ADSORPTION PROPERTIES OF WHEAT STRAW, REED AND DOUGLAS FIR CHARS

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Introduction

As plants grow they absorb CO_2 that is released back to atmosphere when combusted. This is why they are often called carbon neutral - fuel sources with no net release of CO_2 if the cycle of growth and harvest is sustained. In addition, the clear advantage of biofuels is the displacement of CO_2 emissions, which are normally released from the fossil fuel combustion process. Wheat straw biomass is a complex of carbohydrates and is known as a low cost feedstock for ethanol production. Wheat straw, as an agricultural residue, is shown to be suitable for energy production in the Mediterranean region [1]. Shoreline reed is a widespread plant growing in many coastal areas of the world. It is used as a valuable energy resource in Finland, Estonia, Netherlands, Hungary and Romania [2]. The textural properties of chars from various types of woods are widely investigated by the research community [3-6]. Biochars originating from woods are not only obtaining attention as a fuel source, but also as an excellent sorbent material [4]. The textural properties of biomaterials such as wheat straw and coastal reed chars are fairly unknown to the research community, and to our knowledge there are not any systematic studies of their adsorption properties available in the literature.

Experimental

The untreated wheat straw sample (UWS) originates from the Thessaly area of Greece. The same wheat straw sample was treated (TWS) by a simple leaching technique [1] to remove the alkali metals and chlorine. The pine tree pellets (UPP) and Douglas fir wood chips (UDF) originate from the forests of Munich in Germany. The coastal reed (UR) originates from the western shoreline areas of Estonia.

A simple fixed bed reactor operating at atmospheric pressure is used to pyrolyze the biomass samples. The parent samples are heated in the reactor at a rate of 20°C min^{-1} to 800°C in 1 $Lmin^{-1}$ N_2 gas flow and held isothermally for about 15 min before cooling to ambient temperature. The detailed apparatus and process description is described elsewhere [7].

Carbon dioxide isotherms at 273K and nitrogen isotherms at 77K are obtained from physical adsorption measurements by a volumetric technique using a Quantachrome Autosorb-1 instrument. Prior to analysis, all the char samples were out-gassed at 300°C under vacuum overnight to remove the surface contaminants. Due to the pressure limitation of the instrument, the maximum relative pressure of 0.03 is obtained when CO_2 isotherms at 273K are measured ($P_{CO_2}^{sat}$ = 3484.8kPa at 273K). The specific Brunauer, Emmett and Teller (BET) surface areas from the N_2 isotherms of the char samples are determined over the partial pressure (P/Ps) range where the BET equation has the highest correlation coefficient (at least 0.9999). Therefore, the N_2 isotherm specific BET areas are calculated at significantly lower relative pressure values; in some cases as low as 0.01 to 0.05 [8]. The pore size distribution (PSD) of the char samples is determined from the N_2 adsorption isotherms at 77K and from the CO_2 adsorption isotherms at 273K using density functional theory (DFT) [9, 10]. The specific micropore volumes and the micropore surface areas of the biochar samples are determined from the CO_2 isotherms using the Dubinin-Radushkevich (DR) model [8].

Results and Discussion

The CO_2 and N_2 adsorption isotherms of all tested biochars are shown in Figure 1. The UPP, UR and UDF char N_2 adsorption isotherms exhibit type I isotherm behavior (Fig. 1A), with deep "knee" at partial pressures below 0.1, indicating the presence of pores with width less than 0.2 nm in size. Following the partial pressure of 0.1 the N_2 isotherms display nearly horizontal lines to P/Ps=0.95, indicating limited mesoporosity (pores in the range 0.2 nm to 50 nm) in the chars. The TWS char isotherm exhibits nearly type II isotherm behavior, indicating the presence of larger micropores, and mesopores. The UWS shows slight adsorption uptake, indicating little to no accessible pores at all. As seen from Fig. 1A, the wheat straw treatment process makes some of the char pores available for the N_2 adsorbate, which would normally be inaccessible. However, the CO_2 adsorption isotherms, shown in Fig. 1B, reveal no considerable CO_2 uptake differences among the biomass chars tested. As seen from the N_2 isotherm results the UPP char shows the highest and UWS char the lowest CO_2 uptake.

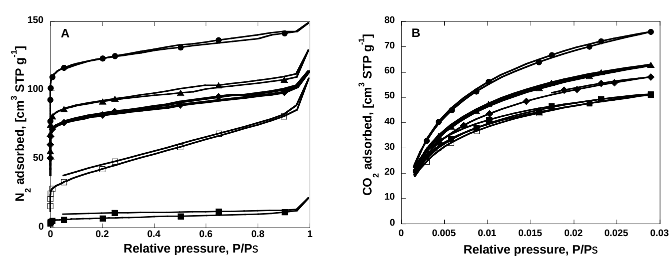

Fig. 1A: N_2 adsorption-desorption isotherms of biochars at 77K, ■ untreated wheat straw, □ treated wheat straw, ● pine wood pellets ▲ coastal reed, ◆ Douglas fir pellets.
B: CO_2 adsorption-desorption isotherms of biochars at 77K, ■ untreated wheat straw, □ treated wheat straw, ● pine wood pellets ▲ coastal reed, ◆ Douglas fir pellets.

Despite the fundamental differences of both BET (assumes layer-by-layer adsorption) and DR models (assumes volume filling adsorption) the specific areas of UDF and UPP chars are quite compareable (see Table 1). However, the N_2 and CO_2 specific BET surface areas of UWS and TWS chars exhibit apparent differences. The specific N_2 BET surface area of UWS is approximately 14 times smaller, while the TWS char BET area is underestimated by approximately 2.3 times. In the literature, Matsumoto et al. [6] reports that the cedar char N_2 adsorbate specific BET area is 184 m^2g^{-1}, and Zhou et al. [5] reports that the pine tree char N_2 specific BET surface area is 379 m^2g^{-1}. Other studies also suggest that the N_2 specific BET areas of other types of wood chars are in the same range of area values if compared to our results presented in Table 1. Based on our results, it could be concluded that some of the published literature N_2 adsorption BET area values for some biochars might be slightly underestimated. It seems quite evident that the use of both adsobates, N_2 and CO_2, is needed when adsorption characteristics of carbonaceous samples with significant microporosity are investigated [3, 11].

Table 1. BET and DR specific surface areas and microporosities of biochars obtained from CO_2 and N_2 isotherms.

Chars	BET (N_2) $m^2\ g^{-1}$	BET (CO_2) $m^2\ g^{-1}$	DR (CO_2) $m^2\ g^{-1}$	DR (N_2) $cm^3\ g^{-1}$	DR (CO_2) $cm^3\ g^{-1}$
UWS	25	348	429	0.009	0.150
TWS	152	354	454	0.051	0.158
UR	357	435	583	0.137	0.203
UDF	305	398	545	0.121	0.190
UPP	485	536	736	0.184	0.257

In order to further investigate the specific pore region of the micropores that are not accessible to N_2, the DFT PSD is calculated from the TWS and UWS CO_2 and N_2 isotherms. The results are presented in Fig. 2A and 2B.

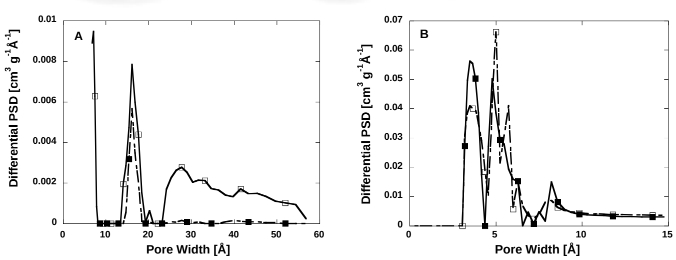

Fig. 2A: N_2 isotherm differential PSD obtained by applying DFT method, ■ untreated wheat straw, □ treated wheat straw. **B:** CO_2 isotherm differential PSD obtained by applying DFT method, ■ untreated wheat straw, □ treated wheat straw.

As shown in Fig. 2A, UWS shows no mesoporosity and some microporosity. However, the TWS char has micropores (pores in size 0.8 and 1.6 nm) and then a wide network of mesopores (pores in sizes 2.5 to 5.5 nm). Treating (leaching) the wheat straw has opened up some of the micro- and mesopores, which seem otherwise to be nearly blocked for N_2 molecules. Perhaps alkali minerals removed by leaching serve as pore-blockers for N_2, and together with the N_2 diffusion limitations at 77K prohibit the access of N_2 to small pores. Fig. 2B shows that both UWS and TWS char samples have quite similar micropore size distribution - supermicropores ranging from 0.4 to 0.8 nm in size. The sample treatment seems to have zero effect to the adsorption characteristics when the CO_2 isotherm is applied in PSD determination.

Conclusions

The adsorption characteristics of the wheat straw, pine pellet, and Douglas fir wood chip chars were determined. The specific DR CO_2 surface area of the pine pellet char is as high as 736 m^2g^{-1}. The wheat straw char surface area ranges from 429 to 454 m^2g^{-1}, and the reed char surface area is 583 m^2g^{-1}. The high surface area of the biochars tested originates mostly from micro- and supermicropores. While investigating the adsorption characteristics of the materials with clearly microporous nature both CO_2 and N_2 techniques should be applied.

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