



# Mechanochemical and chemical activation of lignocellulosic material to prepare powdered activated carbons for adsorption applications



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## ABSTRACT

This work presents a solvent-free mechanochemical approach toward controlled preparation of powdered activated carbons from lignocellulosic residue (horse chestnut shell, CS). The physicochemical changes of the biomass during mechanochemical and chemical activation with  $K_2CO_3$  and the properties of the final materials obtained after pyrolysis at 700 °C have been investigated by means of thermogravimetric analysis (TG–DTG), scanning electron microscopy (SEM), X-ray diffraction (XRD),  $N_2$  adsorption–desorption, infrared and micro-Raman spectroscopy. The results indicated that the mechanochemical activation is superior to the traditional chemical activation in terms of specific surface area, pore development and the degree of structural order of the activated carbons. Furthermore, it has been observed that the later parameters depend on the milling time and the maximal BET surface area (1040 m<sup>2</sup>/g) and total pore volume (1.01 cm<sup>3</sup>/g) of the resulting mesoporous material can be obtained after 3 h milling of the raw material/ $K_2CO_3$  mixture. In addition, malachite green oxalate (MGO) adsorption capacities of the carbons were also examined and adsorption uptake up to 250 mg/g is observed. This study demonstrates the potential use of CS as a precursor in the preparation of activated carbon for adsorption applications and opens up new ways for activation of lignocellulosic materials under ball-milling conditions.

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## 1. Introduction

The preparation of activated carbons (ACs) with appropriate structural and chemical properties has gained much attention over the last decades [16]. Due to their highly developed internal surface area, porous structure and high degree of surface reactivity, ACs are widely used as adsorbents in a variety of industrial fields for water purification, gas separation and catalysis [1–3]. Furthermore, porous carbon materials play an important role in numerous emergent applications such as storage of electrical energy in supercapacitors [4], immobilization and separation of large biomolecules [5], CO<sub>2</sub> capture [6] and hydrogen storage [7]. Activated carbon can be produced from a wide range of carbonaceous precursors such as bituminous coal, wood, coconut shell, peat, petroleum pitch, and polymers [8]. Among all the precursors, lignocellulosic residues have received an increasing attention due to their low-cost, renewability and wide prevalence [9]. A huge number of lignocellulosic biomass based ACs such as bamboo [10], cherry stones [11], rice husk and bagasse [12], coffee endocarp [13], potato peels [14] and peanut shells [15] have been reported.

There are two methods for preparing activated carbon – physical and chemical activation. The physical activation consists of the pyrolysis of the carbonaceous precursor and gasification of the char at high temperatures. In chemical activation (also called wet oxidation) process, the raw material is first impregnated by strongly reacting chemicals such as ZnCl<sub>2</sub>, H<sub>2</sub>SO<sub>4</sub>, NaOH, KOH, K<sub>2</sub>CO<sub>3</sub>, K<sub>2</sub>HPO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub>, followed by thermal activation in an inert atmosphere. In the latter method, the dehydrating effect of the used activating agents hinders the formation of tar which lead to higher AC yield and to lower activation temperature than those reported for the physical activation [16]. In addition, ACs obtained by chemical activation demonstrate higher surface area and better developed mesoporosity than physical activation [17].

Mechanochemical activation of the precursors can be considered as another method for fabrication of AC. Ball-milling has proved to be effective for preparing ceramic powders [18] and nanomaterials [19], for conducting solvent-free organic reactions [20] and for degradation of waste materials [21]. Mechanochemistry offers several benefits over traditional solvent-based protocols like simplicity, mild/short reaction conditions, ease of scale-up and the ability to synthesize metastable phases [22]. Performing reactions without the need of solvents is advantageous, as it is eco-friendly and low-cost process. Nevertheless, as far as we know, this technique has rarely been applied for the activation of carbonaceous precursors in preparation of AC powders.

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In this study, we investigate the potential of mechanochemical treatment of lignocellulosic biomass/activating agent mixtures under solvent-free conditions as an alternative route for preparation of AC. Horse chestnut shell was chosen as a renewable carbon resource. Horse chestnut (*Aesculus hippocastanum*) is a deciduous tree native to the Balkan Peninsula, but grow throughout the Northern Hemisphere [23]. Horse chestnut is one of the most attractive ornamental trees and is planted widely in parks and gardens in both urban and rural areas in Europe, e.g. at least 20,000 horse chestnut trees grow in Vienna and its environs [23]. Although the dried ripe seeds of the tree are of medicinal interest, the horse chestnut shell has no significant industrial and commercial use. Because of the prevalence of the species, horse chestnut shell can be considered as an inexpensive raw material in AC fabrication.

The main goal of the present work is to determine the effects of the solid state mechanochemical activation of chestnut shell in the presence of  $K_2CO_3$  on the physicochemical characteristics and adsorption properties of the as-prepared ACs in comparison to the traditional chemical activation method. In the first part of the paper, the structural and compositional transformations in the course of ball-mill-based mechanochemical activation of horse chestnut shells in the presence of  $K_2CO_3$  are examined. The mechanochemically obtained precursors have been heated at 700 °C in order to obtain porous carbons and their morphological, structural and textural features are reported in the second part of the paper. The prepared materials have also been tested in the adsorption of malachite green oxalate from aqueous solution at room temperature (25 °C). For the sake of comparison, AC prepared by traditional chemical activation method via impregnation of the raw material with  $K_2CO_3$  is also assayed.

## 2. Experimental

### 2.1. Materials

Horse chestnut (*A. hippocastanum*) seeds were collected from a park region in Sofia, washed thoroughly with distilled water, dried at room temperature and peeled to get the shells off. The shells were washed once again, dried at 110 °C for 6 h, crushed and sieved. Fraction with particle size of 1–1.7 mm was used in the rest of our work (denoted as CS). For the characterization of CS proximate and elemental analyses were performed. Moisture, volatile matter, fixed carbon and ash contents of the raw material were determined according to the ASTM standard methods. Elemental analyses were performed with Carlo Erba 1106 combustion elemental analyzer. Sulfur content was determined by Eshka method. The proximate, ultimate and component analyses of CS sample are shown in Table 1.

In order to obtain mechanically activated precursors, the raw material (CS) was mixed with  $K_2CO_3$  at the  $K_2CO_3/CS$  mass ratio of 1:1 and the mixture was milled in a planetary ball mill Pulverisette 5 (Fritsch) at 550 rpm with the ball-to-powder mass ratio of 10:1. Before the experiments, potassium carbonate (>99%, Fisher Chemical) was dehydrated at 120 °C overnight. The samples (denoted as CSK-*t*) were treated for 1, 2, 3 and 4 h (*t*). CS powder was also milled at the same conditions for the same times (samples named CS-*t*). For traditional wet oxidation, CS powder was kneaded with saturated aqueous solution of  $K_2CO_3$  ( $K_2CO_3/CS$  mass ratio of 1:1) at room temperature and the mixture was then dried at 110 °C for 6 h. The obtained impregnated sample is denoted as CSK-W. The carbonization of CSK-*t* and CSK-W samples was performed in a conventional horizontal furnace at 700 °C in nitrogen flow. In each run the activation temperature was reached at a 10 °C/min heating rate and maintained for 1 h. The resulting carbons were washed with doubly distilled water till neutral pH and dried at 110 °C overnight. The activated carbons prepared from CSK-*t* precursors are denoted as AC-*t* and from CSK-W as AC-W.

**Table 1**  
Chemical characteristics of the raw chestnut shells.

Proximate analysis (wt%)		Ultimate analysis (wt%)		Composition <sup>a</sup> (wt%)	
Moisture	6.99	Carbon	47.39	Lignin	59.4 ± 5
Volatile	69.70	Hydrogen	5.71	Holocellulose <sup>b</sup>	48.5 ± 5
Fixed carbon	22.71	Nitrogen	1.48		
Ash	0.60	Oxygen <sup>c</sup>	45.32		
		Sulfur	0.10		

<sup>a</sup> According to Ref [24].

<sup>b</sup> Cellulose and hemicellulose.

<sup>c</sup> By difference.

### 2.2. Methods

The thermal behavior of CS, CS-*t*, CSK-*t* and CSK-W samples were studied by thermogravimetry (TG) and derivative thermogravimetry (DTG) in nitrogen atmosphere, using Perkin-Elmer TGS-2 thermobalance. The total weight losses of the samples were determined from the corresponding TG curves at the final heating temperature of 700 °C. Powder X-ray diffraction (XRD) patterns of the samples were recorded at room temperature on the Bruker D8 Advance diffractometer using  $CuK\alpha$  radiation. The morphology and the microstructure of CS, CS-*t*, CSK-*t*, AC-*t* and AC-W were analyzed by scanning electron microscopy (SEM, JEOL 5510) applying gold coating before the observation. The Fourier transform infrared (FTIR) spectra (KBr pellets) of the studied samples were recorded between 4000 and 400  $cm^{-1}$  by using Nicolet 6790 FT-IR (Thermo Scientific) spectrometer.

Raman spectra of AC-*t* and AC-W samples were measured using micro-Raman spectrometer HR 800 (Jobin Yvon). The grating utilized is 600 g/mm. The excitation is provided by the built-in He-Ne laser, at 632.8 nm. The laser intensity on the sample was <0.06 mW and the spectral accuracy achieved is better than 1  $cm^{-1}$ . Each spectrum is an average of 5 spectra, obtained from 5 different points from the sample with objective  $\times 50$ .

The texture characteristics of activated carbons were determined by low-temperature (77.4 K) nitrogen adsorption in a Quantachrome Instruments NOVA 1200e apparatus. The nitrogen adsorption-desorption isotherms were analyzed to evaluate the following parameters: the specific surface areas ( $S_{BET}$ ) were determined on the basis of the BET equation, the total pore volume ( $V_t$ ) was estimated in accordance with the Gurvich rule at a relative pressure close to 0.99. The volume of the micropores ( $V_{MIC}$ ) and specific surface area connected to micropores ( $S_{MIC}$ ), as well as the external specific surface area ( $S_{EXT}$ ) were evaluated according to V-t-method. Additionally, the pore-size distributions were calculated by DFT method using slit pore, NLDFT (nonlocal density functional theory) equilibrium model. All samples were outgassed for 16 h in vacuum at 120 °C before the measurements.

Batch adsorption experiments were carried out by agitating 0.04 g of AC-*t* and AC-W in 125 mL (100  $mg L^{-1}$ ) of malachite green oxalate (MGO,  $C_{48}H_{50}N_4O_4 \cdot 2C_2H_2O_4$ , 90% dye content, Aldrich) aqueous solutions in an incubator at 25 °C for 72 h to ensure that the adsorption equilibrium is reached. The adsorbed amounts were then calculated from the difference between the initial and equilibrium concentration of the dye, as determined with UV-Vis absorption spectroscopy (Evolution 300 Thermo Scientific Spectrophotometer).

## 3. Results and discussion

### 3.1. Mechanochemical treatment vs impregnation of raw biomass

#### 3.1.1. TG-DTG

The TG and corresponding derivative (DTG) curves for the raw material (CS), CSK-*t* and CSK-W samples are compared in Fig. 1a, b. The

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