

Article

Carbons from Pistachio Nutshells Activated with Phosphoric Acid and Microwave Treatments: Towards Sustainable Sorbents for Treating Water

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Abstract

Activated carbons are usually prepared from natural precursors (e.g., fruit stones or nutshells) by carbonization and activation processes carried out at 400–1000 °C. They exhibit well-developed porosity, and chemical activation introduces hydrophilic functional groups on their surface, providing excellent sorption properties. However, the high temperatures required during thermal treatment increase production costs. In this work, cost-reducing methods for preparing carbon sorbents are proposed. Carbonization of H₃PO₄ activated waste pistachio nutshells was performed using classical pyrolysis (500 or 550 °C, 30 min, N₂ atmosphere) and microwave treatment (power 1000 W, 20 min). The properties of the synthesized carbons were characterized using thermogravimetry and spectroscopic techniques including infrared (ATR), Raman, photoelectron (XPS) spectroscopies, and scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS). Porous structure parameters were determined using nitrogen adsorption experiments. The efficiency of Pb²⁺ removal from spiked ultrapure, tap and river water was evaluated by batch sorption experiments and inductively coupled plasma–mass spectrometry. The most porous carbons were those prepared at 500 and 550 °C, with specific surface areas of 910 and 256 m²/g, respectively. Surface phosphates increased the Pb²⁺ sorption efficiency to 99% from ultrapure water, at an initial concentration of 300 µg Pb²⁺/L. The material obtained with the microwave method was not fully carbonized and remained nonporous, but it also exhibited 99% Pb²⁺ uptake from ultrapure water due to the presence of oxygen-containing surface groups. The Pb²⁺ removal from spiked tap and river water reached up to 84% and 94%, respectively, at the spiking level of 300 µg Pb²⁺/L.

Keywords: pistachio nutshell; carbonization; microwave treatment; TGA; SEM-EDS; XPS; ATR-FTIR; Raman spectroscopy; sorption of Pb²⁺



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1. Introduction

One of the most pressing global challenges is limited access to drinking water. Intensive efforts to address this issue are being carried out worldwide under the United Nations 6th Sustainable Development Goal. Adopted in 2015, the Sustainable Development Goals (SDGs) aim to eradicate poverty, improve health and education, reduce inequalities, and address climate change while promoting the responsible use of natural resources. In particular, SDG 6 emphasizes the need for the sustainable provision and management of water

and sanitation services for all [1]. Growing pressures from climate change, overpopulation, and poverty contribute to the increasing prevalence of waterborne diseases. This problem is particularly evident in rural areas of low-income regions, where water treatment infrastructure is often inadequate [1]. In 2024 the highest proportion of countries with the lowest access to safely managed drinking water services was found in Africa [2]. A key report from the World Health Organization estimates that 3.4 billion people lacked access to safely managed sanitation services in 2024, which directly affects the safety of drinking water [2]. There is also a growing problem of water pollution by heavy metals, exacerbated by global population growth [3]. This pollution leads to ecosystem degradation, and consequently, to a reduction in biodiversity. Some heavy metals—such as lead, cadmium chromium, mercury and arsenic—accumulate in the food chain, and exposure to them from a particular threshold threat to human life [3,4]. In the tissues of living organisms, heavy metals cause cell death, disrupt essential body functions, and ultimately may lead to death [5].

The main source of lead contamination in soil and water is heavy industry, particularly mining. Mining practices such as drilling and blasting release fine particles containing lead, which subsequently settle in the surrounding environment. Furthermore, wastewater generated by the mining industry is also a significant source of this metal, than can seep into the soil and further migrate into surface and groundwater [6]. Lead has also been widely used in the production of components for water supply systems, such as pipes, taps and anti-corrosion coatings for steel pipelines [7]. In the form of micron-sized particles, lead can accumulate in the human body through the respiratory system, while larger particles may enter the body via the digestive system. Its absorption through the skin is limited to the species in the form of organic complex compounds. Children under six years of age are particularly vulnerable to lead toxicity because their bodies absorb the heavy metal more readily than adults. Lead is considered a neurotoxin that disrupts the nervous system and impairs normal brain development and cognitive functions. Excessive lead exposure can also cause kidney damage and adversely affect the reproductive system [8]. Therefore, there is a pressing need for the effective removal of lead (commonly present as Pb^{2+}) from aquatic environments.

Adsorption is a promising alternative to existing biochemical and electrochemical methods of lead removal, due to its simplicity of use, low cost and wide range of options for selecting and modifying the appropriate adsorbent [9]. Carbonaceous materials derived from natural waste are very popular among adsorbents. Owing to their scalability and low production costs, these materials serve as effective substitutes for synthetic adsorbents, and the adsorption is widely recognized as an efficient solution for environmental remediation [10].

Nutshells are an easily accessible waste product used as an adsorbent. The pistachio industry is particularly well developed in the United States. In the 2023–2024, global pistachio production reached 1.07 million metric tons, of which 45–70% was not usefully applied. The nutshells, often mixed with soil, are unsuitable for animal feed. And without further processing, they constitute a byproduct with a very limited use [11,12].

As a natural material of plant origin, pistachio shells consist of cellulose (38–54%), hemicellulose (15–34%), and lignin (25–29%) [11,12] which, as sclerenchyma, form secondary cell walls and serve as the protective tissue of the shell. Secondary cell walls develop through the process of lignification, which involves the formation of a specific three-dimensional structure and helicoidal arrangement of cellulose microfibrils. Lignin acts as a matrix, embedding the cellulose fibrils. This highly organized structure enables efficient energy absorption and consequently provides pistachio shell tissues with excellent mechanical properties, which makes them a particularly attractive sustainable raw material for various applications [13].

Activated carbon, the most effective class of carbon-based adsorbents, can be produced from pistachio nutshells through pyrolysis combined with physical activation using CO₂, steam, or chemical activation using KOH, NaOH, ZnCl₂, K₂CO₃, NH₄NO₃, HCl, or H₂SO₄ [14–18]. Pyrolysis of biomaterials can be performed conventionally, using a standard carbonization furnace or by means of microwave-assisted methods [11,15,19–23]. These processes typically involve heating the material under an inert atmosphere. The efficiency of pyrolysis depends on parameters such as temperature, annealing time, and heating rate [17,20,24,25]. In addition to solid carbon, biogases and biooils are also formed as byproducts [11,23]. In microwave pyrolysis, a modern alternative to conventional methods, heat is delivered to the sample not through convection or conduction, as in the classical approach, but through dipole rotation and ionic conduction within the material's particles [22].

The lignocellulosic matter contained in pistachio shells provides hydroxyl functional groups that enable numerous surface modifications. The most active in this regard are the hydroxyl groups located at the C6 carbon of cellulose (the only methylene group in the cellulose's basic unit) and the hydroxyl substituents on the aromatic rings of lignin. Common modification strategies include esterification, etherification, noncovalent and hydrophobic modifications, alkyne–azide reactions, or cationization [26,27].

One of the most popular chemical activating agents—applied before or during the pyrolysis of biomass containing lignocellulose is phosphoric acid. Its presence promotes the formation of levoglucosenone during the pyrolysis of the raw material. Because of its physicochemical properties, levoglucosenone can undergo polymerization and react with oxygen-containing compounds, facilitating additional structural transformations in the precursor [28,29]. Phosphoric acid (H₃PO₄) is used as a modifier in the carbonization process due to the lower cellulose degradation in comparison to other mineral acids [28,30–32]. At the initial activation stage, the presence of phosphoric acid enables the formation of the first intermediate products with reduced molar mass and the release of volatile gases. At an advanced state in the preparation of the carbon, there is a dispersion of intermediate compounds within the biomass matrix, which is accompanied by the formation of tar and a carbon fraction. In this stage, according to the reactions reported by Neme et al., phosphoric acid begins to decompose. In the final stage porous char is formed in the presence of P₂O₅ [31]. The phosphoric acid activation process is highly temperature-dependent [33]. During the carbonization of lignocellulosic materials, dehydration occurs at temperatures below 350 °C, reducing oxygen and hydrogen content in the biomass precursor. This decreases the efficiency of the initial activation compared with carbonization performed without phosphoric acid. However, at higher temperatures (above 350 °C), the presence of H₃PO₄ significantly enhances carbonization efficiency through increased dehydration [34]. The changes occurring in the precursor during activation involve not only the decomposition of organic matter. Elevated temperature favors also the formation of new chemical bonds between the lignocellulosic precursor and the acid activator. In general, an increase in carbonization temperature is associated with a higher phosphorus content within the carbon structure. However, this trend is not universal and depends strongly on the precursor type as well as processing conditions such as temperature, type of gas atmosphere and the precursor-to-activator ratio [33,35–38]. Studies on activated carbons derived from peach pits and lignosulfonates carbonized at temperatures exceeding 800 °C demonstrated a decrease in phosphorus content, which was attributed to the formation of volatile phosphorus-containing species resulting from the reduction of phosphates to elemental phosphorus [39,40]. Similar behavior has also been observed at lower temperatures. In case of pecan shells precursors, an increase in carbonization temperature from 350 to 475 °C led to a substantial reduction in phosphorus content from 2.6 to 1.5 wt% [41]. Likewise, lignin-based materials exhibited a decrease in phosphorus content from 1.2 to 0.6 wt% when the temperature was raised from 450 to 650 °C [42].

The acidic surface functionalities enable phosphorus-containing carbons to bind metal ions from aqueous solutions. Although the use of phosphoric-acid-activated carbons for metal ion adsorption was patented long time ago, this topic attracted only sporadic research interest until the late 20th century, when carbon materials and their modification once again aroused the interest of scientists. This period has brought enormous progress in research on the development of porous materials with the highest possible porosity and sorption capacity. During this period, new phosphorus-containing carbons were developed, as well. For example Liu et al. synthesized H_3PO_4 activated carbon from lotus stalks and achieved Pb^{2+} adsorption capacities on the level of 139.0 mg/g [43].

An additional advantage of using H_3PO_4 as an activator in the production of activated carbons is the improvement of their thermal stability compared to unmodified materials [31]. Beyond adsorption applications, the porous phosphorus-doped carbons, due to their high porosity and specific surface area, are also used as anode materials for energy storage [44].

Activation of carbons takes place at high temperatures, usually 800–1000 °C. The materials produced under such conditions exhibit a well-developed porous structure and excellent sorption capacity [32,33,38]. Nevertheless, the energy costs associated with their production are increasing due to the rising costs of electricity generation. Carbonizing at lower temperature would be a solution. Another approach can involve the use of microwave reactors, in which the carbonization process is much faster.

In this work, new effective carbon sorbents prepared with enhanced sustainability practices were synthesized. The conditions investigated involved lower carbonization temperatures (500 and 550 °C) and using fast microwave treatment. Pistachio nutshells, classified as “waste” biomass, served as the precursor of the carbon adsorbents. The activation of the carbons was supported by phosphoric acid applied either at room temperature or at the carbonization temperature, resulting in products that differed in porosity and in the amount of phosphorus incorporated into their structure. This work aimed to prepare a new generation of highly effective, scalable adsorbents, developed to make drinking water safer from heavy metals, using green practices and underused safe waste-derived materials. Additionally, energy consumption was compared across different carbonization conditions to demonstrate the economic benefits achievable through reduced processing temperature.

2. Materials and Methods

Pistachio nutshells (PNs) were mechanically crushed and separated into fractions using four sieves with metal mesh sizes of 0.22 mm, 0.326 mm, 0.63 mm, and 1.25 mm. The fraction of the material measuring ≥ 1.25 mm was selected for further studies. In the next step, the acid activation process was preformed according to the following procedure: 45 g of the sieved material was soaked in 16.7 mL of 85% H_3PO_4 (Merck, Darmstadt, Germany) at room temperature and left to dry in open air for several days. The resulting product was divided into two parts. The first one, named PN- H_3PO_4 , was carbonized as received without any additional treatment (carbonization at 500 °C in the presence of the acid). From the second portion, named PN- H_3PO_4 -R, the excess acid was removed by washing. The material was soaked in 50 mL of water overnight and then decanted and filtered off. The procedure was repeated (approximately 6 times) until the water had a neutral pH (determined using pH indicator strips). The sample of pistachio nutshells (15 g) soaked in distilled water (6.5 mL) and dried in open air was utilized as the reference material (PN). Next, the prepared precursors were carbonized (carbonization at 550 °C after rinsing out the acid). The carbonization procedures are depicted in Figure 1. After thermal treatment all samples were purified by washing with acetone (POCH, Gliwice, Poland) and weighed to evaluate the yield of the process.

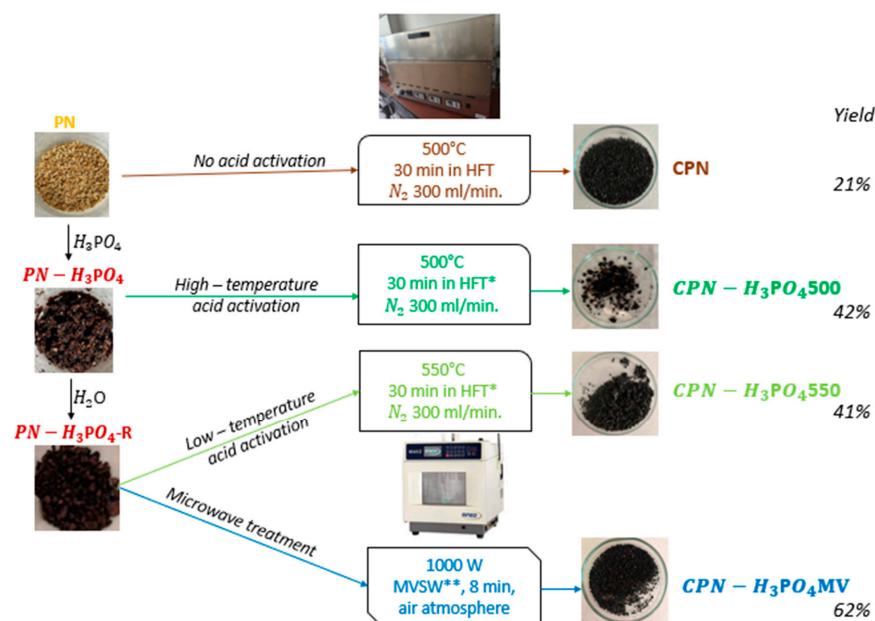


Figure 1. Scheme of activation and carbonization procedure. * HTF—horizontal quartz tube furnace PRW-S 55LM (Czylok, Jastrzębie Zdrój, Poland). ** MVSW—Microwave Synthesis Workstation MAS-II PLUS (Sineo Microwave Chemistry Technology Co., Ltd., Shanghai, China).

Thermogravimetric analyses (TGAs) were performed using an STA 449 F1 Jupiter thermal analyzer (Netzsch, Selb, Germany). Samples of approximately 7 mg were weighed into Al₂O₃ crucibles. Measurements were carried out in the temperature range of 30 to 1000 °C with the heating rate set on 10 °C/min. During analyses, helium or synthetic air atmosphere was maintained with a flow rate of 40 mL/min. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves were processed using Proteus Analysis 6.0.0 software.

Microscopy analyses were accomplished with a Nikon SMZ 1500 optical microscope equipped with an LED light source (Nikon Corporation, Tokyo, Japan), using Touptview image capture software (version 4.11). To obtain more detailed information on the morphology and composition of the carbons, the samples were examined with a Quanta 3D FEG (FEI, Hillsboro, OR, USA) scanning electron microscope (SEM). Before analysis the samples were stuck on circular aluminum stubs using double-sided sticky carbon tape and then coated with Pd/Au. Subsequently, they were transferred to the SEM sample chamber and analyzed at an accelerating potential of 5kV. Energy-dispersive X-ray spectroscopy analysis (EDX) was performed with Octane Elect Plus detector (EDAX Inc., Mahwah, NJ, USA).

X-ray photoelectron spectroscopy (XPS) analyses of the sorbent surface were performed with a Prevac multi-chamber UHV analytical system (Rogów, Poland) using a hemispherical Scienta R4000 electron analyzer with Scienta SAX-100 X-ray source (Al K α , 1486.6 eV, 0.8 eV band) equipped in the XM 650 X-ray Monochromator (0.2 eV band). The pass energy of the analyzer was set to 200 eV for survey spectra (with 500 meV step), and 50 eV for high resolution regions: N2p, O1s and Si2p (with 50–100 meV step). The base pressure in the chamber was 5×10^{-9} mbar, and during the spectra collection, the pressure in the chamber was not higher than 3×10^{-8} mbar. The spectra were analyzed and processed with the CasaXPS 2.3.10 software. The background was approximated by the Shirley algorithm and the detailed spectra were fitted with the Voigt function.

Infrared spectra were collected by means of a TENSOR 27 spectrophotometer (Bruker, Ettlingen, Germany) in Attenuated Total Reflectance mode (ATR-FTIR). The spectra were acquired in the frequency range of 4000 to 600 cm⁻¹ at a resolution 4 cm⁻¹, recording 32 scans per measurement. The collected data were processed with OPUS 6.0 software. The resulting spectra were shown as a function of transmittance versus wavenumber.

Raman spectra were recorded with a MicroRaman Renishaw InVia™ supported with a WiRE 3.3 software (Gloucestershire, UK) and equipped with a Leica DMLM 2700M microscope (Leica Microsystems GmbH, Wetzlar, Germany). The wavelengths of the excitation lasers used were 532 or 633 nm and their power was about 1.4 mW. The intensity of the power of the laser was modulated for optimal sensitivity. One spectrum in the range of 4000 to 100 cm^{-1} , with a resolution of 1 cm^{-1} , was recorded per measurement. These spectra also were processed using OPUS 6.0 software.

The porous structure parameters were evaluated by standard low temperature nitrogen sorption experiments performed with an ASAP 2405 analyzer (Accelerated Surface Area and Porosimetry system, Micromeritics Inc., Norcross, GA, USA). Before the analyses, the samples were outgassed at 70 °C for 1 h. The N_2 adsorption–desorption isotherms were measured at −196 °C. The specific surface area (S_{BET}) was calculated using the standard BET method assuming N_2 molecular cross-sectional area 0.162 nm. The adsorption total pore volume (V_{tot}) was evaluated as single point at $P/P_0 = 0.99$. Micropore volume was obtained with t-Plot method and mesopore volume BJH method (as adsorption cumulative volume of pores between 1.70 nm and 300.00 nm diameter). Pore size distributions were calculated based on the adsorption branches of the isotherms with the SAIEUS software (Micromeritics), free version, www.nldft.com (accessed on 25 March 2019) choosing implemented the 2D-NLDFT for the heterogeneous pore model.

To evaluate the Pb^{2+} sorption capacity of the studied materials, an inductively coupled plasma–mass spectrometry (ICP-MS) model 7700 from Agilent technologies (Santa Clara, CA, USA) was used. The analytical parameters were as follows: peak pattern: 6; replicate: 5; sweeps per replicates: 100. The instrument settings included an RF power of 1500 W; a cool gas (Ar) flow of 16 L/min; auxiliary gas (Ar) flow of 0.9 L/min; nebulizer gas (Ar) flow of 1 L/min; a collision glass (He) flow of 4 L/min. To reduce polyatomic interferences, Kinetic Energy Discrimination with He was applied. Liquid samples were measured in falcon tubes. Standards and sample solutions were adjusted to 2% nitric acid of trace metal quality. The acid was adjusted using dilutions of 67–70% nitric acid (Trace Metal™ Fisher Chemical™) purchased from Thermo Fisher Scientific (Cheshire, UK) were introduced at 0.4 mL/min with a peristaltic pump.

The sorption capacity of lead ions (Pb^{2+}) was examined in batch mode. The samples (200 mg) were immersed in 45 mL of a Pb^{2+} solution at an initial concentration of 300 $\mu\text{g/L}$, stabilized with 2% nitric acid (HNO_3). The mixtures were shaken for 48 h at room temperature to ensure the equilibrium state was reached. The concentrations of lead in the solution were quantified by ICP-MS, employing a calibration curve spanning a range of 5 to 250 $\mu\text{g/L}$, also adjusted to 2% nitric acid. The limit of detection in the ICP-MS was 0.02 $\mu\text{g Pb}^{2+}/\text{L}$. Each concentration measurement was compared with a reference system consisting of water sample (ultrapure, tap and river water) adjusted to 2% nitric acid without added lead ions, serving to account for background signals and matrix effects. The measurement of every sample was carried out in triplicate. Experiments were conducted using three aqueous matrices: ultrapure water, tap water, and river water. River water was collected from the River Thames, near Kingston University. Geographical coordinates of the sampling point were 51.40594; −0.30841. Before use, the river water was filtered through 0.45 μm syringe filters from Thermo Fisher Scientific (UK).

3. Results and Discussion

3.1. Thermal Analysis

In the first stage of our studies, we applied thermogravimetric analysis to choose the most appropriate temperature of the carbonization process. For this purpose, the TGA test was carried out under an inert gas atmosphere. The obtained results are presented

in Figure 2, which evidences that the decomposition process is quite complex and goes through several stages [25,45–47]. Among them, drying (~ 100 °C), torrefaction (200–300 °C), and low-temperature (300–400 °C) and high-temperature (above 400 °C) carbonization can be distinguished [25]. During these processes, lignocellulosic matter undergoes gradual changes. The main temperature ranges attributed to degradation of hemicellulose, cellulose and lignin are 150–350 °C, 220–400 °C and 150–600 °C, respectively [48]. In the case of the studied pristine pistachio nutshells (PNs), at least three well-defined stages can be distinguished, with maxima at approximately 290, 350 and 530 °C (Figure 2), corresponding quite well to the above-mentioned ranges. The right carbonization process occurs in the temperature range from 440 to 560 °C. For this reason, temperatures of 500 and 550 °C were selected to represent the middle and final stages of the process (indicated in Figure 2).

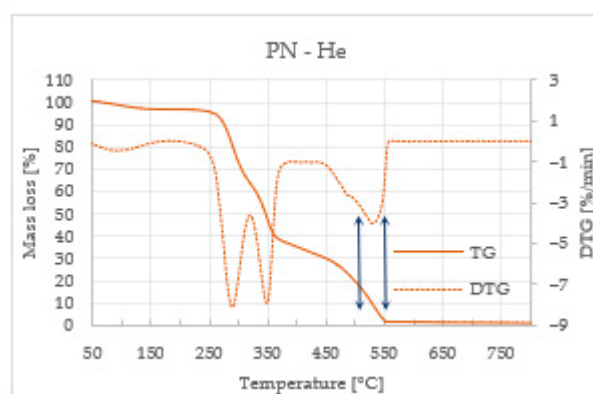


Figure 2. TGA of pistachio nutshells performed under helium atmosphere.

The further thermal characterization of the prepared materials involved determining and comparing their thermal stability in natural conditions, i.e., under the synthetic air atmosphere. TG and DTG curves are presented in Figures 3a and 3b, respectively.

The TG curves in Figure 3a clearly demonstrate differences in the thermal behavior of the analyzed materials, and consequently, the differences in their structural properties. Thermal stability under air atmosphere is predominantly lower than under inert helium atmosphere. This phenomenon can be observed for PN, whose decomposition in air occurs at the temperature range lower by 50 °C than in He. Quite a similar trend in the initial stage is shown by pistachio nutshells modified with phosphoric acid (PN- H_3PO_4 and PN- $\text{H}_3\text{PO}_4\text{-R}$ in Figure 3). However, above 270 °C some differences can be observed. Instead of the two well separated decomposition steps visible for PN at 278 and 340 °C, the modified samples—PN- H_3PO_4 and PN- $\text{H}_3\text{PO}_4\text{-R}$ —exhibit only one step, represented by a broad, not fully resolved peak at 304 °C (Figure 3b). According to the literature, the role of phosphoric acid in the activation of lignocellulosic precursors involves chemical processes such as hydrolysis, dehydration, aromatization and crosslinking, making the overall mechanism very complex [31,34,49,50]. All of them, regardless of their extent, affect the chemical structure of the modified material. As a consequence, the changes in thermal behavior appear not only in the lower temperature range (200–375 °C) but become particularly pronounced above 400 °C. In this region, the decomposition of PN- H_3PO_4 is almost twice as slow as that of PN. It is also worth paying attention to the fact that the thermal behavior of PN- H_3PO_4 and PN- $\text{H}_3\text{PO}_4\text{-R}$, although very similar (Figure 3b), is not identical. In the temperature range of 270 to 290 °C, both the acid-modified precursors have shoulders on the DTG curve indicating the partial removal of hemicellulose. In the case of PN- $\text{H}_3\text{PO}_4\text{-R}$, from which excess acid was washed out, this shoulder is even smaller, suggesting that a greater amount of hemicellulose was removed during the washing process. Such a structural change caused

the decomposition of PN-H₃PO₄-R occurred 0.5–0.9%/min faster. This observation confirms the stabilizing role of phosphoric acid and its flame-retardant effect [50].

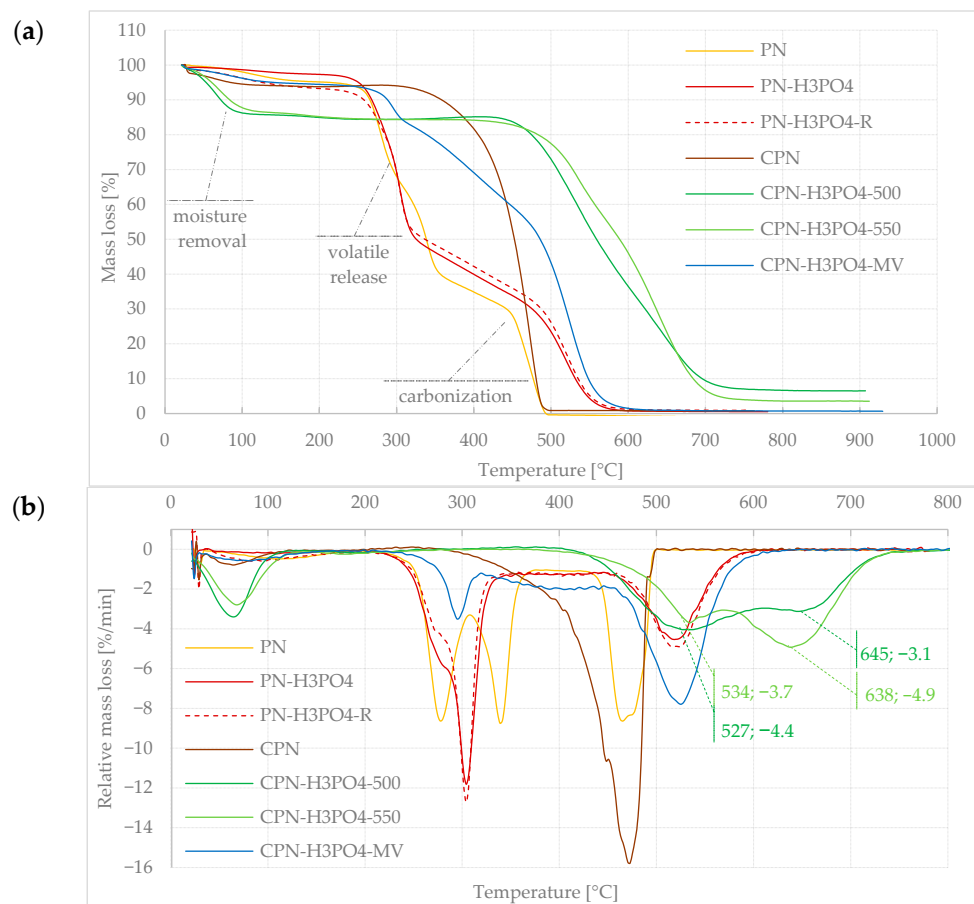


Figure 3. TG (a) and DTG (b) plots of the studied materials conducted under air atmosphere. The values in the peak labels are temperature of the maximum decomposition rate and the rate of decomposition, respectively.

The selection of the precursors—PN, PN-H₃PO₄ and PN-H₃PO₄-R—allowed us to assess the acid's activation effect on the properties of the resulting carbons; furthermore, it also allowed to compare the efficiencies of high- and low-temperature activation. The carbonized pistachio nutshells (CPNs) decomposed rapidly over a broad temperature range (285–500 °C), while CPN-H₃PO₄-500 and CPN-H₃PO₄-550 remained stable up to 400 °C, as shown in Figure 3. Although both the acid-activated carbons underwent thermal degradation in the range of 400–750 °C, and in both cases two stages can be distinguished, these processes proceed in completely different ways (light and dark green plots in Figure 3). The first stage of CPN-H₃PO₄-500 decomposition takes place at a lower temperature (527 °C) (see Figure 3b) and at a higher rate (−4.4%/min) compared with CPN-H₃PO₄-550 (534 °C and −3.7%/min). In the second stage, the situation is completely opposite. There are two possible causes of the observed dissimilarity. The first one is the carbonization temperature. Since CPN-H₃PO₄-550 carbon was prepared at 550 °C, the charring process was more advanced, contributing to the increase in thermal stability. Another reason may be the structural and/or chemical nature of these two materials, which will be discussed in subsequent paragraphs of this article.

The TG curve of the microwave-treated sample (CPN-H₃PO₄-MV) is located between the plots of the precursors (PN-H₃PO₄, PN-H₃PO₄-R—red lines in Figure 3a) and carbons (CPN-H₃PO₄-500, PN-H₃PO₄-550—green lines in Figure 3a). In turn, its DTG curve shows

some analogies to the DTG of $\text{PN-H}_3\text{PO}_4$. The thermal behavior of $\text{CPN-H}_3\text{PO}_4\text{-MV}$ clearly indicates the poor carbonization and limited charring of the precursor. For this reason, the process has not been referred to as carbonization, but rather as microwave treatment or microwave processing.

3.2. Morphology

Figure 4 presents images of the pristine and modified pistachio nutshells obtained using both the optical and the scanning electron microscopes.

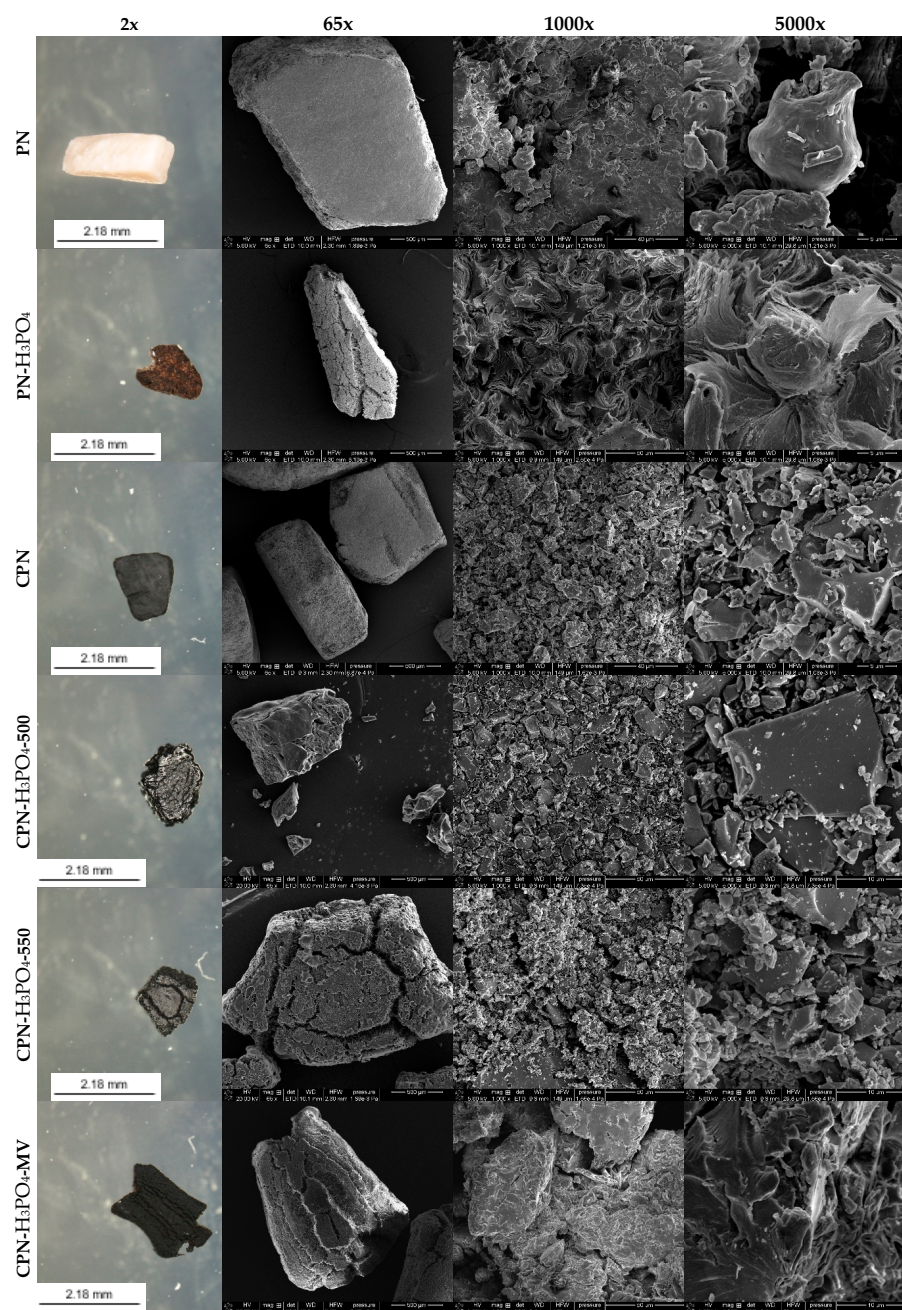


Figure 4. Images of representative samples of the studied materials taken using optical microscopy technique (2× magnification) and SEM (65, 1000 and 5000 fold magnification). WD was 99 ± 2 mm, and HFW was 2.3 mm, 149 and 29.8 μm for respective SEM magnifications.

Both optical and SEM micrographs, clearly how the performed modifications affected the nutshells.

Pistachio nutshells, as a protective tissue of plants, are composed of dead sclerenchyma cells with a fibrous or irregular geometries. Recently, their shape has been described as polylobate. In sclerenchyma secondary cell walls matrix, cellulose forms micro- and macrofibrils accompanied by hemicelluloses. Interface between cells is filled with an aromatic polymer—lignin. Xiao et al. described mature pistachio shell tissue as dense, composed of lamellar layers and spaces resembling ball-joint structures where the cell walls have fractured [13]. The view consistent with this description is visible in the SEM image of PN in Figure 4, which represents the pristine material used in our research.

Upon treatment with phosphoric acid, the shells turned brown (see Figure 4 magnification $2\times$, H_3PO_4) and numerous cracks appeared on their surface. Their presence is the result of a complex mechanism of the activation process. The acid penetrating into the interfibrillar spaces of the organic matter of the shell (e.g., cellulose and hemicellulose) causes the breaking of hydrogen bonds, hydrolysis and depolymerization as well as at higher temperature the formation of phosphate esters. Moreover, highly hygroscopic H_3PO_4 catalyzes dehydration reactions leading to the formation of unsaturated derivatives [28,34]. All these reactions drastically change the morphology of the material which can be easily observed when comparing images of PN and PN- H_3PO_4 at high magnification in Figure 4. In contrast, under optical microscopy, the surface of CPN appears smooth and free of cracks (Figure 4 left). For that sample, numerous folds and cavities can be distinguished with higher magnification. Under carbonization conditions, precursors usually shrink. For this reason, both the lamellae length and cavity diameters were smaller in CPN compared to pristine PN (CPN at magnification of $5000\times$).

The carbons prepared from shells activated with phosphoric acid (CPN- H_3PO_4 -500 and CPN- H_3PO_4 -550) are characterized by a cracked but shiny surface. However, the carbon synthesized at $550\text{ }^\circ\text{C}$ is more fractured than that prepared at $500\text{ }^\circ\text{C}$. In both cases, the primary structural features derived from the plant tissues are almost entirely undetectable. Instead, cavities and slit-shaped voids are present.

The morphology of CPN- H_3PO_4 -MV closely resembles that of PN- H_3PO_4 , and the preserved precursor-like structure supports the conclusion that carbonization efficiency was low. The numerous splits on the surface of CPN- H_3PO_4 -MV are significantly longer and wider than those seen in carbons obtained by conventional high-temperature carbonization, indicating that the course of microwave processing is more intense and disruptive.

3.3. Surface Chemistry

3.3.1. SEM-EDS and XPS

Elemental analyses of the studied materials were performed by means of SEM-EDS and XPS techniques. In the case of SEM-EDS, the samples were examined as received, without any additional preparation procedures. For this reason, the obtained results reflect the composition of their outer surface (up to $1\text{ }\mu\text{m}$ depth of the analyzed layer). Prior to XPS analysis, the samples were ground into a fine powder using an agate mortar and pestle; thus, these data can be considered representative of the bulk materials (ca. $3\text{--}5\text{ nm}$ depth of the analyzed layer). The results are summarized in Table 1.

Table 1. Comparison of SEM-EDS and XPS analysis data.

Material		SEM-EDS			XPS	
		Range of wt%	Mean ¹ wt% $\pm \sigma$	O:P	%At Conc. $\pm$ % σ	C:O O:P
PN	C	63.2–74.1	69.1 ± 1.2		69.4 ± 1.2	2.36
	O	28.6–36.8	31.6 ± 1.2		29.4 ± 1.1	

Table 1. *Cont.*

Material		SEM-EDS			XPS		
		Range of wt%	Mean ¹ wt% $\pm \sigma$	O:P	%At Conc. $\pm$ % σ	C:O	O:P
PN-H ₃ PO ₄	C	62.8–66.6	64.7 $\pm$ 0.9		67.6 $\pm$ 1.5		
	O	33.4–37.2	35.3 $\pm$ 0.9		31.7 $\pm$ 1.5	2.13	
	P	nd	nd		nd		
CPN	C	81.5–89.1	85.9 $\pm$ 0.5		90.6 $\pm$ 1.3		
	O	10.9–18.5	14.1 $\pm$ 0.5		9.4 $\pm$ 1.3	9.69	
CPN-H ₃ PO ₄ -500	C	76.3–86.4	81.4 $\pm$ 0.9		86.4 $\pm$ 1.7		
	O	8.9–15.1	13.2 $\pm$ 1.1	2.45	10.9 $\pm$ 1.4	7.95	4.00
	P	3.5–7.7	5.4 $\pm$ 0.7		2.7 $\pm$ 1.2		
CPN-H ₃ PO ₄ -550	C	67.3–73.6	69.1 $\pm$ 0.3		76.9 $\pm$ 1.8		
	O	17.8–20.7	20.7 $\pm$ 0.2	2.01	16.5 $\pm$ 1.1	4.67	3.00
	P	7.9–14.7	10.3 $\pm$ 0.3		5.5 $\pm$ 1.3		
CPN-H ₃ PO ₄ -MV	C	68.8–78.8	75.8 $\pm$ 1.5		76.3 $\pm$ 1.2		
	O	21.2–31.2	24.1 $\pm$ 1.4		23.7 $\pm$ 1.2	3.22	
	P	nd	nd		nd		

¹ mean from 3–10 measurements carried out on 1–4 pieces of sample. nd—not detected (estimated below 1%).

The comparison of the results presented in Table 1 shows that the highest convergence of the SEM-EDS and XPS results was obtained only for the PN and CPN-H₃PO₄-MV. For other samples, the XPS results differ from the corresponding SEM values by 2.5–7.8%. The lower carbon content and higher oxygen content in SEM-EDS compared to XPS suggests that the outer surfaces of the samples are more oxidized than their interiors. The greatest differences concern the amount of phosphorus [51]. Its twice-higher concentration on the surface compared to the bulk is a consequence of surface impregnation and hindered diffusion of the acid through the lamellar structure of the sclerenchyma. Interestingly, in PN-H₃PO₄ and CPN-H₃PO₄-MV, no phosphorus was detected by either XPS or SEM-EDS. Although impregnation with concentrated phosphoric acid undoubtedly modified the precursor, the process carried out at room temperature did not cause permanent binding of phosphates to the surface of the activated materials; therefore, these moieties remained at low concentration. For this reason, such phosphates groups can be relatively easily removed by extensive rinsing. In contrast, applying elevated temperature 150–400 °C promotes the formation of cross-links via phosphate bridges and leads to the permanent incorporation of phosphorus into the precursor matter [34,49,52].

The percentages of the various elements also served as the basis for calculating the C:O and O:P ratios gathered in the last two columns of Table 1. Two of the lowest C:O ratios were noted for uncarbonized materials PN and PN-H₃PO₄; however, the value for the latter is even lower. This proves impact of the acid on the precursor structure during the modification step. The absence of phosphorus in PN-H₃PO₄ and the increase in oxygen content after acid modification may be related, for example, to the process of hydrolysis/depolymerization of polysaccharides included in sclerenchyma. The carbonized materials are richer in carbon; therefore, their C:O ratios are in the range of 4.7–9.7. The C:O value of CPN-H₃PO₄-MV once again reflects the intermediate properties of this material.

The ratio of P:O for CPN-H₃PO₄-500 in the bulk of the material is 4, just like for the phosphate ion, but on the surface, it is only 2.45, indicating the existence of more condensed or reduced species. A similar trend can be noticed for CPN-H₃PO₄-550, although both the P:O values are lower than those for CPN-H₃PO₄-500. This observation is consistent

with reports in the literature [51,53,54], where the formation of pyrophosphates and other phosphorus-containing derivatives has been proposed [53].

The further analysis of the XPS results was based on data processed using the peak-fitting method. The C 1s envelopes of the analyzed samples were fitted with five or six component peaks, depending on the type of material. In the cases of the precursors (PN and PN-H₃PO₄), fitting was performed to keep the binding energy (BE) of C-C and C-H at 285.0 eV and the next carbon–oxygen functional groups were shifted in relation to the first one by +1.6 (C-OH, C-O-C), +3.0 (C=O), +4.2 (O-C=O) eV, according to the literature recommendations [55–57]. For the carbonized materials, the C=C component was positioned at 284.5 eV and the five following peaks were fixed at +0.3 (C-C, C-H), +1.8 (C-OH, C-O-C), +3.1 (C=O), +4.5 (O-C=O), +6.3 eV (π - π) [51,58–60]. Functionalities such as C-O-PO₂R and C-O-PO₃R can be overlapped with peaks at 286.6 and 287.2 eV, respectively [61].

In O 1s envelope assignment of oxygen–carbon functional groups was fitted to five ranges: 531.3–531.6 (O=C/O=C-O-R/O=P in (PO₄)^{3−} and (P₂O₇)^{4−}), 532.7–533.1 (C-OH/(PO₃)[−]), 533.4–533.6 (C-O-C), 533.6–533.9 (C-O/O=C-O-R) and 534.8–535.1 eV (H₂O/O₂). For the acid-modified carbons additional contributions from C-O-P (533.2 eV) and P-O-P (533.5 eV) species were included in the C-O/O=C-O-R region [60,62–65].

The P 2p spectra were fitted using a single peak with BE ranging from 133.9 to 134.1 eV [53,54,66,67]. Table 2 summarizes the assignments of the individual functional groups and the ranges of their B.E.

Table 2. The assignment of XPS deconvoluted peaks.

Component	This Studies B.E./eV	Lit. B.E./eV	Surface Functional Group Assignment	Description	Ref.
C 1s	284.5 ± 0.2	284.3–284.5	C=C	Sp ² bonded carbons	[51,58–60]
	285.0 ± 0.2	284.8–285.5	C-C/C-H	sp ³ bonded carbons	[51,55–60]
	286.6 ± 0.3	286.0–287.0	C-OH/C-O-C/C-O- PO ₂ -R	Alcohol and ether species, organic phosphates	[51,55–61]
	287.2 ± 0.0	~287.2	C-O-PO ₃ H ₂ /C-O- PO ₃ -R	Organic phosphates and phosphites	[61]
	288.0 ± 0.4	287.5–288.5	C=O	Carbonyl species	[51,55–60]
				Carboxyls, esters, lactones and other moieties where carbon is bonded to two or more the same or different heteroatoms	
	289.2 ± 0.2	289.0–290.0	O-C=O	Aromatic shake-up for primary C-C peak.	[51,55–60]
O 1s	290.8 ± 0.3	291–293	Pi-Pi *		[51,58–60]
	531.4 ± 0.2	531.2–531.6	O=C/O=C-O- R/O=P	Carbonyls (also in carboxyls, lactones) O=P in (PO ₄) ^{3−} and (P ₂ O ₇) ^{4−}	[60,62–65]
	532.8 ± 0.3	532.5–532.9	C-OH/(PO ₃) [−]	Hydroxyl groups, (PO ₃) [−]	[62]
	533.2 ± 0.0	~533.2	C-O-P	C-O-P bonds	[60,62–65]
	533.5 ± 0.1	533.0–533.4	C-O-C/P-O-P	Ether groups, P-O-P bonds	[60,62–65]
	533.8 ± 0.2	534.0–534.8	C-O/O=C-O-R	Ester groups (non-carbonyl oxygen)	[60,62–65]
P 2p	535.0 ± 0.2	534.8–535.2	(O ₂ /H ₂ O) _{ads}	Chemisorbed oxygen/water	[60,62–65]
	-	~133	P-C	C-P bonds	[53,67]
	134.0 ± 0.2	133.9–134.2	P-O-C	C-O-P bonds	[53,54,66–70]
	-	~136	P ₂ O ₅	phosphorus pentoxide	[71]

Figure 5a–d present the details regarding C 1s, O 1s and P 2p moieties.

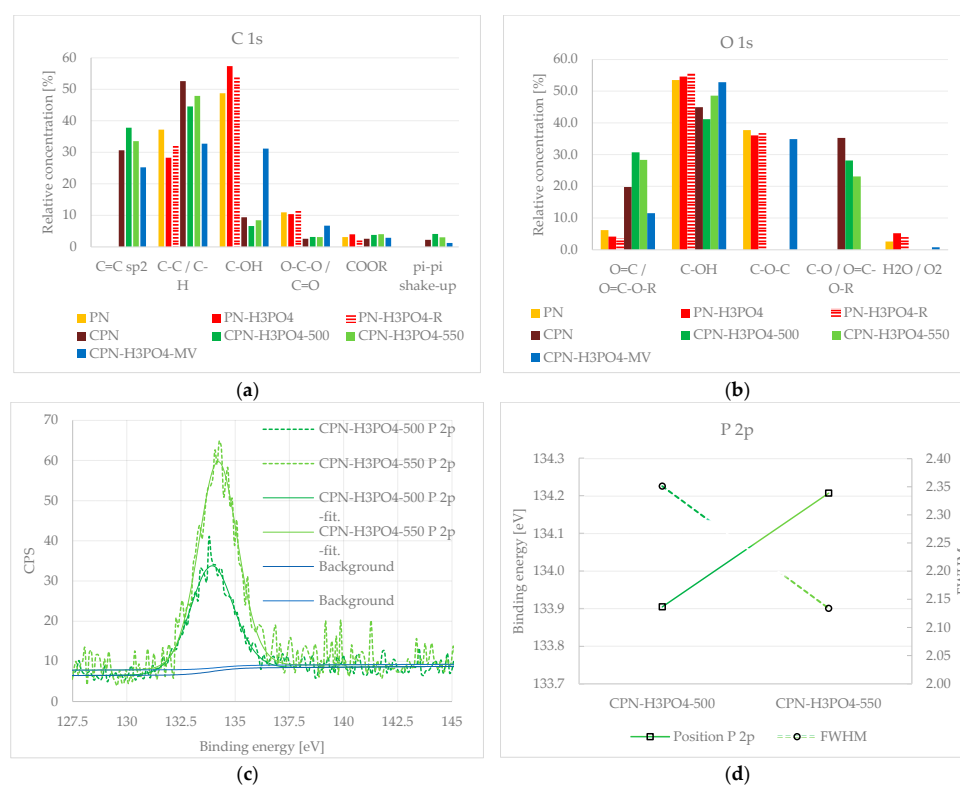


Figure 5. XPS details. Content of carbon species (a). Content of oxygen species (b). Core-level spectra P 2p with fitting (c). Change of P 2p peak position and FWHM for carbons prepared at 500 and 550 °C (d).

• C 1s

The respective bars in Figure 5a reflect the polysaccharide nature of PN and PN-H₃PO₄. The main components of their C 1s envelope are C-OH and C-C/C-H species, accompanied to a lesser extent by O-C-O groups. It is worth noting that the relative concentration of C-OH for PN-H₃PO₄ is somewhat higher compared to PN, which is consistent with the previously proposed hypothesis that hydrolysis takes place during acid modification. Neither C=C nor π - π shake-up are detected, confirming the predominantly aliphatic character of these materials and the very low concentration of lignin [13].

Under carbonization conditions, most of the C-OH groups were lost, replaced by unsaturated bonds, while the number of C-C/C-H contributions increased. Particularly noteworthy is the fact that the proportion of C=C in CPN-H₃PO₄ carbons is higher than in CPN. Moreover, the relative concentration of C=C is greater for CPN-H₃PO₄-500 than for CPN-H₃PO₄-550. Although the former material was carbonized at slightly lower temperature (500 °C), the process occurred in the presence of H₃PO₄; in contrast, the latter was heat-treated at a higher temperature (550 °C), after rinsing out the acid. This finding is in line with the claim that phosphoric acid favors the aromatization process [34,53]. A significant predominance of aliphatic bonds over aromatic ones is a consequence of rather low carbonization temperature, at which the cyclization and aromatization processes just begin [45,47]. Thus, it would be expected that the studied carbons have rather a disordered structure.

CPN-H₃PO₄-MV only lost about half of its C-OH moieties compared to its precursor (PN-H₃PO₄-R), but the level of C-C/C-H remained nearly unchanged. On the other hand, the relative concentration of C=C is almost as high (25.2%) as that of the other carbons (30.7–37.8%). A somewhat different relationship is observed in case of π - π shake-up peaks, as 1.3% for CPN-H₃PO₄-MV is much lower than 2.2–4.1% for the carbons. The presence

of this peaks is caused mainly by " $\pi \rightarrow \pi^*$ type transitions in which electrons in highest occupied molecular orbitals are promoted to lowest unoccupied molecular orbitals" [58]. Materials with a higher content of aromatic rings in their structure exhibit more intense shake-up signals [58]. Paynter also reported that the intensity of these peaks varied with the change in the aromatic ring content [72].

The significantly lower signal of the shake-up peak of CPN-H₃PO₄-MV implies the comparatively low contents of aromatic species in this material. Therefore, the observed relatively high intensity of the C=C component arises primarily from the unsaturated bonds (and, to a much lesser extent, from the aromatic rings). This suggests that the microwave treatment may cause the dehydrogenation, deoxygenation, and dehydration of the precursor via an elimination reaction or cracking processes, leading to the formation of unsaturated bonds [22,73,74]. The possibility of such processes is further supported by the significant reduction in oxygen content in CPN-H₃PO₄-MV compared with PN or PN-H₃PO₄ (Table 1).

- *O 1s*

In the O 1s envelopes of PN and PN-H₃PO₄, similarly to the C 1s, the highest relative concentrations are observed for C-OH and C-O-C groups, which is consistent with their polysaccharide chemical nature [55]. Acid treatment caused in PN-H₃PO₄ an increase in C-OH with a simultaneous decrease in C-O-C and O=C/O=C-O-R, which confirms the partial occurrence of the hydrolysis process of glycosidic bonds. In the carbonized materials C-O-C groups are no longer present, and relative concentration of C-OH is reduced. In their place, more oxidized moieties (C-O/O=C-O-R and O=C/O=C-O-R) were created. It should be kept in mind that these signals are assigned not only to oxygen-carbon connections but also to oxygen-phosphorus ones. Therefore, for CPN-H₃PO₄-500 and CPN-H₃PO₄-550, the presence of phosphates (PO₄^{3−}, P₂O₇^{4−} and PO₃[−]) was comprised in this fitting [51,67,75]. The microwave processed sample (CPN-H₃PO₄-MV) has the relative concentrations of C-OH and C-O-C species on the same level as the acid-modified precursors, but the contents of the carbonyl groups take an intermediate value between the precursor and the carbons. Similar carbons enriched in the -OH and -COOH groups have also been reported under microwave-assisted hydrothermal conditions [74].

- *P 2p*

The P 2p envelope fitting showed only one relatively narrow peak for both carbons CPN-H₃PO₄-500 and CPN-H₃PO₄-550 (Figure 5c). The binding energy of these peaks increased a little with the rise of carbonization temperature, while their width became narrowed (Figure 5d). The observed relationship suggests only slight structural changes.

According to the literature, the B.E range from 133.9 to 134.2 eV, characteristic of phosphorus species, can be assigned to phosphites (PO₃)^{2−} [68], phosphates (H₂PO₄)[−] [67], metaphosphates (PO₃)[−] [69] or pyrophosphates (P₂O₇)^{4−} [70], depending on the chemical environment of the moiety. Organic derivatives such as esters also should be designated to this region, as the B.E. of P-O-C is ~134 and that of P-C is ~133 eV [53,76]. Moreover, Textor et al. demonstrated that even the number of hydrogen atoms attached to the phosphate group can strongly influence the peak position: the greater the number of hydrogens in the phosphate molecule, the higher its binding energy [69].

Table 3 presents the possible reactions of phosphoric acid occurring in the temperature range of the carbonization process, as known from the literature. The gradual loss of water leads to the formation of polyphosphates, whose B.E.s strongly depend on the length of the phosphate chains and increase with the chain elongation: 132.5 (PO₄)^{3−}, 133.3 (P₂O₇)^{4−}, 134.3 (PO₃)[−], 135 P₄O₆ and 135.5 eV for P₄O₁₀ [68–71,76–78].

Table 3. The impact of temperature on H_3PO_4 transformations [31,34,49].

Reaction Equation	Range of Temperatures	Processes
$n\text{H}_3\text{PO}_4 \rightarrow \text{H}_{n+2}\text{P}_n\text{O}_{3n+1} + (n-1)\text{H}_2\text{O}$	100–400 °C	Dehydration, gradual polyphosphate formation data
$\text{H}_{n+2}\text{P}_n\text{O}_{3n+1} \rightarrow \text{P}_4\text{O}_{10} + \text{H}_2\text{O}$	400–700 °C	Dehydration, oxide formation
$\text{P}_4\text{O}_{10} + 2\text{C} \rightarrow \text{P}_4\text{O}_6 + 2\text{CO}_2$		Oxide reduction

The P 2p signals recorded for CPN- H_3PO_4 -500 and CPN- H_3PO_4 -550 are not very broad (Figure 5c,d), which may indicate a high degree of chemical similarity among the functional groups corresponding to these signals. The value of B.E. registered for CPN- H_3PO_4 -500 is 133.9 eV, what can suggest coexistence of $(\text{P}_2\text{O}_7)^{4-}$ and $(\text{PO}_3)^-$ or other intermediate species with comparable structures. The B.E. of CPN- H_3PO_4 -550 is the same as that of $(\text{PO}_3)^-$, which leads to the conclusion that pyrophosphates lost water and were converted into metaphosphates. Nevertheless, the existence of other functionalities with P-C bonds or P_4O_{10} cannot be excluded. Their relative content is not significant enough to cause a visible deformation of the P 2p envelope peak around 133 and 135.5 eV, respectively.

3.3.2. ATR-FTIR Spectroscopy

A complement to the surface chemistry analysis performed with XPS was carried out with ATR-FTIR. The spectrograms of the studied materials, divided into precursors and carbons, are presented in Figures 6a and 6b, respectively. The plot of the material prepared by microwave treatment was placed together with the precursors in panel (a), because of its greater similarity to them than to the carbons.

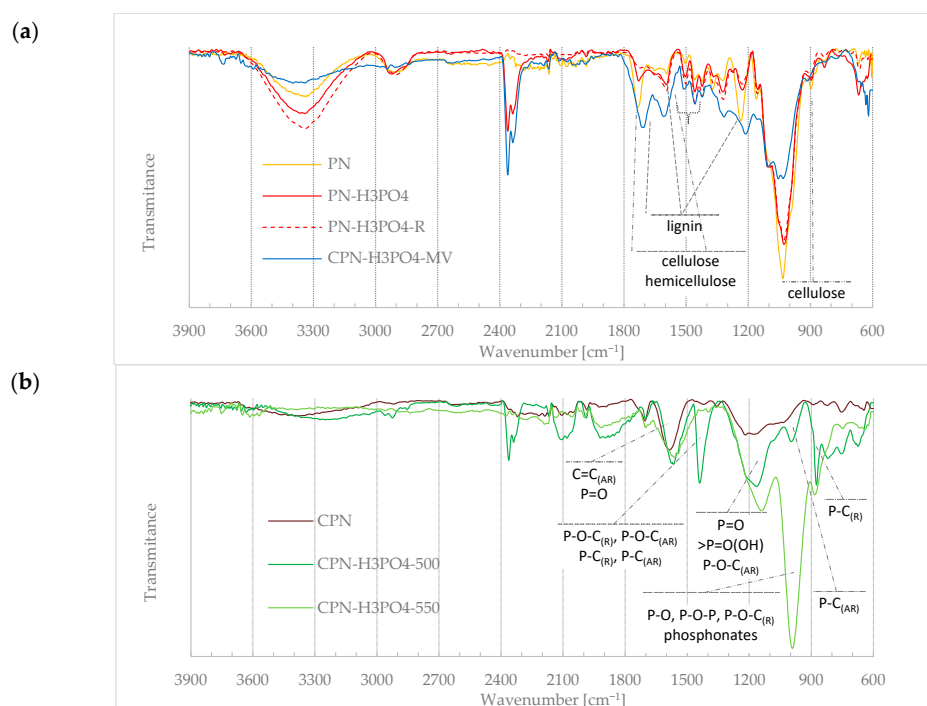


Figure 6. ATR-FTIR spectra of the studied materials. The precursors and CPN- H_3PO_4 -MV(a), and the carbons (b).

The main components of pistachio nutshells are cellulose, hemicellulose and lignin. Cellulose is a linear biopolymer composed of D-glucose units linked by $\beta(1 \rightarrow 4)$ glycosidic bonds. Therefore, in its spectra, characteristic bands of the following groups are present: -OH (stretching (str.) ~ 3350 , deformation or bending (def.) ~ 1618 ~ 1430 , ~ 1402 , ~ 1340 and

1110 cm^{-1}); C-O and C-O-C (str. $\sim 1060 \text{ cm}^{-1}$); C=O (str. $\sim 1738 \text{ cm}^{-1}$); -CH (def $\sim 1375 \text{ cm}^{-1}$); -CH₂- (def. ~ 1458 and $\sim 830 \text{ cm}^{-1}$). Pyranose ring vibrations can be observed at ~ 1170 and ~ 1082 (C-O-C skeletal ring str.), ~ 915 (asym. ring vibr.), ~ 870 (sym. ring breathing), ~ 845 and ~ 890 (def. of anomeric C-H), ~ 867 (def. of equatorial C-H), and $\sim 960 \text{ cm}^{-1}$ (def. of terminal methyl) [18,79,80]. Glycosidic bond vibration can be found at $\sim 896 \text{ cm}^{-1}$ [12]. Hemicellulose differs from cellulose in that its chains are branched due to the presence of not only $\beta(1 \rightarrow 4)$ but also $\beta(1 \rightarrow 3)$ glycosidic bonds. For this reason, its spectrum is very similar to that of cellulose, revealing only some differences in the intensities of OH and C=O bands as well as the appearance of 875 cm^{-1} (sym. ring str.) instead of 896 cm^{-1} [80,81]. As a consequence, distinguishing between these two substances in a sample of natural origin is difficult and prone to uncertainty. The situation is different in the case of lignin, which has numerous aromatic rings substituted with hydroxyl and methoxyl groups in its structure. Characteristic bands of these species are situated as follows: at ~ 1632 , ~ 1613 , ~ 1594 , ~ 1450 and $700\text{--}900 \text{ cm}^{-1}$ for aromatic rings; at ~ 1220 and $\sim 1360 \text{ cm}^{-1}$ for phenolic C-O and O-H; at ~ 1450 and ~ 1232 for methoxyl moieties and C-O-C str. of aryl-alkyl ether linkages, respectively [32,80,82].

In the spectrogram of PN, a broad stretching band of -OH groups forming intra- and inter-molecular hydrogen bonds is visible in the range of 3600 to 3150 cm^{-1} . It can be assigned to alcohols (cellulose, hemicellulose) and phenols (lignin) [18]. Between 2960 and 2850 cm^{-1} , a broad band arising from overlapping stretching vibrations of aliphatic C-H bonds is present. Three characteristic bands of cellulose and hemicellulose are located at 1732 (C=O), 1360 (C-H) and 896 cm^{-1} (β -pyranose). Lignin does not present intense bands at 1648 , 1594 , $1520\text{--}1450$ (aromatic system), 1327 and 1157 cm^{-1} (O-H def. and C-O str.), and 1237 cm^{-1} (O-CH₃). The low intensity of these bands is due to the low lignin content in pistachio nutshells, which was demonstrated by Xiao et al. [13]. In the range of 1130 to 950 cm^{-1} , a broad and very intense C-O str. band with a maximum at 1035 cm^{-1} clearly dominates the spectrum, confirming the predominance of cellulose and hemicellulose in the structure of the shells.

Phosphoric acid treatment changed the surface of the shells. The reduction in the main peak at 1035 cm^{-1} and that at 1237 cm^{-1} accompanied by an increase in the bands at 3330 and 1330 cm^{-1} suggests partial hydrolysis of ether (methoxyl) groups. The band of β -glycosidic bonds has also decreased, revealing the degradation of polysaccharide chains of cellulose and hemicellulose. It is also worth mentioning that the intensities of the $1650\text{--}1450$ and 635 cm^{-1} bands increased indicating the formation of C=C bonds. All these observations are consistent with the XPS analysis data discussed in Section 3.3.1, and with literature reports on the degradation of lignocellulosic biomass followed by the conversion of hemicellulose and cellulose into unsaturated derivatives, like furfurals or levoglucosenone, under the influence of phosphoric acid [28,30].

In the spectrum of CPN-H₃PO₄-MV, the further progress of the initiated changes can be observed, especially in terms of the formation of C=C and aromatic species. The decrease in C-O bands ($1130\text{--}950 \text{ cm}^{-1}$) and O-H band ($3600\text{--}3200 \text{ cm}^{-1}$) together with an increasing intensity of C=O (1703 cm^{-1}) indicate the oxidation of the structure [79].

In Figure 6b, spectrograms of the carbons prepared at 500 and $550 \text{ }^\circ\text{C}$ are depicted. ATR analyses of CPN revealed only a few bands. The most intense is the one at 1587 cm^{-1} , confirming the presence of an aromatic system. Its wide and asymmetric shape implies that it comes from the overlapped vibrations of various aromatic species with condensed rings. Other bands related to aromatic system are present at 912 , 817 and 731 cm^{-1} . At 1705 cm^{-1} , there is also a broad C=O band visible. In the region of strong C-O vibrations ($1300\text{--}1000 \text{ cm}^{-1}$), several peaks can be distinguished (1261 , 1170 , 1050), showing the presence of oxygen functional groups on the surface of the carbon. In this range, the vibrations

of C-C and C-H, having medium or weak intensities, can be observed as well. The not very intense band of OH moieties is hardly visible, indicating the loss of most hydroxyl groups during carbonization [32,79,83].

The spectrograms of the carbons prepared from acid-modified precursors are rather similar in the range from 3600 to 1500 cm^{-1} . In case of CPN- H_3PO_4 -500, the C-H (2950–2850 cm^{-1}) and O-H vibrations (3500–3100 and 2700–2550 cm^{-1}) are more pronounced than for the other carbons. The O-H band is a little shifted toward lower wavenumbers that is the characteristic feature of acidic (e.g., carboxylic) species. Due to the higher carbonization temperature, CPN- H_3PO_4 -550 almost completely lost its O-H and C-H moieties.

Below 1500 cm^{-1} , the spectra of the acid-modified carbons differ significantly, even within the regions associated with characteristic phosphate vibrations. Their locations in the spectra were depicted in Figure 6b.

The carbon CPN- H_3PO_4 -500 has the most intense bands at 1440, 1184, 864 cm^{-1} and weaker at 1080, 995, 842, 750, 675 cm^{-1} . Among them, those at 1184 (str. of P=O), 864 (asymmetric str. P-O-P), 1080 (asymmetric str. P-O in P-OH), 995 (asymmetric str. P-O-P) and 750 cm^{-1} (symmetric str P-O-P) correspond to pyrophosphates [77,79,84]. Vibrations of the ionized form of P^+-O^- , being active in the range of 1170 to 1310 cm^{-1} , may additionally enhance the P=O band. The others at 1440, 1060, 842 and 675 cm^{-1} can be assigned to asymmetric and symmetric stretching of P-O-C and/or P-C vibrations, in which the carbon can be either aliphatic or aromatic [71,85,86]. Additionally, the carbon species previously mentioned for CPN also contribute to the spectrum [32,71,79,87].

The carbon CPN- H_3PO_4 -550 has one dominating band at 991 cm^{-1} and two of medium intensity at 1115 and 883 cm^{-1} . Their presence is caused by stretching of P-O, P=O and P-O-P metaphosphates or polyphosphates, respectively [71,77,88]. These compounds may form a chain or cyclic form. FTIR analysis allows to distinguish them by the presence or absence of the 3300 cm^{-1} band originating from terminal O-H groups [89]. Its lack in the spectrum of CPN- H_3PO_4 -550 allows us to determine that the resulting metaphosphates have rather cyclic structures. Furthermore, the higher intensity of the P-O band proves a proportionally higher phosphate content compared to CPN- H_3PO_4 -500 [71]. On the other hand, the bands from P-O-C are drastically diminished, indicating that most of these bonds were decomposed. Thus, the carbonization temperature was sufficiently high to initiate the final dehydration stage, leading to the formation of the phosphorus oxides (Table 3).

3.3.3. Raman Spectroscopy

Additional insight into the surface chemistry of the studied materials can be obtained from the Raman spectra shown in Figure 7.

Table 4 compiles Raman bands positions for PN and PN- H_3PO_4 . Most of the bands detected are common to lignin and cellulose, although some are specific to only one of them.

Table 4. Assignment of bands in Raman spectra of lignocellulosic biomass [79,90–95].

Component	Band Position [cm^{-1}]		Assignment
	PN	PN- H_3PO_4	
Cellulose Hemicellulose	888	862	C–O–C ring breathing
	3201	3201	C–O–H stretching
	3448	3448	C–O–H stretching
Lignin	634	634	Skeletal modes
	757	746	Aromatic ring modes
	1643	1643	Ring conjugated C=C stretching; C=O stretching
	3044	3044	Aromatic ring modes

Table 4. Cont.

Component	Band Position [cm^{-1}]		Assignment
	PN	PN-H ₃ PO ₄	
Lignin and cellulose	350	-	C-C-C and C-O-C deformations of cellulose ring; aromatic ring deformation
	533	533	Glycosidic C-O-C deformations; lignin skeletal deformation
	1026	1026	C-O stretching; C-O-H bending; ring deformation; CH ₃ wagging
	1157	1157	C-O; C-C; C-H and glycosidic stretching and bending; C-O-C ring breathing
	1300	1318	C-H bending, C-O-H bending, CH ₂ OH related mode
	1456	1456	HCC and HCO bending, cellulose OH stretching
	2894	2894	Aryl-O of aryl OH and aryl O-CH ₃ CH ₂ deformation, lignin O-CH ₃ deformation, CH ₂ scissoring, C-H and CH ₂ stretching
	2894	2894	
Other	1788	1777	C=O stretching
	2057	2057	Acetal mode
	2435	2435	Acetal mode, phosphates
	2596	2596	OH chelated to carbonyl
	2708	-	C-H stretching in CHO

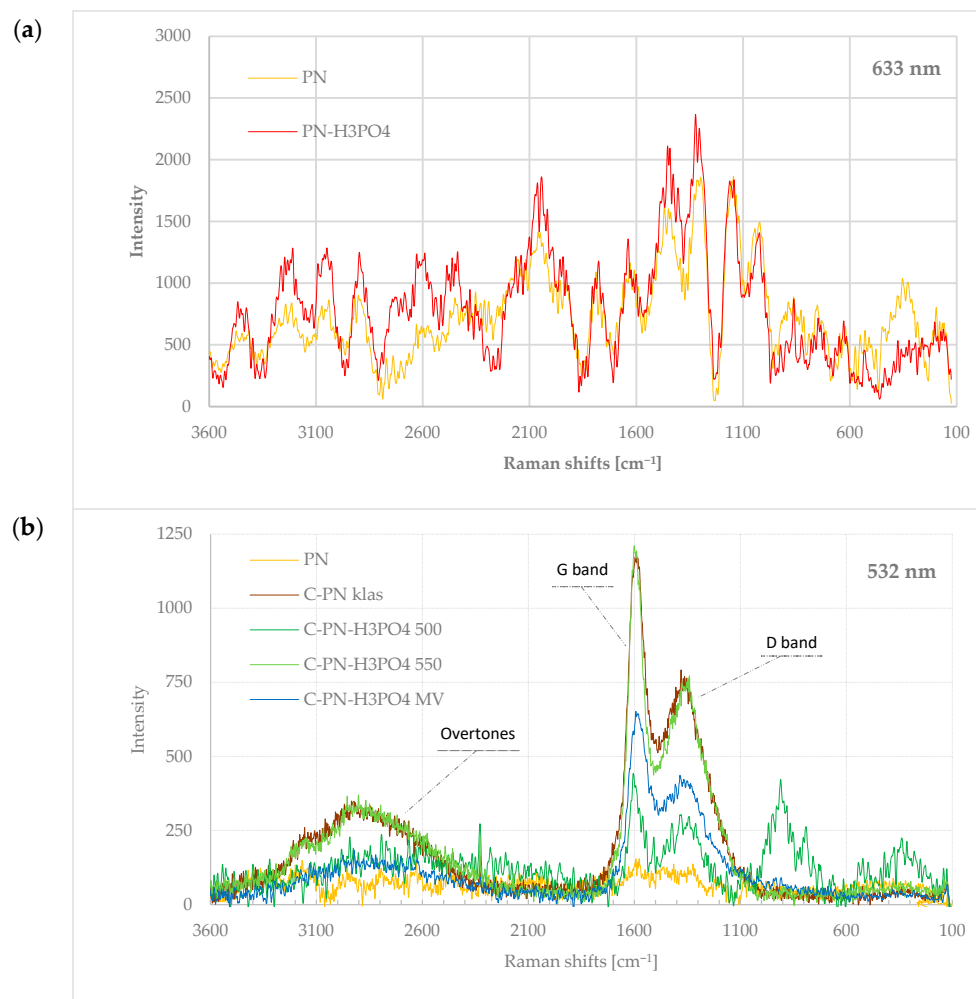


Figure 7. Raman spectra of precursors (a) and carbonized materials (b).

Although the single-scan Raman spectra (Figure 7a) have lower resolutions than the multiple-scan spectra with Fourier transform, they can still be informative; they reveal some structural changes occurring in pistachio shells under acid treatment. The C-O-C band at 350 cm^{-1} became undetectable, while the two bands at 533 and 888 cm^{-1} became narrower, indicating that the reaction with the acid involves both lignin and cellulose species. In the case of $\text{PN-H}_3\text{PO}_4$, two new bands were created at about 2600 and 2710 cm^{-1} due to the presence of aldehyde and its interaction with hydroxyl group.

After the thermal treatment (Figure 7b), the Raman spectra differ significantly. All the materials exhibit two characteristic carbons peaks (Table 5). They are called G and D bands and are situated at ~ 1590 and $\sim 1350\text{ cm}^{-1}$, respectively. The former is associated with the presence of carbon clusters built of regular aromatic rings often represented by polyaromatic hydrocarbons of various sizes; the position of the latter provides information about their dimensions. For large and more symmetric clusters, the D band is located near 1350 cm^{-1} ; as the symmetry and dimensions decrease, it approaches 1400 cm^{-1} . This band is caused by combined breathing and Kekule vibrations of PAHs. Smith et al. noted that the intensity and position of the valley minimum between the G and D bands are sensitive to the carbonization temperature. An increase in the temperature from 400 to $600\text{ }^\circ\text{C}$ lowers the minimum point, while further heating up to $700\text{ }^\circ\text{C}$ leads to a blue shift in its position. These changes were attributed to the loss of oxygen-containing functional groups. They also claimed that heteroatom-related defects can cause a more pronounced red shift [96,97].

Table 5. Positions of the Raman spectra bands.

Material	G Band [cm^{-1}]	D Band [cm^{-1}]	Valley [cm^{-1}]
CPN	1581	1353	1542
CPN- H_3PO_4 -500	1598	1341	1513
CPN- H_3PO_4 -550	1588	1339	1522
CPN- H_3PO_4 -MV	1587	1346	1487

The other bands visible in the spectrograms are located at $\sim 2900\text{ cm}^{-1}$, where a combination of D and G modes gives a second-order vibration band superimposed on the D band overtones at ~ 3100 , ~ 2700 , and $\sim 2400\text{ cm}^{-1}$ [98].

The spectra of CPN and CPN- H_3PO_4 -550 are very similar. Their G bands are narrow, pointing to the formation of carbon clusters. The D bands are wide, but its position for CPN- H_3PO_4 -550 is a little shifted in relation to the CPN one, suggesting larger sizes of clusters formed at higher temperatures. The reduced valley intensity and its red shift in CPN- H_3PO_4 -550 compared to CPN indicate heteroatom defects, as generated by the presence of phosphates.

For CPN- H_3PO_4 -MV, both the bands are broader and are half as intense as those for the two previously described samples, showing poorer carbonization efficiency.

Of all the carbons, CPN- H_3PO_4 -500 has the lowest G and D band intensities, but the location of D band is close to that of CPN- H_3PO_4 -550; moreover, the valley position has a similar value. This suggests that the formation of carbon cluster has been initiated. Moreover, in this spectrogram, in the range of 1100 to 100 cm^{-1} , several extra bands appear that are absent in the other samples. Their existence can be associated with phosphates species. The strongest of them ($\sim 906\text{ cm}^{-1}$) can be assigned to $(\text{P}_2\text{O}_7)^{4-}$. The others, situated at ~ 784 , ~ 522 , and $\sim 324\text{ cm}^{-1}$, may come from the P-O-C bonds, which would confirm the connection of the phosphates with organic matter [79]. Interestingly, such bands are not visible in the case of CPN- H_3PO_4 -550. A possible explanation for this phenomenon may be the temperature-induced transformation of the phosphate species, as described in Sections 3.3.1 and 3.3.2.

Characteristic bands of metaphosphates in Raman spectra are expected at ~ 1200 (strong) and $\sim 650\text{ cm}^{-1}$ (medium) [79]. The former can be entirely covered by a very strong and wide D band; meanwhile, the latter, being of lower intensity, may not be so easily identifiable. That is why they seem to be absent in the spectrogram for CPN- H_3PO_4 -550.

3.4. Textural Properties

In terms of sorption abilities, it is important to know the textural properties of the materials. The results of the nitrogen sorption experiments are summarized in Table 6.

Table 6. Porous structure parameters.

Material	S_{BET}^1 [m^2/g]	V_{Tot}^2 [cm^3/g]	V_{Mi}^3 [cm^3/g]	V_{Me}^4 [cm^3/g]	% Mi	% Me
PN	0.1	0.001	-	0.001	-	-
PN- H_3PO_4	0.2	0.001	-	0.001	-	-
PN- H_3PO_4 -R	0.1	-	-	-	-	-
CPN	93.6	0.038	0.004	0.005	10.5	13.1
CPN- H_3PO_4 -500	909.9	0.477	0.140	0.205	29.4	43.0
CPN- H_3PO_4 -550	255.9	0.127	0.040	0.043	31.5	33.9
CPN- H_3PO_4 -MV	0.1	-	-	-	-	-

¹ S_{BET} —specific surface area; ² V_{Tot} —total pore volume; ³ V_{Mi} —micropore volume; ⁴ V_{Me} —mesopore volume.

CPN- H_3PO_4 -MV is nonporous, like its precursors (PN, PN- H_3PO_4), as indicated by the data presented in Table 6. The carbonization process significantly improves porosity, increasing the specific surface area to about $100\text{ m}^2/\text{g}$ for CPN and 250 or 900 m^2/g for acid-activated carbons. The enlargement of the porous structure parameters is the result of an increase in the volume of micro- and mesopores. However, the percentage of micro- and mesopore volumes in the acid-treated carbons is almost three times higher than that in the CPN. Figure 8 presents the nitrogen sorption isotherms and pore size distribution plots of the studied carbons.

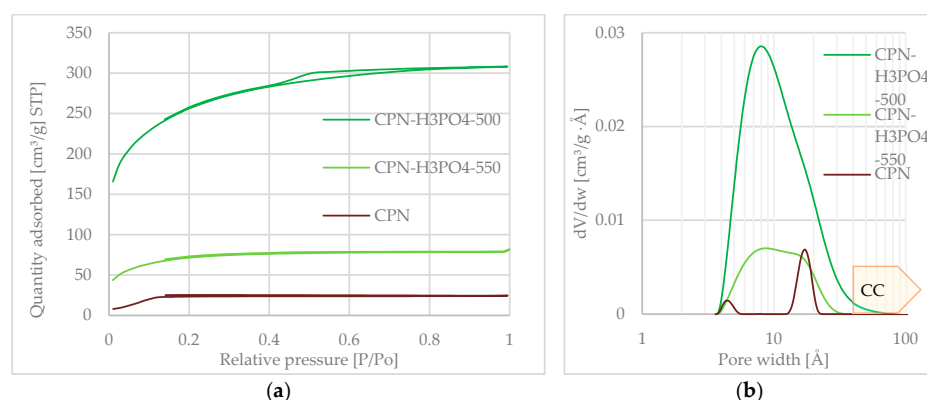


Figure 8. N_2 adsorption–desorption isotherms (a) and pore size distribution (b). CC: capillary condensation.

Although the three carbons have mesopores, only CPN- H_3PO_4 -500 has a well-developed hysteresis loop belonging to type H4, according to the IUPAC classification [99]. This type is a characteristic feature of materials containing slit-shaped micropores connected by macro- and mesopores [54,100,101] with widths exceeding $\sim 4\text{ nm}$, enabling capillary condensation [102–104]. In contrast, the isotherms of CPN and CPN- H_3PO_4 -550 show no hysteresis. Their shapes correspond to type I(b), given by materials of broader distributions of pore sizes, including wider micropores and narrow mesopores ($< 2.5\text{ nm}$) [102]. The above considerations are confirmed by the results shown in Figure 8b. The PSD of CPN is represented by the

bimodal curve with narrow maxima at ~ 4.7 and ~ 18 Å. In contrast, both the acid-activated carbons have PSD curves covering a broad range of widths up to 20 and 70 Å. As one can see, only a small part of the area under the PSD curve of CPN-H₃PO₄-500 coincides with the capillary condensation region, which is marked with an orange arrow labeled CC.

3.5. Adsorption of Pb²⁺

The materials were tested in terms of their effectiveness in removing lead ions. These experiments were performed using three types of aqueous matrices—ultrapure water, tap water and natural river water—to simulate purification systems relevant to laboratory, drinking and wastewater treatment applications. The concentration of lead ions after sorption from studied solutions was measured in triplicate against a 300 µg/L standard. The obtained results are presented in Figure 9 and Table 7. The graphs show the concentrations of Pb²⁺ remaining in solutions after 48 h of shaking 200 mg sorbents with 45 mL of a 300 µg/L lead ions solution.

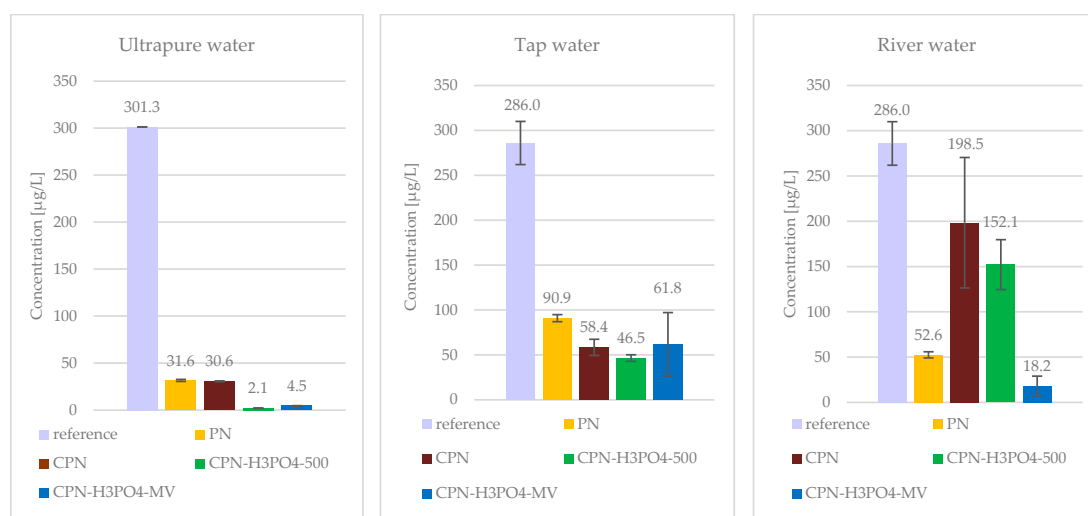


Figure 9. Sorption of Pb²⁺ on the studied sorbents. Each analysis was performed using 200 mg of sorbent and 45 mL of spiked aqueous solutions. The batch experiments were carried out for 48 h (in an orbital shaker at 90 rpm under ~ 20 °C). Reference denoted the initial Pb²⁺ concentration in the spiked waters, the error bars represent $n = 3$ independent replicates. The limit of detection (ICP-MS) was 0.02 µg Pb²⁺/L. Textural and compositional characteristics of the sorbents: PN—nonporous, P%—nd; CPN—93 m²/g, P%—nd; CPN-H₃PO₄-500—910 m²/g, P%—5.4%; CPN-H₃PO₄-MV—nonporous, P%—nd.

Table 7. Sorption efficiency expressed as a percentage of Pb²⁺ adsorbed from aqueous solution.

	Ultrapure Water	Adsorbed Amount [%] Tap Water	River Water
PN	89.5	68.2	81.6
CPN	89.8	79.6	30.6
CPN-H ₃ PO ₄ -500	99.3	83.8	46.8
CPN-H ₃ PO ₄ -MV	98.5	78.4	93.6

The results in Figure 9 and Table 7 show that all the tested materials effectively adsorbed lead ions from water. According to the expectations, the highest Pb²⁺ uptake for all the sorbents was observed in ultrapure water, where interactions between Pb²⁺ and the sorbents surface took place without any interferences. Minerals and inorganic ions are usually present in tap and fresh water. Their presence can cause competition for active sites on a sorbent surface. Such phenomenon will naturally lead to a decrease in lead ion

uptake. River water typically contains a greater proportion of organic matter in comparison with tap and ultrapure water. It is one of the most complicated matrices, in which many different interactions occur. Large organic molecules may deposit on the sorbent surface and block access for analytes. Other mechanisms include interactions between lead ions and organic matter (e.g., chelating or ion exchange), contributing to changes in the sorption characteristic [26,105–107].

In the case of ultrapure water, CPN-H₃PO₄-500 (2.1 µg/L 99.3%) and CPN-H₃PO₄-MV (4.5 µg/L; 98.5%) proved to be the most effective in the removal of lead ions. Pristine pistachio nutshells and CPN sorbed lead with a slightly lower efficiency (the post-sorption concentration was 31.6 µg/L; 89.5% and 30.6 µg/L; 89.8%, in the ultrapure, tap and river water samples, respectively). Lead ions uptake from tap water was not as high as it was for ultrapure water. PN and CPN-H₃PO₄-MV showed the worst sorption ability: we found equilibria Pb²⁺ concentrations at 90.9 µg/L (68.2%) and 61.8 µg/L (78.4%), respectively, compared to CPN and CPN-H₃PO₄-500, where the final concentrations were 58.4 µg/L (79.6%) and 46.5 µg/L (83.8%), respectively. In the experiment conducted with river water, significant differences were observed between the trends presented for the ultrapure and tap water solutions. The best lead ions sorption was demonstrated by CPN-H₃PO₄-MV, where only 18.2 µg/L of Pb²⁺ remained in the solution after sorption. About three times more Pb²⁺ were left in the solution with the sample of PN. The lowest uptake was demonstrated by CPN and CPN-H₃PO₄-500 (198.5 µg/L; 30.6% and 152.1 µg/L; 46.8%, respectively). The large standard deviations for these results (shown in Figure 9) may be attributed to matrix effects arising from interactions between the river water interferents, the sorbents, and the lead ions.

The mechanism of Pb²⁺ sorption on activated carbons involves different types of adsorptive interactions occurring at the adsorbent surface. Carbons, as highly porous materials, have a well-developed system of micro- and mesopores, in which pore filling, driven by weak van der Waals interactions, constitutes the basis of physical adsorption. In addition, the chemical nature of the carbon surface determines the type and energy of the forces affecting the adsorbate. The overall interaction is considered as the sum of independent interactions such as dispersion, electrostatic, dipole–dipole, induced dipole, donor–acceptor, hydrogen bonding and π -electron stacking. Among them, donor–acceptor interactions and hydrogen bridges are more likely, while typical chemical interactions involving electrostatic forces are less common [108].

The lone electron pairs available on oxygen in its functional groups (e.g., OH or C=O) provide active sites for complexation of Pb²⁺ ions. Other functional groups capable of dissociation (e.g., COOH or phosphates) enable cation exchange mechanisms [109].

More recently, chemical precipitation has been proposed as one of the dominant pathways of Pb²⁺ sorption on biochars activated with H₃PO₄ [110]. This mechanism arises from the low solubility of lead phosphates and carbonates in water (0.14 and 0.11 mg/L). Their solubility product values (K_{sp} Pb₃(PO₄)₂ = 3.98×10^{-45} and K_{sp} PbCO₃ = 7.4×10^{-14}) can be readily exceeded, leading to the deposition of solid precipitates [111].

The chemical nature of the studied sorbents, discussed in paragraphs describing the XPS, FT-IR and Raman results, along with textural properties, allow us to divide these materials into two groups: a nonporous but hydrophilic group (PN and CPN-H₃PO₄-MV) and a porous but more hydrophobic group (CPN and CPN-H₃PO₄-500). This division is reflected in their sorption properties. PN and CPN-H₃PO₄-MV exhibit similar trends. Uptake of lead ions in the case of these materials diminishes in the tap water solutions but increases in the river water solutions. This phenomenon can be explained by competitive interactions between the surfaces of the sorbents and the interferents present in the solution. Minerals dissolved in tap water compete with Pb²⁺ for active sites, reducing the efficiency of

the process. In river water, additional effects should be taken into account. The hydrophilic surfaces of the PN and CPN-H₃PO₄-MV can easily interact with polar organic interferents dissolved in this solution. The presence of the organic matrix, on the one hand, can limit the sorption of Pb²⁺ by blocking the sorption sites; on the other hand, it can interact with metal ions and deposit as a conglomerate on the hydrophilic surface of the sorbent. This interaction is helpful in explaining the observed effect of improved sorption. A schematic representation of the described dependencies is shown in Figure 10.

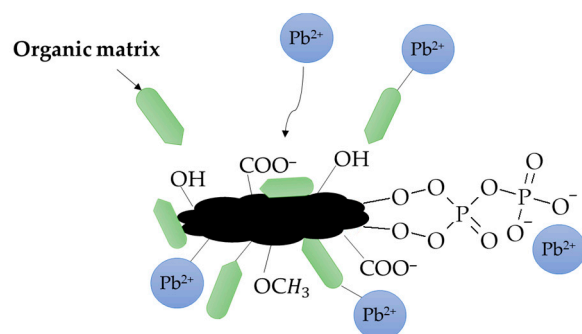


Figure 10. Scheme of interactions between a sorbent, Pb²⁺ and matrix molecules.

For CPN and CPN-H₃PO₄-500, the sorption ability decreases in tap water, and this tendency is even more noticeable in river water. Keeping in mind that their surfaces are more hydrophobic than those of PN, different interaction mechanisms likely govern their sorption behavior. One of the factors influencing the high efficiency of sorption is porosity. Both CPN and CPN-H₃PO₄-500 exhibit quite well-developed porous structures (following from the data in Table 6). Additionally, CPN-H₃PO₄-500 possesses phosphate-derived functionalities on its surface, which can interact electrostatically with Pb²⁺. This results in the better sorption ability of CPN-H₃PO₄-500 compared to PN. Such an effect is observed in both ultrapure and tap water solutions spiked with Pb²⁺; the uptake was slightly lower in tap water, which is possibly due to part of active sites being occupied by interferent substances. Even lower sorption properties in the river water are consequence of two factors. First, more hydrophobic carbon surface limits interactions with polar organic matter. Second, the micro-meso porous structure is filled very quickly by small adsorbate molecules. However, larger molecules of the organic matrix can cover the entrances to the pores, preventing smaller ones such as Pb²⁺ from accessing them. Additionally, phosphates present on CPN-H₃PO₄-500 exhibit acidic character and their negative charge would, in principle, favor the interaction with the targeted contaminant. While this enhances sorption in ultrapure and tap water solutions, in river water, the acidic surface of the sorbent may also shift the local acid–base equilibrium, altering the dominant sorption mechanism.

Table 8 presents some data from the literature on the sorption capacities of various phosphoric-acid-activated carbons. Differences in Pb²⁺ uptake depend strongly on both the experimental conditions and the sorbents properties. Porosity and surface chemistry are created during the synthesis process, which can be multi-step, long-lasting, and energy-consuming. The sorption efficiency obtained in this work is comparable to the values reported by other researchers.

Table 8. The comparison of adsorption capacities of H₃PO₄ activated carbons reported in the literature.

Carbon Precursor	Activator (Impregnation Ratio) Percentage of P	Preparation Conditions.	S _{BET} [m ² /g]	Initial Concentration/ Pb ²⁺ Capacity	% Uptake	Ref.
Date pits	85% H ₃ PO ₄ (1:3) P%-	160 °C, 5 h/215 °C, 0.25 h/500 °C, 0.5 h	864	100 mg/L/ 23 mg/g	60	[112]

Table 8. *Cont.*

Carbon Precursor	Activator (Impregnation Ratio) Percentage of P	Preparation Conditions.	S _{BET} [m ² /g]	Initial Concentration/ Pb ²⁺ Capacity	% Uptake	Ref.
Coffee grounds	85% H ₃ PO ₄ , (1.6:2.2) P%-21.3	450 °C, 1 h/80 °C, 4 h/600 °C, 0.5 h	102	100 mg/L/ 166 mg/g	72.8	[110]
Eichhornia crassipes	1.2 M H ₃ PO ₄ , (25 g:350 mL) P%-0.13	150 °C 1.33 h/r.t., 24 h		20 mg/L	96	[113]
Sucrose	85% H ₃ PO ₄ (ratio 0.6) P%-9.05	100 °C, 12 h/400 °C, 0.5 h	1019	2 × 10 ⁻⁴ M/L 94 mg/g		[114]
water hyacinth	45% H ₃ PO ₄ (2.4:1) P%-0.44	r.t., 24 h/ 450 °C, 2 h	424	150 mg/L 118.8 mg/g	-	[109]
Polygonum orientale Linn	45% H ₃ PO ₄ (2.4:1) P%-	450 °C, 1 h	1398	50-75 mg/L 98.39 mg/g		[115]
Sea-buckthorn stones	Diluted H ₃ PO ₄ (1:2) P%-	r.t., 24 h/550 °C, 3 h	1071	100 mg/L 7.8 mg/g	98.3	[116]
Pistachio nutshells	85% H ₃ PO ₄ (1:1.6) P%-5.5	r.t./24 h 500 °C, 0.5 h	910	0.3 mg/L 7.8 mg/g	99.3	Present study

3.6. Economic Considerations of the Carbonization Process

In order to evaluate the economic benefits associated with carbonization at lower temperatures, the following approach was carried out: The horizontal quartz tube furnace was heated from room temperature to the adjusted 500, 900 or 1000 °C at a heating rate of 10 °C per min. A computer-based control system recorded the real-time energy consumption of the furnace: 60, 115 and 144 kWh for 500, 900 and 1000 °C, respectively. Next, the energy needed to maintain each temperature for 30 min was verified. The obtained values were 8, 28 and 30 kWh, respectively.

From the received data, it is clearly visible that the most energy-consuming step is preheating, while maintaining the constant temperature requires considerably less energy. It should also be emphasized that energy consumption is not a linear function of temperature. Carbonization at 500 °C uses 2.5 times less energy (68 kWh) than at 1000 °C (174 kWh), which is a consequence of the smaller temperature difference between the furnace and the external environment. Increasing the carbonization temperature to 1000 °C substantially raises energy demand, due to greater heat dissipation.

In the case of microwave processing, the consumption of energy was calculated based on data declared by the producer in the device specification sheet. The microwave treatment was performed at a power of 1000 W (rated input power 1360 W) for 8 min, giving an energy consumption on the level of 0.18 kWh, which is significantly lower compared to that of conventional furnace carbonization.

From the above considerations, it follows that the most energy-efficient option is to use a microwave treatment. However, in the case of conventional carbonization, lowering the process temperature brings measurable benefits. Comparing total energy consumption during carbonization at 1000 (174 kWh), 900 (143 kWh) and 500 °C (68 kWh) shows that reducing the temperature by 100 °C allows for energy savings of about 18%, but lowering it to 500 °C saves as much as 61%.

4. Conclusions

In this study, two methods for preparing activated carbon sorbents were investigated, with the aim of improving the sustainability of the process and reducing costs compared to traditional approaches. The first method proposed is based on classical carbonization, performed at a reduced temperature of 500 or 550 °C instead of the typical temperature of 900 or 1000 °C. The second method investigated involved using microwave treatment to prepare the carbons. The physicochemical properties of the synthesized carbons were analyzed

in relation to the pristine and H_3PO_4 -modified pistachio nutshells, which were used as the precursors; these materials are currently considered as waste materials, with very limited use in industry. The research conducted allowed us to draw the following conclusions:

- Activation of the biomass with phosphoric acid improved the thermal stability of the carbonization products by about 100 °C. Increasing in the carbonization temperature by 50 °C (so from 500 °C to 550 °C) resulted in some additional thermal stability. Moreover, by selecting two acid-modified precursors, $\text{PN-H}_3\text{PO}_4$ and $\text{PN-H}_3\text{PO}_4\text{-R}$, we were able to determine which parameter—temperature or the presence of the acid activator—had a stronger influence on the porosity of the resulting carbons. The presence of the acid turned out to be more important than the increase in temperature.
- The product prepared by microwave treatment was poorly carbonized and nonporous.
- A consistent chemical characterization of both the precursors and the carbons was obtained using XPS, ATR and Raman spectroscopies. It has been shown that pretreatment of the precursors at room temperature, even with the concentrated phosphoric acid, did not lead to the permanent binding of phosphate species to their surface. However, when the treatment was applied at elevated temperatures, the incorporation of phosphorus groups was enhanced. It has also been revealed that, as the carbonization temperature increased, the phosphates incorporated into the carbon structure underwent transformation, converting from pyrophosphates to metaphosphates.
- The highest specific surface area (910 m^2/g) was obtained for the carbon prepared at 500 °C in the presence of phosphoric acid (high-temperature acid activation). Such conditions represented a state in which the carbon-formation process is at its most advanced stage, and the changes taking place are furthermore supported by the acid influence. Much lower porosity (256 m^2/g) was generated for the sorbent that had been rinsed from the acid before the carbonization at 550 °C (low-temperature acid activation).
- Both the pistachio nutshells and the products of their chemical and thermal treatment show great potential as low-cost, efficient sorbents for Pb^{2+} removal, even from highly diluted solutions. The metal ions sorption process is strengthened by the presence of functional groups introduced into the structure during the activation step. The sorption experiments performed using ultrapure, tap and river water simulated the potential applications of the prepared sorbents as filter fillings to purify potable water or wastewater. Lead removal efficiencies of 90–99%, 70–80% and 30–90% were achieved for ultrapure, tap and river water, respectively.

Future research should investigate the use of pistachio nutshells in the removal of other important heavy metals, as well as organic contaminants, e.g., pharmaceuticals, artificial dyes, and other pollutants. In terms of the practical applications of the modified pistachio nutshells as a material for tertiary water treatment, kinetic studies should be carried out on a pilot scale to determine the feasibility of full-scale implementation. Pristine pistachio nutshells, even without any modification, have proven to be an advantageous natural sorbent due to their wide availability and low cost. The findings of this study present an alternative option to current sorbents for tertiary water treatment; at present, these processes involve non-sustainable practices (coal mining; activated carbons preparation requires substantial electricity input and associated CO_2 emissions).

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Abbreviations

The following abbreviations are used in this manuscript:

ASAP	Accelerated Surface Area and Porosimetry
ATR-FTIR	Attenuated Total Reflectance–Fourier Transform Infrared spectroscopy
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
CPN	carbon prepared from pistachio nutshells
CPN-H ₃ PO ₄	carbon prepared from pistachio nutshells activated with H ₃ PO ₄
DTG	differential thermogravimetric analysis
FWHM	full width at half maximum
HFW	horizontal field width
HTF	horizontal quartz tube furnace
ICP-MS	inductively coupled plasma–mass spectrometry
LED	light-emitting diode
MV	microwave
MVSW	Microwave Synthesis Workstation
PN	pistachio nutshells
PN-H ₃ PO ₄	pistachio nutshells chemically modified with H ₃ PO ₄
PN-H ₃ PO ₄ -R	H ₃ PO ₄ activated pistachio nutshells rinsed with distilled water
PSD	pore size distribution
SEM-EDS	scanning electron microscope with energy dispersive X-ray spectroscopy detector
TG	thermogravimetry
TGA	thermogravimetric analysis
WD	working distance
XPS	photoelectron spectroscopy analysis

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