

Activated Carbon from Hydrochar Produced by Hydrothermal Carbonization of Wastes

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Hydrothermal carbonization (HTC) is a thermo-chemical process for recovery and valorization of biomass and organic waste that uses sub-critical liquid water as a reaction medium for converting feedstock into value-added products. HTC treatment produces a carbonaceous solid, named hydrochar, with attractive characteristics that can be used in a variety of applications, such as activated carbon or soil amendment. In this study, activated carbons were prepared by KOH chemical activation of hydrochars obtained from hydrothermal carbonization of green waste and municipal solid waste. The effects of precursors and different KOH/char mass ratios on physical characteristics of the activated carbon were investigated. Methylene blue and iodine numbers were determined to evaluate the adsorption properties of obtained activated carbons. The results have shown a significant increase of porosity and a change in hydrochar structure by KOH activation method. The amount of mesopores and micropores increase with increasing KOH/char ratio. In particular, the sample by treatment of hydrochar from green waste activated with a 2:1 KOH/char weight ratio presented good mesoporosity, with a methylene blue number of 385 mg/g, and a well-developed micropore structure, with iodine number of 747 mg/g. Therefore, the application of KOH activated hydrochar as activated carbon appears to be promising.

1. Introduction

Hydrothermal carbonization (HTC) is a thermo-chemical process to upgrade diverse biomass feedstocks. HTC simulates natural coalification in coal petrology, involving the decomposition and carbonization of biomass material in water medium at desired temperature and autogenous pressure.

During HTC, biomass is converted in sub-critical water as reaction medium at mild temperature (180-250°C) and self-generated pressure (up to 2 MPa) for several hours (Fiori et al., 2014) to give three products: the solid carbonaceous product (hydrochar), a water-soluble organic fraction (sugars, acetic acid and other organic acids) and a gas fraction (mainly CO₂). Different feedstocks, process conditions, and production technologies may result in differences in hydrochar properties (Kambo and Dutta, 2015).

Hydrochar is a carbon-rich solid with physical structure and chemical characteristics comparable to lignite (Oliveira et al., 2013). For these characteristics, hydrochar can be effectively used as fuel, replacing traditional fossil coal. Recent studies report good performance obtained from hydrochar applications in the chemical industry, such as fertilizer for soil amendment in agriculture (Rillig et al., 2010), filler in composite materials and adsorbent for gas and liquid contaminants removal. Indeed, its high surface area and the presence of diverse surface sites such as carboxylic, hydroxyl, and carbonyl groups make it a suitable candidate for use as precursor for activated carbon (Park et al., 2013). Activation can be carried out by chemical or physical methods. In physical activation, the precursor is first carbonized in an inert atmosphere then activated using oxidizing agents such as steam or CO₂ (Rashidi and Yusup, 2015); whereas during chemical activation, carbonization and activation occur in a single step by carrying out thermal decomposition of the raw material impregnated with chemical agent, such as zinc chloride (ZnCl₂) (Tay et al., 2001), potassium hydroxide (KOH) (Mao et al., 2015) or phosphoric acid (H₃PO₄) (Belgacem et al., 2013).

In this work, hydrochar from two different feedstocks, green waste and municipal solid waste, was chemically activated with KOH. Activation conditions were varied, studying different KOH/char ratios fixing time and temperature of the thermal treatment to produce high surface area activated carbon. These resulting samples were characterized by morphologic, thermal and adsorption analysis by using methylene blue and iodine indexes for surface area and porosity measurements.

2. Experimental

2.1 Materials

Two different types of hydrochar, obtained respectively from HTC treatment of green waste (GW-HC) and municipal solid waste (MSW-HC), were supplied by Ingelia Srl (Valencia). The samples were first dried at 105 °C for 24 h, then ground in an agate mortar for 3 hr and sieved to particle size less than 75 µm. Potassium hydroxide, KOH, was used as chemical activating agent (Sigma Aldrich Co. Llc, Analytical grade chemicals, pellets).

2.2 Activated carbon preparation and characterization

Chemical activation with KOH of both hydrochars was carried out by using two different KOH/char ratio (weight terms), 1:1 (samples GW-AC1 and MSW-AC1) and 2:1 (samples GW-AC2 and MSW-AC2). Physical mixtures of around 3 g of sample with corresponding amount of KOH pellets were prepared and then heated up to 600 °C for 1 hr in a steel tubular reactor, under nitrogen atmosphere (180 ml/min of N₂). Both temperature increase and decrease ramping rates were set to 5 °C/min. During cooling of samples at room temperature, N₂ flow rate was set to 60 ml/min. The activated char samples were mixed with HCl 5 M and then washed with deionized water until they reached a pH of 7. Finally, the samples were dried at 105 °C for 15 h.

Moisture, volatile matter, fixed carbon and ash content of GW and MSW hydrochar were determined by thermogravimetric analysis using a TA Instruments Q-500 thermobalance. The runs were conducted under nitrogen flow (100 mL/min) in the temperature range from 30 °C to 900 °C, at a heating rate of 20 °C/min. Next, the temperature was set to 800°C and flow switched to air in order to determine the ash content of the samples. Ultimate analysis was carried out with a LECO TruSpec CHN Elemental Analyzer.

The morphology of precursors and activated chars were observed by using a JEOL 5600LV Scanning Electron Microscope (SEM). The samples were coated with Au on a SEM coating device (Edwards Sputter Coater S150B) to induce electro conductivity. A homogeneous layer of metal of 5-6 nm thickness coated the entire sample surface.

The adsorption capacity of activated char samples was determined by using methylene blue and iodine number. Multi-points isotherm adsorption studies were conducted for methylene blue number estimation, according to Raposo et al. (2009). 10 mg of activated carbon were placed in contact with 10 mL of a methylene blue solution at different concentrations for 15 hr at room temperature (approximately 20 °C). The remaining concentration of methylene blue is analyzed using a UV/Vis spectrophotometer Shimadzu UV-1700 PharmaSpec at 665 nm. The amount of methylene blue adsorbed from each solution, q_e , was calculated by the Eq(1):

$$q_e \left(\frac{mg}{g} \right) = \frac{(C_0 - C_e) \cdot V}{M} \quad (1)$$

where C_0 is the initial concentration of the methylene blue solution in mg/L, C_e is the concentration of the methylene blue solution at equilibrium time in mg/L, V is the volume in L of the treated solution and M is the mass in g of the adsorbent. In order to evaluate the maximum amount of methylene blue adsorbed by each sample, that is not dependent on the initial concentration of the solution, was applied the Langmuir model, described by Eq(2):

$$q_e = \frac{q_{max} \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (2)$$

where q_{max} is the Langmuir maximum monolayer adsorption capacity in mg/g and b is the Langmuir equilibrium constant in L/mg. Linearization of the Langmuir model was made by using Weber equation, Eq(3), to find Langmuir adsorption parameters:

$$\frac{C_e}{q_e} = \frac{1}{b \cdot q_{max}} + \frac{C_e}{q_{max}} \quad (3)$$

The methylene blue number was expressed by q_{\max} , as the maximum amount of dye (in mg) adsorbed by 1 g of adsorbent.

The iodine number was determined applying a method based on ASTM D4607 and expressed in milligrams of iodine adsorbed by 1 g of activated carbon. 10 mg of sample were placed in contact with 10 mL of a 0.01 N iodine solution, stirred for 30 seconds and then filtered by gravity through filter paper. After filtration, 5 mL of solution were titrated with $\text{Na}_2\text{S}_2\text{O}_3$ 0.001 N to evaluate the remaining concentration of iodine solution.

3. Results and discussion

The elemental composition and the proximate analysis of GW and MSW hydrochars are reported in Table 1 and Table 2, respectively. The results show that the elemental and fixed carbon content in GW hydrochar is higher than in MSW. Whereas, ashes content is higher for MSW hydrochar.

The relationship among the type of precursors and the KOH chemical activation was investigated varying KOH/char ratio, keeping fixed temperature and time of activation.

The SEM micrographs of hydrochars and activated chars are reported in Figure 1. SEM images show that for both precursors the KOH chemical activation leads to a morphological change, developing a porous structure that increase with increasing of KOH/char ratio. Figures 1c and 1d display a non-complete porosity development for samples activated with 1:1 KOH/char ratio, with particles that have similar structure to starting hydrochar. Whereas 2:1 ratio (Figure 1e and 1f) allows to obtain a uniform porous structure. This can be attributed to the amount of KOH, which for samples GW-AC1 and MSW-AC1 is not sufficient to ensure a good contact of activating agent with hydrochar. By increasing the KOH/char ratio, the activation process is strengthened.

The effect of KOH/char ratio on adsorption properties of activated chars was studied. Both methylene blue and iodine number are indexes used to express the adsorption capacity, surface area and porosity of an activated carbon. In particular, iodine number denotes the amount of micropores, due to its small dimensions (surface area of iodine molecule of 0.40 nm^2); whereas methylene blue number has fairly large molecules (molecule surface area of 2.08 nm^2), therefore indicates the amount of mesopores of the activated carbon.

Figures 2 and 3 show, respectively, the methylene blue and iodine numbers as a function of KOH/char ratio. Starting GW and MSW hydrochars present a mesoporosity similar to that of a commercial activated carbon, since adsorb 244 and 263 mg/g of methylene blue, respectively. Methylene blue number of a commercial activated carbon is in the range 250 - 300 mg/g (Tounsadi et al., 2016). The amount of iodine adsorbed by raw hydrochars is lower (149 and 208 mg/g, respectively), indicating the presence of a small amount of micropores. A typical iodine number for activated carbon is 900 mg/g, with values greater than 1000 mg/g for high-grade activated carbon (Yang, 2003). Therefore, the adsorption capacity of raw hydrochars is very limited compared to that of a typical activated carbon.

Table 1: Elemental analysis of green waste (GW) and municipal solid waste (MSW) hydrochar.

Sample	Carbon (%)*	Nitrogen (%)*	Hydrogen (%)*	Oxygen (%)*
GW	41.27	4.02	0.97	36.16
MSW	23.63	2.60	1.07	35.04

* dry basis

Table 2: Proximate analysis of green waste (GW) and municipal solid waste (MSW) hydrochar.

Sample	Moisture (wt%)	Volatile matter (wt%)*	Ashes (wt%)*	Fixed carbon (wt%)*
GW	8.03	63.72	17.58	18.70
MSW	9.37	52.99	37.66	9.35

* dry basis

For KOH activated chars, the adsorption of methylene blue and iodine increase with increasing KOH/char ratio, as confirmed by SEM images (Figure 1). The development of porosity is associated with the reaction of KOH with C under inert conditions, that leads to the formation of different potassium species (K_2O , K, K_2CO_3) during the activation step. These species diffuse within the structure of hydrochar, widening existing pores and creating new pores (Mao et al., 2015). As shown in Figure 3, the iodine number of MSW-AC is lower than that of GW-AC, which can be due to the higher amount of carbon in GW-HC. The higher volatile content in GW-HC allows the formation of interconnected pores, which promote the diffusion of KOH into char particles, resulting in a well-developed micropore structure (Mao et al., 2015).

The adsorption of methylene blue (Figure 2), is greater for GW-AC than MSW-AC, except for 2:1 KOH/char ratio. In particular, methylene blue number of GW-AC remain nearly constant when KOH/char ratio increases from 1 to 2 (from 370 to 385 mg/g), whereas it sharply increases for MSW-AC (from 303 to 588 mg/g). This can be attributed to the different structure of raw hydrochars: GW-HC has a more heterogeneous composition and a fibrous structure than MSW-HC and the interaction with KOH during activation could be different. That leads to obtain pore of greater dimensions for MSW-AC, while for GW-AC there is a remarkable increase in iodine number, concerning the increase of micropores (Falco, 2013).

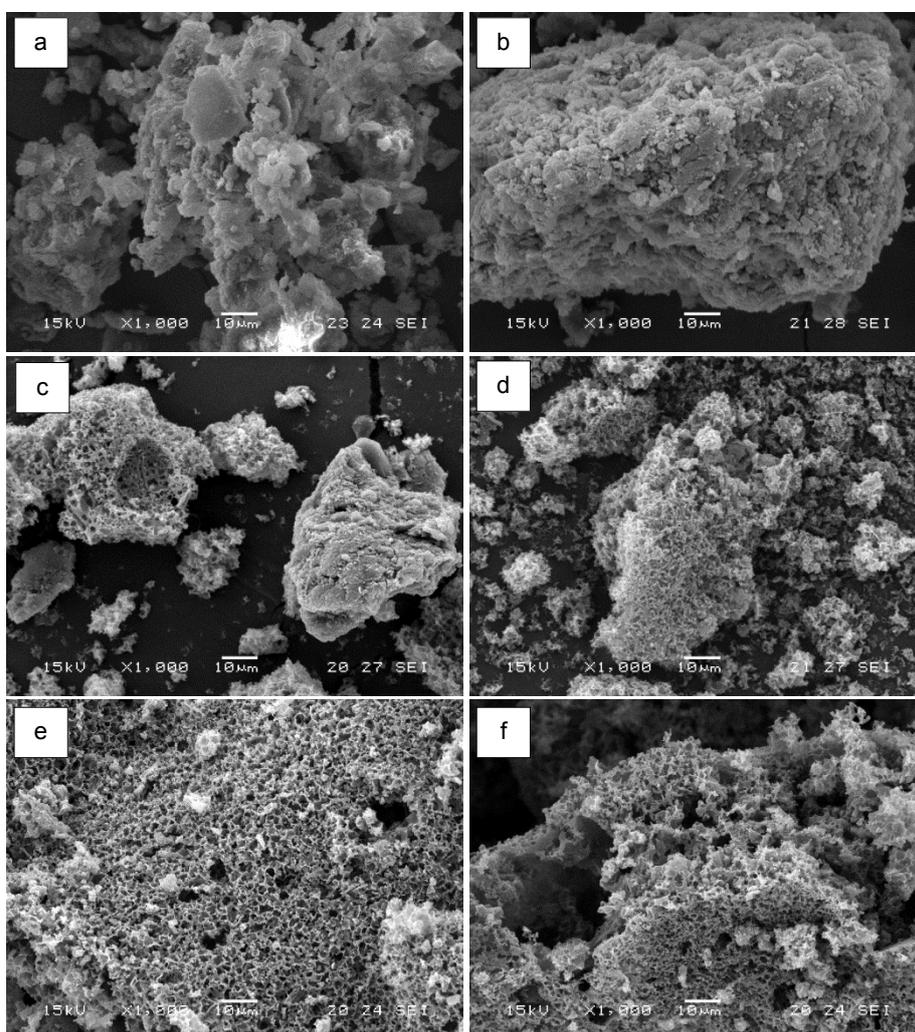


Figure 1: SEM images of hydrochar before and after chemical activation: (a) hydrochar from green waste (GW-HC); (b) hydrochar from municipal solid waste (MSW-HC); (c) GW-AC1 (1:1 KOH/char ratio); (d) MSW-AC1 (1:1 KOH/char ratio); (e) GW-AC2 (2:1 KOH/char ratio); (f) MSW-AC2 (2:1 KOH/char ratio).

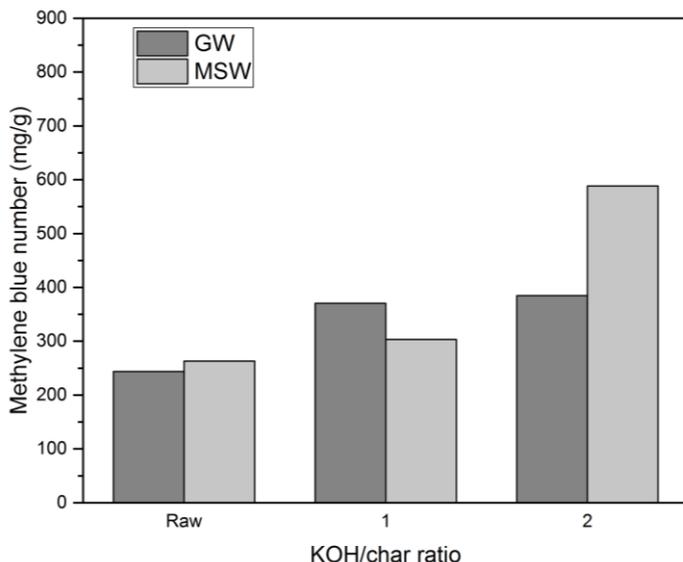


Figure 2: Methylene blue numbers of activated chars from GW and MSW as a function of KOH/char ratio.

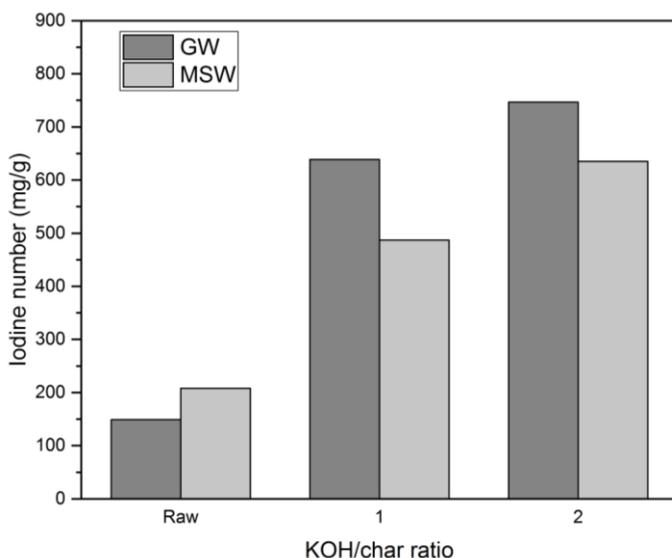


Figure 3: Iodine numbers of activated chars from GW and MSW as a function of KOH/char ratio.

4. Conclusions

The objective of this work was the valorization of hydrochar obtained from HTC treatment of waste biomasses (green waste and municipal solid waste). In particular, the study aimed to assess the use of hydrochar as activated carbon after chemical activation. The results showed that HTC carbons are potential precursors for the synthesis of activated carbons via chemical activation with KOH. Methylene blue and iodine indexes were used to evaluate the adsorption capacity. Both numbers increased with increasing KOH/char ratio. A KOH/char ratio of 2 allows to obtain activated chars with adsorption characteristics similar to that of a commercial activated carbon. In particular, sample GW-AC2 presented good mesoporosity, with a methylene blue number of 385 mg/g, and a well-developed micropore structure, with iodine number of 747 mg/g. Activated carbons from municipal solid waste (MSW-AC) showed lower properties in terms of iodine adsorption, however the methylene blue number of MSW-AC2 reached higher values (588 mg/g).

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