

Composition of Surface Groups and Adsorption Properties of Activated Carbons Derived from Different Bio-Precursors

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Activated carbons (AC) are widely used in a variety of applications because of their controllable porosity and surface functionalities. In this work, AC were prepared from different hard woods through one- and two-step pyrolysis/activation for the adsorption of organic pollutants in water. Water vapor was used as the activating agent. The influence of the precursor and preparation methods on the properties of the resulting AC was evaluated through multiple techniques. Temperature-programmed oxidation (TPO) measured the reactivity toward oxygen of chars and AC, while temperature-programmed desorption coupled with mass spectrometry (TPD/MS) revealed functional groups on AC surface. Methylene blue adsorption tests evaluated the adsorption capacity of the prepared AC and the presence of mesopores. Depending on the oxidation reactivity of the char produced by pyrolysis, the resulting AC show different surface composition and adsorption performance. With the increasing char oxidation reactivity, the AC has higher degree of surface functionalization and enhanced adsorption toward methylene blue. In particular, Red Maple char is the more reactive one, followed by Birch and Ironwood. Thus, Red Maple AC prepared through the two-step process, exhibits lower activation yield, higher concentration of surface functionalities and improved methylene blue adsorption. TPO technique could predict the degree of surface functionalization and adsorption properties of the final AC.

1. Introduction

Activated carbon (AC) is commonly used in purification and separation processes on a large scale due to its large specific surface area and porous structure (Ma et al., 2017). Beside the low operating cost and simple system design, the environmental and economic advantages of using AC increase when this material is obtained from renewable biomass and available in large quantities (Ruiz-Rosas et al., 2019). Surface area and porosity together with the surface chemistry affect the AC performance in many different applications. Still, controlling and tuning these properties for specific applications remains a challenge for researchers. AC can be prepared from a wide variety of raw materials using a chemical or physical activation process to create the desired porosity and surface composition. Chemical activation requires an activating agent and relatively low temperatures compared to physical activation which is conventionally performed with steam or carbon dioxide following the carbonization of the raw materials. A one-step pyrolysis/activation method was also reported in the literature where water vapor is introduced during the pyrolysis of biomass or other raw materials (Gergova, 1996). Oxygen-containing groups are the most abundant on the AC surface. The nature and concentration of surface groups is modified through different treatments, such as oxidative treatments which can increase their concentration (Figueiredo et al., 1999) or thermal treatments in inert atmosphere which remove some of them (Szymanski et al., 2002). Multiple methods characterize the surface of carbonaceous materials, such as potentiometric titrations, electrochemical methods, temperature-programmed desorption (TPD) and spectroscopic methods (Bandosz, 2008). Moreover, temperature-programmed desorption can be coupled with mass spectrometry (TPD/MS) to determine the composition of gases evolved upon heating the samples in an inert atmosphere. Since oxidation reactions are involved in the activation and surface functionalization of AC, the oxidation reactivity of carbons becomes an important property which can be determined through temperature-programmed oxidation (TPO) analysis (Andreoli, 2020).

The principal focus of this study was to prepare mesoporous AC to remove methylene blue used as model pollutant. AC were prepared from different types of wood through one- and two-step activation with water vapor. The surface composition, oxidation reactivity, and adsorption capacity of the prepared materials were investigated and related to the AC precursors properties and preparation methods.

2. Materials and Methods

Lignocellulosic materials, like wood, account for around 45 % of the total raw materials used for the manufacture of activated carbon (Dobele et al., 2012). In this study, the starting materials for AC (Red Maple, Birch and Ironwood) were selected among hard wood species which have a higher content of cellulose and hemicellulose with respect to the soft woods which are rich in lignin (Bhaskar et al. 2008). Cellulose and lignin contents are 45 % and 23 % for Red Maple, 38 % and 22 % for Birch (Fengel, 1989), 44-45 % and 22 % for Ironwood (Kiaei et al., 2015), respectively.

2.1 AC preparation

AC were prepared from three different hard woods by a one-step pyrolysis/activation and a more conventional two-step procedure. A diagram of the experimental set up used for the pyrolysis/activation experiments is reported in Figure 1.

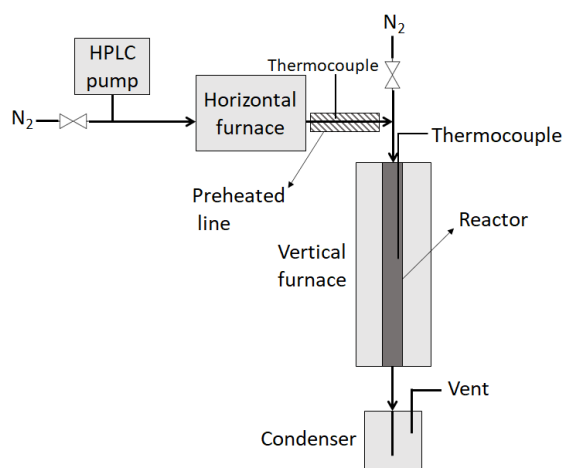


Figure 1: Diagram of the experimental set up used for pyrolysis/activation experiments.

Pyrolysis and activation take place in a vertical furnace while a horizontal furnace (set at 120 °C) and a HPLC pump are used for water vapor generation. For the two-step procedure, 10 g samples of each wood (18-40 mesh) were pyrolyzed in a stainless-steel tube reactor at 550 °C for 30 minutes under nitrogen flow. After cooling down, the char was heated and activated at 750 °C for 30 minutes with water vapor introduced in the reactor with a liquid water flow rate of 1 mL/min. For the one-step procedure, 10 g samples of each wood were heated at 20 °C/min to 750 °C and maintained at that temperature for 30 minutes. In this case water vapor was introduced in the reactor at the beginning of the pyrolysis/activation at the same rate of two-steps procedure.

2.2 AC characterization

For the composition of the surface functional groups, temperature-programmed desorption and mass-spectrometry (TPD/MS) experiments were carried out on 60-80 mg of sample with a Micromeritics TPD/TPR 2910 equipment. After degassing at 120 °C for 30 minutes, samples were heated at 10 °C/min to 900 °C and maintained at that temperature for 10 minutes under argon flow (20 mL/min). An on-line quadrupole mass spectrometer (Ametek Dycor, USA) analysed the exit gas stream and the amounts of CO and CO₂ evolved were obtained by integration of the area under the corresponding peaks. Temperature-programmed oxidation (TPO) analyses were carried out in a LECO RC612 Multi-phase Carbon Analyzer with 50 mg of ground samples under a continuous flow of oxygen (1 L/min) from 100 to 550 °C. All carbon species from carbon oxidation were converted to CO₂ on a downstream CuO catalyst bed and the amount of evolving CO₂ was quantified with a calibrated IR detector. Methylene blue adsorption tests were performed on 20 mg of AC placed in 100 mL of dye solution (0.1 g/L) and stirred at room temperature. After 24 hours, the amount of methylene blue left in the solution was measured with a Milton Roy Spectronic 401 at 663 nm after dilution.

3. Results and discussion

The AC samples, prepared as described above, were characterized with respect of their oxidation reactivity, surface composition and adsorption capacity. Results from the different characterization techniques will be discussed in the following sections. Moreover, yields for the pyrolysis/activation were examined based on the different precursors and number of steps used for AC preparation.

3.1 Char and activated carbon yields

Type of precursors and number of steps for pyrolysis/activation are reported in Table 1. For the one-step procedure, only the final yield was calculated since pyrolysis and activation were performed at the same time. The activation yield for the two-step process was calculated using the weight of the char (after pyrolysis) as the starting weight.

Table 1: AC precursors, number of steps for pyrolysis/activation and corresponding yields.

AC precursors	Number of steps	Pyrolysis Yield (%)	Activation Yield (%)	Final Yield (%)
Ironwood	1	-	-	18
Ironwood	2	22	73	16
Red Maple	1	-	-	4
Red Maple	2	27	48	14
Birch	1	-	-	4
Birch	2	26	65	17

Ironwood yields from one- and two-step procedures are comparable, 18 and 16 %, respectively. However, for the other two wood samples, the yield for the one-step preparation was very low (4 %), compared to the two-step method, which gave 14 % for Red Maple and 17 % for Birch. After one-step pyrolysis/activation, Red Maple and Birch gave very low yields compared to Ironwood. The difference in the yield values for different biomasses treated under the same conditions is often related to their lignin content. However, in this study, different yield values were observed despite the similar content of lignin of the considered woods (22-23 %). This can be explained by the lower density of Red Maple and Birch compared to Ironwood. The high density of Ironwood could prevent the migration of volatile matters to the surface of the wood and consequently favour the formation of secondary charcoal, as suggested by Dofourny et al. (2019). For the two-step process, the pyrolysis yields were found to be comparable for the different precursors (22-27 %), while the activation yields of Ironwood was higher (73 %) than Birch (65 %) and Red Maple (48 %). Beside the density of the starting woods, the differences in the activation yields could be explained by TPO results shown in the next section.

3.2 Oxidation reactivity of chars and activated carbons

TPO technique was used to characterize the oxidation reactivity of chars and activated carbons (Figure 2).

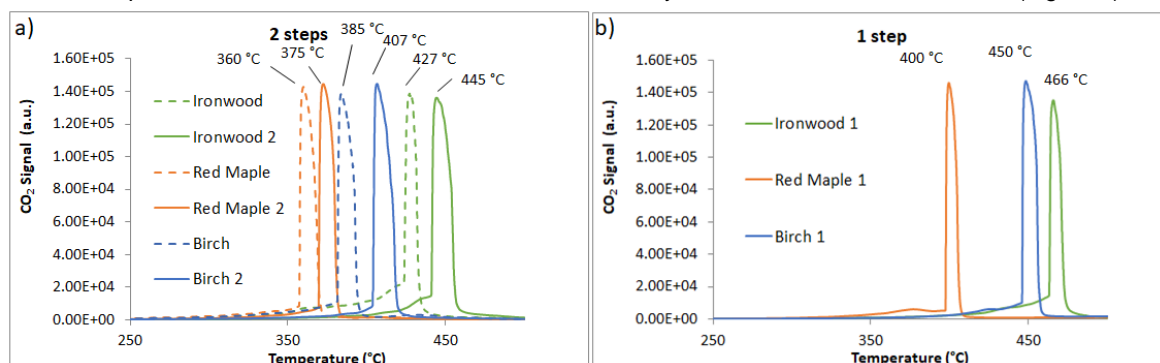


Figure 2: a) TPO profiles for two-step chars (dashed lines) and AC (solid lines); b) TPO profiles for AC from one-step procedure. Number of steps is indicated with 1 for one-step and 2 for two-step.

During TPO, the reaction of solid carbon with molecular oxygen takes place on specific active sites, including structural defects. Thus, there is a relationship between the intrinsic oxygen reactivity of solid carbons and their structure (Alonso-Morales et al., 2013). In the TPO profiles of carbonaceous substances, the more reactive species shows oxidation peaks at lower temperatures, while the less reactive species is oxidized at higher temperatures.

In Figure 2a, the chars and corresponding AC, obtained from the three wood samples through two-step process, show oxidation activity in a wide temperature range between 300 and 500 °C and the temperatures of maximum rate of CO₂ evolution vary in the range from 360 to 445 °C, suggesting significant differences in the reactivities of the chars and AC samples. This is an interesting observation considering that the pyrolysis of the wood samples and the subsequent activation of pyrolysis chars were conducted under the same conditions, respectively. For all samples, the AC profile peaks are shifted to higher temperatures compared to the parent chars, as expected, because the more reactive part of the chars is removed by oxidation. Moreover, the char and AC derived from Red Maple are the most reactive ones, followed by the Birch and the Ironwood products, respectively. To summarize, the nature of the starting wood has a strong effect on the oxidation reactivity of the pyrolysis chars and the corresponding activated carbons.

The TPO profiles of the two-step products (Figured 2a) can be related to the differences observed among the corresponding AC yields. The Red Maple sample that has the highest oxidation reactivity gave the lowest yield (48%) after activation because this material is more prone to oxidation. The Birch sample shows an intermediate reactivity followed by the Ironwood sample which is the least reactive among the three. Hence, the AC yield is intermediate for Birch (65%) and the highest for Ironwood (73%). At the same time Ironwood has the highest density among the three woods. Thus, the density of the starting woods appears to be an important factor that could affect the oxidation reactivity. Referring back to Table 1, the overall AC yields based on the starting wood sample are not very different, 13, 16, and 17 %, for Red Maple, Ironwood, and Birch, respectively, while the AC yields from the corresponding chars vary widely, 48, 73, and 65 %, in the same order. Thus, the principal influence of the nature of different woods is manifested in the reactivity of the pyrolysis chars, and, consequently, in the AC yields obtained from the pyrolysis chars.

In Figure 2b, the AC produced through one-step pyrolysis/activation show a reactivity trend similar to the AC derived from the two-step process. Indeed, Red Maple AC has the higher reactivity with a maximum of CO₂ evolution around 400 °C, followed by Birch AC at 450 °C and Ironwood AC at 466 °C. Comparing the temperatures at which the maximum evolution of CO₂ is observed, there is a shift toward higher temperature for one-step derived AC, suggesting a lower reactivity for these samples with respect to the two-step AC. This observation is consistent with an earlier report proving that the presence of water vapor introduced at the beginning of the pyrolysis could lead to a considerable activation of the carbon (Gergova, 1996). Thus, a considerable portion of the more reactive part of carbonaceous material was removed during the pyrolysis/activation. This could explain also the very low yields of AC (4 %) obtained from the Red Maple and Birch samples, the woods with the lower density compared to Ironwood which gave a rather high AC yield (18 %) comparable to that obtained by the two-step run (16 %).

3.3 Surface functionalities

TPD/MS analysis provides quantitative information on the concentration of functional groups on carbon surfaces. TPD/MS data may help explain the relationships between the oxidation reactivity of pyrolysis chars and the composition of the surface functional groups associated with the different AC. Table 2 shows the amounts of CO₂ and CO evolved from the AC samples during the TPD/MS analyses.

Table 2: Amount of CO₂ and CO evolved during the TPD/MS analyses from the activated carbons obtained by one- and two-step runs from the three samples, as indicated with 1 for one-step, and 2 for two-step.

Sample	CO ₂ amount (μmol/g)	CO amount (μmol/g)
Ironwood 1	687	429
Ironwood 2	307	359
Red Maple 1	985	664
Red Maple 2	871	928
Birch 1	2171	1057
Birch 2	602	739

During TPD analysis, carbonaceous materials are heated in inert atmosphere and their surface functionalities decompose releasing primarily CO₂, CO and H₂O. Carboxylic acids and lactones generate CO₂. Carboxylic

anhydrides produce simultaneously CO and CO₂. Phenols, ethers and carbonyl groups release CO (Aksoylu et al., 2001). Therefore, the higher the amount of CO₂ and CO released, the larger is the extent of functionalization on sample surfaces. Amounts of CO₂ and CO released are of the same order of magnitude reported for commercial activated carbons (Pereira et al., 2003). In general, AC produced through one-step activation released larger amounts of CO₂ compared to those derived from the two-step runs. As reported in the section regarding the oxidation reactivity of chars and activated carbons, the presence of water vapor introduced at the beginning of the pyrolysis could lead to a considerable activation of the carbon. Thus, a higher amount of surface functionalities could be expected for the one-step AC. In particular, the difference is more marked for the amount of CO₂ released from Birch AC after one- and two-step procedures. At the same time, a larger shift toward higher temperature was observed for Birch AC from one- and two-step procedure in the TPO profiles. Indeed, the temperature for the maximum of CO₂ evolution was 43 °C higher for the one-step birch AC with respect to the corresponding two-step sample. For the one-step AC derived from Red Maple and Ironwood, a smaller shift was observed with respect to the corresponding two-step AC, 25 and 21 °C, respectively. Same trend is observed for the CO amounts, with the exception of Red Maple AC (Red Maple 2) sample which shows a higher amount of CO although it was produced through the two-step process. This may be explained by the higher reactivity of Red Maple char. AC derived from different sources through the two-step procedure show difference in surface composition and the reason of this can be found again in the reactivity of the parent chars. From TPO analysis, Red Maple was found to be the more reactive char and the corresponding AC (Red Maple 2) shows the higher amount of surface functionalities (higher amount of CO₂ and CO). Chars from Birch and Ironwood showed respectively an intermediate and lower reactivity. Indeed, CO₂ and CO amounts from TPD/MS analysis are intermediate for Birch (Birch 2) and lower for Ironwood (Ironwood 2) derived AC. Thus, TPO technique could predict the extent of surface functionalization based on the tendency of the char to oxidize during the activation process. The higher the oxidation tendency of the char, the larger the amount of surface functionalities on AC is.

3.4 Methylene blue adsorption

Methylene blue adsorption tests indicate the capacity of AC to adsorb molecules having similar dimensions to methylene blue and to determine the presence of pores larger than 1.5 nm (Hui, 2015). The presence of surface functionalities, as well as the porous structure, are known to affect the adsorption performance of AC (Spagnoli et al., 2017). Methylene blue can interact with carbonaceous adsorbent through electrostatic interactions, like dipole-dipole interaction between methylene blue and surface phenols or hydrogen bonding between hydroxyl group of phenols and aromatic ring of methylene blue (Spagnoli et al., 2017). Moreover, an increase in adsorption of methylene blue was observed for materials having carboxylic acid groups on the surface (Laksaci et al., 2017). Figure 3 shows the trend of methylene blue adsorption for two-step AC with the amount of CO and CO₂ evolved from the decomposition of surface functionalities.

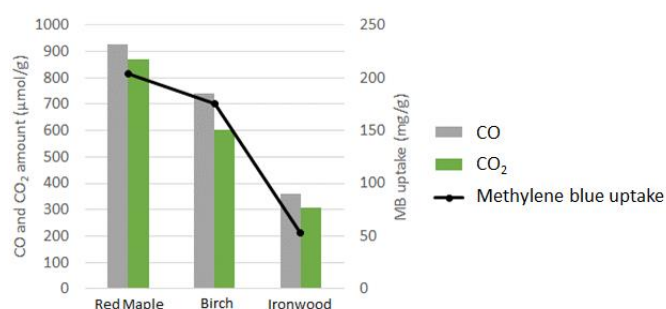


Figure 3: CO and CO₂ amounts and methylene blue uptake for two-step AC.

The Red Maple AC shows the higher amount of surface groups and the higher methylene blue uptake, followed by Birch and Ironwood AC. This trend suggests that the presence of surface groups improved the adsorption performance. However, in the adsorption process, the porosity could play an important role as well. The adsorption capacity toward methylene blue of the prepared AC is comparable to the one reported by Zubair et al. (2020) for biomass-derived AC.

4. Conclusions

Significant differences in the yields, oxidation reactivities, surface compositions and adsorption properties were observed for wood samples pyrolyzed and activated under the same conditions. Char reactivity toward oxygen

and density of starting woods affect the pyrolysis/activation yields and the properties of the resulting materials. Ironwood has the higher density and provides higher yields. Red Maple char shows a higher tendency to oxidation and formed AC with lower yield, higher content of surface functionalities and improved adsorption toward methylene blue. Determining the oxidation reactivity of chars through TPO may help in predicting the properties of the resulting AC as extent of surface functionalization which affects the adsorption performance.

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