



Physico-Chemical Properties and Use of Waste Biomass-Derived Activated Carbons

Riikka Lahti^{a,b}, Davide Bergna^{a,b}, Henrik Romar^{a,b}, Tero Tuuttila^b, Tao Hu^a, Ulla Lassi^{a,b}

^aUniversity of Oulu, Research Unit of Sustainable Chemistry, P.O.Box 3000, FI-90014 University of Oulu, Finland

^bUniversity of Jyväskylä, Kokkola University Consortium Chydenius, Applied Chemistry, P.O.Box 567, FI-67101 Kokkola, Finland

riikka.lahti@chydenius.fi

Activated carbons are widely used in different industrial processes for example as adsorbents or as support materials. Advantageously these carbons can be prepared from residual or waste biomass materials. Different raw material type and activation procedure plays an important role in the physico-chemical characteristics of activated carbon e.g. surface area, porosity and pore distribution. In this study, activated carbon has been prepared from lignocellulosic waste materials (e.g. saw dust, lignin residue) and characterized by a number of methods. Further, adsorption properties of carbons were evaluated. Adsorption capacity of dyes and metals was high (methylene blue dye 86 % and zinc metal 97 % removal) onto prepared activated carbons.

1. Introduction

Activated carbons (AC) are widely used in different industrial processes for example as adsorbents in the water purification process or as support materials because of its high surface area and well-developed porous structure. Typically activated carbons has been prepared from carbonaceous materials e.g. coal. Advantageously these carbons can be prepared from residual or waste biomass materials, which are alternative low-cost raw materials. Different raw material type and activation procedure has an important role in the physico-chemical characteristics of activated carbon e.g. surface area, porosity, and pore distribution, and surface functional groups which are all important properties for supports and adsorbents. For preparation of activated carbon, thermal procedures carbonization and activation are used. Activation can be prepared by chemical or physical activation process. In the carbonization step temperature is raised to high temperatures (~400-900 °C), and followed by the activation step in which activating agent: steam, carbon dioxide, air, or a mixture of these is fed in the system for the proper surface activation. (Serp and Machado, 2015)

Activated carbon is widely used as an adsorbent in the water purification processes. For example, textile industry produces large number of dyed wastewater (Wang and Zhu, 2007). Other pollutants that are produced in the industry are for example heavy metals, sulphates, nitrates and phosphates and excess of these needs to be removed from wastewater. Other possibly use for activated carbon can be as a support for metal catalysts. Dyes, metals and ions can be adsorbed onto surface of AC. During the adsorption, dissolved species such as organic or inorganic materials diffuse into the pores of adsorbent. Because adsorption takes place on the surface, a large surface area with number of pores is necessary for adsorbent. With high porosity, adsorbents can have a pore volume of 0.1 to 0.8 mL/g and a surface area ranging from 400 to 1500 m²/g. As a result, the adsorption capacity can be as high as 0.2 g of adsorbate per gram of adsorbent, depending on the adsorbate concentration and type. The size of the adsorbate that can enter a pore is limited by the size of the pore. Pore sizes (diameter d_p) in the AC can according to IUPAC be classified into micropores: $d_p < 2$ nm, mesopores: $2 \text{ nm} < d_p < 50$ nm and macropores: $50 \text{ nm} < d_p$. (Howe et. al. 2012; Ioannidou and Zabaniotou, 2007)

In our earlier studies (Kilpimaa et al., 2014, 2015; Runtti et al., 2014, 2016), we have used carbon residues from biomass gasification process as raw material for ACs and used it as adsorbent for metal cations, phosphate, nitrate and sulphate removal. In this study, activated carbon is prepared by physical activation of

raw material by steam after carbonation step at temperature 800 °C in an inert atmosphere. As a raw material, lignocellulosic waste materials: saw dust of birch, spruce, pine and willow, and also Kraft lignin, fraction from pulping process, has been used. These prepared activated carbons have been characterized by a number of methods including carbon content (TC), specific surface area, pore size distribution and scanning electron microscopy (SEM). Adsorption properties of carbons were also evaluated.

2. Materials and methods

2.1 Raw materials

Waste fractions of lignocellulosic biomass; saw dust of birch, spruce, pine and willow, and Kraft lignin from pulping process were used. All samples were from northern Finland.

2.2 Chemical analysis of wood samples

The moisture content of the samples was obtained by drying the samples in an oven at 105 °C until the weight of the samples were constant. The ash content was determined using procedure described by Sluiter et al. (2008). Wood samples (3 g) were extracted with 150 mL of acetone for 4 hours by soxhlet extraction equipment in order to remove organic extractives (Tappi, 1999). Extractives-free samples were utilized to determinate lignin and holocellulose content. Klason lignin was determined by the slightly modified procedure described by Rowel et al. (2005). 200 mg of extractives-free wood samples were weighed in the test tubes, and 4 mL of 72 % H₂SO₄ was added. The test tubes placed in the water bath at 30 °C for 1 hour. The samples were stirred occasionally with a glass rod. Subsequently, the mixture was transferred to the autoclave bottle, and 112 mL of distilled water was added. The samples were autoclaved at 121 °C and 1 bar for 60 min. The lignin was filtered and washed with hot water. The lignin was dried in oven at 105° and weighed. Holocellulose was prepared from extractives-free samples applying the previously published procedure (Rowell et al. 2005). Generally, 1.5 g of extractives-free sample, 48 mL of distilled water, and 0.3 mL of Acetic acid and 0.75 g of sodium chlorite were allowed to react in a 250 mL Erlenmeyer flask in a water bath (70-75 °C). After 60 minutes additional 0.3 mL of Acetic acid and 0.75 g of NaClO₂ were added. After each succeeding hour, fresh portion of 0.3 mL of Acetic acid and 0.75 g of NaClO₂ was added. After 6 hours, the flask was allowed to cool and the holocellulose was filtered. The residue was washed with distilled water until the yellowish color was removed, and finally dried in an oven at 105 °C. The residual lignin content in holocellulose was determined by the above-mentioned methods. The α-cellulose content was determined from the holocellulose, applying the previously published procedures (Yokohama et al., 2002; Styarini et al., 2012). 0.75 g of holocellulose and 37.5 mL of 17.5 % NaOH was placed in a 250 mL Erlenmeyer flask and stirred until holocellulose was completely dispersed. The stirrer was then removed and washed with 12.5 mL of 17.5 % NaOH to make total reagent content in the flask 50 mL. The flask was placed in a water bath at 25°C. After a period of 30 min from the first addition of the NaOH reagent, 50 mL of distilled water was added to the suspension and stirred thoroughly with glass rod. The flask was left in the bath for another 30 min. At the end of 60 min, the suspension was stirred and filtered. The solid α-cellulose was washed first with distilled water, then with 20 mL of 10 % Acetic acid, and finally with distilled water until the filtrate was neutral. The hemicellulose content was obtained by subtracting α-cellulose fraction from holocellulose. The results are presented as a mean value of the duplicates.

Metal contents of samples were measured by inductively coupled optical emission spectrometry (ICP-OES) using a Perkin Elmer Optima 5300 DV ICP–OES instrument. 0.10-0.12 g samples were added in 63 % nitric acid and hydrogen peroxide, then digesting in a microwave oven (MARS, CEM Corporation) at 200 °C for 10 min. After digestion, the solution was diluted to 50 mL and measured by ICP-OES.

2.3 Preparation of activated carbons

The dried and sieved lignocellulosic biomass was carbonized and steam activated in a one-step process in a rotating quartz reactor (Nabertherm GmbH RSRB 80). The thermal process was divided into two parts: the first carbonization step, in which the temperature was raised to 800 °C, followed by the activation step. During the activation, temperature was kept at 800 °C for 120 min with a stream of steam, for the proper surface activation. During the whole process, the reactor was flushed with an inert gas, N₂. The resulting AC was characterized for yields, carbon content (TC), specific surface area, pore size distribution and scanning electron microscopy (SEM).

2.4 Calculations of yields and total carbon determinations

The mass yield from each sample was calculated as the mass of activated carbon measured divided by the initial sample mass used for carbonization and activation. The content of carbon present in each sample, given as total carbon (TC) percent, was measured using a solid phase carbon analyzer (Skalar Primacs

MCS). Dried samples were weighted in quartz crucibles, combusted at 1100 °C in an atmosphere of pure oxygen and the formed CO₂ was analyzed by an IR analyzer. Carbon content values were obtained by reading the signal of IR analyzer from a calibration curve derived from known masses of a standard substance, oxalic acid. The total mass of carbon was calculated as a percent of the mass initially weighted and was measured after the carbonization and activation step.

2.5 Specific surface area and pore size distribution

Prior to measurements samples (about 200 mg) were pretreated at low pressures and high temperatures to clean the surfaces. Sample tubes were immersed in liquid nitrogen (-197 °C) and nitrogen gas was added to the samples in small steps and the resulting isotherms were obtained. Specific surface areas were calculated from adsorption isotherms according to the BET method (Brunauer et al., 1938) and pore size distributions were calculated using the BJH algorithm (Barrett et al., 1951).

2.6 A field emission scanning electron microscope

A field emission scanning electron microscope (FESEM) Zeiss Ultra Plus equipped with an energy-dispersive X-ray spectroscopy (EDS) analysis system at the Center of Microscopy and Nanotechnology, University of Oulu was used to study the microstructure of the catalysts and for elemental analyses.

Scanning electron images were taken under an acceleration voltage of 5 KV and working distance around 5 mm without any coating. The AZtec software (Oxford Instruments) was used for EDS analyze.

2.7 Adsorptive properties

The formed AC's adsorption properties were tested with different adsorption procedures. Adsorption capacity of basic dyes including methylene blue and gentian violet (Raposo et al., 2009; Wang and Zhu, 2007) were tested onto activated carbons. A solution containing 300 mg/l of dye was prepared, 100 mL of this solution was transferred into Erlenmeyer flask with 100 mg of activated carbon and the solution were continuously agitated for 24 hours in order to achieve equilibrium between adsorption and desorption of the test dye. Portions of each solution were filtered and, if needed, diluted, and the absorbance of the solution was measured at 664 nm (methylene blue) or 582 nm (gentian violet) on a Shimadzu UV-1800 double-beam spectrophotometer. The concentration of the solution was calculated from a calibration line obtained with known concentrations. The adsorbed mass was calculated using Eq(1) and the percent removed was calculated using Eq(2)

$$q(ads) = (C_0 - C_t) \cdot V/m \quad (1)$$

$$\% \text{ removed} = (C_0 - C_t) / C_0 \quad (2)$$

Where C_0 is initial concentration (mg/L), C_t is measured concentration after 24 h, V is volume of the solution used and m is mass of the activated carbon used.

Also adsorption capacity of zinc, nitrate, sulphate and phosphate ions were tested with selected carbons. A solution containing 50 mg/L of Zn²⁺ metal ion or NO₃²⁻/SO₄²⁻/PO₄³⁻ ions was prepared; 25 mL of initial solution was transferred into Erlenmeyer flask with 5 g/L of AC. Since the pH of the AC's prepared from lignocellulosic biomasses is quite alkaline (pH ~10), pH of the solution was adjusted to 4 with 0.1 M HCl, preventing the formation of unwanted precipitation. After the pH adjustment solution were continuously agitated for 24 hours. Portions of each solution were filtered, diluted, and the concentration of the metal in the solution were measured with atomic absorption spectroscopy (AAS) Perkin-Elmer AAnalyst 200 and ion concentrations were measured with ion chromatography (IC) Metrohm Compact using an anion column and a carbonate based eluent. Adsorption capacities of metal and anions were calculated as previous using Eqs. (1) and (2).

3. Results and discussion

Organic and inorganic materials were determined from raw materials. Moreover, elemental analysis of heteroatoms (carbon, hydrogen and nitrogen) was determined. In Table 1 is presented percentage of TC, ash, extractives, lignin, holocellulose and elemental analysis from birch, spruce and pine. From Table 1 can be seen that there are some variations in composition of the samples. Pine contains least and spruce the most of inorganic (ash) material. Elemental analysis showed that birch contains more nitrogen and hydrogen, and less carbon than other samples. The most abundant fraction from organic compounds was holocellulose, which includes α -cellulose and hemicellulose. From the samples, pine contained most of α -cellulose. Birch had more hemicellulose than other samples. Metal content from the samples were also determined and presented in Table 2. In all samples the biggest fractions of metals were calcium (>840 mg/kg) and potassium (>560 mg/kg). From raw materials, spruce contained most of calcium (1540 mg/kg) and potassium (626 mg/kg).

From raw materials pine contained most aluminium, iron, chromium and nickel. Birch had higher values of phosphorous, sulphur and zinc than other samples.

Table 1. Content of total carbon, ash, extractives, lignin, holocellulose and elemental analysis from birch, spruce and pine.

| Sample | Unit | Birch | Spruce | Pine |
|------------------------|------|-------|--------|------|
| Total carbon | (%) | 46.9 | 47.0 | 45.8 |
| Ash | (%) | 0.55 | 0.65 | 0.43 |
| Extractives | (%) | 3.7 | 2.7 | 3.3 |
| Lignin | (%) | 23.4 | 27.7 | 27.6 |
| Holocellulose | (%) | 69.3 | 63.5 | 70.9 |
| α-Cellulose | | 37.4 | 40.2 | 44.4 |
| Hemicellulose | | 31.9 | 23.3 | 26.5 |
| Elemental analysis (%) | | | | |
| C | | 50.5 | 51.1 | 51.8 |
| H | | 6.67 | 6.48 | 6.51 |
| N | | 0.24 | 0.20 | 0.17 |

Table 2. Metals in lignocellulosic raw material (birch, spruce and pine).

| Sample | Unit | Birch | Spruce | Pine |
|--------|---------|-------|--------|------|
| Al | (mg/kg) | 11.9 | 27.8 | 65.9 |
| B | | 3.39 | 2.73 | 2.24 |
| Ca | | 1240 | 1540 | 844 |
| Cd | | 0.16 | 0.07 | 0.17 |
| Cr | | 0.97 | 2.68 | 10.1 |
| Cu | | 1.26 | 1.20 | 1.45 |
| Fe | | 16.1 | 28.1 | 63.8 |
| K | | 611 | 626 | 563 |
| Mg | | 234 | 151 | 213 |
| Mn | | 95.4 | 119.0 | 78.6 |
| Na | | 6.05 | 7.17 | 7.00 |
| Ni | | 0.47 | 1.20 | 4.79 |
| P | | 131.0 | 85.0 | 94.2 |
| Pb | | <1.0 | <1.0 | <1.0 |
| S | | 89.4 | 70.5 | 76.1 |
| Zn | | 47.7 | 27.6 | 27.4 |

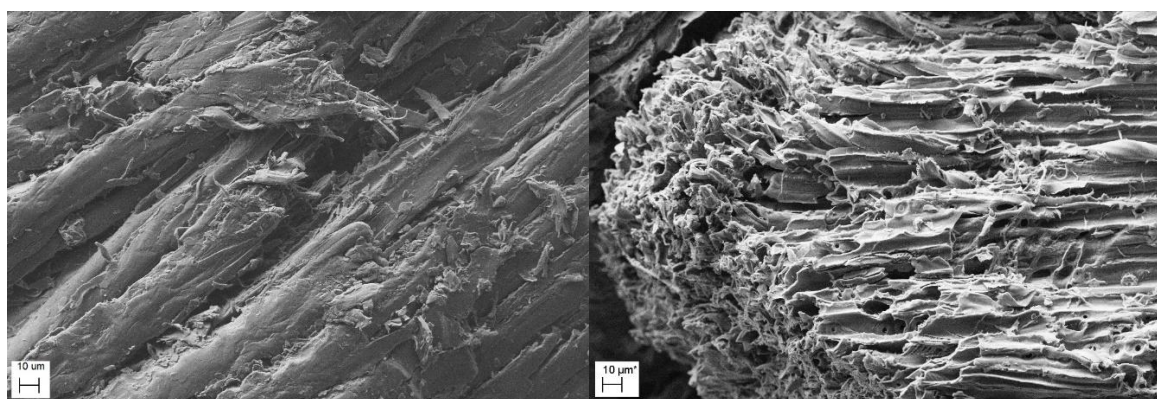


Figure 1. FESEM images of the raw lignocellulosic biomass of pine (on the left) and activated carbon prepared from pine (on the right).

Table 3. Yields, total carbon content, surface areas, pore volumes and mean pore sizes of the prepared activated carbons and raw lignin as a reference material.

| Sample AC | Yield (%) | TC (%) | BET | | | BJH | | |
|------------|-----------|--------|---|----------------------------------|------------------------|---------------|--------------|---------------|
| | | | Specific surface area (m ² /g) | Pore volume (cm ³ /g) | Average pore size (nm) | Micropore (%) | Mesopore (%) | Macropore (%) |
| Birch | 10 | 97 | 860 | 0.61 | 2.8 | 14 | 84 | 2 |
| Spruce | 10 | 88 | 1080 | 0.80 | 3.0 | 18 | 78 | 4 |
| Pine* | 12 | 91 | 336 | 0.24 | 2.9 | 18 | 76 | 6 |
| Willow | 13 | 89 | 660 | 0.40 | 2.4 | 18 | 78 | 4 |
| Lignin | 13 | 93 | 750 | 0.62 | 3.3 | 32 | 62 | 6 |
| Raw lignin | - | 65 | >5 | 0.02 | 18 | | | |

*Pine activation time 4h, other sample's activation time 2h

FESEM images of raw material was taken before and after the carbonization and activation process. Formed porous structure can be seen clearly from Figure 1. Yield, total carbon content, specific surface area, pore volume and mean pore sizes of the prepared activated carbons are presented in Table 3 and values are compared to raw lignin without carbonization and activation. Activation with steam creates high, porous surface structure that varies with different raw materials. Carbon content in raw materials was about 50 % (see Table 1) and after carbonization and activation the total carbon content increased to about 90 % and surface area increased from almost zero (<5 m²/g) to 300-1000 m²/g. Spruce had the largest surface area (over 1000 m²/g) and pore volume (0.8 cm³/g). Inorganic material (ash) content in the raw material might correlate to porous structure. The more raw material contained ash (see Table 1) the more porous structure; higher surface area and pore volume is formed during the activation (see Table 3). Meso- and macroporous structure was high for sawdust's, over 80 %, which is important if bigger molecules are wanted to adsorb into the pores. AC of Kraft lignin had a higher microporous (32 %) and less mesoporous structure (62 %) than other AC samples. According to Correa et. al (2017) the higher micropore volumes might correlate with a higher content of lignin in the biomass.

From the prepared activated carbons, AC of birch was selected for adsorption test. Adsorption properties of dyes methylene blue and gentian violet were tested onto prepared AC of birch (Table 4.). Further metal adsorption and anion adsorption were tested (Table 4.). After 24-hour test, adsorption capacity of dyes was high. With dye methylene blue, adsorption was 240 mg per gram of AC and the adsorption percentage was 86 %. With gentian violet adsorption was little bit lower, 74 %. Adsorption properties of metal was tested with zinc metal and 97 % of metal was adsorbed onto the AC from solution. Anions of nitrate, sulphate and phosphate were also tested for the adsorption properties of activated carbon and the capacity was from 30 to 40 % (PO₄³⁻ < SO₄²⁻ < NO₃²⁻). According to literature, activated carbons shows lower adsorption towards anionic pollutants (Bhatnagar and Sillanpää, 2011). The lower adsorption capacity of anions indicate that prepared AC might have more negatively charged adsorption sites on the surface where cations can bind more strongly than negatively charged anions.

Table 4. Adsorption equilibrium concentrations of dyes methylene blue (MB), gentian violet (GV), zinc metal, and nitrate, phosphate and sulphate ion onto AC prepared from birch after 24h adsorption test.

| Adsorbate | Adsorption (mg/g) | Adsorption (%) |
|-------------------------------|-------------------|----------------|
| MB | 258 | 86 |
| GV | 222 | 74 |
| Zn ²⁺ | 9.9 | 97 |
| NO ₃ ²⁻ | 4.2 | 43 |
| SO ₄ ²⁻ | 4.0 | 36 |
| PO ₄ ³⁻ | 1.6 | 31 |

4. Conclusions

In this study, a number of activated carbon from lignocellulosic waste materials were prepared and characterized. Different raw materials and their composition seemed to have role in the preparation step and further properties of prepared activated carbons, e.g specific surface area and porosity. From the prepared activated carbons, especially spruce and birch AC had high carbon contents, high specific surface areas and pore size distribution containing mainly mesopores. Metal and lignin content in the raw material might

correlate to the porous structure of the AC. Prepared activated carbon from waste materials were also tested for their adsorption properties of dyes, metals and anions. Adsorption capacity of metal cations and dyes was high onto activated carbon prepared from birch. With zinc metal removal was 97 % and with methylene blue dye 86 %. Removal of anions was lower from ~30 to 40 % ($\text{PO}_4^{3-} < \text{SO}_4^{2-} < \text{NO}_3^{2-}$).

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