

# Activated carbons prepared from hazelnut shells, walnut shells and peanut shells for high CO<sub>2</sub> adsorption

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Research treats about producing activated carbons for CO<sub>2</sub> capture from hazelnut shells (HN), walnut shells (WN) and peanut shells (PN). Saturated solution of KOH was used as an activating agent in ratio 1:1. Samples were carbonized in the furnace in the range of temperatures 600°C–900°C. Properties of carbons were tested by N<sub>2</sub> adsorption method, using BET equation, DFT method and volumetric CO<sub>2</sub> adsorption method. With the increase of carbonization temperature specific surface area of studied samples increased. The largest surface area was calculated for samples carbonized at 900°C and the highest values of CO<sub>2</sub> adsorption had samples: PN900 at 0°C (5.5 mmol/g) and WN900 at 25°C (4.34 mmol/g). All of the samples had a well-developed microporous structure.

**Keywords:** activated carbon, biomass, nutshells, CO<sub>2</sub> adsorption.

## INTRODUCTION

CO<sub>2</sub> as well as CH<sub>4</sub> are considered as one of the greenhouse gases that contribute to anthropogenic global warming. Global warming has a destructive effect on climate, it can change ecosystems, increase contagious diseases and enlarge ozone hole. CO<sub>2</sub> is exchanged among land surface, atmosphere and ocean. However, its excess disturbs natural balance and have a negative influence on Earth's climate. Combustion of fossil fuels and industrial gas emission are a major source of atmosphere pollution. Climate change is a quickly growing issue and governments start to look for new methods of preventing it. Natural reduction of pollution would take ages and is not possible because of the scale of the problem. These are the reasons why developing new techniques of capturing CO<sub>2</sub><sup>1–7</sup> are the main interest of many existing studies but the methods of CO<sub>2</sub> conversion are developed as well<sup>8–12</sup>. Methane conversion to methanol<sup>13–15</sup>, formaldehyde<sup>13, 16, 17</sup>, methyl bisulfate<sup>18–23</sup>, carbon nanomaterials<sup>24–29</sup>, hydrogen<sup>30–35</sup> is investigated very deeply but methane can be used as an alternative fuel vehicle<sup>36–38</sup>.

Most of the commercial activated carbons show too low CO<sub>2</sub> adsorption capacity, therefore finding and developing new type of porous carbons was necessary<sup>39–44</sup>. Activated carbons can be prepared from the wide range of organic materials, such as agricultural wastes. Raw agricultural by-products can be used as a promising material for carbons production due to their many qualities<sup>45</sup>. They are extensively studied because of their good chemical stability, low ash content, porous structure, great adsorption capacity and low cost<sup>35, 39, 45, 46</sup>. Carbon adsorbents are broadly exploited for water<sup>47</sup> and gas purification<sup>48, 49</sup>, removal of metal ions<sup>50, 51</sup> and dyes<sup>52, 53</sup> and production of high purity substances<sup>45, 54</sup> but they can find many applications e.g. as catalysts<sup>55–57</sup>.

Biomass derived activated carbons are cheap and usually solve problem of wastes utilization. For example corncobs<sup>4</sup>, rice husks<sup>58</sup>, almond shells<sup>58</sup>, coconut shells<sup>59</sup>, fruit stones<sup>60</sup>, molasses<sup>36, 61, 62</sup>, pomegranate peels<sup>63</sup>, tinder fungus<sup>63</sup>, mistletoe branches and leaves<sup>63</sup>, carrot peels<sup>63</sup>, kiwi fruit peels<sup>63</sup>, fern leaves<sup>63</sup>, sugar beet pulp<sup>63</sup>, sun flo-

wer shells<sup>64</sup>, demineralized kraft lignin<sup>65</sup>, ebony wood<sup>66, 67</sup>, mahogany wood<sup>66</sup>, and nutshells<sup>67–70</sup> were described as carbon precursors. Porous carbons can be prepared and activated in many different ways. The ability of activated carbons to capture CO<sub>2</sub> depends on several factors that include activation method and type of starting material. These elements have a direct influence on the properties of the carbon, such as its porosity and surface area<sup>60</sup>.

There are not many studies describing the preparation of activated carbons from nutshells for CO<sub>2</sub> capture. Most of the studies are focused on removing metal ions and dyes from aqueous solutions. Moreover, methods of preparation activated carbons are more complex than the one presented in this study. In other studies, physical activation or other activating agents were used<sup>64, 71–74</sup>. There are no studies considering the preparation of activated carbons from hazelnut shells for CO<sub>2</sub> adsorption. Furthermore, none of the publications compare three types of nutshells presented in this study.

The aim of this study was to evaluate CO<sub>2</sub> adsorption capacity of activated carbons prepared from hazelnut shells, walnut shells and peanut shells at different carbonization temperatures, as well as to assess the size of the specific surface area and pore volume.

## EXPERIMENTAL

Hazelnut shells (HN), walnut shells (WN) and peanut shells (PN) were crushed to the particle size 0.3–1.6 mm. Obtained material was mixed with saturated solution of potassium hydroxide in ratio 1:1 and left in the room temperature for 3 h. Afterwards, impregnated samples were dried at 200°C for 19 h. In the next step, material was grounded and put into quartz boats. Then pyrolyzed in a furnace at required temperature (600°C, 700°C, 800°C, and 900°C) which was maintained for 1 h in constant nitrogen flow 18 dm<sup>3</sup>/min. After pyrolysis samples were grounded again. Obtained powder was washed with distilled water to neutral pH. Then all materials were soaked with hydrochloric acid in concentration 1 mol/dm<sup>3</sup> for 19 h and washed again with distilled water until the filtrate became neutral.

Structure characterization of carbonaceous materials was carried out by  $N_2$  adsorption-desorption isotherms measured at  $-196^\circ\text{C}$  using Quantochrome Autosorb Instrument. Before analysis all samples were degassed at  $200^\circ\text{C}$  under vacuum for 16h. The specific surface area was estimated using the Brunauer-Emmett-Teller equation. Micropore volume was assessed by DFT model used to the nitrogen adsorption. The total pore volumes were calculated on the basis of the volume of  $N_2$  adsorbed at a relative pressure.  $\text{CO}_2$  adsorption capacity at  $0^\circ\text{C}$  and at  $25^\circ\text{C}$  was determined using Quantachrome Autosorb Instrument.

## RESULTS AND DISCUSSION

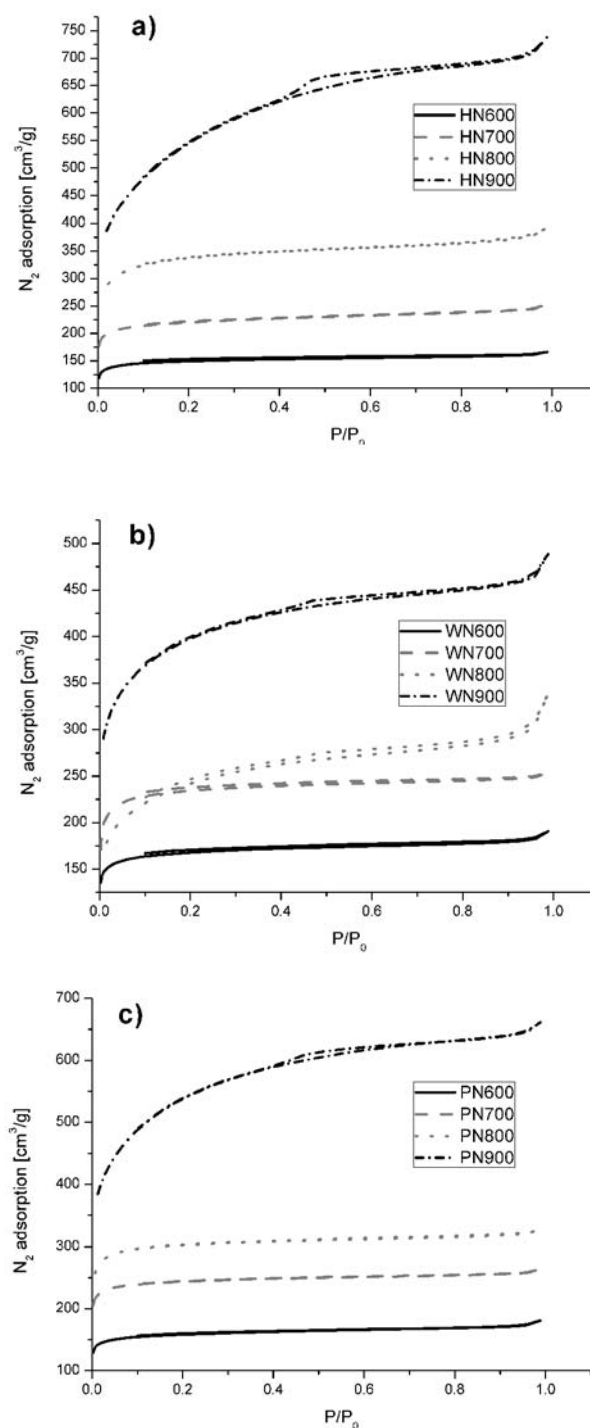
The results of surface properties of all activated carbons are gathered in Table 1. It can be noticed that the highest specific surface area ( $S_{\text{BET}}$ ) values were found for samples carbonized at  $900^\circ\text{C}$ . The values of  $S_{\text{BET}}$  of HN900, WN900 and PN900 were  $1963\text{ m}^2/\text{g}$ ,  $1468\text{ m}^2/\text{g}$  and  $1962\text{ m}^2/\text{g}$  respectively. Furthermore,  $S_{\text{BET}}$  increased with the rise of carbonization temperature. Carbonization temperature also had an influence on micropore volume ( $V_{\text{mic}}$ ) and total pore volume ( $V_{\text{tot}}$ ) of examined samples. The highest values of  $V_{\text{mic}}$  and  $V_{\text{tot}}$  were obtained for samples carbonized at  $900^\circ\text{C}$ . The values of  $V_{\text{mic}}$  and  $V_{\text{tot}}$  were in the range  $0.22\text{--}0.68\text{ cm}^3/\text{g}$  and  $0.26\text{--}1.15\text{ cm}^3/\text{g}$  respectively.

**Table 1.** Activated carbons surface properties

Sample	$S_{\text{BET}}$ [ $\text{m}^2/\text{g}$ ]	$V_{\text{mic}}$ [ $\text{cm}^3/\text{g}$ ]	$V_{\text{tot}}$ [ $\text{cm}^3/\text{g}$ ]
HN600	591	0.22	0.26
HN700	870	0.31	0.39
HN800	1297	0.47	0.61
HN900	1963	0.64	1.15
WN600	663	0.24	0.30
WN700	927	0.34	0.39
WN800	1277	0.44	0.74
WN900	1468	0.52	0.76
PN600	629	0.24	0.28
PN700	979	0.35	0.41
PN800	1212	0.43	0.51
PN900	1962	0.68	1.03

Figure 1. shows nitrogen adsorption-desorption isotherms of activated carbons made from hazelnut shells (Fig. 1a), walnut shells (Fig. 1b) and peanut shells (Fig. 1c). These isotherms are type I which means that at the lowest relative pressure the  $N_2$  uptake is the highest. When the relative pressure increases the uptake of gas starts to plateau. This result indicates that examined activated carbons had a well-developed microporous structure. No hysteresis loops or very small ones (mainly for samples carbonized at  $900^\circ\text{C}$ ) were found which suggests the lack of mesopores or their very low volume and implies the advantage of micropores.

Pore size distribution was calculated by applying DFT theory to  $\text{CO}_2$  adsorption data at  $0^\circ\text{C}$  and  $N_2$  adsorption data at  $-196^\circ\text{C}$ . Figure 2. shows the micropore size distribution curves of all examined samples (HN, WN and PN). The pore diameter range ( $0.3\text{--}0.8\text{ nm}$ ) indicates that studied activated carbons developed a microporous structure. In addition, the presence of very low volume mesopores was noticed (Fig. 3). The largest mesopore



**Figure 1.** Adsorption and desorption isotherms of  $N_2$  for hazelnut shells (a), walnut shells (b) and peanut shells (c)

volume up to  $6\text{--}8\text{ nm}$  was found for samples carbonized at  $900^\circ\text{C}$ .

The size and volume of micropores have a crucial effect on  $\text{CO}_2$  adsorption capacity. The more microporous is the activated carbon the more effective is the gas adsorption. Adsorption temperatures have an influence on pore volume of activated carbons and their ability to capture  $\text{CO}_2$ .

To quantify the accurate range of micropores for  $\text{CO}_2$  adsorption at  $0^\circ\text{C}$  and  $25^\circ\text{C}$ , the correlation between the amounts of  $\text{CO}_2$  adsorbed on all activated carbons and their pore volume in the specific ranges was studied. The plots of  $\text{CO}_2$  adsorption capacity versus pore volume in

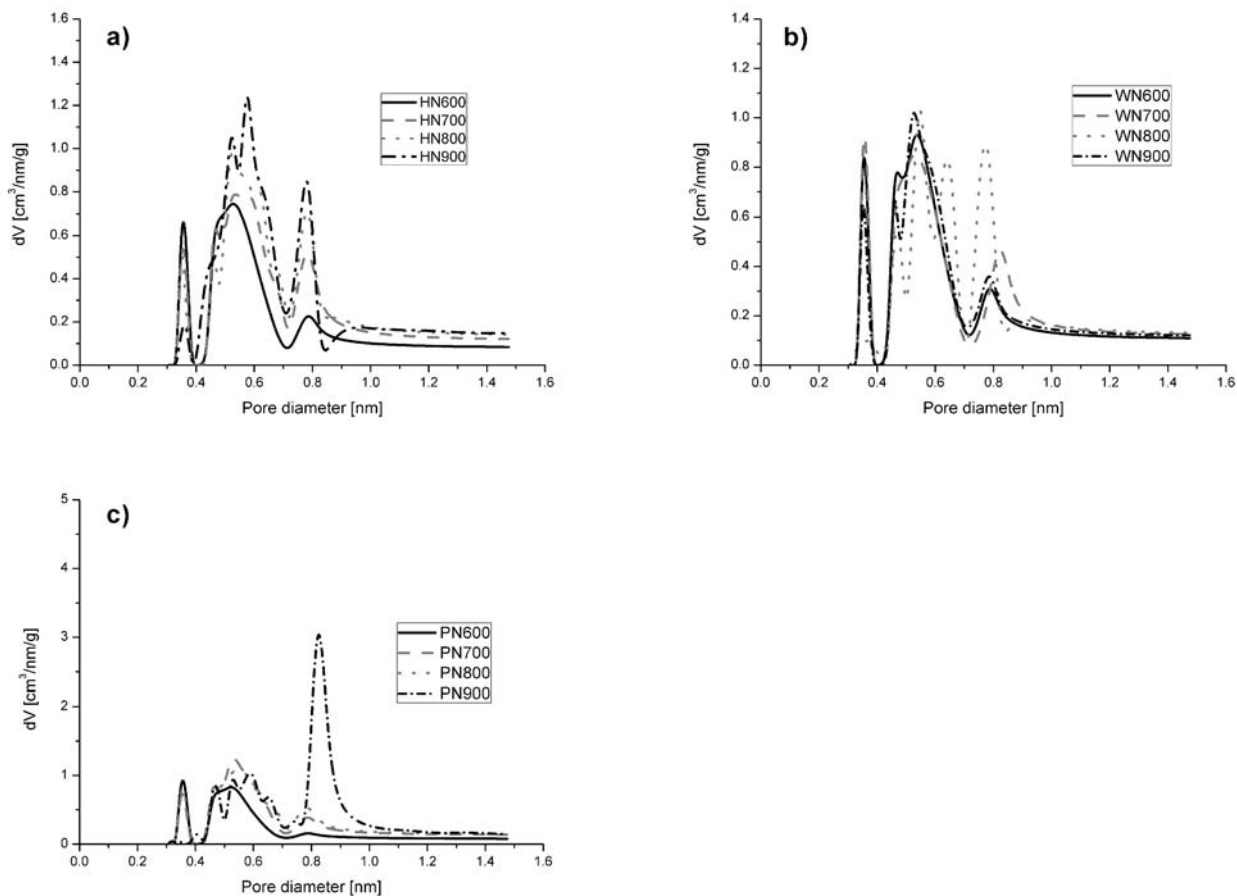


Figure 2. Micropore size distribution curves of activated carbons from hazelnut shells (a), walnut shells (b) and peanut shells (c)

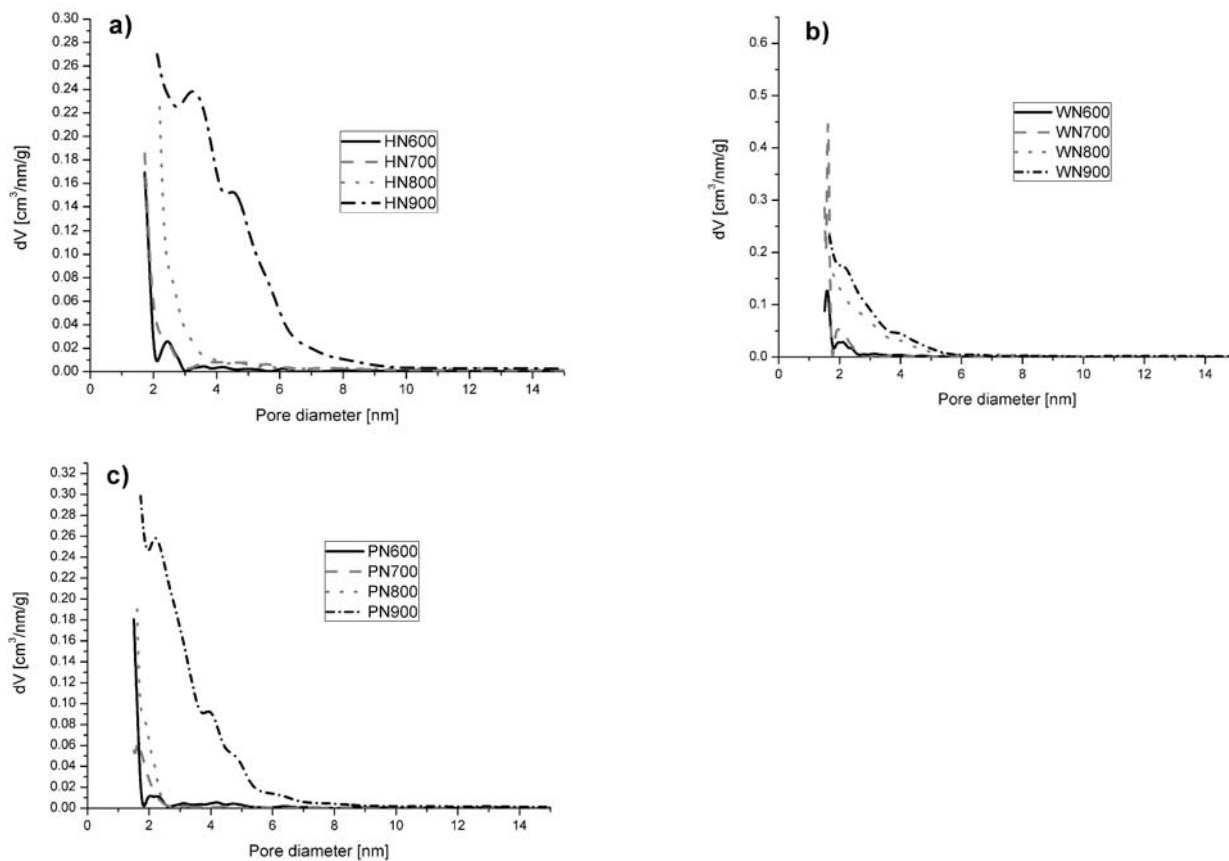
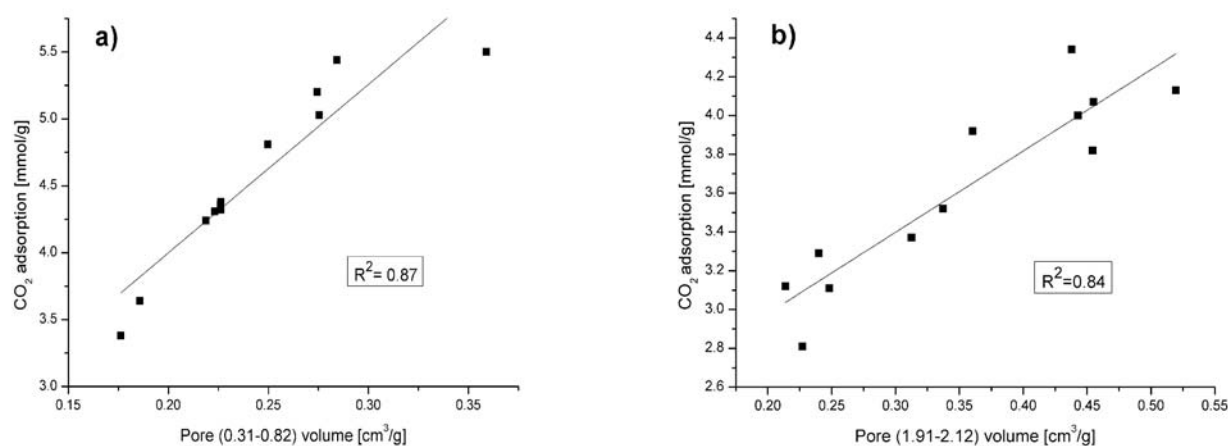
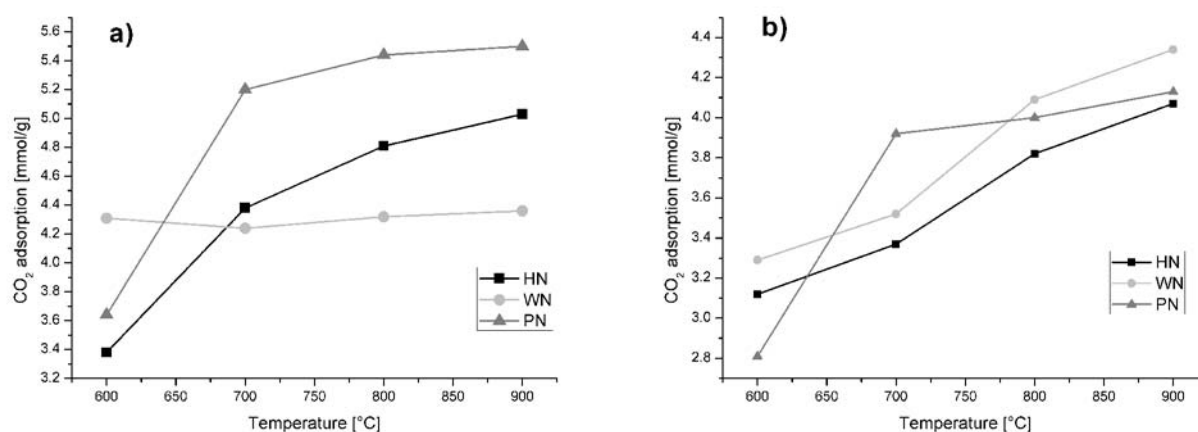


Figure 3. Micropore and mesopore size distribution curves of activated carbons from hazelnut shells (a), walnut shells (b) and peanut shells (c)



**Figure 4.** The best linear relationship between the volume of pores in correlation to CO<sub>2</sub> adsorption at 0°C (a) and 25°C (b)



**Figure 5.** CO<sub>2</sub> adsorption levels at 0°C (a) and 25°C (b) in correlation to carbonization temperature

obtained in this study. For activated carbon, carbonized at 700°C, CO<sub>2</sub> adsorption value was 1.54 mmol/g at 25°C, whereas the value of CO<sub>2</sub> adsorption on activated carbon produced in the same conditions in this research was 3.92 mmol/g. This result can be caused by differences in the preparation of activated carbons, such as carbonization of raw material before the activation process.

## CONCLUSIONS

Activated carbons prepared from hazelnut shells, walnut shells and peanut shells can be used as an effective and cheap adsorbent of CO<sub>2</sub> with high surface areas. With the increase of carbonization temperature specific surface area of studied samples increased. The highest S<sub>BET</sub> values and CO<sub>2</sub> adsorption levels at 0°C and 25°C were found for samples carbonized at 900°C. The nitrogen adsorption-desorption isotherms and the micropore size distribution curves show that activated carbons had a well-developed microporous structure. At 0°C the CO<sub>2</sub> adsorption took place mostly in micropores in the range of 0.31–0.82 nm and at 25°C in the pores from 1.91 nm to 2.12 nm. Preliminary carbonization of raw material before activation, especially of peanut shells, have a negative influence on adsorption properties of activated carbons.

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