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Cent. Eur. J. Chem. • 11(1) • 2013 • 78-85
DOI: 10.2478/s11532-012-0140-0

Central European Journal of **Chemistry**

The effect of chemical activation method on properties of activated carbons obtained from pine cones

Research Article

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Received 16 April 2012; Accepted 3 September 2012

Abstract: A method for obtaining carbonaceous adsorbents from pine cones by chemical activation with NaOH is described. Activated carbons were obtained by two methods of activation (physical mixing and impregnation) and two variants of thermal treatment. It has been shown that pine cones can be successfully used as cheap precursor of carbonaceous adsorbents of well-developed surface area, large pore volume and good sorption properties. All activated carbon samples obtained show strongly microporous structure and surface of acidic character. The best physicochemical properties and greatest sorption capacity towards iodine were found for the carbon samples obtained by physical mixing of the precursor with the activating agent and then subjected to thermal activation at 600ºC.

Keywords: *Pine cones • Chemical activation • Impregnation • Physicochemical properties*

1. Introduction

Activated carbons are highly crystalline materials of large pore volume and surface area with many different functional groups on the surface. Their properties, in particular their sorption capacity, are determined by the type of precursor as well as method and conditions of the processes leading to the final product [1,2]

Activated carbons are obtained by physical activation (thermal) [3] or by chemical activation [4,5]. Physical activation usually requires pyrolysis of the precursor followed by gasification of the char obtained or direct activation of the precursor by such activating agents as steam, oxygen, or CO_2. These processes lead to selective elimination of carbon atoms and generation of the product structure. Chemical activation takes place in lower temperatures and needs a shorter time than physical activation, moreover it gives activated carbons a better developed porous structure. The yield of carbons obtained by chemical activation is usually higher as the activating agents (KOH, NaOH, H_3PO_4) show dehydrogenation properties and thus slow down the formation of tar and volatiles [6,7].

Activated carbon can be obtained from various materials of organic origin such as wood, peat, and fossil coal [8]. Growing demand for carbon adsorbents related to development of many branches of industry and increasing restrictions of the rules concerning protection of the natural environment, have stimulated the search for new substrates and new technologies of activated carbon production. Of considerable economical importance is the use for this purpose of waste products, whose utilisation or safe dumping and neutralisation would be a serious ecological problem. The use of such waste products as precursors of activated carbon is a very attractive solution.

In recent years, different agricultural by-products have been very often used as precursors for activated carbons production such as walnut shells, pine sawdust, plum stones, walnut shells, pistachio-nut shells, and olive stones [3,9-15]. Their use permits getting activated carbons of new properties and new applications. It

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has been established that the properties of activated carbons and hence their possible applications, depend on the type of precursor as well as on the method and conditions of production. For obvious reasons, much attention has been paid to the use of the most accessible and the cheapest precursors ensuring production of effective activated carbons.

The main aim of this study was to obtain cheap activated carbons from pine cones as a precursor by chemical activation in different variants and characterise their physicochemical and sorption properties.

Pine cones have been for some time already of interest as precursors of activated carbon or biosorbents. Duman *et al*. [16] have studied the effectiveness of removal of methylene blue, phenol, and Cr(VI) by carbon obtained from pine cones and activated by zinc chloride and phosphoric acid. The authors applied different variants of pine cone treatment and obtained a wide range of mesoporous activated carbon samples displaying different acid-base surface properties and different sorption capacities towards the above pollutants. The same authors have proved that more effective in removal of phenol and Cr(VI) are the carbon samples activated by phosphoric acid, while the sorption capacities of the carbons activated with $ZnCl_2$ and H_3PO_4 are comparable.

Momcilovic *et al*. [17] have studied activated carbon samples from pine cones activated by 85% H_3PO_4. The material they obtained was mesoporous and had a significant amount of oxygen functional groups on the surface. It showed good sorptive capacity towards Pb(II) ions. The adsorption efficiency of lead ions increased with increasing adsorbent dosage and pH of the solution.

Removal of heavy metals by activated carbon obtained from pine cones has been also the subject of study of Argun *et al*. [18]. By exposing pine cones to Fenton's reagent, the authors obtained a good sorbent of Pb(II) and Cd(II) ions, characterised by the efficiency of about 30 mg g^{-1}. They have also evidenced that the carbon ability to remove heavy metals depends on the pH of the solution and contact duration.

A wide gamut of biosorbents showing high sorption capacity towards Cu(II) ions have been obtained and studied by Ofomaja *et al*. [19], by activation of pine cones with NaOH solutions of different concentrations. The sorption capacity of these materials depended on the temperature of adsorption and concentration of the NaOH solution used for the modification.

Not much can be found in literature on the obtaining of activated carbon by chemical activation with NaOH, which seemed an interesting subject for us.

2. Experimental procedure

2.1. Materials and preparation of activated carbons

The initial sample of raw pine cones (C, W^a = 9.7 wt.%, Ash^d = 0.6 wt.%, VM^{daf} = 77.7 wt.%) was dried in a drier, crushed and sieved to collect the grain size fraction of 2-4 mm. The material obtained was divided into two parts and then subjected to modification.

The pyrolysis (P) was carried out in a horizontal furnace under a stream of argon at the flow rate of 170 mL min^{-1}. The sample was heated (5°C min^{-1}) from room temperature to the final pyrolysis temperature of 400°C. In the final temperature, the sample was kept for 15 min and then it was cooled in inert atmosphere.

The activation was performed in a horizontal pipe reactor heated by a resistance furnace, at 600°C (increasing rate of 10°C min^{-1}), for 20 minutes in an argon atmosphere supplied at the flow rate of 170 mL min^{-1}. The activating agent was sodium hydroxide. The activation process was realised in two variants:

Method I (A) – by physical mixing of the precursor with refined activating agent at the 2:1 weight ratio of NaOH/ precursor.

Method II (IA) – by impregnation of the precursor with a solution of NaOH, keeping the 2:1 weight ratio of NaOH/precursor. The precursor was mixed with a water solution of NaOH by a magnetic stirrer and then the mixture was dried at 105°C for 24 hours to a constant mass.

For each method of activation two variants of thermal treatment were applied:

Variant I (1) – a boat with the sample was placed in a furnace heated to 600°C, to rest till stabilisation of temperature. Thermal activation was performed for 20 minutes, counted from the moment the furnace temperature reached 600°C.

Variant II (2) – the sample was heated from room temperature to the final temperature of 600°C increasing at the rate 10°C min^{-1}. After reaching 600°C the sample was kept at this temperature for 20 minutes

Thermal activation was applied to the initial precursor and char, but the char was activated only according to variant 1. The activated carbons obtained were washed with a 5% HCl solution to remove the excess of NaOH, and then with hot distilled water to remove chlorides, and dried at 105°C.

2.2. Analytical procedures

Elemental analyses of the materials under investigation were performed on an elemental analyzer CHNS Vario EL III (Elementar Analysensysteme GmbH, Germany).

Table 1. Elemental analysis of initial sample and char obtained at 400°C [wt.%].

Sample	A^{d}	C^{daf}	H^{daf}	N^{daf}	S^{daf}	O^{daf*}
C	0.6	51.2	6.4	0.3	0.0	42.1
CP	1.6	72.1	4.5	0.5	0.0	22.9

^{d} – dry basis, ^{daf} – dry ash-free basis, * – by difference, C – raw pine cones, CP – pyrolysed pine cones.

Table 2. Elemental analysis of activated carbons obtained [wt.%].

Sample	A^{d}	C^{daf}	H^{daf}	N^{daf}	S^{daf}	O^{daf*}
CA1	0.7	82.8	2.0	0.4	0.0	14.8
CA2	0.7	82.3	1.8	0.5	0.0	15.4
CIA1	0.5	83.2	2.3	0.2	0.0	14.3
CIA2	1.4	81.8	2.3	0.2	0.0	15.7
CPA1	0.5	83.2	1.5	0.4	0.0	14.9
CPIA1	0.8	85.3	2.3	0.5	0.0	11.7

^{d} – dry basis, ^{daf} – dry ash-free basis, * – by difference, CA1 and CIA1 – activation at a constant temperature (600°C), CA2 and CIA2 - activation with temperature increased at the step of 10°C min^{-1}, I – stands for impregnation.

The content of ash was performed according to the Data National Standards ISO 1171:2002.

Characterization of the pore structure of obtained materials was performed on the grounds of low-temperature nitrogen adsorption-desorption isotherms measured on a sorptometer ASAP 2010 manufactured by Micromeritics Instrument Corp. (USA). Prior to the isotherm measurements, the samples were outgassed at 150°C for 10 h. Surface area was calculated by BET (Brunauer-Emmett-Teller) method based on the evaluation of the monolayer capacity - the number of adsorbed molecules in the monolayer on the surface of a material and BJH (Barrett-Joyner-Halenda) methods, respectively [20]. Total pore volume and average pore diameter were determined as well. Micropore volume and micropore area were calculated using the t-plot method.

SEM images were obtained using a scanning electron microscope made by PHILIPS (Netherlands) in the following conditions: working distance of 14 mm, accelerating voltage of 15 kV and digital image recording by DISS.

The surface properties were evaluated using potentiometric titration experiments using 809 Titrando equipment manufactured by Metrohm. The instrument was set at the mode when the equilibrium pH was collected. Materials studied of about 0.100 g in 50 mL 0.01 M $NaNO_3$ were placed in a container thermostated at 25°C and equilibrated overnight with the electrolyte solution. To eliminate the influence of atmospheric CO_2, the suspension was continuously saturated with N_2. The carbon suspension was stirred throughout the measurements. Volumetric standard NaOH (0.1 M) or HCl (0.1 M) were used as the titrants.

The iodine sorption ability of the activated carbon samples, expressed as the efficiency of adsorption of molecular iodine from a water solution, was determined according to the ASTM Standard [ASTM D4607-94 (2006)]. This method permits estimation of the ability of the adsorbents obtained to remove substances whose molecules have the size close to that of iodine molecules, so of diameters close to 1 nm, from the liquid phase. To measure the adsorption capacity of the materials in a powdered form, the granular samples were pulverized manually in a mortar.

3. Results and discussion

Elemental analysis of the char obtained as a result of pyrolysis of raw pine cones at 400°C, see Table 1, prove a significant increase in carbon and a decrease in the content of hydrogen and oxygen. These changes are caused by evolution of volatiles on pyrolysis, leading to enrichment in carbon and formation of the primary porous structure. A small increase in the content of nitrogen is noted, which suggests that pine cones can contain nitrogen permanently built into their structure, and an increase in mineral substance (ashes) as a result of exposure to high temperature.

Raw pine cones and the char obtained from them were subjected to chemical activation by NaOH realised in a few variants, described in section 2.1. The elemental compositions of all activated carbon samples obtained and the yield of their obtaining are given in Table 2.

As follows from the data from Table 2, irrespective of the method of activation it results in an increase in the content of carbon and a decrease in oxygen with respect

Table 3. Textural parameters of the activated samples obtained.

Sample	Total surface area (BET) [$m^2 g^{-1}$]	Micropore area [$m^2 g^{-1}$]	Total pore volume [$cm^3 g^{-1}$]	Micropore volume [$cm^3 g^{-1}$]	V_{mic}/V_t	Average pore diameter [nm]
CA1	848	835	0.42	0.39	0.93	1.96
CA2	652	637	0.32	0.30	0.94	1.98
CIA1	506	489	0.30	0.23	0.78	2.07
CIA2	589	568	0.30	0.27	0.90	2.07
CPA1	965	953	0.47	0.45	0.96	1.93
CPIA1	465	449	0.24	0.21	0.88	2.10

to their levels in the char. All samples subjected to activation reveal a decrease in the content of hydrogen, most probably caused by aromatisation of the carbon structure. Analysis of the content of nitrogen in the activated carbon samples shows that in samples CIA1 and CIA2 its content decreases with respect to that in the initial char, which can be a result of a low resistance of nitrogen groups to the activating agent (NaOH) and temperature of activation (600ºC). In the other samples (CA1, CA2, CPA1 and CPIA1) the content of nitrogen practically does not change.

To characterise the porous structure of the activated carbons, their specific surface area was determined on the basis of BET isotherm measurements.

According to the results, presented in Table 3, the method of activation determines the structural parameters of the activated carbon samples obtained. Irrespective of the variant of thermal treatment, the activated carbons samples obtained by physical mixing of the precursor and the activating agent (CPA1, CA1, CA2) have a better developed porous structure and greater pore volume than the samples obtained by impregnation of the precursor with an NaOH solution (CIA1, CIA2, CPIA1).

According to Table 3, in the porous structure of all activated carbon samples obtained from pine cones the dominant are micropores. In samples CA1, CA2, CPA1 they make over 90% of all pores, while in the other samples the contribution of mesopores increases with reaching a maximum for sample CIA1, in which the contribution of mesopores is 22%. The highest volumes of micropores were found in the samples obtained by the activation of the precursor and char physically mixed with the activating agent, so samples CA1 (0.39 $cm^3 g^{-1}$), CPA1 (0.45 $cm^3 g^{-1}$), while in the samples obtained by impregnation of the precursor or char the volume of micropores is lower and the lowest for CPIA1 (0.21 $cm^3 g^{-1}$).

Fig. 1 presents the nitrogen adsorption/desorption isotherms recorded for activated carbons obtained from pine cones. All of them have the shape close to that of the reversible type I isotherm assigned to microporous solids. They have hysteresis loops of H4 type, which confirms the contribution of mesopores in the porous structure of the samples studied.

To illustrate the structures of the activated carbon samples obtained, their SEM images are presented in Fig. 2.

The SEM images presented reveal considerable differences in morphology of grains of the carbon samples activated by different methods. According to the data obtained in the study, the activated carbon samples differ not only in the shape and size of pores, but also in the way of their connection and arrangement. The SEM images of samples CPA1 and CPIA1 suggest that the carbons obtained by pyrolysis of pine cones followed by chemical activation of the chars show greater density than the analogous materials subjected only to activation

To get the information on the chemical character of the activated carbon surfaces, the content of the surface oxygen functional groups was estimated. The results presented in Table 4 evidence a high content of surface oxygen functional groups and definitely acidic surface character, irrespective of the method of activation and variant of thermal treatment. From among the samples obtained by activation of raw pine cones, the samples subjected to thermal treatment according to variant II (CA2 and CIA2) have higher total content of surface oxygen groups than the samples subjected to thermal treatment according to variant II (CA1 and CIA1), although the content of surface oxygen groups of acidic character is definitely higher in the samples thermally treated according to variant I (CA1 and CIA1). The content of basic oxygen surface groups is higher in the samples thermally treated according to variant I only for the samples obtained by physical mixing of the precursor with solid NaOH (CA).

From among the samples obtained by precursor impregnation with a solution of NaOH (CIA) the content of basic surface oxygen groups is higher in the samples thermally treated according to variant II. From among

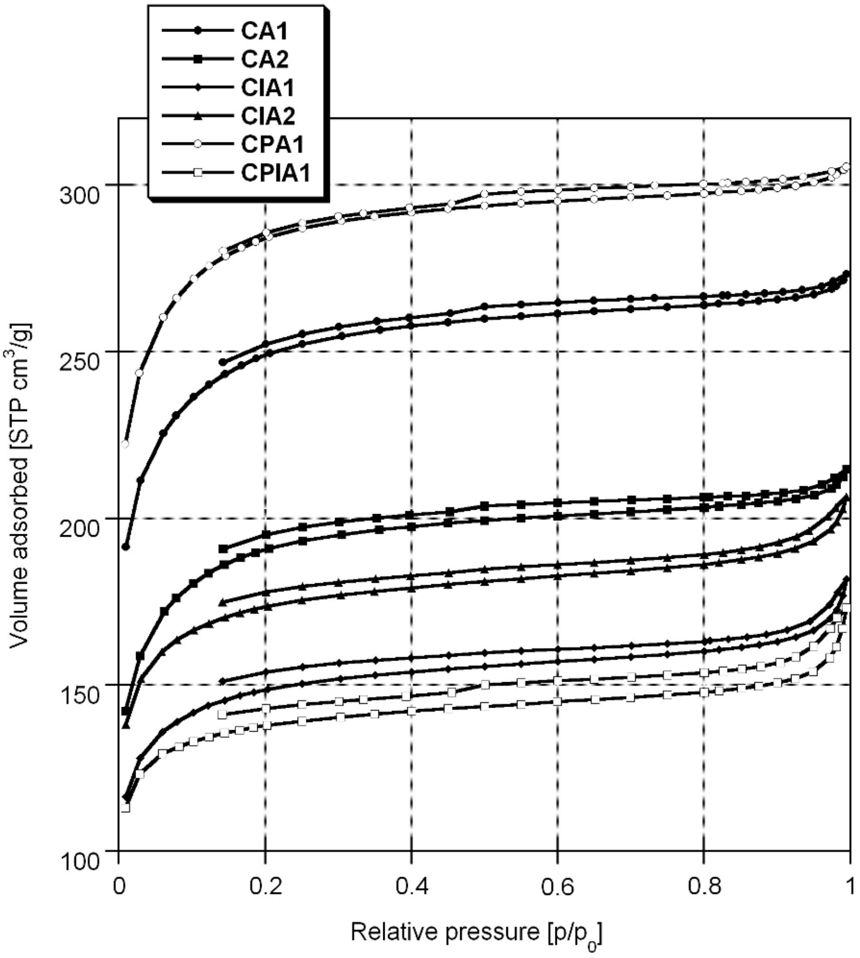

Figure 1. Nitrogen adsorption isotherms of the activated carbons obtained.

Table 4. Acid-base properties of obtained activated carbons.

Sample	Total content of surface oxides [mmol g^{-1}]	Acidic groups [mmol g^{-1}]	Basic groups [mmol g^{-1}]
CA1	3.28	2.76	0.52
CA2	2.33	1.89	0.44
CIA1	2.78	2.36	0.42
CIA2	2.94	2.29	0.65
CPA1	2.86	2.38	0.48
CPIA1	1.80	1.31	0.49

the activated carbon samples obtained from char (CPA1, CPIA1), much higher content of total and acidic surface oxygen groups was found in the sample obtained by physical mixing of char with solid NaOH (CPA1). The content of basic surface oxygen groups was almost the same in these two samples.

In order to establish the influence of the method of activation and variant of thermal treatment on the sorption properties of the samples obtained, the iodine adsorption number was determined. For the sake of comparison, the sorption capacities of the precursor and char were measured. The results are given in Fig. 3 and show that the char (CP) has a lower iodine sorption capacity (179 mg g^{-1}) than the initial precursor (C 228 mg g^{-1}). This result can be interpreted as related to the presence of non-carbonised fragments in the precursor or the presence of the products of tar decomposition in the char pores.

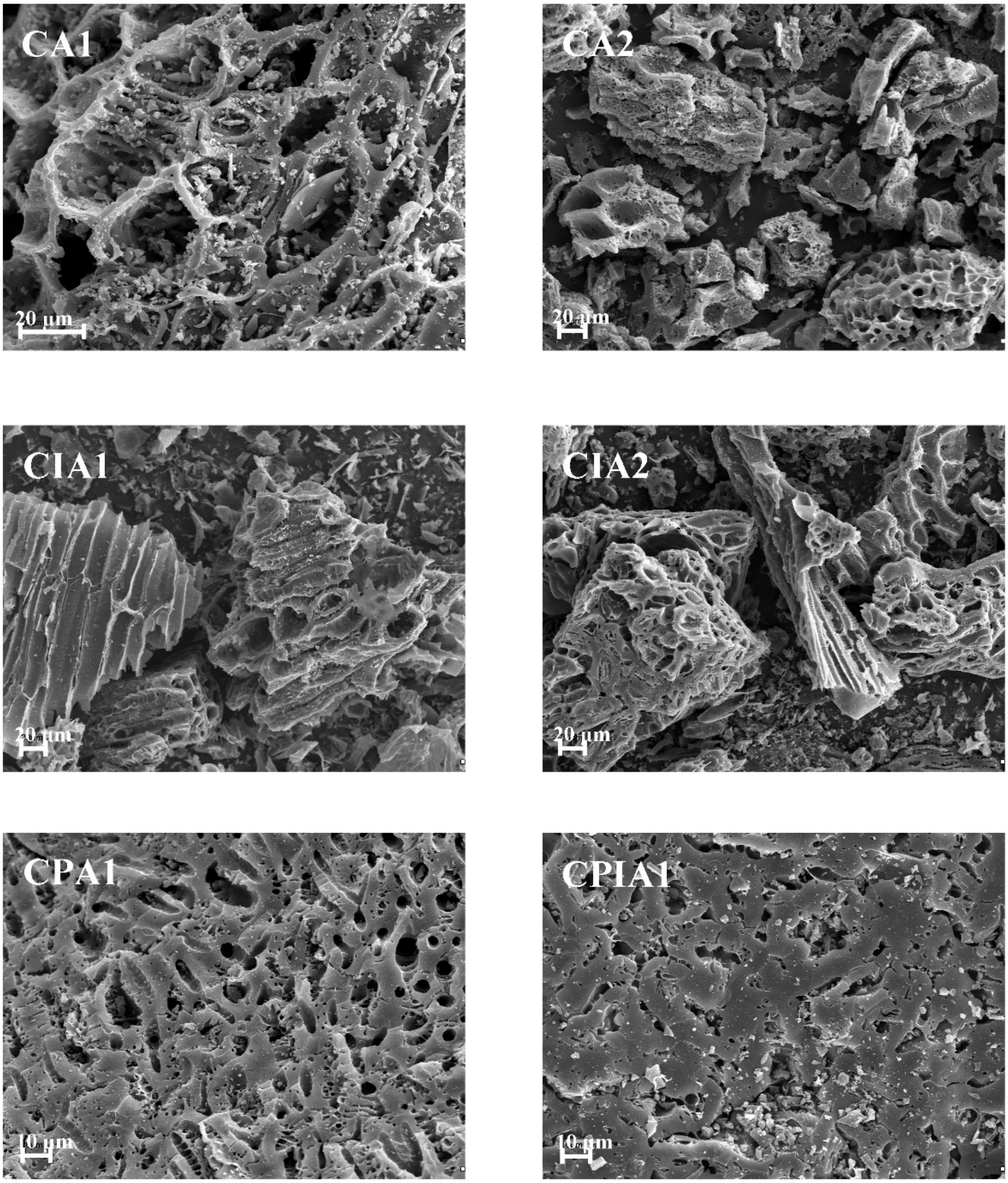

Figure 2. SEM images of the activated carbon samples obtained.

After activation of the precursor and char, the iodine adsorption number of the activated carbons obtained is much higher, which means that the activation has resulted in effective development of the porous structure as is also confirmed by the data from Table 3.

Analysis of these data reveals that the iodine adsorption number depends on the method of activation and the variant of thermal treatment. The highest iodine adsorption number was found for the activated carbon obtained by physical mixing of precursor or char with solid NaOH and thermal treatment at 600ºC (variant I – CA1 897 mg g^{-1} and CPA1 913 mg g^{-1}).

The iodine adsorption number also depends on the textural parameters of the activated carbon obtained, specific surface area, total pore volume and volume of micropores as the highest iodine adsorption number was determined for samples CA1 and CPIA1, Fig. 3,

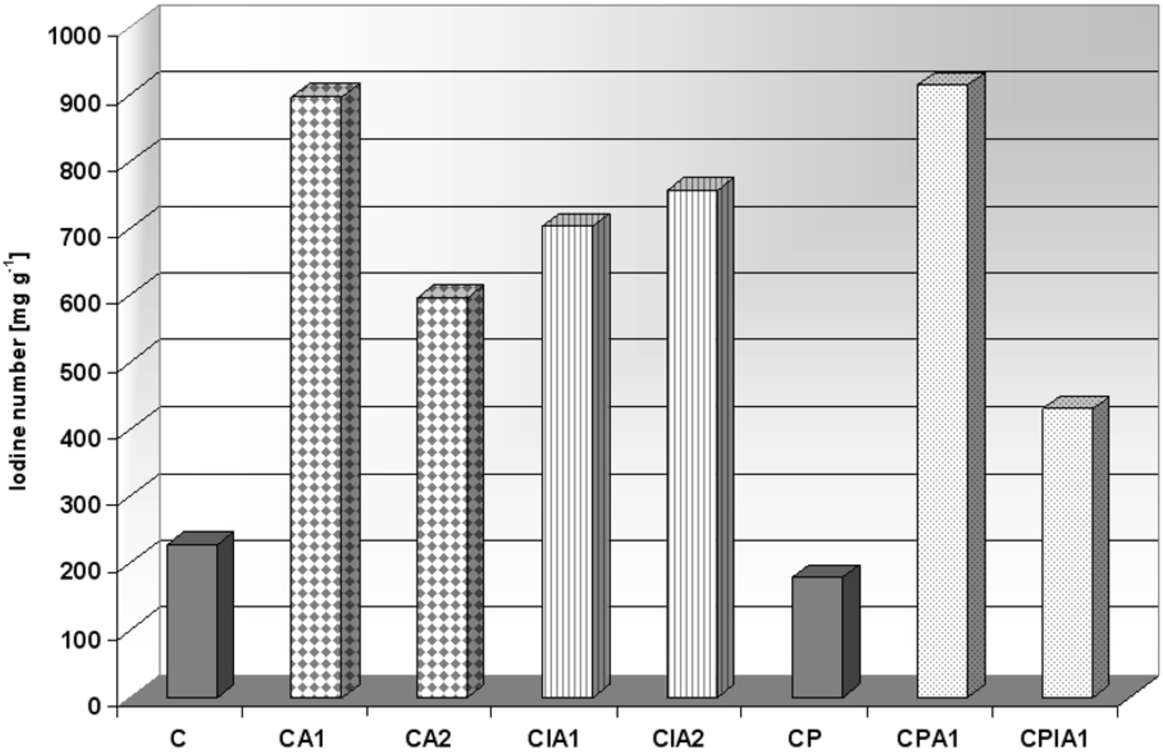

Figure 3. Iodine number for initial sample, char and activated carbons obtained.

characterised by the largest specific surface area and the greatest total pore volume (Table 3).

Analysis of the results collected for the samples based on the raw pine cones (series C) shows that for samples (CA1 and CA2) obtained by physical mixing with solid NaOH, the sample thermally treated according to variant I has a higher iodine adsorption number. From among the samples obtained by impregnation with NaOH solution, samples (CIA1 and CIA2) the activated carbon thermally treated according to variant II was found to have a higher adsorption capacity.

From among the activated carbon samples obtained from char (CPA1, CPIA1), higher (and the highest of all samples) sorption capacity has the sample obtained by physical mixing with solid NaOH, while the sample obtained by char impregnation and activation has the worse physicochemical properties of all activated carbon samples studied.

4. Conclusions

The previously described results have shown that pine cones can be successfully used as a cheap precursor of carbon adsorbents of well-developed surface area, high pore volume, and good sorption capacity. Physicochemical and sorption properties of the activated carbons obtained depend on the activation method and the variant of thermal treatment applied. The porous structure of all activated carbon samples studied was shown to be made mainly of micropores, but the samples obtained by activation of impregnated precursor or char were found to have poorer developed surface areas and lower pore volumes. The samples obtained by physical mixing with solid NaOH had the largest specific surface areas. All activated carbon samples obtained from pine cones contained a high number of surface oxygen groups among which those of acidic character were dominant. The activated carbon samples obtained by activation of the raw pine cones or a char physically mixed with solid NaOH were established to be characterised by the highest sorption capacity (highest iodine adsorption number), comparable with that of the commercial products.

Acknowledgments

This work was supported by The Polish Ministry of Science and Higher Education project No. N N204 277537. Piotr Nowicki wishes to thank the Foundation for Polish Science for fellowship.

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