



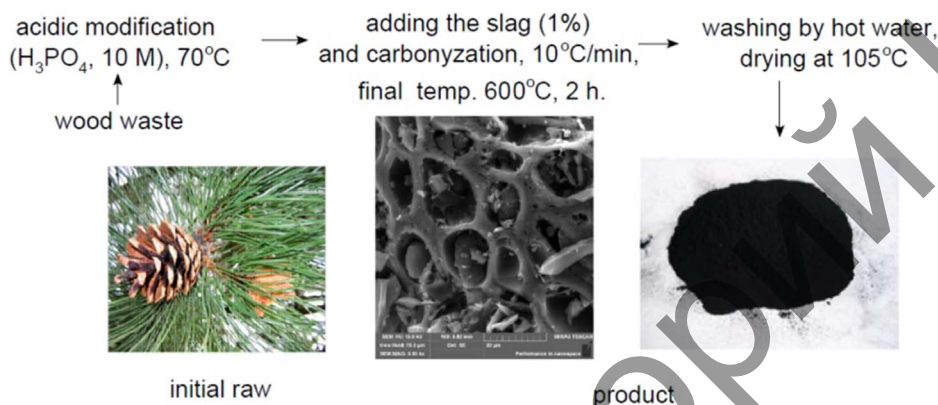
The active carbons modified by industrial wastes in process of sorption concentration of toxic organic compounds and heavy metals ions



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GRAPHICAL ABSTRACT



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ABSTRACT

The results of investigation of active carbons, obtained from the pine waste (lat. *Pinus sylvestris*) by modifying phosphoric acid and industrial (metallurgical slag) wastes, are discussed. The structure, composition and properties of obtained sorbent have been investigated by using FT-IR-spectroscopy, elemental analysis, DTA/TGA, SEM. The iodine adsorption activity and adsorption values toward to some inorganic and organic pollutants of sorbent have been evaluated. Based on laboratory test results, it was established that the sorbent on the base of activated carbons prepared by chemical modification, followed by carbonization in the presence of metallurgical slag and water treatment, has a porous structure. It was shown that sorbent can be used in the processes of sorption concentration of phenol, chloroform, pyridine, aniline, and also heavy metals ions from aqueous solutions.

1. Introduction

Activated carbon fiber materials and wastes of energy sector (ash and slag) have a well-developed porosity, specific surface area, as well as combination of high filtration and sorption-kinetic properties. A large number of active carbon materials have been studied including

wood chemical waste and secondary raw materials (energy sector waste) [1–5]. Specifically, activated carbons derived from pine waste (lat. *Pinus sylvestris*), have specific applications as sorbents for chlorine-, nitrogen- and oxygen-containing organic compounds and heavy metal ions. Moreover, it has been demonstrated that these materials exhibit a high degree of purification in comparison with known sorbents such as

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sorbents based on sawdust [1], activated carbon (also referred to as Sigma C-3014) [6], coconut coir and sugarcane bagasse [7].

The aim of this work is the synthesis and characterization of activated carbons, specifically, activated carbons obtained from pine waste (lat. *Pinus sylvestris*). Specifically, activated carbons were produced by the chemical modification of phosphoric acid and industrial (metallurgical) wastes, owing to their subsequent applications in the process of sorption concentration of chlorine-, nitrogen- and oxygen-containing organic compounds and heavy metal ions. The novelty of this material is significant because of application of wood (pine) wastes after chemical modification and carbonization in the presence of metallurgical slag.

2. Synthesis and experimental

2.1. Chemicals, reagents and materials

The wood pulp ($d = 0.5\text{--}2.0$ mm), obtained from the pine waste (lat. *Pinus sylvestris*), was used as a raw material, with 8% moisture and 12.2% of volatile substances. All the reagents (phenol, chloroform, pyridine, aniline, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, KI, $\text{Na}_2\text{S}_2\text{O}_3$, NaOH, HCl and H_3PO_4) used were of analytical grade or better. In order to avoid contamination during the chemical reactions, distilled water was used throughout the synthesis.

2.2. Preparation of sorbent

Pine waste was impregnated by a solution of 10 mol L^{-1} of orthophosphoric acid by constant stirring at a temperature of 70°C . The weight ratio of initial mass to modifying agent was 1:5. The material slurry was then subjected to evaporation until the wet residue was left. To this residue, metallurgical (1% by weight of the sorbent) was added, thermal treatment at the temperature range: $300\text{--}600^\circ\text{C}$ with holding the sorbent at final temperature for 120 min. After temperature treatment, the obtained carbonized material was washed with hot distilled water heated to 90°C (3 times), then dried at 105°C . Then obtained product (active carbons) was used as sorbent in adsorption tests.

2.3. Experimental characterization of sorbent

Elemental analysis (C, H and O) of the activated carbons was carried out on the Perkin Elmer 240 °C Elemental Analyzer. X-ray fluorescence analysis of the samples was carried out on the X-ray fluorescence analyzer Olympus Delta XRF Innov-X Systems. Electron microscopic images of the sorbents were taken on the scanning electron microscope Mira 3 Tescan at 25–2000 times magnification.

Fourier transform infrared (FT-IR) spectroscopic measurements were carried out by using on a FSM 1201 FTIR spectrometer operating at frequency range between 4000 and 400 cm^{-1} . For FTIR measurements, the sorbent samples were placed in KBr pellets.

Thermal analyses (TGA and DTA) analyses were performed on the Labsys DTA/DSC device. The solid sorbent samples were placed in an aluminum sample holder and then heated from 32°C to 1000°C in steps of $10^\circ\text{C min}^{-1}$ in the presence of N_2 atmosphere.

For determining the total pore volume, the sorbent was filling of pores by water at boiling a sample of active carbons in water and removing excess water from the grain surface by aspiration using water jet pump. The common porosity (%) is defined as the ratio of the total pore volume to the volume of the active carbons sample. The total pore volume (V_Σ) in $\text{cm}^3 \text{ g}^{-1}$ is calculated by the formula:

$$V_\Sigma = \frac{m_1 - m}{m \cdot \rho} \quad (1)$$

where m is the mass of active carbons in dry state, g; m_1 is the mass of wet coal, g; ρ is the density of water, $\text{g} (\text{cm}^3)^{-1}$. The error of determination is not more than $\pm 0.7\%$.

Adsorption isotherms were determined at the temperatures 25 and 45°C by using stoppered flasks containing 1.0 g of activated carbon dissolved in 30 mL of solution. The solutions of HCl (2.88 mol L^{-1}) and NaOH (2.77 mol L^{-1}) were used to control the pH of the solutions. Initially, activated sorbent was immersed in an aqueous solution (pH 3, 4, 7, 8, 9) of the sorbate, with a concentration of (1, 3, 5 mg L^{-1} in the case of organic compounds, and $20\text{--}100 \text{ mg g}^{-1}$ for the inorganic toxicants). Then, this mixture in a container was thermostated for 60 min with constant stirring until equilibration. Then this solution was filtered.

The residual concentration of Fe(III), Co(II), Ni(II) ions was determined by atomic absorption spectroscopy by using Varian AA140 spectrometer. The concentrations of the organic compounds adsorbed by the sorbent were determined by liquid chromatography method coupled with mass spectrometry (LCMS Agilent 7890A). Specifically, for the case of phenol, the determination of the residual concentration after adsorption was carried out by using common spectrophotometric method at $\lambda = 420 \text{ nm}$, the 4-aminoantipyrine was used as a light-substance.

1.5 g of active carbons was being shaken into 100 mL of 0.1 mol L^{-1} solution of potassium iodide (KI) for 45 min for determination of iodine number. Iodine concentration was determined by titration with 0.1 mol L^{-1} sodium thiosulphate ($\text{Na}_2\text{S}_2\text{O}_3$), with using a starch solution as an end-point indicator. The iodine number equals to the adsorbed amount of iodine in%.

In order to evaluate the accuracy and reproducibility, the aforementioned experimental measurements were carried out repeatedly for at least three times. All values stated in this paper are the mean values taken over three readings, with a standard deviation, S_x , does not exceeding ± 0.05 .

3. Results and discussion

3.1. Composition, surface morphology and structural aspects of sorbent

Sorbent samples were prepared by chemically activating pine waste with 10 mol L^{-1} orthophosphoric acid for two hours at the temperature range between 300 and 600°C . Orthophosphoric acid is a widely used as a pore-forming agent, that stimulates carbonization reactions usually occur at much lower temperatures than standard pyrolysis, essentially by consisting – radical processes resulting in disproportionation reactions and tar formation [8]. Followed by a 2-h carbonization reaction, the sorbent had been subjected to high-temperature water treatment by washing the material three times with hot (heated to 90°C) water. As a result of the above steps the following changes have been taken place: (i) formation of carbon mass with a characteristic porous structure, (ii) delicate surface morphology and texture, (iii) reduced process time, temperature drop and losses for gasification. Specifically, during the carbonization of the sorbent material at the temperature range between 300 and 600°C , porous sorbent structures are formed enabling the material to capturing specific organic compounds and exchanging cations and ions depending on the size and shape of the porous structure of the sorbent. In the present study, the metallurgical slag added to carbon mass was a solid powder ($\pm 0.074 \mu\text{m}$), the elemental composition of which is presented in Table 1.

Elemental analyses suggest that the composition of chemically modified active carbon by using orthophosphoric acid consists of (%) C 65.68; H 4.40; O 20.12; C/H 14.92; C/O 3.26, while the elemental composition of the same material after adding wastes was (%) C 81.95; H 4.76; O 22.42; C/H 17.21; C/O 3.65. On the basis of these distinct elemental compositions, it could be hypothesized that the increase ratio of C/O from 3.26 to 3.65 is possibly due to the carbonization process. The results clearly indicate that the oxidation of active carbons with subsequent carbonization influences the atomic C/H and C/O ratios. The increase in the atomic C/H ratio in the pyrolysis products compared with initials indicate that the material has undergone

Table 1
Mineralogical composition of metallurgical slag (additives to sorbent).

Fe	Al ₂ O ₃	CaO	SiO ₂	MgO	MnO	P ₂ O ₅	S	Na ₂ O	K ₂ O	Co	Cr	Pb	Σ
31.40	14.12	6.87	42.56	0.36	0.72	0.35	0.16	0.71	1.45	0.01	0.10	0.004	98.814

significant changes in terms of the internal structure of the cellulose. We hypothesize that these structural changes are linked to the degree of carbonization. Moreover, the atomic C/H ratio increases with increase in the temperature of the pyrolysis. Thus, a higher value of the atomic C/H ratio is more likely to occur in oxidized carbons and it demonstrates that increase of the condensation degree of the nuclear part in the process of oxidative decomposition. The pore volumes are significantly increased with increase of temperature of carbonization reaction (Table 2).

It is to be noted that the catalytic activation may also be promoted by the addition of mineral additives, i.e., transition metals. Transition metals are known to be effective catalysts for promoting the carbonization reaction of cellulose, lignin and other wood components [9,10]. Moreover, the presence of transition metals also invokes the thermal transformations such as cellulose effect, possibly by shifting the decomposition processes towards a lower temperature region and increasing the yield of carbon residue [11].

Furthermore, the amount of oxygen-containing functional groups on surface of the activated pine waste has been determined by the Boehm [12] method. The concentrations of acidic functional groups as a function of temperature are listed in Table 3.

The burning of the carbon walls causing the separation of walls of the pores from each other is most likely to happen at certain “critical” temperature. This process is expected to increase the volume of pores accordingly. The large number of pores on the surface of obtained materials can serve as an excellent transport system, in which the channels required for adsorbing material may move from the liquid phase transfer to the internal pores, located at a great distance from the surface of carbon materials. Reactions of depolymerization, decarboxylation, decarbonylation with formation of low molecular products of decomposition, also aromatization processes to form a graphite layers occurring in the temperature range from 150 to 800 °C, to form weight products.

Thermal analysis of activated carbon sorbent is presented Fig. 1. The weight loss of the cellulose can be described in three steps. The first step of the TG curve (green) is in the temperature range of 55–110 °C corresponds to the desorption process of physically bounded water, followed by the dehydration process that occurs presumably in the temperature range of 110–150 °C, finally resulting the decomposition of the carbon mass at temperatures greater than 600 °C. Analysis of DTA curve (blue) of active carbons carbonized at 600 °C showed that the thermal destruction of the sorbent followed by two endothermic effects in 67–212 and 803–980 °C respectively are associated to the dehydration and destruction of organic matter adsorbent processes.

Scanning Electron Microscopy (SEM) characterization (Fig. 2) indicates that the carbonized sorbent has discrete porous nature with variable wall thicknesses and pore sizes. This SEM data could be interpreted to the morphological features of the material such as bulges in the outer wall, the channel structure of macrospores, which are characteristic of a surface structure of the carbonized pine waste.

To further evaluate the structural aspects of the sorbent, we carried out Fourier-Transform Infrared spectroscopy (FT-IR) characterization.

Table 2
The common porosity of the sorbent.

Temperature (°C)	300	400	500	600
Porosity (%)	33.03	39.07	44.26	49.07

The FT-IR spectra (Fig. 3) of initial material and modified sorbent have an intense broad absorption band assigned to valence vibrations of different OH functional groups with a maximum at ~3650 cm⁻¹. Valence vibrations of C–O–C groups of esters, ethers, phenols and alcohols can characterize the absorption bands at the 1350–1050 cm⁻¹. The absorption bands at the 1710 cm⁻¹ were assigned to fluctuations ν_{CO} of carboxyl groups, intensities of which increase with an increase in temperature. FT-IR analysis also suggests that sorbent modified by orthophosphoric acid after carbonization in the presence of mineral additives can be described as the hydrophobic samples surface which appears as absorption bands at the 650, 1350, 700, 1500, 1800, 3650, 3700 cm⁻¹. This indicates the presence of phosphate groups, carboxyl groups, aromatic and aliphatic acids, esters on the surface (as reaction centers).

On the basis of elemental composition, thermal analyses, microscopy and spectroscopy characterization, it can be reasonably concluded from the obtained data that the tested adsorbents are porous sorbents, which have cation exchange properties. Total acidity mostly determined by the Boehm method is due to the presence of carboxyl groups responsible for ion-exchange.

3.1. Adsorption of cation, anion and small molecules on active carbon sorbents

The oxidation of the pine waste carbon surfaces by phosphoric acid, followed by a thermal activation resulted in a sorbent that is expected to have ion-exchange properties. To evaluate the sorbent activity of activated carbons, the sorbent material was treated with cations, anions and small organic molecules. Adsorption isotherms for cations and organic molecules are presented in Figs. 4 and 5, and the adsorption values for anion (iodine) is give in Table 4. The adsorption values (mg g⁻¹) have been calculated from the obtained experimental data of adsorption of inorganic and organic toxicants from individual solutions by active carbons:

$$A = \frac{(C_{init} - C_{res})V}{m} \quad (2)$$

where C_{init} and C_{res} are initial and residual concentrations of toxic compounds (or ions) in liquid (mg L⁻¹), V is volume of solution (L) and m is mass of sorbent (g).

It is clear from Fig. 4, the adsorption value increases at increasing the adsorptive concentration. The adsorption of isotherms has inflection point. It can be assumed that in the system the poly molecular adsorption occurs, it is probably, that adsorbed molecules are tending to stay on the surface as ionic chains [13]. It is found that adsorption ability of metal ions would increase if ion charge is increased from Ni (II) to Fe(III) ions.

Analysis of sorption isotherms by Hils classification leads to the conclusion that the interaction between the adsorbed molecules is

Table 3
The acidic functional group concentration of surface.

Temperature, °C	Total acidic functional group, mmol L ⁻¹	Carboxylic group, mmol L ⁻¹
300	9.0	7.9
400	9.5	8.2
500	9.6	8.5
600	10.2	8.8

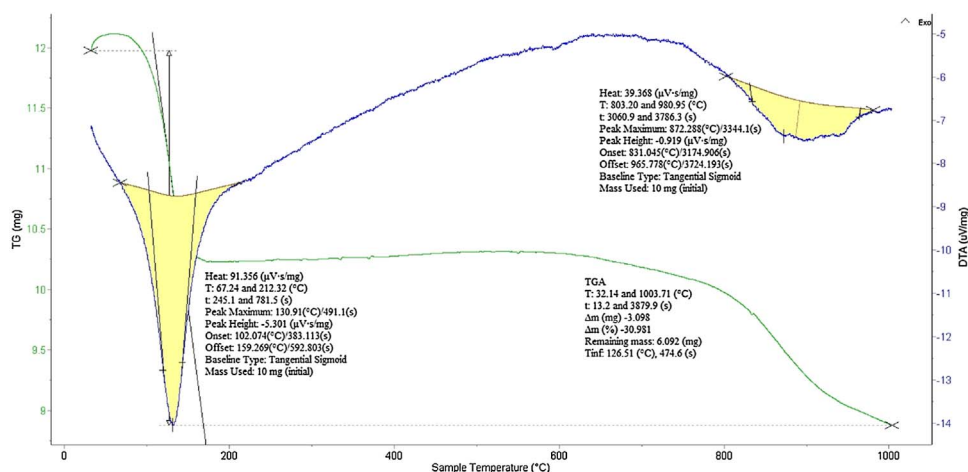


Fig. 1. TGA and DTA curves of activated carbons obtained by carbonization at 600 °C.

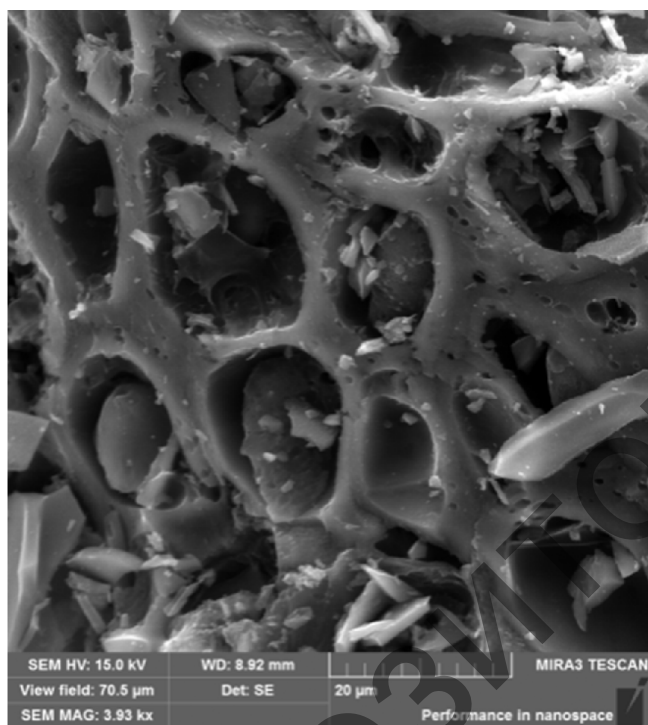


Fig. 2. Scanning Electron—Microscope (SEM) image of the sorbent carbonized at 600 °C.

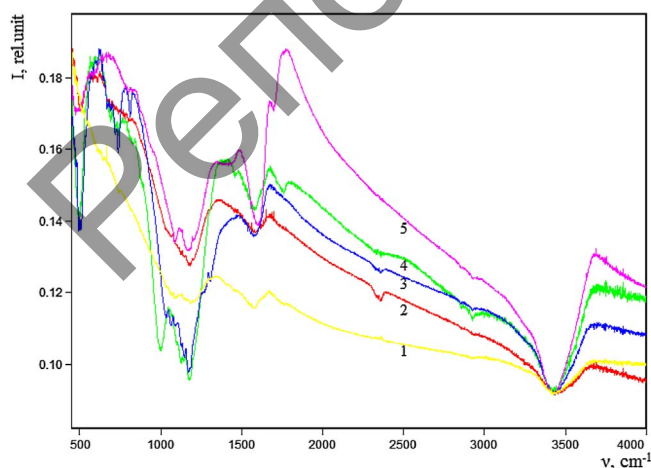


Fig. 3. FT-IR-spectra of initial pine wastes, 1 and modified sorbent carbonized at variable temperatures: 300 °, 400 °C, 500 °C and 600 °C depicted in 2, 3, 4, and 5 respectively.

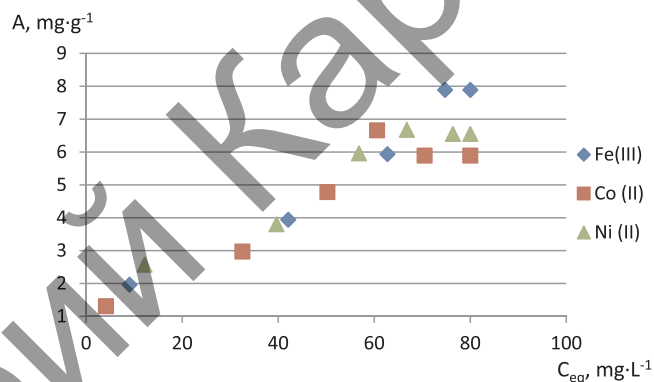


Fig. 4. Adsorption isotherms of metal ions (Fe^{3+} at pH 7, Co^{2+} and Ni^{2+} at pH 8) on sorbent at 25 °C.

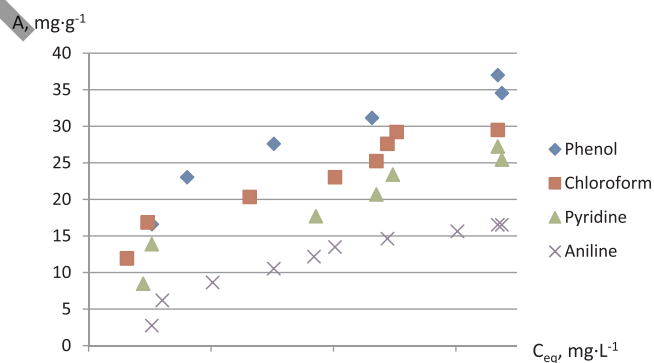


Fig. 5. Adsorption isotherms of phenol (pH 7), chloroform (pH 9), pyridine (pH 4) and aniline (pH 3) on sorbent at 25 °C.

Table 4
Iodine adsorption results.

T, °C	300	400	500	600
X, %	27.34	35.56	63.57	90.17

small, and the activation energy does not depend on filling degree of the sorbent surface. The degree of adsorption of small molecules on sorbent was found to be phenol > chloroform > pyridine > aniline. According to the classification Hils, in this case, the adsorption of isotherms in shape corresponds to the H1-type, which describes a very strong adsorption of adsorbate at low concentrations due to the high affinity between adsorbate and adsorbate.

The data presented in Table 4 shows that iodine sorption activity of sorbent increases with temperature and equals to 90.17% at 600 °C.

4. Conclusions

The structure of the products obtained in the carbonization process of pine wastes of modified H₃PO₄ in the presence of metallurgical slag additives after water processing has been investigated. It was shown that porous material having iodine adsorption 90.17% has been formed as a result. Also it is shown that these active carbons can be used as sorbents in water purification from Fe(III), Co(II), Ni(II) ions and organic toxicants.

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