Preparation and use of activated carbon based on *Pinus nigra* cones

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Research Article

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Abstract

Water pollution caused by inorganic and organic compounds is one of the most important challenges worldwide. In recent years, the use of alternative precursors for AC preparation has gained attention. The study highlights *Pinus nigra* cone–derived microwave-activated carbons as promising and sustainable adsorbents for the treatment of complex wastewater matrices containing co-occurring pharmaceuticals and heavy metals.

In this work, five samples of carbon based on *Pinus nigra* (PN) cones (PN-P, PN-NaOH, PN-Na_2CO_3, PN-KOH, and PN-K_2CO_3) were prepared and tested for the removal of pharmaceuticals (metformin, caffeine, telmisartan) and heavy metals (copper (II), cadmium (II), lead (II)) from water.

1 Introduction

Contamination of ground and surface waters is a serious problem worldwide. The water can be contaminated by various inorganic substances (such as heavy metals, nitrates, and phosphates) and organic substances (including pharmaceuticals, pesticides, or dyes). The presence of these contaminants in water resources can pose a threat to both the environment and human health.

Many methods are investigated to improve wastewater treatment for the removal of hazardous compounds; adsorption on activated carbon (AC) is one of the most popular due to its sustainability and high effectiveness [1].

In recent years, the preparation of activated carbon from various biomass-based alternative precursors has been investigated [2–7]. *Pinus nigra* is commonly chosen for activated carbon production, especially from its cones, due to its abundant availability as a forestry by-product in Central Europe, low cost, and advantageous physicochemical properties that produce high-performance adsorbents [8]. The cones naturally contain a high percentage (around 50%) of carbon, providing a solid foundation for carbonization. Moreover, their lignin content, ranging from 25% to 39%, enhances the structural integrity and forms a stable char matrix during pyrolysis, which facilitates the development of microporosity upon activation [9, 10]. Chemical activation influences the dense, lignocellulosic structure of the cones to produce activated carbons with high surface areas [11] and remarkable adsorption capacities for dyes such as methylene blue and malachite green, as well as organic pollutants like BTEX and bisphenol A. Several studies have also shown the effective removal of heavy metals, including Pb^{2+} and Cu^{2+}, using pine-derived activated carbons [12–15]. These qualities, combined with sustainability and regional abundance, make *Pinus nigra* cones an eco-friendly, preferred feedstock for large-scale activated carbon production.

Pharmaceuticals are widely present in water resources; therefore, their potential exposure to humans and other living organisms is of interest [16]. Long-time exposure to contaminated water can lead to numerous health problems [17]. Metformin is an anti-hypoglycaemic drug and cancer suppression medicament used worldwide. Caffeine is a central nervous system stimulant of natural origin that occurs in approximately 60 plant species and is contained in coffee or tea and several pharmaceutical products [18]. Telmisartan is an antihypertensive whose presence in water can cause severe allergic reactions, difficulty in breathing, depression, or vision problems in human bodies after prolonged exposure [19]. Heavy metal contamination also poses serious environmental hazards. Unlike organic pollutants, heavy metals are difficult to degrade into environmentally friendly substances by biodegradation [20]. Their presence in water leads to their accumulation in organisms, which presents a danger for these organisms and potentially for human health [20–22]. Copper (II) enters the water environment mainly from household plumbing systems, roofing, or its alloys [23, 24]. The main source of cadmium (II) in water is various chemical industries (metal refineries, pigment manufacturing) [23, 25]. Lead (II) ions main sources in water are the chemical industry, smelting, or lead-containing water pipes [26, 27].

Most of the published works on pharmaceutical adsorption are conducted using single-component solutions, while only a minority address binary or multicomponent systems. Even at the environmental level, monitoring data typically report individual or pairwise occurrences of contaminants. Furthermore, a minority of the published studies are focused on the effect of the choice of an activating agent on the adsorption properties, and there is a lack of studies focused on the effect of activating agent selection on the competitive adsorption from multicomponent solutions. Therefore, we decided to investigate the effect of the activating agent selection on the textural properties of microwave-assisted *Pinus nigra* cones-based activated carbon, as well as on their adsorption efficiencies and selectivity in mixtures of contaminants. In this work, five samples of *Pinus nigra* cone-based microwave-assisted ACs were prepared and tested for the remediation of two mixtures: one of pharmaceuticals (metformin, caffeine, telmisartan) and another one of heavy metals (copper (II), cadmium (II), and lead (II)).

2 Materials and methods

2.1 Preparation of microwave-assisted activated carbons

Cones fallen from the *Pinus nigra* trees were collected in Ostrava, Czech Republic (49.838145N, 18.162228E). The cones were crushed, sieved and mixed with an activation agent and carbon. The carbon was prepared conventionally in a nitrogen atmosphere and served for the adsorption of microwaves. After mixing, the sample was placed into the quartz flask and rinsed with a nitrogen flow before the start of the radiation. After the microwave irradiation, the material was cooled in a nitrogen flow. The prepared carbonaceous material was washed with diluted HCl, hot demineralized water, and cold demineralized water to a stabilized neutral pH. Finally, the sample was dried to constant weight.

The prepared activated carbons were labelled PN-NaOH, PN-Na_2CO_3, PN-KOH, and PN-K_2CO_3, respectively, based on the activation agent used. The sample prepared without any activation agents was marked PN-P.

2.2 Characterization of prepared ACs

The mass concentration of the pyrolysis products (carbonaceous solids PN-C, liquid condensate PN-L and pyrolysis gas PN-G) was calculated using Eq. 1, with PN-G serving as the balancing component to reach a total yield of 100%.

PN-G = 100% – (PN-C + PN-L) (1)

Nitrogen physisorption was conducted using a 3Flex instrument (Micromeritics, USA). The nitrogen adsorption-desorption data were modeled using the Brunauer–Emmett–Teller (BET) theory to determine the specific surface area, SBET (m^2/g) [28]. The t-plot [29] and the BJH [29, 30] methods were employed on the adsorption branch of the isotherm using the Carbon Black STSA standard isotherm and assuming cylindrical-pore geometry to obtain the mesopore surface area (S(meso), m^2/g) and the mesopore-macropore size distribution.

A scanning electron microscope (SEM) Tescan Vega (TESCAN, Czech Republic) with a tungsten cathode was employed for the microscopic examination of the biochar. Microphotographs were obtained in secondary electron (SE) and backscattered electron (BSE) mode. Before imaging, the samples were sputtered with gold to ensure adequate electron conductivity.

The FTIR spectra of the biochars were obtained using a Thermo Scientific Nicolet iS10 FTIR Spectrometer (Thermo Scientific, USA). The measurements were conducted within the range of 500–4000 cm^{-1} with a resolution of 2 cm^{-1} in ATR mode. Each sample spectrum was subsequently ratioed.

The zeta potentials of the samples were measured using a Malvern Zetasizer Ultra (Malvern Instruments Ltd., Worcestershire, UK). Before each analysis, the solid sample was dispersed in deionized water by ultrasonication. The dispersed sample was placed in a sample container, which was then attached to an MPT-3 Multi-purpose titrator and titrated.

2.3 Adsorption of pharmaceuticals on *Pinus nigra* cones-based AC

Pure standards of metformin hydrochloride (Sigma Aldrich, USA), caffeine (Sigma Aldrich, USA), and telmisartan (Merck, Germany) were used in this work. First, the solutions of a concentration of 1 mg L^{-1} were prepared. Then, the equimolar solution of all three substances was mixed up. The mixed solution was put into Erlenmeyer flasks, mixed with AC, and shaken on a laboratory shaker (Standard Analog Shaker, Model 3500, agitation speed 200 rpm, VWR, Radnor, PA, USA). The solution was collected in different periods, filtered through mixed cellulose ester (MCE) membrane filters (0.45 µm, Macherey-Nagel GmbH, Germany) and analysed using liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS; Nexera XL series HPLC instrument (Shimadzu, Japan) coupled to a QTRAP 6500 + mass spectrometer (Sciex, USA) with an electrospray ionization source).

2.4 Adsorption of heavy metals on *Pinus nigra* cones-based AC

Single-component solutions of $CuSO_4 \cdot 5H_2O$ (PENTA, Czech Republic), $CdSO_4 \cdot 8/3H_2O$ (VWR, USA), and $PbNO_3$ (PENTA, Czech Republic) were prepared and used as the source solutions for an equimolar ternary solution of Cu (II), Cd (II), and Pb (II). Then, the ternary solution was mixed with AC for different periods, and the volume of 5 mL for each heavy metal was filtered through nylon membrane filters (0.45 μm, Labicom, Czech Republic) and analysed using an atomic absorption spectrometer (AAS) contrAA 700 (Analytik Jena, Germany).

3 Results and discussion

3.1 Characterization of prepared ACs

Three distinct pyrolysis products were identified: carbonaceous solid (PN-C), liquid condensate (PN-L), and pyrolysis gas (PN-G). Figure 1 shows the mass balance for *Pinus nigra* cones with different activating agents.

The SEM images (Fig. 2) reveal that the structures of PN-KOH and PN-K_2CO_3 are considerably more disrupted than those of PN-P, PN-NaOH, and PN-Na_2CO_3. Sodium-based activators are milder than potassium-based ones; therefore, their use does not lead to extensive structure cracking.

The FTIR analysis revealed no significant structural differences between the adsorbents. In Fig. 3, it can be seen that these are mainly less intense and broader peak bands, suggesting that this will be a rather amorphous material [31].

3.2 Competitive adsorption of pharmaceuticals

During the process of drug adsorption, metformin demonstrated the most rapid rate of adsorption on potassium-based activated carbon. PN-NaOH had a significantly slower initial rate of adsorption than PN-KOH, PN-K_2CO_3, and PN-Na_2CO_3. The adsorption rate of PN-P was much slower than that of activated adsorbents.

Caffeine was effectively removed by all four samples of AC prepared with an activator. PN-KOH showed slightly poorer adsorption behaviour compared to PN-NaOH, PN-Na_2CO_3, and PN-K_2CO_3. Similarly to the case of metformin, PN-P had by far the worst adsorption properties.

The trends between the telmisartan adsorption performances of the studied carbons were very similar to those of caffeine; both materials activated with sodium-based agents reached equilibrium much faster than PN-K_2CO_3 and PN-KOH. Unlike in the previous two cases, the adsorption properties of PN-P were comparable with those of activated adsorbents.

3.3 Competitive adsorption of heavy metals

The order of adsorption efficiencies for the studied metals is PN-Na_2CO_3 > PN-KOH > PN-K_2CO_3 > PN-NaOH > PN-P. Two materials, namely PN-Na_2CO_3 and PN-KOH, were selected for the time-dependent adsorption studies. The adsorption performances of both adsorbents were similar for Pb (II) removal and only slightly different for Cu (II) and Cd (II) removal.

Cu (II) and Pb (II) cations were removed much more efficiently than Cd (II); the removal efficiency of both Pb (II) and Cu (II) at given condition exceeded 80%, whereas only about 10–15% Cd (II) was removed.

4 Conclusion

Five samples of microwave-assisted activated carbon prepared from *Pinus nigra* cones were studied for the adsorption of pharmaceuticals and heavy metals from water. One sample was prepared without activating agents (PN-P), and the other four were prepared with activating agents mentioned in their names (PN-NaOH, PN-Na_2CO_3, PN-KOH, PN-K_2CO_3). The adsorbents were used for the competitive adsorption from the mixtures in order to assess the effect of the choice of an activating agent on the adsorption efficiency a selectivity.

Metformin was most efficiently removed by PN-KOH and PN-K_2CO_3 samples, caffeine and telmisartan were best attached to PN-NaOH, PN-Na_2CO_3, and PN-K_2CO_3. The carbons PN-Na_2CO_3 and PN-KOH showed the best performance in the removal of Cu (II), Cd (II), and Pb (II). Pb (II) and Cu (II) were attached in preference to Cd (II) on all studied activated carbons.

Declarations

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Ultra.

Data availability

Open research data will be available on Zenodo in the final version of the manuscript.

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Figures

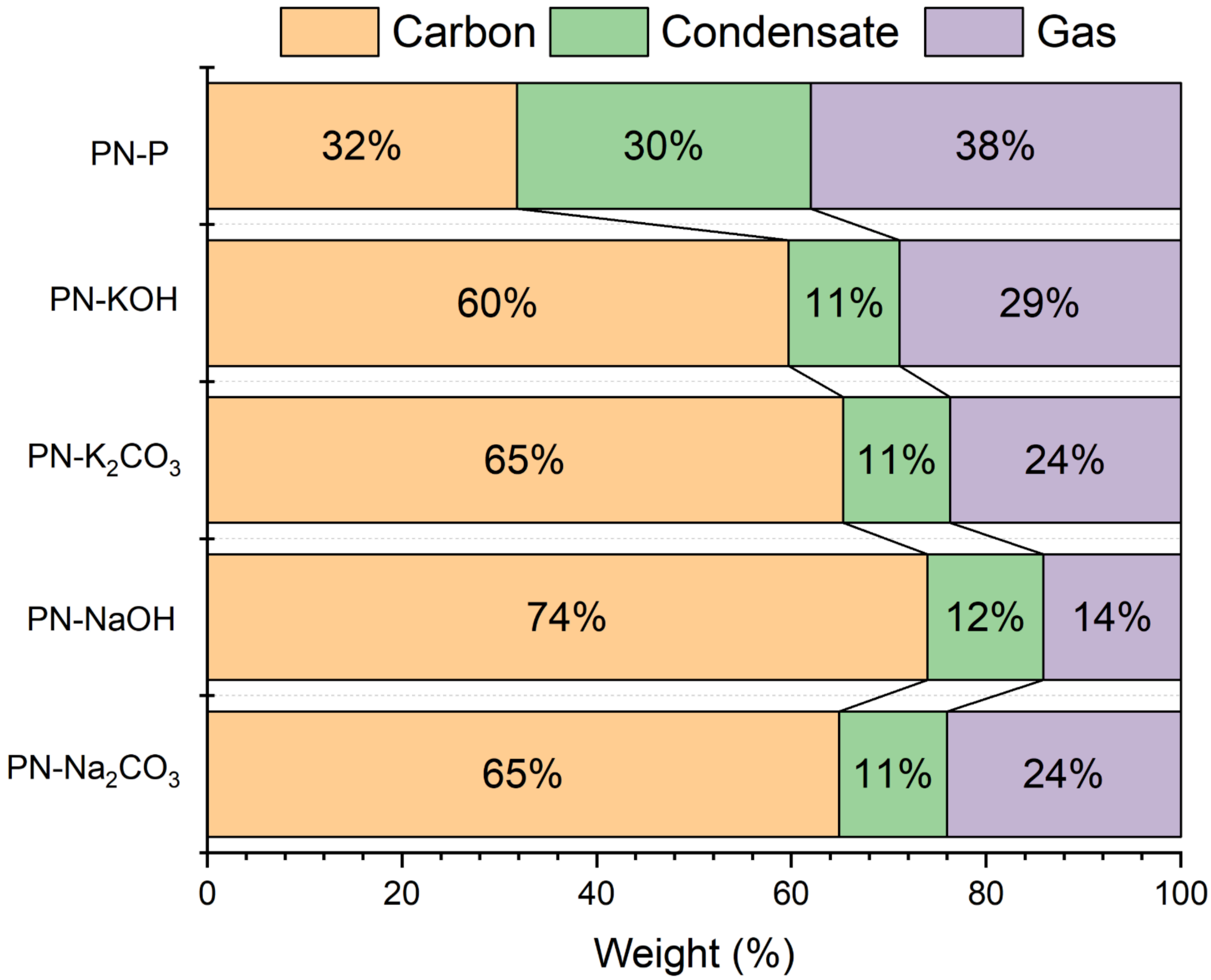

Figure 1

The PN-C : PN-L : PN-G ratios of prepared ACs

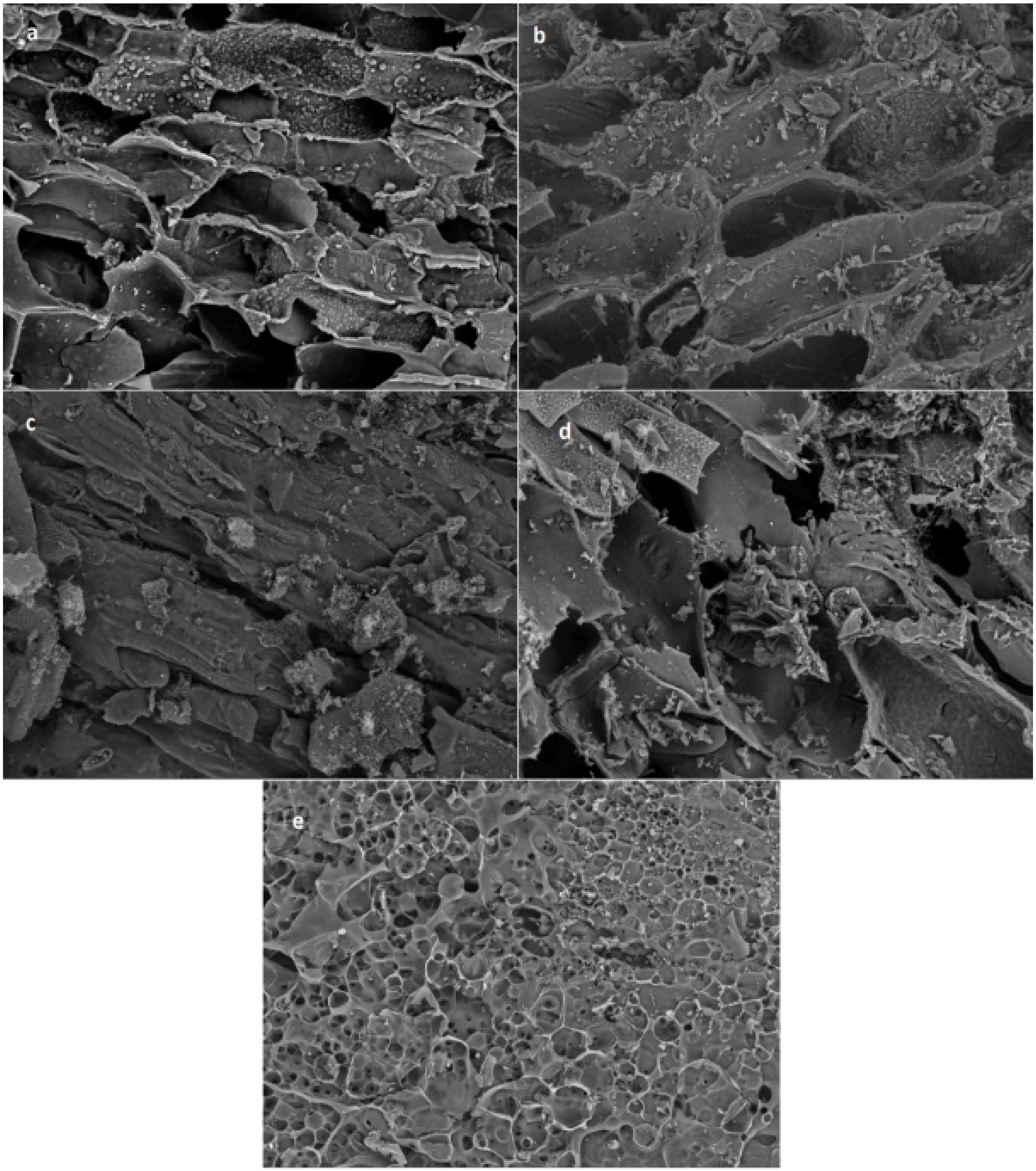

Figure 2

SEM images of prepared activated carbons (a) PN-P, b) PN-NaOH, c) PN-Na_2CO_3, d) PN-KOH, e) PN-K_2CO_3

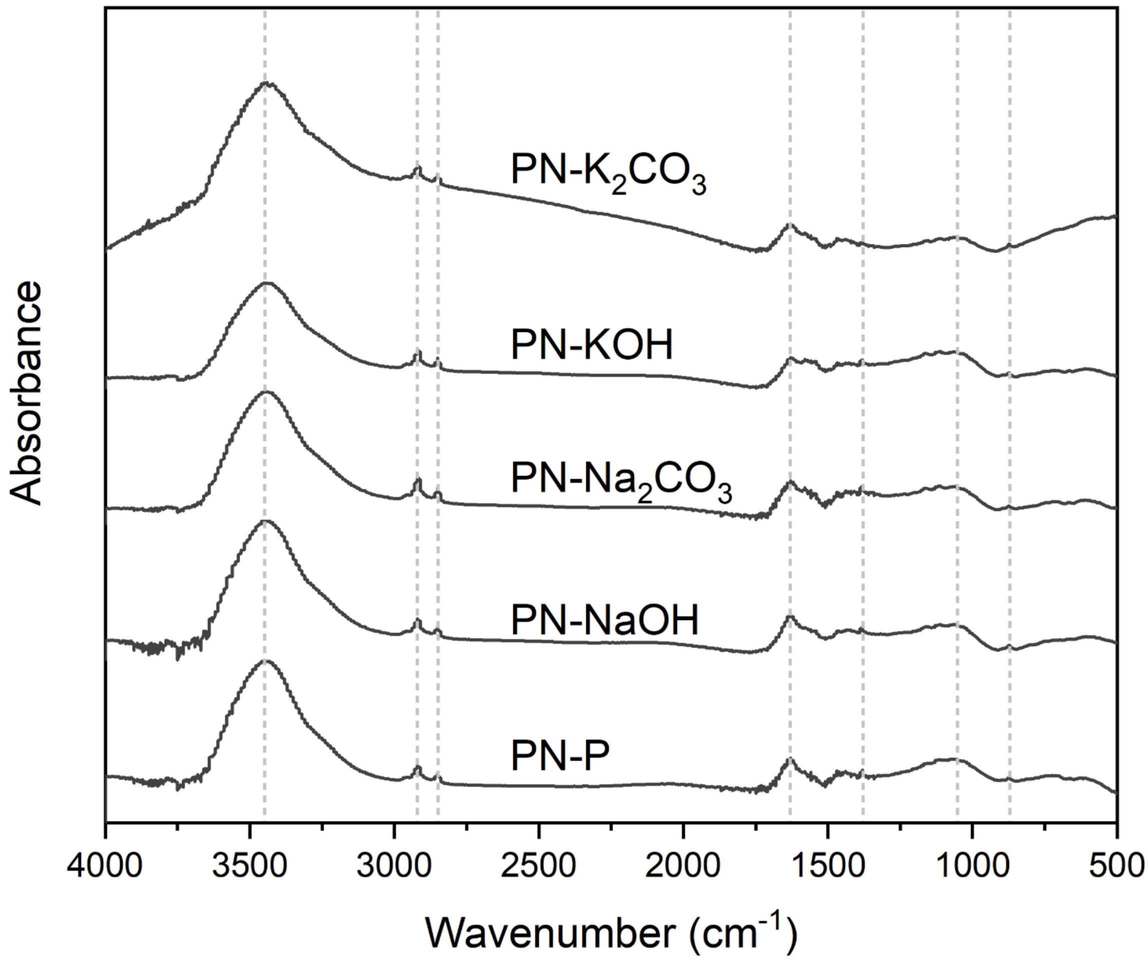

Figure 3

FTIR spectra of the prepared activated carbons