spheres may also form clusters and agglomerates (Fig. 1b). A closer inspection of panel Fig. 1c (pH 9.0) reveals described smoothness characteristic for unimpaired CS. Broken spheres exhibit textural irregularities inside the breaches, which reveal deeper structural layers of a sphere. Additionally, for spheres obtained at higher pH values, due to more pronounced uniformity, CS may also self-assemble into larger periodic structures, which has been shown in the background of Fig. 1d. This feature is also confirmed in the literature to date [39,40].





Fig. 1. SEM images of carbon spheres synthesised at pH: 7.50 (Fig. 1a); 8.85 (Fig. 1b); 9.00 (Fig. 1c); 9.25 (Fig. 1d); 9.50 (Fig. 1e); 10.00 (Fig. 1f) (above) and histograms representing the distribution of the diameter values of the carbon spheres obtained at different pH values and their basic statistics (below).

In comparison, the structures obtained at an increased pH value of 9.50 (Fig. 1e) and a pH value of 10.00 (Fig. 1f) are noticeably less regular, since the material consists of not fully spherical shape, with an increased tendency to agglomerate. With higher amounts of ammonia water present in the reaction system, surface of obtained CSs in the sample becomes rougher and more irregular, due to the presence of carbon non-spherical structures on the surface, which reduces the overall homogeneity of the material. The most agglomerated material was obtained at a pH value of 10 (Fig. 1f).

Histograms resulting from analyzed SEM images (Fig. 1) reveal that for the regular, smooth spheres – obtained at pH = [7.50; 9.25] - typical spheres' diameters (TSD, modes) vary in range from about 390 nm to 860 nm. Analysis of the diameter distribution for smooth spheres range shows a trend for the TSD to decrease with increasing pH of the initial mixture. Increased pH value causes an increase in the polymerization rate of resorcinol-formaldehyde resin. The mechanism of the polymerization of resin is as follows: during the first step, the addition reaction, resorcinol anions react with formaldehyde to form hydroxymethyl derivatives. The second step, condensation, consists of a formation of the methylene and methylene ether bridged compounds [41]. The addition reaction can be accelerated by the incorporation of a catalyst. At high pH values deprotonation of resorcinol in the first step occurs, which favors the appearance of hydroxymethyl derivatives. As a consequence, the higher the pH values, the smaller size of the finally obtained colloidal particles [42]. The enhanced rate of polycondensation and emulsification process at elevated pH value probably caused also additional agglomeration of the spheres for the sample RF\_EtOH\_10.00 [43]. The occurrence of this trend itself is confirmed in other publications, but for either other types of CS [44] or acidic conditions [42], so this paper confirms that described relation between pH and diameter size is also true for RF in basic conditions. Rey-Raap et al. [42] found that an increase in the pH value from 3 to 5, changed with the use of sodium hydroxide, led to carbon spheres with sizes of 4 µm and 3.5 µm, respectively. Additionally, it is worth noting that, as it was claimed by the authors of the work [42], it is possible to get smaller spheres, which might be an advantage for some applications, but these methods require solvents [43,45,46], long synthesis times [47,24,48] and even surfactants [49], which hinders their industrial implementation and increases their production cost. In our work, the time required to prepare carbon spheres is shorter, thanks to the use of the microwave reactor, in comparison with the methods where usually autoclaves are applied [50]. Further comparison with the results presented in the work [44] allows to suggest, that since TSD for RF EtOH 9.00 and for Jiang's counterpart obtained at pH = 9.00 has around 100 nm discrepancy in value, the use of different carbon precursor greatly influences both the TSD value and overall diameter distribution in fixed conditions. The presence of smaller particles was also explained by the formation of smaller emulsion droplets containing larger amounts of ethylenediamine [51] or cysteine-assisted synthesis [52].

Upon analysis of Fig. 1, it has been determined, that with the pH rise, diameter distribution undergoes a gradual narrowing up to pH = 9.00 (where the smallest value of  $\times = 0.075$  was obtained) and then subsequent widening above the mentioned value. This observation implies, that for RF spheres certain conditions exist in which the desired highest uniformity of sample is obtainable. The comparison of histograms presented in Fig. 1 also shows that with the pH values increased above the 9.25 mark, irregularity of the spheres, indicated by a sharp rise in  $\times$  values, is more pronounced for RF\_EtOH\_10.00 (the value of  $\times$  is 3.7 times higher than the optimum). For this sample obtaining smaller spheres' size, as well as merging effect is a consequence of reaction conditions, namely enhanced rate of polycondensation and emulsification process [43].

All histograms of the diameter distribution of the spheres show a negative skewness, indicating that spheres smaller than TSD are more frequently obtained in those conditions. This effect may be associated with the premature termination of the polymerization process (before the optimum sphere forms), which occurs under all pH conditions. Spheres' diameter distribution may be both leptokurtic or platykurtic, which depends on the exact conditions of the synthesis, but in general: CS samples with higher uniformity tend to be quasi-mesokurtic, resembling Gaussian distribution.

The surface composition of samples RF\_EtOH\_9.00, ARF\_EtOH\_9.00 and ARF\_EtOH\_10.00 was examined utilizing X-ray photoelectron spectroscopy. On the surface of all samples, carbon and oxygen were identified. The surface of the sample ARF\_EtOH\_9.00 contained also traces of potassium. The content of this element was apparently due to non-ideal cleaning of the material after modification.

The oxygen present on the surface of the studied materials contributed a very small fraction of all atoms observed by XPS. Oxygen atoms on sample RF\_EtOH\_9.00 accounted for only 1 % of the surface. The atomic concentration of oxygen in the other samples was slightly higher, for sample ARF\_EtOH\_10.00 it was about 5 %, and for sample ARF\_EtOH\_9.00 it reached 7 %. These data confirm that the surface modification introduced additional oxygen atoms into the material.

The XPS C 1 s spectra presented in Fig. 2a confirm the high surface purity of the studied samples. The maximum of the spectrum for each sample is located at identical binding energy, 284.5 eV, which corresponds to the graphitic carbon. In the binding energy range between 286 eV and 292 eV, a low intensity "tail" is observed. Its presence confirms the presence of various functional groups containing C—O bonds, but does not allow for an unambiguous indication of their types. In the case of sample ARF\_EtOH\_9.00, at binding energies around 293 eV and 296 eV two maxima of very low intensity are observed, which correspond to a doublet of K 2p3/2 and K 2p1/2 lines.



**Fig. 2.** Photoelectron spectra for non-activated and activated materials: panel a) contains XPS C 1 s spectrum and panel b) contains XPS O 1 s spectrum.

Somewhat better insight into the presence of carbon-oxygen bonds on the surface of the studied samples is provided by the analysis of the XPS O 1 s spectra shown in Fig. 2b. The O 1 s line observed for the surface of the reference sample, RF\_EtOH\_9.00, is relatively narrow and shows a slight asymmetry towards lower binding energies. The maximum of this line is located at a binding energy of 533.1 eV, as depicted as a thick black line above the spectra. Assuming that the observed XPS line corresponds only to bonds of oxygen atoms with carbon (or with hydrogen atoms not observed by XPS method), this position corresponds to C-O bonds or bonds in hydroxyl groups. The occurrence of the asymmetry of this line on the low binding energy side may be due to a small contribution of C=O bonds, for which the position of the O 1 s line is about 531.5 eV (depicted as a thick line above the spectra).

In the modified sample ARF EtOH 10.00 the O 1 s line was significantly broadened in comparison to the reference sample. The position of the maximum of this line has shifted slightly to the binding energy value of 532.5 eV. However, the center of gravity of the spectrum remains near the binding energy value of 533 eV. It may be explained by the fact that after the modification an additional group of C=O bonds appeared on the surface, which agrees with the increase of the concentration of surface oxygen.

The surface of the sample ARF\_EtOH\_9.00 has changed the most in comparison to the reference material. The position of the maximum of this line at the binding energy of 532.6 eV is similar to the position of the maxima of the O 1 s line observed for the other two samples. However, the envelope of this line is significantly broadened and extends to the binding energy range of about 530 eV. It should be recalled that potassium atoms were detected on the surface of this material. For the type of materials discussed in this paper, potassium should be present in the oxidized form. The O 1 s line for oxidized potassium compounds is located around the binding energy of 530 eV. Therefore, it can be suggested that in the case of the latter sample, the surface modification led to the incorporation of additional oxygen atoms in the form of C=O bonds, and that oxidized potassium compounds are also present on the surface. The obtained results confirm that the organic spheres are composed of primary particles with a great amount of surface oxygenated groups [53]. Their presence may be one of the reasons why a certain degree of spheres agglomeration exists. [54]. SEM investigations of the samples obtained at 10 pH and presented in Fig. 3b confirm that observation. What is interesting is that carbon spheres prepared at 9 pH and activated using potassium hydroxide did not show any agglomeration tendency (Fig. 3a), which can confirm that the presence of oxygen on the carbon surface is connected mainly with the oxidized potassium compounds.

Based on the low-temperature (-196 °C) nitrogen adsorption

isotherms, presented in Fig. 4 and in Fig. S1 (supplementary materials), the specific surface area (S<sub>BET</sub>), total pore volume (TPV), the volume of micropores (V<sub>m</sub> < 2 nm), and volume of mesopores (V<sub>meso</sub>) of the nonactivated materials have been determined. The calculated values are listed in Table 1. The obtained results show that the change in pH during the preparation of non-activated samples does not significantly affect the value of the specific surface area. The SBET of the tested samples ranged from 443  $m^2/g$  to 461  $m^2/g$ . More careful analysis of the results, reveals a slight change in the values of SBET in relation to pH values, which is presented in Fig. 5. For the sample obtained at the lowest pH of 7.50, calculated  $S_{BET}$  equaled 449 m<sup>2</sup>/g. Together with the increase of pH, the increase of S<sub>BET</sub> was noticed reaching a maximum value, 461 m<sup>2</sup>/g, for RF\_EtOH\_8.85. Further increase of the initial pH value caused a slight decrease in the surface area values of the obtained samples. The lowest value, equal to  $443 \text{ m}^2/\text{g}$ , was reached for the sample prepared at the lowest pH = 10.00.

Much greater differences were observed in the case of the total pore volume results and the shape and course of N2 adsorption isotherms. The data in Table 1 show that the samples obtained between pH 7.50 to 9.25 are characterized by lower TPV, than the samples obtained at higher pH, and practically the same values for all samples were received,  $0.25 \text{ cm}^3/$ g or 0.26 cm<sup>3</sup>/g. In Fig. 4, we can see that the  $N_2$  adsorption isotherms for these samples exhibited a type I of physisorption isotherm [55,56],



Fig. 4. Nitrogen adsorption-desorption isotherms of non-activated samples obtained at pH 7.50, 9.50 and 10.00.



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Fig. 3. SEM image of the activated sample obtained at 9 pH (Fig. 3a) and 10 pH (Fig. 3b).

#### Table 1

rextural parameters and GO <sub>2</sub> sorption capacities for the non-activated and activated carbon spheres obtained at different pri-	Textural	parameters and	CO <sub>2</sub> sorption	1 capacities for the second se	ne non-activated and	activated c	arbon spheres of	obtained at d	ifferent pH.
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	S <sub>BET</sub>	TPV	v <sub>s</sub> (<1nm)	V <sub>m</sub> (<2nm)	V <sub>meso</sub>	CO <sub>2</sub> 0 °C	CO <sub>2</sub> 25 °C
	[m <sup>2</sup> /g]	[cm <sup>3</sup> /g]	[cm <sup>3</sup> /g]	[cm <sup>3</sup> /g]	[cm <sup>3</sup> /g]	[mmol/g]	[mmol/g]
RF_EtOH_7.50	449	0.25	0.19	0.22	0.03	3.44	2.33
RF_EtOH_8.60	455	0.26	0,19	0,22	0,04	3.25	2.45
RF_EtOH_ 8.85	461	0.26	0.20	0.22	0.04	3.56	2.40
RF_EtOH_9.00	459	0.25	0.19	0.21	0.04	3.50	2.36
RF_EtOH_9.25	458	0.26	0.19	0.21	0.05	3.50	2.33
RF_EtOH_9.50	455	0.34	0.18	0.20	0.14	3.31	2.32
RF_EtOH_10.00	443	0.31	0.18	0.20	0.11	3.28	2.30
ARF_EtOH_7.50	916	0.49	0.34	0.43	0.06	5.55	3.39
ARF_EtOH_8.60	765	0.45	0.27	0.36	0.09	4.63	3.04
ARF_EtOH_8.85	840	0.46	0.29	0.40	0,06	5.06	3.11
ARF_EtOH_9.00	1030	0.58	0.32	0.48	0.10	5.37	3.24
ARF_EtOH_10.00	756	0.49	0.28	0.35	0.14	4.83	3.08

 $S_{BET}$  - specific surface area; TPV - total pore volume; vs - the volume of ultramicropores with diameter smaller than 1 nm;  $V_m$  - the volume of micropores with diameter smaller than 2 nm;  $V_{meso}$  - the volume of mesopores with diameter from 2 to 50 nm.



Fig. 5. Graphical comparison of the BET surface area values obtained for the non-activated samples.

which corresponds to microporous materials. For these materials, only a small volume of mesopores was noticed and ranged between 0.03 cm<sup>3</sup>/g for RF\_EtOH\_7.50, and 0.05 cm<sup>3</sup>/g for RF\_EtOH\_9.25. The volume of micropores was also similar and amounted to  $0.22 \text{ cm}^3/\text{g}$  for the samples RF\_EtOH\_7.50, RF\_EtOH\_8.60, RF\_EtOH\_8.85 and 0.21 cm<sup>3</sup>/g for the samples RF\_EtOH\_9.00 and RF\_EtOH\_9.25. The pore size distributions of the sample obtained at the lowest pH (7.50) are shown in Fig. 6 and confirms that almost only the micropores existed in this material. A much greater content of mesopores, 0.14  $\rm cm^3/g,$  and 0.11  $\rm cm^3/g,$  was observed in the case of non-activated samples obtained at pH 9.50, and 10.00, respectively. The volume of micropores for both samples was at the level of 0.20 cm<sup>3</sup>/g. Fig. 4 shows the  $N_2$  adsorption and desorption isotherms of these samples. It is clearly visible that the shape of N2 adsorption isotherms changed, which is connected with the greater contribution of mesopores in these materials. In these cases, type II adsorption isotherms with a H4 type hysteresis loop (sample obtained in pH 9.50) and a mixed type of hysteresis loop of H2 and H4 type (sample obtained in pH 10.00) was noticed, as in works [55,56]. The H4 type hysteresis loop is characteristic of micro-mesoporous carbon materials [55–58]. From the analysis of N<sub>2</sub> adsorption–desorption isotherm of the sample obtained at pH 9.50, could be noticed that the sample possesses a three step shaped adsorption isotherm (Fig. 4). The sudden increase in the adsorption isotherm in the low relative pressure range up to (P/P0) 0.01 is due to the presence of micropores with a size below 2 nm.



**Fig. 6.** Pore size distributions of the non-activated samples obtained at pH 7.50; 9.50 and 10.00 corresponding to the nitrogen adsorption isotherms shown in Fig. 4.

Capillary condensation leading to a hysteresis loop in relative pressure (P/P0) around 0.5 indicates the formation of mesopores [58]. Another steeper and stronger adsorption at (P/P0) close to 1.0 may result from the presence of macropores or mesopores in the voids of the intermolecular carbon spheres [59,60,61]. The shape of the hysteresis loop can be attributed to the presence of specific pore structures. In the sample obtained at pH 9.50, the shape of the hysteresis loop can be attributed to the presence of narrow slit-like pores [55]. Sample obtained at pH 10.00 has a little different N2 adsorption-desorption isotherm. Specifically, two typical regions can be observed: first a sharp increase at low pressure (P/P0) < 0.01 confirms the presence of micropores; second when (P/P0) is increased from 0.45 to 0.99. A large hysteresis loop in the isotherm curves indicates the existence of mesopores. The pore size distributions of this sample were shown in Fig. 6 where the presence of mesopores in the range from 3 nm to 25 nm was observed. For the material obtained at pH = 10, the higher content of mesopores in the range from 7 nm to 14 nm was noticed, in comparison with the sample obtained at pH = 9.50. In this sample, probably a mixed type of hysteresis loop composed of type H2 and type H4 existed. The H4 loop has been attributed to adsorption-desorption in a narrow slit-like pores [55,56,62,63]. The H2 loop is especially difficult to interpret and corresponds to pores with narrow necks and wide bodies [55,56,63,64]. In the sample obtained at pH 10.00, the adsorption/desorption hysteresis may indicate a very large ratio of the length of the pores to their width or

the so-called "bottle" shape of the pores - the pores are wider in the grain's depth of the material than at its edge. The shape of the hysteresis loop in this sample may also indicate the presence of more complicated pore structures in which, in addition to capillary condensation, poreblocking phenomena or percolation may occur [55,56,64].

The adsorption properties of the non-activated materials were evaluated in detail by examining CO<sub>2</sub> adsorption from the gas phase. The values of CO<sub>2</sub> adsorption, calculated based on the isotherms obtained at 0 °C (presented in Fig. 7 and Fig. S.2 - supplementary materials), and 25 °C, are given in Table 1. It was found that the differences in the values of the adsorbed carbon dioxide were insignificant. For the samples obtained at pH 7.50 and 8.60, CO<sub>2</sub> adsorption was 3.44 mmol/g and 3.25 mmol/g, respectively. Similar values were noticed for the materials prepared with pH between 7.50 and 9.25, and amounted to 3.44 mmol/ g for RF\_EtOH\_7.50 and 3.50 mmol/g for RF\_EtOH\_9.25. For the samples above 9.25 pH slightly lower values were noticed, reaching 3.31 mmol/ g and 3.28 mmol/g for RF EtOH 9.50 and RF EtOH 10.00, respectively.

The obtained values did not correlate with the values of the total pore volume. From the available data [65,66,67,68] and our previous studies [69,70] it is known that for the adsorption of CO<sub>2</sub> at ambient conditions the micropores below 0.8 nm play a major role and are responsible for this process. The volume of ultramicropores Vs with dimensions below 1.0 nm was determined from the CO<sub>2</sub> adsorption isotherm at 0 °C (Fig. 7 and Fig. S2) and calculated by integrating the pore volume distribution function using the NLDFT method. The results are presented in Fig. 8 and Table 1. All the non-activated materials have a similar content of micropores. However for the materials with the highest CO<sub>2</sub> adsorption, a higher content of pores of 0.35 nm in size was detected. Moreover, a slight increase in pores of 0.55 nm in size was noticed in these samples. The lowest contribution of pores of 0.35 nm and 0.55 nm in size was observed for the sample obtained in pH 9.50 and 10.00. Consequently, these samples expressed the lowest CO<sub>2</sub> adsorption values.

In contrast to non-activated samples, the activation of carbonaceous materials using potassium hydroxide had an observable and significant impact on the values of the specific surface area and thus on the  $CO_2$  adsorption values. The values of  $S_{BET}$  (calculated based on the  $N_2$  adsorption isotherms presented in Fig. 9 and Fig. S3 – supplementary materials) and  $CO_2$  uptake (calculated based on the  $CO_2$  adsorption isotherms presented in Fig. 5.2 – supplementary materials) are listed in Table 1. As expected, for all tested samples the increase of both  $S_{BET}$  and  $CO_2$  adsorption capacity values was noticed in comparison with a non-activated materials. Concerning a dependency between specific



Fig. 7.  $CO_2$  sorption isotherms of the non-activated and activated sample obtained at pH = 7.50.



Fig. 8. Pore size distributions of the non-activated samples corresponding to  $CO_2$  adsorption isotherms shown in Fig. 7 and Fig. S2.



Fig. 9. Nitrogen adsorption–desorption isotherms of activated samples obtained at  $p\mathrm{H}=7.50$  and 10.00.

surface area and pH, the observable tendency was similar as in the case of non-activated sample, which means that SBET increased together with the increase of pH value. For the activated materials obtained at 8.60, 8.85, and 9.00 the specific surface area equaled to 765  $m^2/g$ , 840  $m^2/g$ , and even 1030 m<sup>2</sup>/g, respectively. A high value of  $S_{BET}$  (916 m<sup>2</sup>/g) was also noted for ARF\_EtOH\_7.50 material. It is worth noting that a further increase of pH, above 9.00, resulted in a considerable drop of SBET value, and for ARF\_EtOH\_10.00 equaled to 756 m<sup>2</sup>/g. CO<sub>2</sub> adsorption capacity showed exactly the same tendency. The increase in pH value resulted in the increase of  $CO_2$  adsorption from 4.63 mmol/g at pH = 8.60 up to 5.37 mmol/g at pH = 9.00. The highest value of  $CO_2$  adsorption was noticed for the material prepared at pH = 7.50 and equaled to 5.55 mmol/g. A clear tendency between the pH value of the prepared materials and CO2 adsorption values could not be observed, however in general a decrease in adsorption was noticed together with an increase of pH, and for the sample ARF EtOH 10.00 amounted to 4.83 mmol/g. This phenomenon can be connected with the diameters of carbon spheres and their morphology. The decrease in the diameter of the carbon spheres, as observed with the increase of pH and shown in Fig. 1, may be the cause of easier access of the activating agent to the carbon volume and as a consequence more effective activation process. By extension, the sample prepared at pH = 10.00 should possess the highest specific surface area. Despite the fact that carbon spheres obtained at 10.00 pH had the smallest diameters (Fig. 1), simultaneously a certain degree of merging was observed, resulting in clustered spheres and large carbon structures which hindered even the distribution of potassium ions.

Based on the adsorption isotherms of the KOH-activated samples, presented in Fig. 9 and Fig. S3 - supplementary materials, it was found that the mixed type of H2 and H4 hysteresis loop was observed only in the sample obtained at pH 10.00. The shape of the adsorption-desorption isotherms of this sample is very similar to that observed in the non-activated sample obtained at pH 10.00. Specifically, region when P/P0 is increased from around 0.5 to 0.99, a large hysteresis loop in the isotherm curve indicates the existence of mesopores [71]. The pore size distributions of this sample are shown in Fig. 10 and the presence of mesopores in the range from 3 nm to 25 nm is clearly visible. A region where can be observed a sharp increase at low pressure (P/P0) < 0.01 confirms the presence of micropores in this sample. The shape of the isotherms of the remaining samples (Fig. 9. and Fig S3 – supplementary materials) is very similar and characteristic of microporous materials. The pore size distributions of the sample obtained at pH 7.50 are presented in Fig. 10 and confirm the presence of mainly micropores in this sample. A small number of mesopores was observed only in the range from 2.0 nm to 2.8 nm.

Comparing the activated materials it was found that the highest ultramicropores Vs contributions, 0.34 cm<sup>3</sup>/g, and 0.32 cm<sup>3</sup>/g, were noticed for the materials composed of separated spheres obtained at pH = 7.50 and 9.00, respectively. Although the content of the 0.35 nm pores for the sample ARF\_EtOH\_7.50 is limited, the overall Vs content is compensated by the high contribution of 0.55 nm and 0.8 nm pores as shown in the Fig. 11. The lower ultramicroporosity expressed the activated sample obtained at pH = 8.60, equaled 0.27 cm<sup>3</sup>/g. For the material obtained at pH = 10, the highest content of mesopores was noticed, 0.14 cm<sup>3</sup>/g in comparison with the sample obtained at pH = 9.00, but both micropores and ultramicropores decreased up to 0.35 cm<sup>3</sup>/g and 0.28 cm<sup>3</sup>/g, respectively, which resulted in lower CO<sub>2</sub> uptake values.

#### 4. Conclusions

Taking into account the morphology of the synthetized materials at different pH, it can be found that together with the change of pH, the changes in the diameter of the carbon spheres were noticed. Carbon spheres had diameters ranging 780–920 nm and 80–150 nm for the





Fig. 11. Pore size distributions of the activated samples corresponding to  $CO_2$  adsorption isotherm shown in Fig. 7 and Fig. S2.

sample obtained at the lowest pH (7.50) and the highest pH (10.00), respectively. It is worth to note, that carbon spheres obtained between 7.50 and 9.25 pH had high regularity in size and spherical shape with a smooth outer surface. Generally, spheres existed in rather individual form. Increased pH value of 9.50 and of 10.00 resulted in less regular material, consisting of not fully spherical particles, with an increased tendency to agglomerate. With greater amounts of ammonia water present in the reaction system, the surface of obtained CS becomes rougher and more irregular.

The value of pH did not significantly affect the adsorption capacity of the non-activated materials, however, a slight dependency was noticed. Activation process resulted in a significant increase in the CO<sub>2</sub> adsorption values as well as surface area values of the samples regardless of the morphology of the spheres and a similar dependence was observed in the case of non-activated materials. It means that the increase of adsorption capacity for the samples obtained up to pH = 9 was observed, and above this value, the decrease of  $CO_2$  uptake was noticed. Probably a better separation and smaller diameters of carbon spheres achieved at pH up to 9 allowed for better distribution of potassium ions during activation and in consequence – higher adsorption performance.

It was confirmed that samples obtained above pH 9 had a much larger contribution of mesopores, which, however, did not affect significantly the values of CO<sub>2</sub> adsorption. For efficient CO<sub>2</sub> adsorption, the pores below 0.8 nm in size were essential. Considerable development of the ultramicroporosity was noticed together with an increase of pH, causing the development of the pores 0.35 nm and 0.55 nm in size, and reaching maximum for the activated sample obtained at pH = 9. For this material, the best adsoption results were observed and reached 5.32 mmol/g at 0 °C.

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**Data Availability Statement:** The data presented in this study will be available upon request.

#### CRediT authorship contribution statement

Konrad S. Sobczuk: Writing – original draft, Investigation, Formal analysis, Conceptualization, Methodology. Iwona Pelech: Writing – review & editing, Formal analysis, Conceptualization, Methodology, Writing – original draft. Urszula Narkiewicz: Funding acquisition, Supervision, Writing – review & editing, Conceptualization. Piotr Staciwa: Visualization, Writing – original draft, Investigation, Formal analysis, Methodology. **Daniel Sibera:** Visualization, Writing – original draft, Investigation, Formal analysis, Methodology. **Dariusz Moszyński:** Visualization, Writing – original draft, Methodology.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Data availability

Data will be made available on request.

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# Appendix A. Supplementary data

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Applied Surface Science 608 (2023) 155196

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