ADSORPTION OF Cu(II) IONS ON NEWLY PREPARED ACTIVATED CARBON FROM HAZELNUT SHELLS: TEXTURAL ANALYSIS AND EFFICIENCY EVALUATION

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ABSTRACT

The present study aims to obtain and characterize activated carbon obtained from hazelnut shells and evaluate its adsorption capacity towards Cu^{2+} ions. The synthesis includes pyrolysis at 700°C and subsequent chemical activation with KOH (1:1 ratio) at 500°C. The obtained activated carbon (ACH) was characterized by elemental analysis, nitrogen adsorption (BET method), FT-IR spectroscopy and scanning electron microscopy (SEM). The results show the formation of carbon with a well-developed microporous structure and high specific surface area. The performed FT-IR analysis confirms the presence of oxygen-containing functional groups on the surface. Adsorption tests demonstrate high efficiency of ACH in removing Cu^{2+} ions from aqueous solutions. The obtained data prove that hazelnut shells are a suitable raw material to produce activated carbon, which appears as a promising and sustainable adsorbent for water purification from heavy metals.

Keywords: activated carbon, hazelnut shells, chemical activation, adsorption, cuprum ions, water purification.

INTRODUCTION

In recent years, there has been increased interest in producing activated carbon from waste biomass as a sustainable alternative to conventional carbon materials [1 - 3]. This interest is driven by both the need for effective utilization of waste resources and the growing environmental requirements for water purification and reduction of environmental pollution [4].

Hazelnut shells represent a significant residue of agricultural production, especially in countries with intensive hazelnut production, such as Türkiye, where in 2019-year production reached 776 046 tons according to data from the Food and Agriculture Organization of the United Nations [5, 6]. They represent a widespread biowaste with a high carbon content and low ash, nitrogen and sulfur content, which makes them particularly suitable for the synthesis of activated carbon with desired physicochemical properties [7]. In this regard, hazelnut shells stand out as a promising resource for the production of activated carbon with high adsorption capacity.

According to Milenkovic et al., activated carbon produced from hazelnut shells, have an specific surface area of about 1600 $m^2 g^{-1}$, porous structure dominated with micropores and mesopores, and good structural and chemical stability [8].

Among the chemical activating agents used for activated carbon synthesis, potassium hydroxide (KOH) has been found to be effective in obtaining highly microporous materials, as well as in increasing the content of -OH functional groups on the surface of activated carbon [9]. The higher efficiency of activation with KOH compared to other chemical activating agents is due to the ability of potassium to easily form compounds with carbon. In addition, K_2O formed during the activation process is reduced by carbon to metallic K, which leads to gasification of the carbon matrix and

release of CO_2, thereby forming and developing a porous structure [10].

The mechanism of chemical activation with KOH involves a series of reactions between potassium hydroxide and the carbon matrix, which are represented by the following chemical Eq. (1 - 4):

$$6\ KOH + 2\ C \rightarrow 2\ K + 3\ H_2 + 2\ K_2CO_3 \quad (1)$$

$$K_2CO_3 \rightarrow K_2O + CO_2 \quad (2)$$

$$K_2O + C \rightarrow 2\ K + CO \quad (3)$$

$$CO_2 + C \rightarrow 2\ CO \quad (4)$$

As a result of the described chemical transformations, activated carbon is formed, which should find widespread use as an effective adsorbent for removing pollutants from aquatic systems.

Water pollution with heavy metals is a serious environmental and health problem due to the toxicity of metals, their difficult biodegradability and their ability to accumulate in living organisms, i.e. copper ions (Cu^{2+}), although necessary in small quantities for biological systems, at elevated concentrations can have an adverse impact on aquatic ecosystems and human health [11 - 14].

For these reasons, activated carbon adsorption is considered one of the most effective and economically advantageous methods for removing heavy metals from aqueous solutions thanks to its high adsorption capacity, ease of application and the possibility of regeneration of the adsorbent [15 - 17].

Activated carbons derived from plant biomass have attracted considerable attention as sustainable adsorbents for the removal of various pollutants in water, including Cu^{2+} ions, due to their developed porous structure and the presence of surface functional groups that facilitate the interaction between metal ions and the adsorbent surface [18].

Despite the wide range of possible applications of activated carbon, the present study is focused on its use for effective purification of polluted waters. The main objective of this work is the development of activated carbon from hazelnut shells by pyrolysis followed by chemical activation with potassium hydroxide (KOH), as well as the systematic investigation of its adsorption properties towards copper ions (Cu^{2+}) in aqueous solutions, with the aim of evaluating its potential as a sustainable and highly efficient adsorbent for environmental applications.

EXPERIMENTAL

Synthesis of activated carbon

Hazelnut shells were used as an alternative organic raw material to produce activated carbon. They were crushed and subjected to a pyrolysis process at a temperature of 700°C for 1 h. The obtained carbonized material (CH) was mixed with the activating agent KOH (Merck, p.a.) in a ratio of CH : KOH (1:1). The chemical activation process was carried out in a tube vacuum furnace at a temperature of 500°C for 1 h. The resulting activated carbon sample was designated as ACH (Activated Carbon from Hazelnut Shells). After the activation process, the sample was neutralized with 10 % solution of HCl (Valerus, p.a.) to remove residual chemicals after activation and washed several times with distilled water until neutral pH was reached, after which it was dried at 110°C for 12 h. The process of the carbon preparation and activation is schematically presented in Fig. 1.

Analysis of elemental composition

The elemental composition of the tested samples was determined with an apparatus Vario Macro Cube (Elementar Analyzensysteme GmbH, Langenselbold, Germany). Concentrations of C, H, N, S and O was determinated.

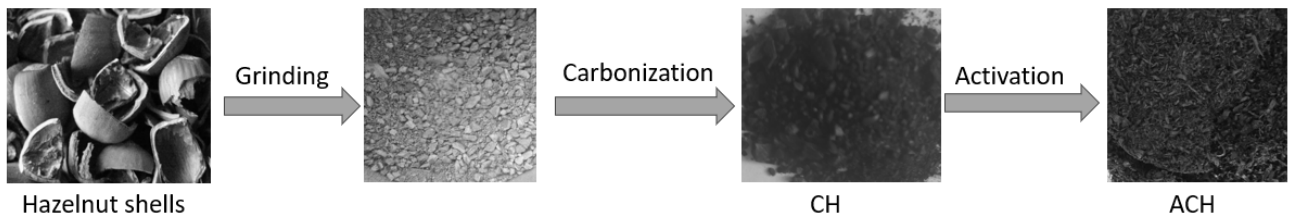

Fig. 1. Scheme of obtaining of ACH.

Brunauer-Emmett-Teller analysis

The functional application of ACH is determined to the greatest extent by its specific surface area and its textural parameters, which were recorded by low-temperature adsorption on nitrogen (N_2, 77 K). The specific surface area was determined using Brunauer-Emmett-Teller (BET) method. The total pore volume (V_t) was determined at a relative pressure $P_i/P_0 = 0.98$ [19].

Fourier Transform Infrared analysis

The infrared spectra of the samples were recorded on a Nicolet Avatar 360 FT-IR spectrophotometer, Germany. KBr pellets were used as a matrix. The spectra were recorded in the region 4000 - 500 cm^{-1}.

Scanning Electron Microscopy study

The surface morphology of the samples was characterized by SEM (Philips, Germany). A small amount of AC sample was placed on the conductive tape and fixed on a holder and then by JFC - 1100 sputter coater thin film platinum coating was obtained. The measurement was done in mode 10 kV, 0^o and 0.1 mm scan spacing.

Adsorption capacity of the ACH to copper ions

The adsorption capacity of the activated carbons regarding Cu^{2+} ions was determined using the following methodology: solution of $CuSO_4.5H_2O$ (Valerus, p.a.) with concentration 5 g L^{-1} was prepared. Aliquots of the obtained $CuSO_4.5H_2O$ solution (10, 20, 30, 40 and 50 mL) were transferred into 50 mL volumetric flasks (samples S1 - S5) and was diluted to the mark with distilled water. Subsequently, 0.2 g of the obtained activated carbon was added into each flask and were homogenized for 1 h. The initial and residual concentration of the Cu^{2+} ions in the solutions was determined with UV-Vis Spectrophotometer, by using the Cuprizone (Cuprizone, Alfa Aesar, p.a.) method at 600 nm (Table 3) [20].

RESULTS AND DISCUSSIONS

Elemental composition

The elemental composition of the samples before and after chemical activation with KOH is presented in Table 1.

The obtained results from the elemental analysis (Table 1) show that the non-activated lignocellulosic material (CH) based on hazelnut shells is characterized by a high carbon content (82.46 wt. %), which is typical for carbonized materials on this basis. The reduction in carbon content after chemical activation (63.59 wt. %) is due to gasification processes at the high activation temperature of 700^oC, which leads to the interaction of the carbon matrix with the activating agent potassium hydroxide and the release of CO and CO_2, according to chemical reactions (2), (3) and (4). As a result, a microporous structure is formed in the activated material (ACH), which is associated with an increase in the specific surface area, confirmed by BET analysis. An increase in the oxygen content to 32.90 wt. %, after chemical activation is due to the formation of oxygen-containing functional groups, as well as possible mineral residues.

Brunauer-Emmett-Teller analysis

The textural parameters of the CH and ACH samples are presented in Table 2, and Figs. 2 - 5.

The results of the BET analysis (Table 2) show that after chemical activation with KOH, the specific surface area (S_{BET}) of the activated samples increases from 150 $m^2 g^{-1}$ to 410 $m^2 g^{-1}$. The total pore volume

Table 1. Elemental composition before and after chemical activation process.

Sample	C, wt. %	H, wt. %	N, wt. %	S, wt. %	O, wt. %
CH	82.460	2.858	0.650	0.268	13.746
ACH	63.590	2.385	0.700	0.427	32.898

Table 2. Specific surface area and basic textural parameters.

Sample	S_{BET}, $m^2 g^{-1}$	Vt, $cm^3 g^{-1}$	V_{micro}, $cm^3 g^{-1}$	V_{mezo}, $cm^3 g^{-1}$	V_{micro}, %	V_{mezo}, %
CH	150	0.012	0.007	0.005	58.33	41.67
ACH	410	0.02	0.01	0.010	50.0	50.0

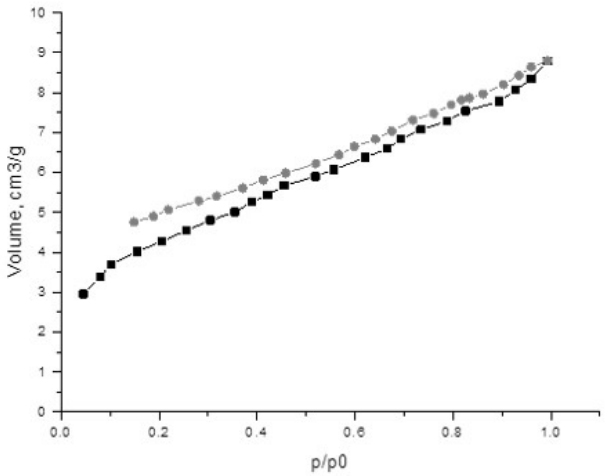

Fig. 2. Low-temperature nitrogen adsorption isotherm at 77.4 K of the sample CH.

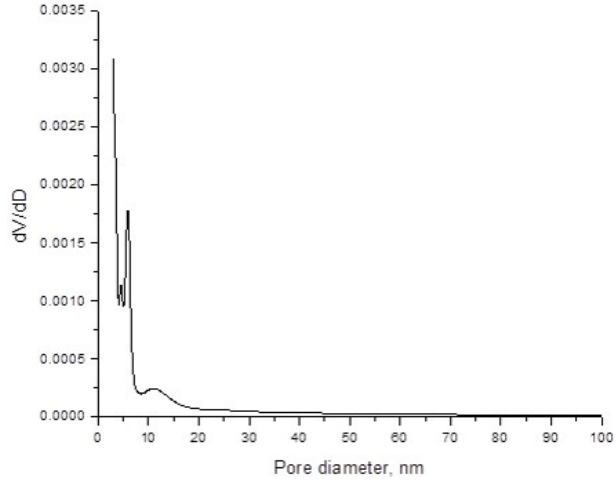

Fig. 3. Pore volume distribution curve by size of CH.

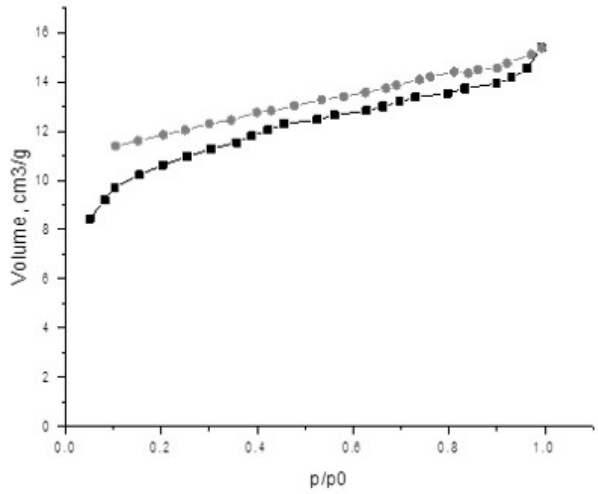

Fig. 4. Low-temperature nitrogen adsorption isotherm at 77.4 K of the sample ACH.

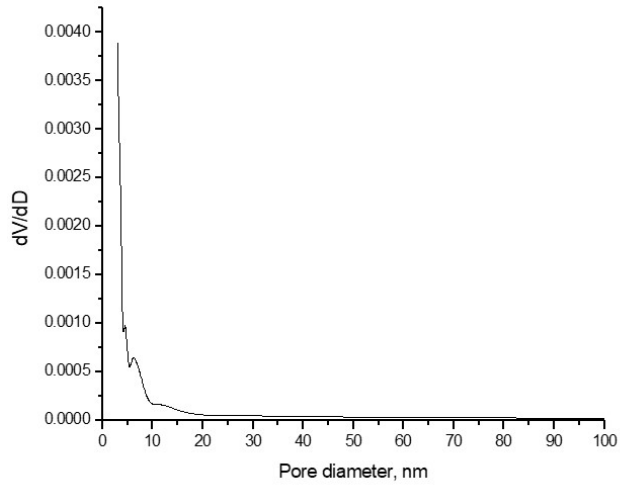

Fig. 5. Pore volume distribution curve by size of ACH.

(Vt) increases from 0.012 to 0.020 $m^2 g^{-1}$ (about 67 %). Although the volume of micropores increases (from 0.007 to 0.010 $m^2 g^{-1}$),
their relative share decreases from 58 % to 50 %, which indicates the development of larger mesopores after activation.

From data about the pore size distribution (Fig. 3), the non-activated sample, which has a low specific surface area S_{BET} = 150 $m^2 g^{-1}$, has a predominantly microporous structure, with a clearly pronounced maximum in the range < 2 nm.

The adsorption-desorption isotherm (Fig. 4) shows significantly higher adsorption in the entire pressure range P/Po, which according to the IUPAC classification is a mixed type I - IV isotherm [21].

Fig. 5 presents the pore size distribution for the chemically activated ACH sample. The figure shows a significantly wider range of pore distribution, with an intense peak in the micropore region, as well as the presence of 5 - 8 nm mesopores, with almost no pores with sizes in the range > 10 nm.

All these data lead to the assumption that chemical activation with KOH leads to a significant increase in the specific surface area S_{BET} = 410 $m^2 g^{-1}$, an increase in the

porous structure and a transition from a predominantly microporous to a micro-mesoporous structure in the activated sample.

Fourier Transform Infrared analysis

The FT-IR analysis data (Fig. 6) show the presence of a characteristic peak around 3400 cm^{-1}, typical of -OH groups, which can be attributed to the presence of surface hydroxyl groups in the samples. The peak around 1700 cm^{-1} reflects the presence of carbonyl groups (C=O), and the absorption lines in the region 1570-1630 cm^{-1} can be mainly associated with aromatic C=C vibrations. The peaks reported at around 1400 cm^{-1} can be associated with oxygen functional groups, such as C=O and C–O. The observed peak around 1200-1000 cm^{-1} is typical of C–O in ether, phenolic and ester groups.

Scanning electron microscopy

The results of scanning electron microscopy show the development of a highly porous surface after chemical activation. The micropores, with a size of < 2 nm, are densely distributed, forming the porous structure of the material. Their development leads to an increase in the specific surface area. The mesopores, with a size of (2-50 nm), which facilitate diffusion and access to the micropores, are noticeable as evenly distributed round or elliptical pores (Fig. 7).

Adsorption capacity of the ACH to copper ions

The initial and residual concentration of the Cu^{2+} ions in the solutions was determined with UV-Vis Spectrophotometry. Here, a necessary standard curve of absorption was made (Fig. 8). The amount of absorbed from AC, cuprum ions is determined as the difference between the initial ion concentration and that determined after the homogenization process with ACH. The used solutions and obtained data from the UV-Vis analysis are shown in Table 3.

The observed values for the concentration of copper ions after treatment with the obtained activated carbon from hazelnut shells are too low and fall outside the range of the calibration curve used. This logically leads to the conclusion that even if there is a residual content of free copper ions in the solution (the method reports low extinction values in the range between 0.007 - 0.035, at the measured characteristic wavelength), their concentration is too low and the main amount of ions should have been sorbed from the surface of the applied activated carbon.

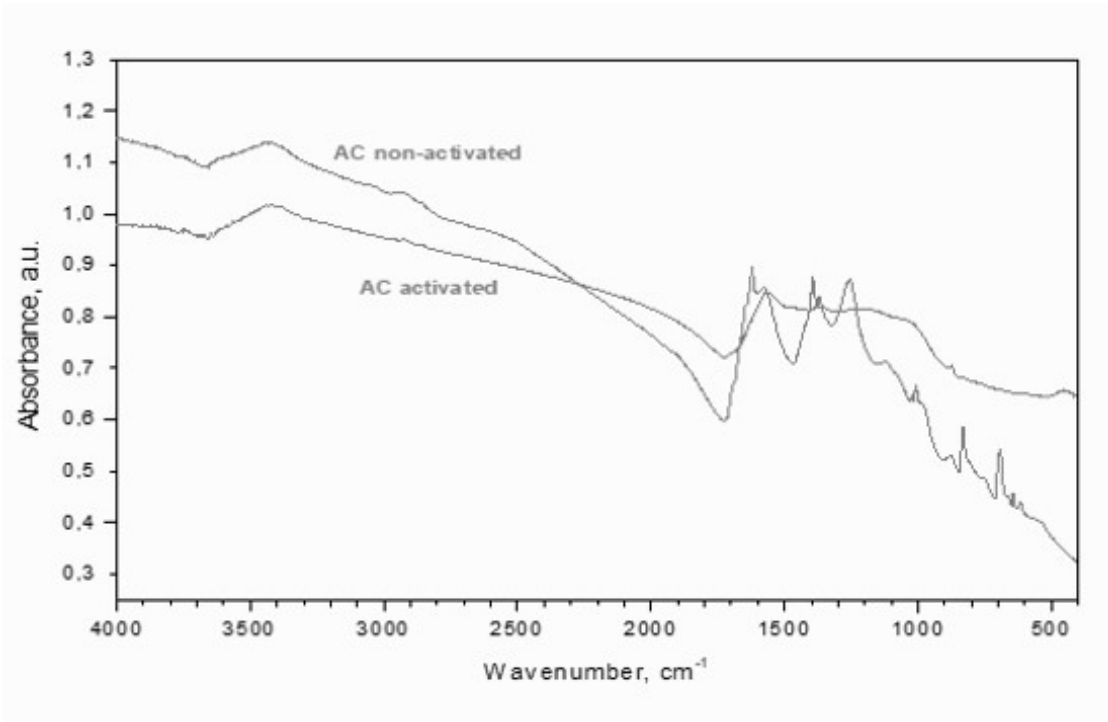

Fig. 6. FT-IR spectra of the samples CH and ACH.

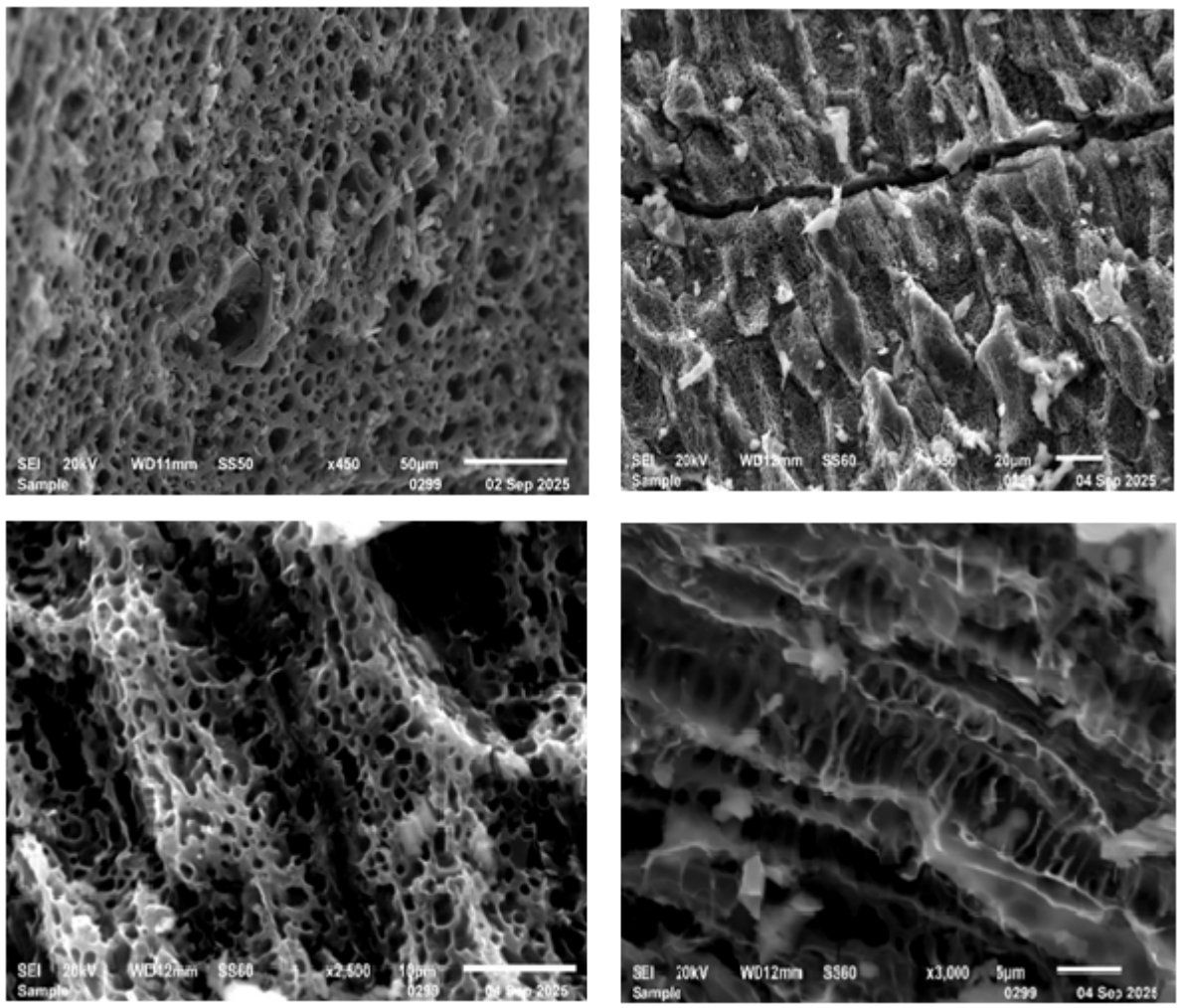

Fig. 7. SEM images of the obtained ACH.

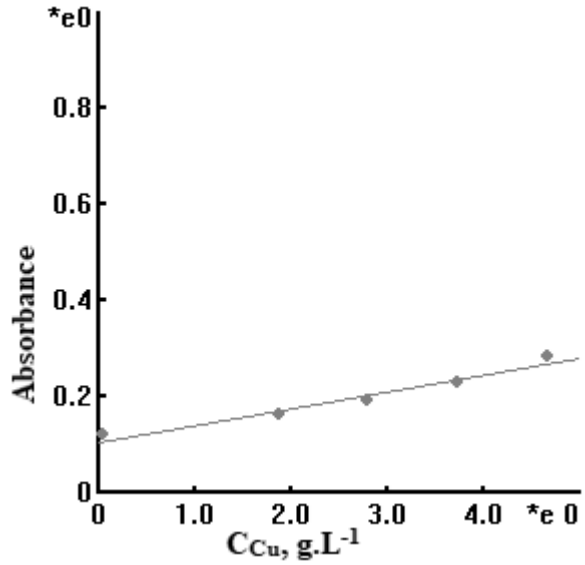

Fig. 8. Standard curve.

Table 3. Results from UV-Vis analysis.

Solution	Initial concentration of Cu^{2+}, g L^{-1}	Residual concentration of Cu^{2+}, g L^{-1}
S1	0.033	< DL
S2	1.867	< DL
S3	2.800	< DL
S4	3.734	< DL
S5	4.667	< DL

< DL - under detection limits (0.025 g L^{-1}).

CONCLUSIONS

The result of the elemental analysis shows a decrease in carbon content (from 82.46 % to 63.53 %) and an increase in oxygen content (from 13.75 % to 32.90 %) after the chemical activation of the hazelnut shells.

The activation of the CH material with KOH leads to a significant development of the surface area and porous texture, accompanied by the formation of oxygen functional groups, which play an important role in the adsorption properties of the resulting activated carbon. The presence of these functional groups is confirmed by the FT-IR analysis, the results of which show the presence of the following oxygen-containing functional groups: –OH, C=O, C–O, recorded at the corresponding characteristic lines 3400 cm^{-1}, 1700 cm^{-1} and 1400 cm^{-1}.

SEM images reveal a well-developed and uniformly distributed porous surface, characterized by densely spaced micropores and clearly defined mesopores, which favours the diffusion and retention of metal ions in the adsorbent structure.

The results of the UV-Vis analysis confirm that the activated carbon produced on the basis hazelnut shells reduces the concentration of copper ions in the investigated solutions - all of residue concentration are below detection limit.

The results show that activated carbon produced based on this type of material has good physicochemical characteristics, from which it should be assumed that KOH-activated hazelnut shell carbon is a highly efficient and environmentally sustainable adsorbent, suitable for the purification of water contaminated with copper ions.

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Authors' contributions

L.M., M.M., K.R., N. B.: Experimental work, Writing; M.M.: Review and editing. All authors approved the final version of the manuscript.

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