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POROUS STRUCTURE OF CHARS OBTAINED FROM AGRO-WASTES

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Abstract: *Increasing concentrations of agricultural wastes, posing a serious environmental problem, require the development of policies and practices intending the minimization of these wastes and their recycling into value added products. In this regard, the aim of the current research is the valorization of agro-wastes, i.e. rice husks (RH), vine rods (VR), almond shells (AS) and walnut shells (WS), through pyrolysis into bio-chars that may have broad practical application as adsorbents. The porous structure of the chars is assessed using low temperature* N_2 *adsorption and Surfer apparatus (Thermo Scientific). It has been revealed that RH based char is mesoporous material with* S_{BET} *and* $V_{0.95}$ *of 76* $m^2\ g^{-1}$ *and 0.1593* $cm^3\ g^{-1}$*, respectively. Bio-chars produced from VR, AS and WS are characterized by better developed porous structure represented mainly by micropores (*$V_{DR,\ micro}$ *= 83 – 85%). The calculated* S_{BET} *and* $V_{0.95}$ *are respectively in the range of 362 – 463* $m^2\ g^{-1}$ *and 0.1734 – 0.2148* $cm^3\ g^{-1}$*, maximizing in the case of WS based bio-char.*

Keywords: *pyrolysis, chars, porous structure, nitrogen adsorption isotherms.*

INTRODUCTION

The strong demand in energy and materials markets, limited reserves of fossil fuels and high environmental requirements towards emissions originating from their processing, imposed a search for sustainable, ecologically friendly and economically feasible renewable resources that overcome these shortages. In this regard, along with the use of renewable energy sources like wind and sun, thermochemical conversion, i.e. pyrolysis, of a variety of biomass wastes, posing a serious ecological concern, has recently gained importance. It not only reduces environmental contamination and fossil fuels dependency but also provides production of different chemicals and high valued materials having various industrial applications (Gonsalvesh et al., 2017a, Yaman, 2004, Gonsalvesh et al., 2016, Ro et al., 2010).

Currently, diverse agro-biological wastes are valorized through pyrolysis combined with physical or chemical activation treatments into carbon based adsorbents and catalyst supports (Budinova et al., 2009, Tsyntsarski et al., 2015, Gonsalvesh et al., 2016, Gonsalvesh et al., 2017a, Gonsalvesh et al., 2017b, Dimitrov et al., 2012). The obtained low cost materials are characterized by features and performance comparable in many cases to those of commercial adsorbents. However the specific application of those products depend on their porous texture and surface chemistry characteristics, which can be tailored through proper precursor and treatment conditions selection. The objective of the current research is the valorization of agro-wastes, i.e. rice husks, vine rods, almond shells and walnut shells, through pyrolysis into bio-chars and assessment of their porous structure.

EXPOSITION

Materials and methods

In the current study, four biomass waste samples, i.e. rice husks (RH), vine rods (VR), almond shells (AS) and walnut shells (WS), were valorized and used as carbon precursor feedstocks for production of porous materials. Prior to use, all air-dried biomass samples were ground in a high-speed rotary cutting mill, sieved (< 2 mm) and oven dried at 110ºC. Thus prepared samples were subjected to carbonization or so called slow pyrolysis in an inert atmosphere in a lab-scale muffle furnance at slow heating rate of 10°C min^{-1} up to pyrolysis temperature of 500°C kept further isothermal for 1 h.

The porous structure characterization was carried out by measuring nitrogen adsorption isotherms at 77K on an automatic apparatus Surfer (Thermo Scientific). The specific surface area of bio-chars is determind by using N_2 adsorption data in the range of relative pressures 0.05-0.28 (for isotherms of type IV) or up to 7.3×10^{-2} (for isotherms of type I) and the linear form of *BET* equation (ISO 9277:2010, 2010, Brunauer et al., 1938, Vlaev, 2014). The total pore volume, known as volume of *Gurvich*, is determined based on the volume of adsorbate $V_{0,95}$, recorded on the desorption branch of the adsorption isotherm at a relative pressure $P_i/P_0 = 0.95$. The micropore volume ($V_{DR,micro}$) is calculated by using the Dubinin-Radushkevich equation up to $P_i/P_0 \leq 0.16$ (Stoeckli et al., 2001). The pore size distribution and pore diameters L_0 are obtained by applying the Non Local Density Functional Theory (NLDFT) on data of adsorption branch of N_2 isotherms (IBS ISO 15901-3:2007, 2007).

Results and discussion

Porous structure of biochars may significantly vary depending on the used precursor and processing technology. Inasmuch as porous structure of a certain material determines its beneficial specific application, the proper porous texture evalution and characterization is important. Porous characteristics of the bio-chars under consideration can be deduced from N_2 adsorption isotherms presented on Fig. 1. The RH based char (Fig. 1A) is characterized by IV type adsorption isotherm according IUPAC classification, which is typical for mesoporous structures. Inasmuch as a discrepancy between the adsorption and desorption branches occurs, a hysteresis loop of H-3 type, according to IUPAC clasification, is observed in N_2 adsorption-desorption isotherm of RH based char. In general, the presence of various hysteresis loops in the isotherms is related to capillary condensation phenomenon in pores of different shape – cylindrical, toroidal, bottle-like shaped or laminar. H-3 type is related to the presence of toroidal pores and(or) to bottle-like shaped pores with narrow and long throats of different sizes and approximately the same size of the bodies (Vlaev, 2014). Porous structures with wedge pores closed sideways and open at both ends are also characterized by an analogous hysteresis loop.

According to IUPAC classification N_2 isotherms of VR, AS and WS based bio-chars (Fig. 1B, C and D) represent type I isotherm. The initial part of this type of isotherm is very steep at low relative pressure with a sharp knee at the relative pressure P_i/P_0 about 0.01. This behavior of the adsorption isotherms reflects the significant role of microporous structure on adsorption process and shows that the porous structure of VR, AS and WS based bio-chars is predominantly microporous, with a narrow pore size distribution. At high relative pressures, a hysteresis loop of H4 type appears in the isotherms, which can be mainly attributed to the presence of a certain amount of narrow slit-like mesopores.

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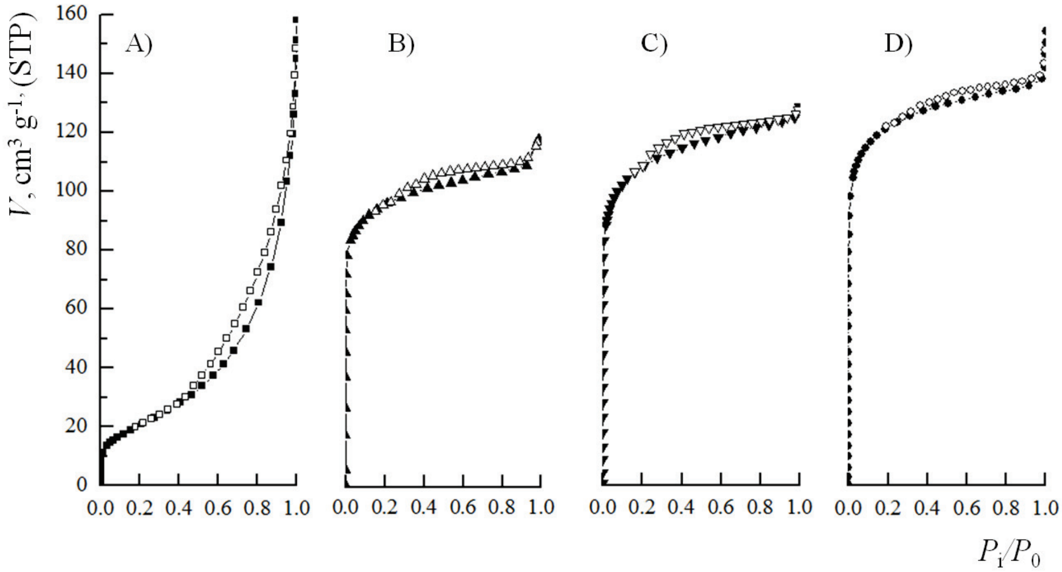

Fig. 1. N_2 adsorption isotherms of bio-chars obtained from agro-wastes:
A) rice husks; B) vine rods; C) almond shells; D) walnut shells.

Specific surface areas S_{BET} and physicochemical constants C for chars under consideration are determined using the linear form of the *BET* equation (Fig. 2). In general, *BET* equation is applicable for determining the specific surface area of mesoporous materials, but its application to determine the specific surface area of microporous adsorbents is problematic due to difficulties to distinguish mono- and polylayer adsorption during micropores volumetric filling (ISO 9277:2010, 2010). Linear *BET* dependence for mesoporous material is valid in the range of P_i/P_0=0.05-0.28, while for microporous materials is shifted to a lower relative pressures compared to mesoporous material and can be determined by applying *Rouquerol* criteria (Rouquerol et al., 2007). The linear form of *BET* equation and criteria of *Rouquerol* for investigated sample are shown on Fig. 2. The obtained results together with the total pore volume of *Gurvich* and micro- and mesoporore volumes of investigated chars are summarized in Table 1. The detailed analysis of the isotherms and calculated porous texture parameters clearly show that pyrolytic utilization of the studied precursors lead to production of porous chars with different internal specific surface area and porous structure. However, the obtained porous chars can be classified in two groups:

Mesoporous char, i.e. RH based char, since V_{meso} (about 85%) significantly prevails over $V_{DR,micro}$. This sample is characterized with the lowest S_{BET} and $V_{0.95}$ among studied chars, 76 m^2 g^{-1} and 0.1593 cm^3 g^{-1}, respectively.

Microporous chars, i.e. VR, AS and WS based chars ($V_{DR,micro}$= 83-85%) For these samples, significantly higher S_{BET} and $V_{0.95}$ are calculated compared to RH based char. S_{BET} and $V_{0.95}$ vary respectively in the range of 362-463 m^2 g^{-1} and 0.1734-0.2148 cm^3 g^{-1}, with a maximum for WS based char.

It should be mentioned that thermal destruction at proper experimental conditions of agrobiological samples leads to the production of materials that are highly dispersed with a well developed system of pores and capillaries (Vlaev, 2014). Typically, the structure of newly obtained pyrolytic product, i.e. char, retain the structure of the parental material as the formed pores are being oriented in a preferred direction corresponding to that of the precursor. This phenomenon is called *pseudomorphism*. It is the reason to observe the aforementioned pecularities of the investigated chars. The RH based char differs so significantly from the other chars due to the high contents of biogenic amorphous SiO_2 (17-22%) in the raw RH (Genieva et al., 2011, Vlaev, 2014). Such high sillica content in plants and plant wastes is unusual and there is no other plant in nature that concentrates such large amounts of SiO_2 (Vlaev, 2014). Morphological studies of raw rice husks show that its structure is a globular (Genieva et al., 2011). This globular structure is retained in the pyrolytic product as well due to the high thermal stability of the sillica, which is about 54% in the final carbon and probably the main factor influencing the porous texture of this char.

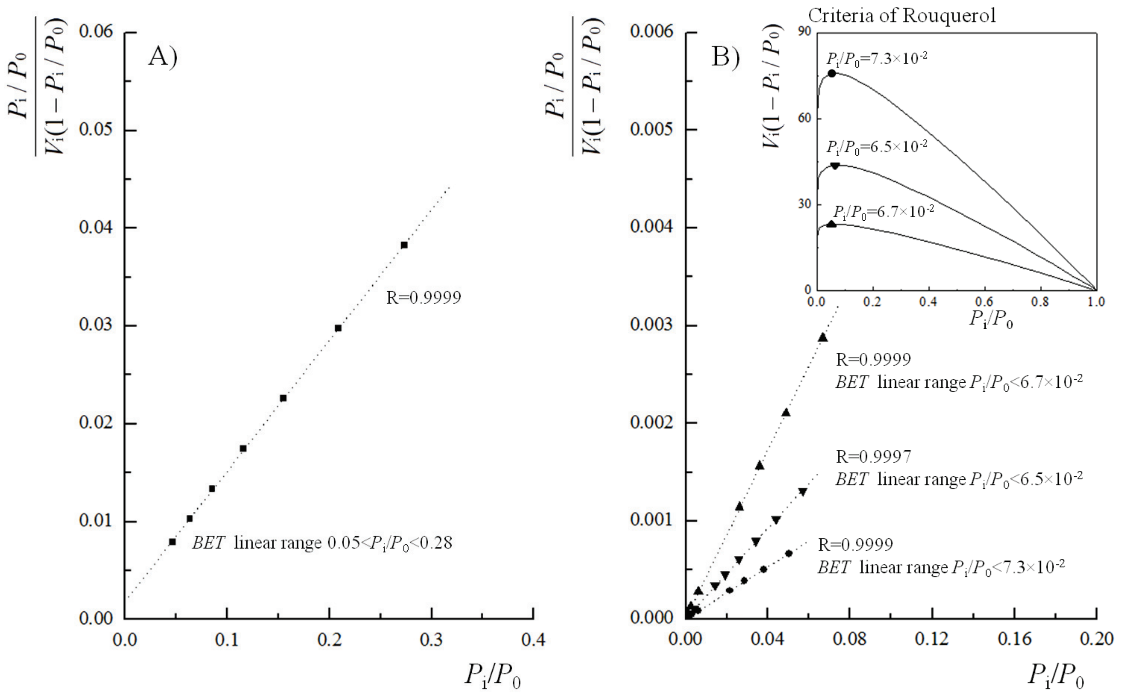

Fig. 2. Graphical presentation of linear form of the *BET* equation and criteria of *Rouquerol* for bio-chars obtained from agro-wastes: A) rice husks (■); B) vine rods (▲), almond shells (▼) and walnut shells (●)

Table 1. Textural properties of prepared agro-waste based chars

Samples	RH	VR	AS	WS
$V_{0.95}$ (cm^3 g^{-1})	0.1593	0.1734	0.1948	0.2148
S_{BET} (m^2 g^{-1})	76	362	404	463
C	68.7	6646.5	4827.9	6356.7
$V_{DR, micro}$ (cm^3 g^{-1})	0.0245	0.1444	0.1619	0.1827
V_{meso}* (cm^3 g^{-1})	0.1348	0.0290	0.0329	0.0321
$V_{DR, micro}$ (%)	15	83	83	85
V_{mezo} (%)	85	17	17	15

$V_{meso}{}^{*} = V_{0.95} - V_{DR,micro}$

Pore size distribution (PSD) of investigated chars is also assessed applying NLDFT theory. For VR, AS and WS based chars the n2c77_cyl kernel, developed for carbon microporous and mezoporous materials based on a cylindrical pore model, is used for NLDFT computation. The theoretical adsorption isotherms described by using this kernel is in best agreement with the registered experimental adsorption isotherms of these chars. In the case of RH based char, best agreement between theoretical and experimental adsorption isotherms is obtained by using

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n2si77_cyl kernel developed for silica materials based on a cylindrical pore model, probably due to the high present of SiO_2 in that char. The obtained pore size distributions of investigated chars are presented in Fig.3. The maximums in the PSD curve correspond to the prevailing pore sizes of the investigated samples. Among investigated microporous materials, the VR and AS based chars are characterized rather by a monomodal pore volume distribution with prevailing pore size L_0 about 1.7 nm. In the PSD curves of these samples, slight maxima in the mesoporous region are also observed, i.e. L_0 about 2.8 nm for VR based char and L_0 about 2.5 and 2.8 nm for AS based char. In the case WS based char, a trimodal pore volume distribution with prevailing pore sizes L_0 about 1.5, 1.8 and 2.0 nm are registered. With regards to RH based char as expected a number of maxima, altough not very well defined, in the mesoporous region are observed, i.e L_0 about 2.0-27.0 nm.

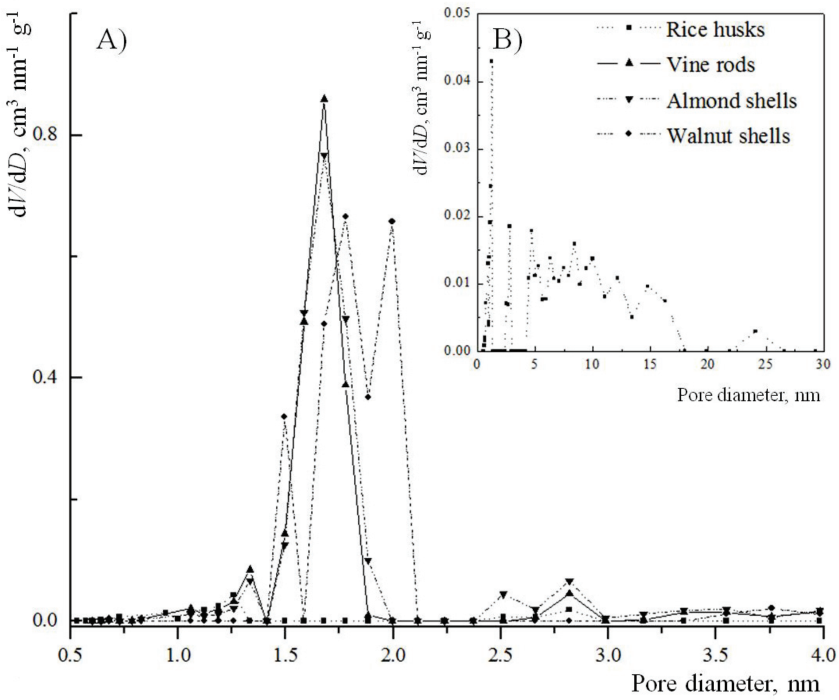

Fig. 3. Pore size distribution of agro-wastes based chars

CONCLUSION

The conducted research clearly shows that the pyrolytic valorization of agro-waste, i.e. RH, VR, AS and WH, leads to production of low cost porous carbon materials. The obtaiend chars, and especially VR, AS and WS based chars, have microporous texture characteristics even without performing an additional physical or chemical activation. These samples have a sufficiently high specific surface area and pore volume to be used as adsorbents, respectively in the range of 362 – 463 m^2 g^{-1} and 0.1734 – 0.2148 cm^3 g^{-1}, maximizing in the case of WS based bio-char.

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