

## EFFECT OF KOH ACTIVATION ON HYDROCHAR SURFACE: FT-IR ANALYSIS\*

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**Abstract.** Hydrothermal carbonization has been proven as one of the simplest and most efficient technologies to produce a variety of carbon-based hydrochars with various applications. Like other types of biochars, hydrochar has reactive, functionalized/aromatic surfaces. Those properties make hydrochar a potential low-cost adsorbent for water purification and soil remediation. In order to increase its ability to remove heavy metal contaminants from aqueous solutions, chemical modification/activation of hydrochar surface using KOH has been suggested. The presented FT-IR spectroscopy analysis of hydrochars obtained from grape pomace and miscanthus (*Miscanthus×giganteus*) showed that KOH modification increased the oxygen-containing functional groups on hydrochar surfaces and its aromaticity. As a result, activated hydrochars may demonstrate enhanced sorption efficiency.

**Key words:** Hydrochar, grape pomace, miscanthus, FTIR, alkali activation

### 1. INTRODUCTION

The primary objective of the contemporary waste management strategy is to increase the utilization of the “whole biomass waste” by implementing innovative, environmentally sound and cost-effective production technologies. However, the reuse of agricultural and food industry residues for production of value-added products is still insufficient [1]. Despite many novel technologies for waste biomass processing, these by-products have been generally under-utilized and many times considered as waste and/or a problem. Furthermore, wet lignocellulosic biomass is mainly unattractive feedstock for further utilization due to increased transport costs, energy consumptive pre-processing thermal treatments (e.g., combustion, pyrolysis), and also environmental issues related to the unpleasant odor and potential spreading of biological pathogens. Therefore, hydrothermal carbonization (HTC) has gained much attention as a potential conversion route for biomass waste, especially for that of very high water content (>50 wt %) [1].

The common HTC process is carried out in water as reaction medium at an elevated pressure and temperatures between 180 and 300 °C [2]. It is a low-emission and safe process, during which most of the carbon from the plants (up to 80%) remains bounded in the solid phase [3]. The produced solid, hydrochar (HC), created via reactions between subcritical water

and lignocellulosic residues, is a hydrophobic, porous, solid material with high carbon content [2]- [4].

HCs from various feedstocks have been extensively studied for different applications [5]-[8]. Due to their characteristic structure and abundance of oxygen-containing functional groups, HCs represent suitable alternative lower-cost sorbents for removal of a wide spectrum of water contaminants [9]. A good adsorption ability of different HCs for different heavy metals and radionuclides has been demonstrated [10]-[12]. Furthermore, significant improvement of adsorption efficiency of switchgrass HC for some heavy metals has been attained by chemical activation using hydroxides [13].

Inspired by the study of Regmi et al. [13], the aim of this work is to investigate the influence of cold alkali activation (using 2M KOH) on the surface structure of the HC obtained from grape pomace (GP) and miscanthus (MIS) (*Miscanthus×giganteus* Greef et Deu.) which should improve its surface reactivity and consequently enhance its adsorption efficiency. Activated hydrochars (AHCs) will be compared with the corresponding non-activated HCs, for their potentially different structural characteristics using FT-IR spectroscopy.

### 2. EXPERIMENTAL

The used GP (skin, stalk and seeds) was collected after the processing of the red grape, grown on a test

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plot Radmilovac, Belgrade, Serbia. The used MIS was grown on test sites of the Institute for the Application of Nuclear Energy (INEP), Zemun, Serbia. Both biomasses were air-dried until constant weight and extensively ground in order to obtain homogeneity of samples, whereupon the fraction of 0.5 mm was used in HTC experiments.

The preparation of grape pomace hydrochar (HC-GP) at 220 °C we have previously described elsewhere [14]. Hydrochar from miscanthus (HC-MIS) was prepared by the identical procedure, using HTC at 220 °C.

Alkali activation of both HC samples was carried out by stirring 2g of HC with 250 mL of 2M KOH solution for 1 h ( $25 \pm 0.5$  °C). Obtained AHCs (AHC-GP and AHC-MIS) were filtered, rinsed with distilled water and adjusted to the neutral pH with 0.1 M HNO<sub>3</sub>/KOH solution. Afterwards, both AHC samples were again filtered and dried at 105 °C.

Spectroscopic analyses were conducted using the Thermo Scientific Nicolet iS50 FT-IR spectrometer. The KBr pastilles with 0.8 mg of sample and 80 mg of KBr have been recorded in transmission mode to identify functional groups present on the HC and AHC surface. The spectra were obtained in the spectral range of 4000-400 cm<sup>-1</sup>.

### 3. RESULTS AND DISCUSSION

The FTIR spectra of analyzed HC-GP and AHC-GP samples are presented in Fig. 1 in relevant spectral regions (3700–2800 cm<sup>-1</sup> and 1850–500 cm<sup>-1</sup>). The O-H stretching band between 3600-3000 cm<sup>-1</sup>, which can be attributed to hydroxyl groups of water, alcohol groups from cellulose and phenols from lignin, increases in intensity with alkali activation. The position of this broad band shifts toward higher wavenumbers, which is most probably due to the assembly of intermolecular H-bonds established by OH groups following KOH treatment. Similarly, the peak at 1616 cm<sup>-1</sup>, attributed to C=C bonds from aromatic rings of lignin and a band of C-O stretching of syringyl groups between 1369 and 1389 cm<sup>-1</sup> [15], became broader, shifted towards higher wavenumbers and became more apparent (Fig.1). These groups play a major role during interactions between reactive surface groups of lignocellulosic residues and metal ions [16].

Conversely, bands at 1459 cm<sup>-1</sup> (C-H deformation in the lignin and carbohydrates), between 1318 and 1205 cm<sup>-1</sup> (C-O stretch from alcohols, carboxylic acid, esters and ethers between), 1161 (-C-O-C- from cellulose) and 783 cm<sup>-1</sup> (aromatic -CH<sub>3</sub>) [15], decreased in intensities. Bands at 1701 cm<sup>-1</sup> (C=O from cellulose and lignin) and 1514 cm<sup>-1</sup> (C=C from the aromatic ring) completely disappeared after alkali activation. The reduction of these bands' intensities may indicate that the addition of KOH causes a partial hydrolytic degradation of cellulose and lignin remained in HC after HTC. According to Regmi *et al.* [13], this may induce increased porosity of AHCs and thus enhance its adsorption of heavy metals.

Spectral bands between 2926 and 2851 cm<sup>-1</sup>, attributed to -C-H stretching of the methylene groups as an indication of increasing unsaturation, are similar

in both samples, HC and AHC of GP. The same is the case with peaks in the region between 1060 and 1030 cm<sup>-1</sup>, attributed to alcohol and/alkyl substituted ethers groups [14].

The FTIR spectra of analyzed HC-MIS and AHC-MIS samples are presented in spectral regions between

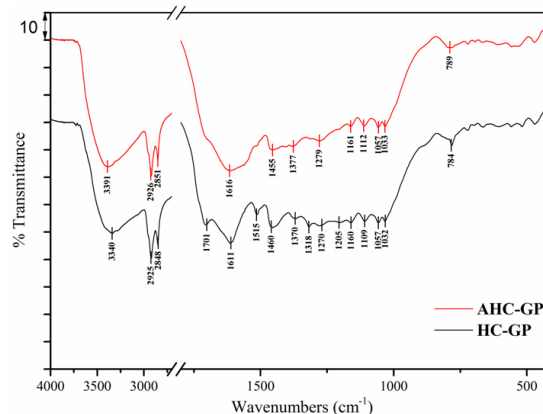


Figure 1. FTIR spectra of grape pomace HC and AHC

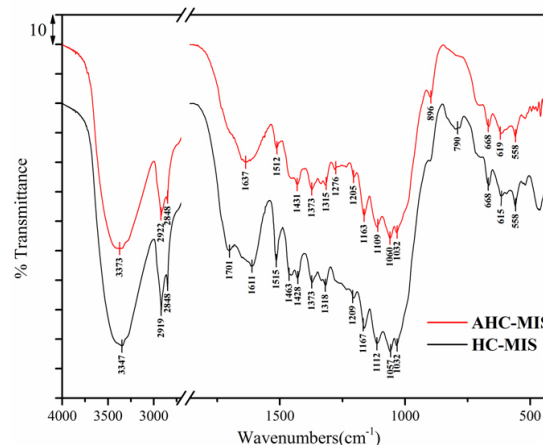


Figure 2. FTIR spectra of miscanthus HC and AHC

Similarly to the HC-GP, due to alkali activation, the position of O-H stretching band around 3347 cm<sup>-1</sup> in HC-MIS was shifted towards higher wavenumbers. Also, the peak at 1611 cm<sup>-1</sup> (C=C bonds from aromatic rings of lignin) became broader and shifted towards 1637 cm<sup>-1</sup>, while peaks at 1701 cm<sup>-1</sup> (C=O from cellulose and lignin) and 789 cm<sup>-1</sup> (aromatic C-H deformations) present in HC-MIS completely disappeared in AHC-MIS (Fig.2). However, KOH activation affected the manifestation of alkyl aryl ethers methoxy groups at 1276 cm<sup>-1</sup> and formation of aromatic C-H out-of-plane bend peak at 896 cm<sup>-1</sup> [15].

Peaks between 2920 and 2840 cm<sup>-1</sup> (-C-H of the methylene groups), at 1515 cm<sup>-1</sup> (C=C stretching of aromatic rings), 1450 (-CH<sub>2</sub>-) and 1373 cm<sup>-1</sup> (C-O stretching of syringyl groups from lignin) [15] slightly decreased in intensity after KOH treatment, but remain quite similar in both HC-MIS and AHC-MIS. Alkali activation did not affect the groups around 1320 cm<sup>-1</sup>

(C-O stretch), 1161  $\text{cm}^{-1}$  (-C-O-C- from cellulose), between 1060 and 1030  $\text{cm}^{-1}$  (C-OH alcohol and/alkyl substituted ethers groups) and bands between 720 and 590  $\text{cm}^{-1}$  attributed to alcohol, -OH out-of-plane bend [15].

#### 4. CONCLUSION

FTIR spectroscopy of HTC HCs and alkali activated HCs of both GP and MIS, revealed slight differences in the presence of surface functional groups. The increased intensity of hydroxyl groups and the overall aromaticity in both HCs samples after KOH treatment was noticed. Oppositely, intensities of carbonyl peaks, originating from cellulose and lignin, present in both HC samples, were reduced after activation, probably due to their partially hydrolytic degradation with KOH [13]. Unsaturation of both AHC samples was preserved upon activation.

Since oxygen-containing functional groups at the HC surface play major role in interactions with metal ions, presented results suggest that AHCs of GP and MIS may demonstrate enhanced sorption efficiency compared to the non-activated hydrochars. Furthermore, a more pronounced aromaticity of both AHCs may induce its increased porosity and additionally enhance its adsorption ability for heavy metals. Both observations are supported by the literature data in which the cold alkaline activation of HCs contributed to better adsorption of divalent metals from the solution [13].

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