Preparation of nitrogen-enriched pine sawdust-based activated carbons and their application for copper removal from the aquatic environment

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Abstract
In this research study, compressed pellets of pine wood sawdust were carbonized at a temperature of 600 °C and then physically activated at 800 °C to obtain activated carbons (ACs). Then, some of the samples were enriched with nitrogen by reaction with urea at 300 °C. The AC samples prepared in this way were examined for the removal of Cu(II) in adsorption processes. Pine wood sawdust is waste resulting from processing in the wood industry and is a promising material to be reused for metal ions recovery. For this purpose, firstly, the AC was characterized using several analytical methods, including ash content, elemental composition, TGA, specific surface area and pore diameter (BET), pore size distribution (BJH), micropore volume, the content of surface acidic and basic functional groups, pH, FTIR and SEM morphology. Secondly, these materials before and after modification with nitrogen were used in experiments on the adsorptive removal of Cu(II) ions from aqueous solutions. The influence of parameters, such as initial pH, adsorbent dosage, initial Cu(II) concentration and contact time on the process, was investigated. Thirdly, adsorption kinetics and sorption isotherms were analyzed. According to the research results, it was reported that maximum sorption efficiency was equal to 99.9 and 99.8% at pH 5 for activated carbon AC (TK6AF1/2) and nitrogen-modified activated carbon NMAC (TK6MAF1/2), respectively. This proves that the examined waste materials exhibit satisfactory sorption properties in relation to Cu(II) ions and can be used as low-cost adsorbents in industrial wastewater treatment processes. These studies are in line with current global trends in sustainable and circular economy. Future research may focus on performing adsorption processes of copper and other metals at various temperatures as well as dynamic flow, studying metal ion competition, performing regeneration to reuse the adsorbents, carrying out realistic wastewater studies and cost estimation of entire processes on a laboratory and industrial scale.
Introduction

In nature, copper is usually found in the form of minerals, such as sulfide (chalcopyrite, chalcocite, covelin), oxide (cuprite), carbonate (malachite, azurite), silicate (chrysocolla) and less often in the form of homogeneous deposits (nuggets). Copper is the 26th most abundant element in the earth’s crust, and its deposits are mainly located in Poland, but also in South America, Chile, Peru, USA, Zaire, Zambia, Canada and Russia. Pure copper is obtained in hydrometallurgical, pyrometallurgical and electrolytic processes (Lingqin et al. 2020; Keber et al. 2020). Copper is usually obtained from metal ores containing chalcocite, chalcopyrite, pyrite and metal sulfides (Pb, Zn, Ni). Methods of enriching copper ores in flotation processes were also developed, making it possible to process ores with a copper content of less than 1% (Han et al. 2018). The metal has chalcophilic properties and is usually found in the form of a divalent cation in minerals and sorption complexes (Lund et al. 2008).

Copper pollution in the natural environment mainly concerns the contamination of surface waters, which is a consequence of mining and metallurgy activities, textile, dyeing, rubber and pharmaceutical industries, processes related to the use of copper such as electroplating, the production of copper alloys and others. One of the pathways leading to copper contamination is the irresponsible management of plant protection products containing copper sulfate. This metal has a tendency to accumulate in the environment, for example in small aquatic organisms. Copper excess is usually observed in wastewater, which is a source of danger to surface waters. Its excessive supply in water reservoirs inhibits the self-purification process of water. Its increased content can sometimes be found in tap water due to the presence of copper alloys in plumbing pipes (Ahmed et al. 2018; Kalak et al. 2021; Kalak et al. 2021a, b). The issue of environmental contamination with heavy metals, including Cu, Pb, Cd, Ni, Cr, As and Zn, is associated with the occurrence of many dangers. Due to the ability to dissolve in the aquatic environment, heavy metals can get into living organisms. Once in the food chain, they can accumulate in high concentrations in animal and human organisms, which contributes to serious organ diseases, cancer and even death. Therefore, treatment of metal-contaminated wastewater before discharging into the aquatic environment is imperative. The progressive industrialization contributes to emission to the environment of more and more hazardous substances that require neutralization. This goal can be achieved by conventional purification processes, such as chemical precipitation, filtration, coagulation, oxidation, ion exchange, electrochemical methods and many others. In addition to the advantages, these processes also have significant disadvantages, such as high process costs, incomplete removal, unsatisfactory efficiency, even ineffectiveness, high energy requirements or the production of toxic sludge (Cheng et al. 2021a, b, 2022; Wojciechowska et al. 2022). Hence, there is a constant need to develop new alternative methods of metal removal, including adsorption processes with the use of low-cost adsorbents. An interesting and promising solution may be activated carbons obtained from waste biomass (Bansal and Goyal 2005; Kalak and Tachibana 2021).
Activated carbon (AC) can be obtained from various raw materials containing a high content of elemental carbon as well as a low content of inorganic volatile substances. The best features of raw materials include high thermal and chemical resistance, easy availability and low price. The most commonly used materials include wood, fossil coal, peat or coconut shells (Menéndez-Díaz and Martín-Gullón 2006). In the literature, there are reports of methods for obtaining AC from various types of plant waste, such as corn cobs, straw, nut shells, sawdust, fruit seeds, as well as industrial waste, including plastics, used tires, paper or sludge from sewage treatment plants (Nowicki et al. 2012; Gayathiri et al. 2022). The main method of obtaining AC is physical activation. This process takes place at a temperature not exceeding 1000 °C in two stages. The first one is the carbonization of the raw carbon material at a temperature below 800 °C in an inert atmosphere, and the second step is the activation of the carbonized product at a higher temperature in the range of 800–1000 °C (Bansal and Goyal 2005). Physical activation consists in subjecting the char to high temperature in the range of 800–1000 °C with the addition of an oxidant in the form of water vapor, carbon dioxide or their mixture. Another method may be direct activation of the precursor, that is, simultaneous pyrolysis and activation occur at the same time (Nowicki and Pietrzak 2012). In turn, chemical activation is a smooth and uniform process. It takes place during the carbonization process at high temperature in the presence of an inert gas (nitrogen or argon) as a result of contact of a precursor with an activator, i.e., KOH, ZnCl₂ or H₃PO₄ (Marsh and Rodriguez-Reinoso 2006). High reactivity of chemical activators used allows to omit or eliminate the form of a typical carbonization process by lowering temperature and also allows to shorten time needed to develop an appropriate porous AC structure. Although the efficiency of the process is high, costs are also higher due to the use of activating agents and secondary processes associated with them (Nowicki and Pietrzak 2012). According to experiments conducted previously in the laboratories, activated carbons, obtained from sawdust pellets coming from coniferous trees, were activated using microwave radiation and then used as adsorbents for the removal of methylene blue from aqueous solutions. In these studies, satisfactory results were obtained with the adsorption capacity equal to 40 mg/g at pH 6 (Kazmierczak-Razna et al. 2018). In another research, activated carbons obtained by chemical activation and ammoxidation of Polish brown coal were used to adsorb copper and zinc ions. The highest adsorption capacities were obtained at pH 8 for Cu²⁺ ions (47.4 mg/g) and pH 6 for Zn²⁺ ions (31.5 mg/g) (Kazmierczak-Razna et al. 2021). Adsorption NO₂ in wet and dry conditions was carried out with the use of nitrogen-enriched activated carbons obtained from coniferous tree sawdust by activation of the precursor and physical activation with CO₂. High sorption capacity was 69 and 46 mg NO₂/g in dry and wet conditions, respectively (Nowicki et al. 2013).

Nitrogen-modified activated carbons (NMACs) exhibit unique physicochemical properties, which enables their wide application. As a result, there are numerous ideas to search for new, effective methods of enriching carbons with this element. The first method involves subjecting the carbon material to thermal treatment in the presence of a nitrogen-containing compound called N-reagent. Ammonia, urea, melamine or nitrogen oxides may be examples of the reagents. Pyrrole, hydrogen cyanide, formamide, hydroxylamine, hydrazine, carbazole or acridine are used much
less frequently. The type of N-reagent used for the AC modification determines the medium in which the modification process takes place, for example in liquid phase with the use of amines, in solid phase with urea modification, or in gas phase when nitrogen oxides or ammonia is used. Both modification conditions and the type of a reagent directly affect the amount and type of nitrogen groups obtained (Burg et al. 2002). Another frequently used method of obtaining nitrogen functional groups is amination process. It consists in intensive heating of AC in the atmosphere of ammonia at a temperature range of 400–900 °C. This solution allows introduction of nitrogen mainly in the form of imides and lactams, which can be transformed by further thermal treatment. Efficiency of the process can be increased by oxidizing carbon materials earlier, which promotes the addition of nitrogen functional groups (Rehman et al. 2019). Another common method of nitrogen modification is ammoxidation process. In this process, the carbon material is simultaneously nitrogenated and oxidized, most often by using a mixture of ammonia and air. The ammoxidation efficiency depends on the degree of raw material metamorphism, process temperature, volume ratio of NH₃ and air in the mixture, activation method, and selection of activated carbon production stage for the nitrogen modification process (Pietrzak et al. 2007, 2009). The types of nitrogen groups present in the structure and on the surface of activated carbons are shown in Fig. 1.

The purpose of this study was to examine the possibility of Cu(II) ions removal from aqueous solutions with the use of activated carbons AC (TK6AF1/2) and nitrogen-modified activated carbons NMACs (TK6MAF1/2) obtained as a result of physical activation of pine wood sawdust. The adsorbents were examined for their physicochemical properties, and then, the influence of parameters such as initial pH, adsorbent dosage, initial concentration, contact time on the efficiency of the adsorption process was examined. Additionally, adsorption kinetics and isotherms were analyzed.

**Experimental procedure**

**Materials and methods**

**Preparation of nitrogen-modified activated carbon (NMAC)**

The starting material used for the research was compressed pine wood sawdust in the form of pellets with a diameter of about 0.5 cm and a length of 1.0 cm (Fig. 2A). This biomass material was treated with pyrolysis (carbonization) in a quartz tubular reactor heated using a horizontal furnace (10 °C/min) from room temperature to the final temperature of 600 °C and held for 30 min. The carbonization efficiency was equal
to 26.5% w/w. Next, the obtained TK6AF1/2 carbon was subjected to physical activation with CO₂ at 800 °C for 30 min (Fig. 2B), and the efficiency was 66.3% w/w. The TK6MAF1/2 carbon was obtained analogously, with the difference that after the carbonization process, the sample was enriched with nitrogen by reaction with urea (weight ratio 1:1) at a temperature of 300 °C for 60 min (Fig. 2C) and the yield of the process was 88.4% w/w. The efficiency of physical activation of N-modified TK6MAF1/2 samples was 51.6% w/w. All the modification experiments were performed in porcelain crucibles heated with the use of microwave muffle furnace Phoenix (CEM Corporation, Matthews, North Carolina, USA). The N-modified AC sample prepared in this way was used in experiments. All chemicals used were pure for analysis, and distilled water was used in these studies.

Characterization of adsorbents

The TK6AF1/2 and nitrogen-modified TK6MAF1/2 activated carbons were used in the research studies. Firstly, physicochemical properties of the materials were analyzed using various analytical methods, such as ash content, elemental composition, X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), specific surface area and pore diameter (BET), pore size distribution (BJH), micropore volume, the content of surface acidic and basic functional groups, pH, FTIR, and SEM morphology. Detailed explanation of the methods used is attached as supplementary material (SM Methods).
Procedure of Cu(II) ions adsorption

The Cu(II) adsorption process was investigated in batch experiments at room temperature. A standard solution (Cu(II), 1 g/L, Sigma-Aldrich) was applied. Samples of TK6AF1/2 and TK6MAF1/2 adsorbents (1.5 g/L, 2.5 g/L) with a grain diameter of less than 0.212 mm and the Cu(II) stock solution at a concentration of 10 mg/L (volume $V = 10$ mL) and at an initial pH 2 – 5 were shaken in conical flasks (200 rpm) for 60 min. The pH of Cu(II) stock solutions was adjusted by adding appropriate amounts of 0.1 M NaOH and/or 0.1 M HCl solutions. After shaking, phases in the solutions were separated by centrifugation (4000 rpm) for 15 min. The content of Cu(II) ions was determined using atomic absorption spectrometry with acetylene–air flame atomization (F-AAS) by means of SpectrAA 800 spectrophotometer (at a wavelength $\lambda = 324.8$ nm for copper, Varian, Palo Alto, USA). The measurements were taken in three repetitions at room temperature and normal pressure. All reagents used were analytically pure, and distilled water was used.

The adsorption efficiency $R$ (%) and adsorption capacity $q_e$ (mg/g) are calculated from Eqs. 1 and 2:

$$R = \left[ \frac{C_0 - C_e}{C_0} \right] \times 100\%$$

$$q_e = \frac{(C_0 - C_e) \times V}{m}$$

where $m$ (g)—the mass of the sorbent, $V$ (L)—the volume of solution, $C_0$ (mg/L)—the initial concentration of Cu(II) ions, $C_e$ (mg/L)—the equilibrium concentration of Cu(II) ions after time $t$.

The adsorption of Cu(II) ions on TK6AF1/2 and TK6MAF1/2 materials was analyzed using the pseudo-first-order model (PFO) and the pseudo-second-order model (PSO) in accordance with Eqs. 3 and 4, respectively:

$$q_t = q_e(1 - e^{-k_1t})$$

$$q_t = \frac{q_e^2 k_2 t}{1 + q_ek_2t}$$

where $k_1$ (1/min.)—the rate constant of pseudo-first-order adsorption, $k_2$ (g/(mg·min.))—the rate constant of pseudo-second-order adsorption, $q_t$ (mg/g)—the amount of Cu(II) ions adsorbed at any time $t$ (min.); $q_e$ (mg/g)—the maximum amount of Cu(II) ions adsorbed per mass of the adsorbent at equilibrium.

Adsorption equilibrium on examined adsorbents was studied using Langmuir and Freundlich isotherm models based on Eqs. 5 and 6, respectively:

$$q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e}$$
\[ q_e = K_F C_e^{1/n} \]  \hfill (6)


\[ q_e (\text{mg/g}) \]—the amount of Cu(II) ions adsorbed at equilibrium, \( q_{\text{max}} (\text{mg/g}) \)—the maximum adsorption capacity, \( K_L (\text{L/mg}) \)—the characteristic constant of the Langmuir isotherm; \( K_F (\text{mg/g·(L/mg)^{1/n}}) \)—the adsorption capacity characteristic of the Freundlich model, \( 1/n \)—the Freundlich constant related to the surface heterogeneity.

**Results and discussion**

**Characterization of activated carbon (AC)**

Following the data presented in Table 1, the pine wood sawdust-based activated carbon TK6AF1/2 is characterized by high C\(^{\text{daf}}\) content (94.4%, m/m), small amount of oxygen (4.8%, m/m) and mineral ash (2.1%, m/m), and negligible content of non-carbon organic components. As it is seen, modification with nitrogen caused changes in the chemical composition of the starting material. The sample prepared by the reaction with urea at the temperature of 300 °C shows an increase in nitrogen content from 0.2 to 2.9% and a decrease in the content of mineral ash and carbon atom at the same time. In addition, a trace increase in the content of hydrogen and oxygen was observed.

In accordance with the data shown in Table 2, modification also leads to significant changes in acid–base properties of the starting AC. Thermochemical modification contributed to an increase in the total content of surface functional groups, where three times more acidic groups and slightly more basic groups were observed compared to the unmodified AC. The changes are confirmed by a decrease in pH value (8.41). This is most likely a consequence of the urea reaction at elevated temperature (300 °C), which favors the formation of more acidic functional groups, and also leads to the maintenance of basic groups on the carbon surface at an almost equal level.

The research results summarized in Table 3 and Figs. 3 and 4 show that the examined samples represent very similar textural parameters, and modification with nitrogen slightly improved them. A surface area development of 57 m\(^2\)/g with a porous structure with dominant micropores was observed, while pore volume did not change properly. Further analysis of the textural results showed that the modification with nitrogen influenced the formation of additional micropores in its porous

| Table 1 | Elemental composition of AC samples |
|---------|----------------------------------|
| AC sample | Elemental analysis (%: m/m) |
|          | Ash\(^d\) | C\(^{\text{daf}}\) | H\(^{\text{daf}}\) | N\(^{\text{daf}}\) | S\(^{\text{daf}}\) | O\(^{\text{diff}}\) |
| TK6AF1/2 | 2.1  | 94.4 | 0.6  | 0.2 | 0.0 | 4.8 |
| TK6MAF1/2| 1.8  | 91.3 | 0.9  | 2.9 | 0.0 | 4.9 |

\(d\)—dry basis, \(^{\text{daf}}\)—dry ash-free basis, \(^{\text{diff}}\)—calculated by difference
structure (an increase by 66 m²/g). This phenomenon is also confirmed by the smaller average pore diameter compared to TK6AF1/2 sample.

The isotherms of AC samples are presented in Fig. 3. Their shape suggests that they belong to type IV isotherms, which is the characteristic of microporous or mesoporous materials. As it is seen, the isotherm curve grows gradually in the initial relative pressure range from 0 to ~0.5, which can be explained by the sorption of monomolecular and multiparticle layers in mesopores and micropores. With the next increase in relative pressure, capillary condensation in the mesopores occurs, which is associated with a wide hysteresis loop. The lack of curve stabilization in the relative pressure range and a rapid increase in the sorption capacity at the pressure close to the value 1 (p/p₀) indicate the presence of macropores. Figure 4 shows the pore size distribution curves. The analysis confirmed that significant part of the porous structure are mesopores with diameters ranging from 1.9 to 12 nm.

Table 2 Acidic and basic properties of AC samples

| AC sample  | pH  | Acidic groups (mmol/g) | Basic groups (mmol/g) | Total content (mmol/g) |
|------------|-----|------------------------|-----------------------|------------------------|
| TK6AF1/2   | 10.54 | 0.23                  | 0.91                  | 1.14                  |
| TK6MAF1/2  | 8.41  | 0.75                  | 0.94                  | 1.69                  |

Table 3 Textural parameters of AC samples

| AC sample  | Surface area (m²/g) | Pore volume (cm³/g) | Micropore contribution Vₘ/Vᵣ | Average pore diameter (nm) |
|------------|---------------------|---------------------|------------------------------|---------------------------|
|            | Total               | Micropore           | Total                        | Micropore                 |
| TK6AF1/2   | 539                 | 503                 | 0.31                         | 0.24                      | 0.77                        | 2.20                        |
| TK6MAF1/2  | 596                 | 569                 | 0.32                         | 0.28                      | 0.87                        | 1.95                        |

Fig. 3 Nitrogen adsorption/desorption isotherms of the activated carbons TK6AF1/2 and TK6MAF1/2
The SEM–EDS method was applied to determine elemental composition, and the results are shown in Figs. 5 and 6 and Table 4. The following elements were determined in the materials: C, O, Mg, Si, S, K, Ca, Fe, Cu. As can be seen, carbon and oxygen are the most abundant elements, which is the characteristic of the activated carbon material. The SEM–EDS measurement was taken on the sample surface. Hence, slight differences in the content of elements in different places of samples are possible due to the heterogeneity of the materials. Moreover, the distribution of various elements was determined using the SEM–EDS mapping method. According to the results, the following distribution of elements was reported: a) TK6AF1/2: C (91%), O (2%), K (3%), Ca (3%), b) TK6MAF1/2: C (93%), O (3%), K (2%), Ca (3%). The intensity of distribution depends on the material properties and type of element (supplementary material, Figures SM1–SM2).

The tested samples were subjected to thermogravimetric analysis (Figs. 7 and 8). It was possible to determine thermal stability and the information about the change in mass loss during the temperature increase. At the beginning, a sharp decrease in the DTG curve was observed and the minimum was achieved at 46.5 °C (−0.9%/min) and 56.2 °C (−1.47%/min) for TK6AF1/2 and TK6MAF1/2, respectively. It may be a consequence of the desorption of absorbed water particles (mass loss of 2.16 and 4.15% for TK6AF1/2 and TK6MAF1/2, respectively) due to the presence of hydroxyl groups. Overall, a gradual mass loss of the materials occurred with an increase in temperature. It was observed that there were no significant mass changes in the temperature range from about 110–400 °C for both samples TK6AF1/2 and TK6MAF1/2. Above the temperature of about 400 °C, the samples begin to lose mass very quickly. According to the literature, carbons with nitrogen atoms incorporated exhibit greater thermal stability (Liu et al. 2012; Masumura et al. 2018).

To analyze the morphological structure of the obtained AC samples, their SEM images are presented in Fig. 9. According to the images, both AC show a
similar morphology. The structure of the materials exhibits numerous pores of various shapes and sizes. Shape irregularities are seen with both larger and smaller particles. The particle structure is not homogeneous and developed flat surfaces are observed. Both AC (TK6AF1/2) and NMAC (TK6MAF1/2) are characterized by developed porous systems but also unevenly distributed. Clear, fine, and irregular particle fragments may indicate the presence of ash. However, it is seen on the surface of the TK6MAF1/2 carbon that the modification with nitrogen influenced the enlargement and deepening of pores, which is manifested by the characteristic larger cracks in the structure. Similar observations have been observed in the literature on activated carbons of various origins (Efeovbokhan et al. 2019; Nowicki et al. 2013; Nowicki 2016).

FTIR analysis was attempted on the tested AC samples before and after adsorption processes. Unfortunately, no readable peaks were found in the spectra. The only very faint peak was seen at a wavelength of 1000–1100 cm\(^{-1}\), which can be attributed to C–O stretching vibrations probably from CO\(_2\) (Yang et al. 2016).
Adsorption studies of Cu(II) ions

Effect of adsorbent dosage

The effect of AC dosage on removal efficiency of Cu(II) ions was analyzed, and the results are presented in Fig. 10 and Figure SM3 (supplementary material). The experiments were conducted under the following conditions: AC dosage 1.5–5 g/L, initial concentration of Cu(II) ions 10.0 mg/L, initial pH 2.4–5, agitation speed 200 rpm, T = 23 °C, contact time 60 min. Generally speaking, increasing the dose of sorbents from 1.5 to 5 g/L increased the adsorption efficiency. The results indicate that sorbent dosages of 3.5 and 5 g/L showed the best results in the entire initial pH range. It should be noted that at pH 4 and 5, maximum adsorption for both AC and NMAC was achieved: TK6AF1/2 (dosage 3.5 g/L, pH 4–98.8%; pH 5–98.3%; 5 g/L, pH 4–99.4%, pH 5–99.8%), nitrogen-modified TK6MAF1/2 (dosage 3.5 g/L, pH 4–98.2%, pH 5–99.3%; 5 g/L, pH 4–99.4%, pH 5–99.8%). It is not advisable to further increase the dose of sorbents at different pH, as the optimal values of the process at the highest level have already been obtained. As can be seen, modification with nitrogen did not significantly improve Cu(II) adsorption, and it can be concluded that the results are comparable. Furthermore, the highest adsorption capacity was achieved at pH 4 and 5 for dosage 3.5 g/L (2.86–2.94 mg/g). Above this dose, sorption capacity tended to decrease (Figure SM3). This phenomenon can be associated with larger specific surface area of AC, which resulted in better removal of Cu(II) ions. Higher metal removal rates are associated with lower sorption capacity. This can be explained by the fact that some active sites are still unsaturated during the adsorption process. However, increasing the AC dose increased the number of active sites, initiating an increase in the efficiency of the adsorption process until the optimum was reached. A further increase in the adsorbent dose was not necessary as it did not affect the adsorption process. These observations are in line with others previously published in the literature (Saif et al. 2015; Ramesh et al. 2005).

Effect of initial concentration of Cu(II)

The influence of initial concentration of Cu(II) ions on sorption efficiency was studied, and the results are presented in Fig. 11 and Figure SM4. The research was performed under the following conditions based on the previous results: adsorbent dosage 5 g/L, initial concentration of Cu(II) ions (2.0–100 mg/L), initial pH 5.0, contact time 60 min, agitation speed 200 rpm, T = 23 °C. In the initial concentration range of 2–10 mg/L, adsorption efficiency was achieved in the range of 80 to 90%.
Fig. 7  Thermogravimetric curves of the AC (TK6AF1/2)

Fig. 8  Thermogravimetric curves of the nitrogen-enriched NMAC (TK6MAF1/2)

Fig. 9  SEM images of AC (scale bar: 20 μm): a TK6AF12, b TK6MAF12
A further increase in the initial concentration up to 100 mg/L resulted in a gradual reduction in adsorption efficiency, with lower values obtained for nitrogen-modified carbon. However, as initial concentration increased from 2 to 60 mg/L, an increase in adsorption capacity was noted. The maximum values are as follows: TK6AF1/2 \((C_e = 60 \text{ mg/L}, \ q_e = 11.98 \text{ mg/g})\), TK6MAF1/2 \((C_e = 42.5 \text{ mg/L}, \ q_e = 9.31 \text{ mg/g})\). At concentrations above 60 mg/L, a gradual decrease in sorption capacity was observed to the value of 2.4 mg/g (100 mg/L).

**Effect of initial pH**

The effect of initial pH on the adsorption efficiency and adsorption capacity was analyzed, and the results are shown in Fig. 12 and Figure SM5 (supplementary material). The following experimental conditions were used in these studies: initial concentration of Cu(II) ions 10.0 mg/L, AC dosage 1.5–5.0 g/L, initial pH 2–5, contact time 60 min, agitation speed 200 rpm, \(T = 23 \degree C\). The lowest adsorption efficiency was observed at lower initial pH 2—3. Only above initial pH 3 there was a significant improvement in adsorption and the best results were recorded at pH 4–5. Maximum efficiency was reported for the following AC doses: TK6AF1/2: 3.5 g/L (pH 4–98.8%, pH 5–98.3%), 5 g/L (pH 3–99.9%, pH 4–99.9%, pH 5–99.9%); TK6MAF1/2: 3.5 g/L (pH 4–98.2%, pH 5–99.3%), 5.0 g/L (pH 4–99.4%, pH 5–99.8%). The binding of Cu\(^{2+}\) ions in the aqueous solution could be accompanied by a cation exchange mechanism. The influence of initial pH on adsorption may be related to the charge distribution of the carbon surface groups and the overall proton equilibrium. Hence, each type of oxygen surface group (neutral, protonated or deprotonated) plays a significant role in the overall adsorption process. The decrease in adsorption at lower initial pH may be caused by the competition of Cu\(^{2+}\) ions with hydronium ions, the concentration of which is much higher in acidic solutions. In this case, electrostatic repulsion interfered with the adsorption of positively charged

![Fig. 10 Effect of AC dosage on adsorption efficiency of Cu(II) ions: TK6AF1/2 (a), nitrogen-modified TK6MAF1/2 (b)](image-url)
copper ions. When initial pH increased to 3—4, the surface of AC sorbents became more negatively electrostatically charged. There was a deprotonation of functional groups, which translated into an increase in electrostatic affinity and the initiation of ion exchange, which resulted in the binding of more copper ions (Chen et al. 2022; Gao et al. 2018).

**Effect of contact time**

The effect of contact time on the adsorption process was also analyzed, and the research results are shown in Fig. 13 and Figure SM6. Based on the previously performed research, the following experimental conditions were proposed in these studies: contact time 15–180 min, initial concentration of Cu(II) 10 mg/L, initial pH 2.4, AC dosage 1.5 and 2.5 g/L, agitation speed 200 rpm, \( T = 23 \, ^{\circ}\text{C} \). In case of the adsorbent dose of 1.5 and 2.5 g/L, the equilibrium of the adsorption process was properly established during the first 30–90 min of shaking for both AC samples. As can be seen from Fig. 13, it was not necessary to conduct further experiments over a longer period of time, as the adsorption efficiency remained at the same level.

**Analysis of adsorption kinetics**

In the present study, kinetics analysis of the Cu(II) removal was investigated. Pseudo-first-order (PFO) and pseudo-second-order (PSO) models were applied to better understand the sorption processes. The calculated parameters are presented in Table 5, and the kinetic plots are attached as supplementary files (Figures SM7–SM14). The equilibrium of the adsorption process was achieved after about
30 min. According to the calculated kinetic parameters, it can be concluded that the Cu(II) ion adsorption process on AC samples fits better into the pseudo-second reaction model. This kinetic model indicates possible ion exchange and sharing of electrons between copper ions and the surface of activated carbons. During the adsorption process, diffusion and ion exchange could occur. Copper ions could be electrostatically attracted by the active sites of the AC surface. As a result, the phenomenon of adhesion to the surface of AC materials and the formation of chemical bonds took place.

Analysis of adsorption isotherms

Langmuir and Freundlich isotherms were used to analyze the adsorption processes of Cu(II) ions. The calculated parameters are shown in Table 6, and isotherms are enclosed as supplementary material (Figures SM15–SM18). In accordance with the obtained data, it should be stated that higher correlation coefficients $R^2$ were obtained in case of Langmuir model. Thus, the research results comply with the isotherm model. Similar results were obtained by other researchers and are published in the literature (Saif et al. 2015; Chen et al. 2022; Demiral and Güngör 2016; Shu et al. 2017; Teker et al. 1999; Zheng et al. 2018). Based on the Langmuir equation, adsorption capacity for TK6AF1/2 and nitrogen-modified TK6MAF1/2 is equal to 12.07 and 11.30 mg/g, respectively. Sorption capacity of examined AC materials for the removal of Cu(II) ions was compared to other selected sorption materials and is shown in Table 7.

Mechanism of Cu(II) ion adsorption

On the AC surface, there are several functional groups that may participate in the metal ion binding mechanism (Fig. 1). Among them there are $>\text{C} = \text{C}$ unsaturated

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**Fig. 12** Effect of initial pH on adsorption efficiency of Cu(II) ions with AC: TK6AF1/2 (a), nitrogen-modified TK6MAF1/2 (b)
bonds that bind oxygen during oxidation processes, forming surface oxygen groups such as acid and basic groups. The acid groups are polar and exist in the form of carboxyl and lactone groups, while the basic groups exist in the form of quinone groups. If AC is placed in aqueous solution, acidic surface groups ionize to form $\text{H}^+$ ions according to the following equation:

$$ > \text{C}–\text{COOH} \rightarrow > \text{C}–\text{COO}^- + \text{H}^+ $$  \hspace{1cm} (7)

When $\text{H}^+$ ions pass into aqueous phase, they leave places with negatively charged $>\text{C}–\text{COO}^-$ groups on the carbon surface. This leads to competition for available active sites on the AC surface, between $\text{H}^+$ ions and $\text{Cu}^{2+}$ ions in the solution. An oxidation process increases the number of free spots and negatively charged groups on the AC surface, which translates into more effective adsorption of $\text{Cu}^{2+}$ ions on oxidized carbons. In turn, the annealing process (in gradually increasing temperature) causes disappearance and elimination of acid groups from the AC surface, which results in a decrease in the number of negatively charged places with $>\text{C}–\text{COO}^-$ groups, which reduces the adsorption of Cu(II) ions. Almost complete disappearance of oxygen groups is observed after reaching the annealing temperature at 950 °C. Then, the AC surface loses its negatively charged character and sometimes becomes positively charged, which causes a repulsion between Cu(II) ions and the AC surface, as a result of a decrease in the adsorption of copper ions (Bansal and Goyal 2005).

**Conclusions**

Activated carbons AC (TK6AF1/2) and nitrogen-modified activated carbons NMAC (TK6MAF1/2) were examined for the removal of Cu(II) ions from aqueous solutions. The materials were obtained as a result of pine wood sawdust carbonization process at a temperature of 600 °C followed by physical activation at 800 °C. Nitrogen enrichment was realized by reaction with urea at 300 °C.

![Fig. 13](image.png)  
Fig. 13 Impact of contact time on the Cu(II) ions adsorption efficiency (adsorbent dosage: 1.5 and 2.5 g/L)
Firstly, sorbent materials prepared in this way were analyzed in terms of their physicochemical properties. Secondly, adsorption processes of Cu(II) ions were carried out in many experiments, taking into account the effect of selected parameters on the processes, including initial pH, initial concentration of Cu(II) ions, adsorbent dosage and contact time. It was revealed that adsorption efficiency for both TK6AF1/2 and nitrogen-modified TK6MAF1/2 was comparable. Maximum adsorption efficiency was equal to 99.9% and 99.8% for TK6AF1/2 and TK6MAF1/2, respectively, under the following conditions: adsorbent dosage 5 g/L, initial pH 5, initial concentration of Cu(II) ions 10 mg/L, contact time 60 min, T = 23 °C, agitation speed 200 rpm. Thirdly, studies on adsorption kinetics and isotherms were investigated. Based on the analysis, it was reported that pseudo-second-order kinetic model and Langmuir isotherm model fit better with the studied adsorption processes. The calculated maximum sorption capacity was equal to 12.07 and 11.30 mg/g for TK6AF1/2 and TK6MAF1/2, respectively.

To conclude, it should be emphasized that under certain experimental conditions, the AC materials obtained as a result of physical activation of pine wood sawdust exhibit high adsorption efficiency of removing Cu(II) ions from aqueous solutions. The use of pine wood sawdust waste from the wood industry for carbonization and activation processes and then for removing metals from wastewater is fully justified and fits well with the current pro-ecological trends. Water purification and improvement of its quality with the use of analyzed processed waste are part of the area of sustainable development and circular economy.

A literature review revealed research gaps related to the removal of metal ions with the use of pine wood sawdust pellets after carbonization. Hence, these materials require further research and many experiments. Future research could be to carry out copper and other metal adsorption processes at different temperatures in a dynamic flow, to study metal ion competition, to perform regeneration to reuse the adsorbents,

| Adsorbent   | Adsorbent dosage (g/L) | PFO model | PSO model |
|-------------|------------------------|-----------|-----------|
|             | $k_{ad}$ (min$^{-1}$)  | $q_e$ (mg/g) | $R^2$ | $k$ (g/mg min) | $q_e$ (mg/g) | $R^2$ |
| TK6AF1/2    | 1.5                    | 0.017      | 0.724     | 0.864 | 4.065 | 1.086 | 0.977 |
| TK6AF1/2    | 2.5                    | 0.041      | 0.410     | 0.965 | 9.721 | 0.702 | 0.996 |
| TK6MAF1/2   | 1.5                    | 0.011      | 0.979     | 0.791 | 1.932 | 1.575 | 0.995 |
| TK6MAF1/2   | 2.5                    | 0.043      | 1.332     | 0.948 | 73.887 | 0.255 | 0.980 |

| Adsorbent   | Adsorbent dosage (g/L) | Langmuir isotherm | Freundlich isotherm |
|-------------|------------------------|-------------------|---------------------|
|             | $q_m$ (mg/g) | $K_L$ (L/mg) | $R^2$ | $K_f$ (mg/g) | ($L/mg$)$^{1/n}$ | $n$ | $R^2$ |
| TK6AF1/2    | 2.5        | 12.07      | 0.234     | 0.998 | 2.066 | 1.645 | 0.961 |
| TK6MAF1/2   | 2.5        | 11.30      | 0.232     | 0.998 | 1.961 | 1.607 | 0.947 |
to conduct studies on realistic wastewater, as well as to estimate the cost of entire processes on a laboratory and industrial scale. Adsorption studies should additionally be performed under realistic conditions as competing ions may reduce or increase the yield of the adsorbents. Research may focus on understanding the factors influencing adsorbent reuse to estimate adsorbent lifetime. Reusing the same adsorbents is of environmental and economic importance.

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Declarations

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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| Adsorbents                                      | pH | q<sub>max</sub> (mg/g) | References                        |
|------------------------------------------------|----|------------------------|-----------------------------------|
| TK6AF1/2                                        | 5  | 12.07                  | This study                        |
| TK6MAF1/2                                       | 5  | 11.30                  | This study                        |
| Waste wood-based panels derived AC              | 5  | 25.04                  | Chen et al. (2022)                |
| OAC                                             | 5  | 53.99                  | Chen et al. (2022)                |
| IDA-OAC                                         | 5  | 83.75                  | Chen et al. (2022)                |
| IRC86 cation-exchange resin                     | 5  | 47.21                  | Chandramohan and Marinimuthu (2011) |
| PN-Fe3O4-IDA                                    | 5  | 47.66                  | Aryee et al. (2020)               |
| PEI-WS                                          | 6  | 52.2                   | Dong et al. (2019)                |
| PVDF-g-G3 PAMAM membrane                        | 5  | 153.8                  | Sun et al. (2021)                 |
| GO-IDA                                          | 6.5| 108.4                  | Pytlakowska et al. (2018)         |
| Fe3O4@SiO2-EDTA                                 | 5.3| 36.86                  | Liu et al. (2016)                 |
| SBA-TETA                                        | 4  | 23.9                   | Lachowicz et al. (2019)           |
| AC derived from pine cones of *Pinus roxburghii* | 5  | 48.54                  | Saif et al. (2015)                |
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