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Effect of Activating Agent on the Preparation of Bamboo-Based High Surface Area Activated Carbon by Microwave Heating

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Abstract: The present work attempts to convert bamboo into a high surface area activated carbon via microwave heating. Different chemical activating agents such as KOH, NaOH, K_2CO_3 and Na_2CO_3 were utilized to identify a most suitable activating agent. Among the activating agents tested KOH was found to generate carbon with the highest porosity and surface area. The effect of KOH/C ratio on the porous nature of the activated carbon has been assessed. An optimal KOH/C ratio of 4 was identified, beyond which the surface area as well as the pore volume were found to decrease. At the optimized KOH/C ratio the surface area and the pore volume were estimated to be 3,441 m^2/g and 2.093 ml/g, respectively, with the significant proportion of which being microporous (62.3%). Activated carbon prepared under the optimum conditions was further characterized using Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM). Activated carbons with so high surface area and pore volume are very rarely reported, which could be owed to the nature of the precursor and the optimal conditions of mixture ratio adopted in the present work.

Keywords: high surface area activated carbon, microwave heating, activating agent, bamboo

Introduction

Bamboo is a green construction material which possesses lots of advantages such as sustainability, the capability of being reused or recycled and environmental friendliness [1]. Bamboo is regarded as a promising resource in the future because of the rapid growth, high production and low cost [2]. Activated carbon can be produced from different raw carbon resources like lignite, peat, coke and biomass resources such as wood, sawdust, coconut shells and so on [3–6]. The properties of the activated carbon depend on the type of precursor utilized as well as the processing methods adopted [7]. In common opinion, advantages of activated carbon are low cost, hydrophobicity and flexibility in terms of porous texture and surface properties [8]. Due to its well-developed pore structure, high active surface area and good mechanical characteristics, activated carbon is a well-known material used in ever increasing numbers of environmental applications, in water and wastewater treatment, in environment protection, in gas filters, etc. [9–13].

In principle, the methods for preparing an activated carbon can be divided into two categories: physical activation and chemical activation [14]. In physical (thermal) activation, the gasification of char is performed at high temperature (usually above 1,073 K) with steam, carbon dioxide or a mixture of them [15–18]. In chemical activation, the precursor is impregnated with chemical agents like KOH [19, 20], K_2CO_3 [21, 22], $ZnCl_2$ [23], H_3PO_4 [24, 25] and activated at comparatively lower temperatures than the physical activation, however involving a washing

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stage, wherein the respective salts are removed from the activated material.

The conventional heating methods result in surface heating from the hearth wall, which do not ensure a uniform temperature as it is based on heat transfer through conduction and convection [26]. Microwave heating is volumetric and the heat is generated from inside the material as the materials receive energy through dipole rotations and ionic conduction [27]. Microwave heating has been proved beyond doubt to possess qualities such as fast heating, energy efficient, easy to control, small thermal inertia and selective heating. Application of microwave heating is increasingly being adopted for processes such as drying, leaching, reducing, roasting, grinding and so on [28–31].

The present work attempts to utilize microwave heating to prepare activated carbon from the precursor bamboo. Four different popular activating agents namely KOH, NaOH, K_2CO_3 and Na_2CO_3 were utilized to identify the most promising activating agent. The effect of mixture ratio is assessed for the activating agent that resulted in best quality activated carbon. The resultant products are characterized using the nitrogen adsorption isotherm, Fourier transform infrared spectroscopy (FTIR) and scanning electron microscope (SEM) analysis.

Experimental

Materials and methods

Bamboo is selected as the raw material to prepare for the activated carbon. The main reagents utilized in the experiments are KOH (AR), NaOH (AR), K_2CO_3 (AR), Na_2CO_3 (AR), HCl (AR).

The carbonization of raw precursors is carried out by loading 1,000 g of precursor into a high-temperature conventional resistance furnace and heated to a carbonization temperature of 600°C at a heating rate of 10°C/min and was held for 2 h at the carbonization temperature in an inert atmosphere. The carbonized materials are cooled to the room temperature with continued flow of the inert gas. Subsequently, a certain weight of activating agent and carbonized samples mixed completely according to a fixed ratio for chemical activation process. Then, these were placed in a ceramic crucible and heated for a certain time at different microwave power in nitrogen atmosphere. A self-made microwave furnace is employed for activating the impregnated samples, which had the output power of 0–700 W at a microwave frequency of 2.45 GHz. The samples are hot quenched in a distilled water to promote the removal of respective salts from the samples, through repeated washing. Then, the samples are washed with 1:1 volume ratio of HCl, followed by rinsing with distilled water. The filtered wet samples are dried in a laboratory oven at a temperature of 105°C for 8 h and stored for characterization quenched.

Characterization of activated carbon

BET surface area of the high specific surface area activated carbon is measured through nitrogen adsorption isotherm at 77 K (Autosorb-1-C, Quantachrome). The total pore volume is determined by the nitrogen adsorption isotherm generated until a relative pressure of p/p_0 of 0.98. The pore size distribution is determined utilizing non-localization density functional theory (NLDFT). The FTIR is applied to qualitatively identify the chemical function groups. FTIR spectra are generated in the range of 4,000–400 cm^{-1} by using Nicolet 8700 spectrophotometer. The transmission spectra of samples are prepared by mixing with KBr crystals and pressed into a pellet. The microstructures are analyzed by the SEM (Philips XL30ESEM-TMP).

Results and discussion

Effect of performance of activating agent

Activated carbon is prepared at a microwave power of 700 W for 15 min, with different activating agents. Based on a survey the mixture ratios were chosen different for different activating agents. An activating agent/C ratio of 4 was utilized for activating agents KOH and NaOH while it was 2 for K_2CO_3 and Na_2CO_3. The nitrogen adsorption isotherms of the activated carbon prepared with different activating agents are assessed using the Autosorb instrument at 77 K and the results are shown in Figure 1. The pore structural parameters deduced from the isotherms are summarized in Table 1.

Figure 1 shows an increase in the nitrogen adsorption capacity with increase in the relative pressure, with steep increase at low pressures. The isotherms based on the IUPAC classification can be categorized to be type I or

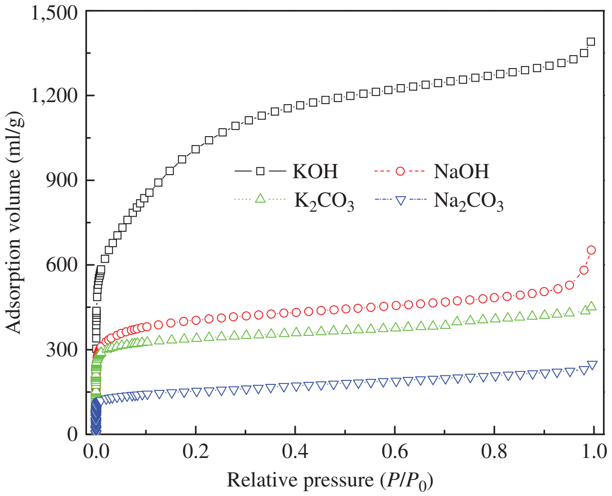

Figure 1: Nitrogen adsorption isotherm of the activated carbon with different activating agents.

type IV isotherm. Type I isotherms correspond to micro porous material indicated negligible increase in the adsorption capacity beyond a p/p_0 of 0.1. Type IV isotherms correspond to material that possess significant quantity of mesopores evidenced through continued increase in the adsorption capacity until a p/p_0 of 1, which could be due to the multilayer filling of the pores due to condensation. Table 1 compiles the results of the adsorption isotherms in terms of surface area, micropore volume and total pore volume. The highest surface area of 3,441 m^2/g corresponds to the KOH activation due to the much higher pore volume as compared to the other activating agents. Additionally the contribution of micropore volume to the total pore volume is significant rendering the surface area to be much higher than the other activating agents. The Na_2CO_3 activating agent resulted in a very low surface area of 484 m^2/g. Based on the fact that the activating agents KOH performed much better than the other activating agent in terms of its ability to produce very high surface area carbon, KOH was subjected to additional assessment though variation of its mixture ratio.

Figure 2 shows the yield of activated carbon obtained using different activating agents. It can be seen that the lowest of yield correspond to KOH while the highest of yield correspond to Na_2CO_3. The yield of activated carbon is 39.82% using KOH activation and yield of activated carbon is 54.25% using Na_2CO_3 activation. An increase in the porosity of the carbon contributes to the reduction in the yield of carbon or in other words higher the porosity of the carbon the lower would be the resultant yield. Similar yield have been reported in literatures for other precursors, namely for holm-oak sawdust (25.5%) and rockrose (20%) [32].

According to classification of International Union of Pure Applied Chemistry (IUPAC) [33], pores are divided into micropore ($<$ 20 Å), mesopore (20–500 Å) and macropore ($>$ 500 Å). Pore size distribution of activated carbon with the different activating agents is presented in Figure 3. A distinct variation in the pore size distribution could be observed, with the differential pore volume higher for the higher surface area carbon. However, the activating agent K_2CO_3 seems to generate a significantly higher proportion of ultra micropores as compared with the other activating agents. The contribution of KOH is distinctly higher throughout but for the ultra micropore range where both K_2CO_3 as well as NaOH generates significantly higher proportion of ultra micropores.

Effect of KOH/C ratio

The nitrogen adsorption isotherm of the effect of KOH/C ratio is shown in Figure 4. Table 2 shows the details of pore structure while Figure 5 shows the effect of KOH/C ratio on the yield of activated carbon. It can be seen observed that the adsorption volume increases sharply at low relative pressure, which indicates the process of filling the micropores. When relative pressure is reached 0.1, adsorption is about 61–75% of saturation adsorption. As the relative pressure continues to increase, adsorption increases slowly and the isotherm is seen as an upwardly

Table 1: Details of pore structure of activated carbon with different activating agents.

Sample	S_{BET}(m^2/g)	S_{mic} (m^2/g)	$S_{External}$ (m^2/g)	V_{tot} (ml/g)	V_{mic} (ml/g)	V_{mic}/V_{tot} (%)
AC-KOH	3,441	2,591	850.1	2.093	1.304	62.30
AC-NaOH	1,263	1,002	261.1	0.9019	0.5177	57.40
AC-K_2CO_3	1,044	877.2	166.9	0.6769	0.4581	67.68
AC-Na_2CO_3	484.5	315	169.5	0.3561	0.1670	46.90

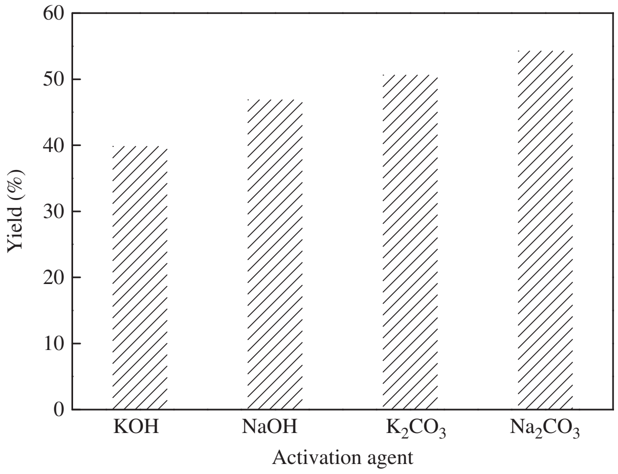

Figure 2: Effects of activating agents to the yield of activated carbon.

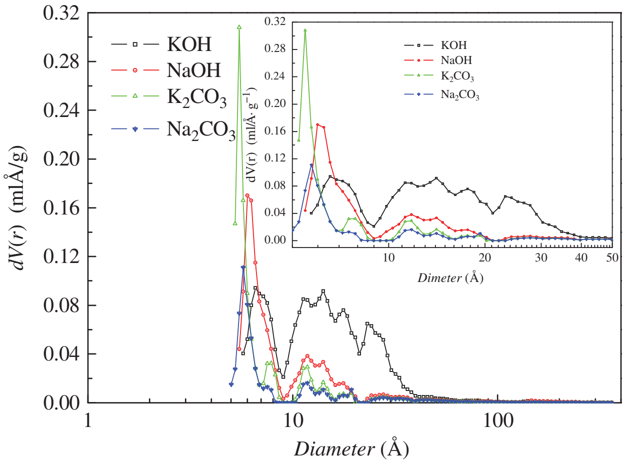

Figure 3: Pore size distribution chart for different activating agents.

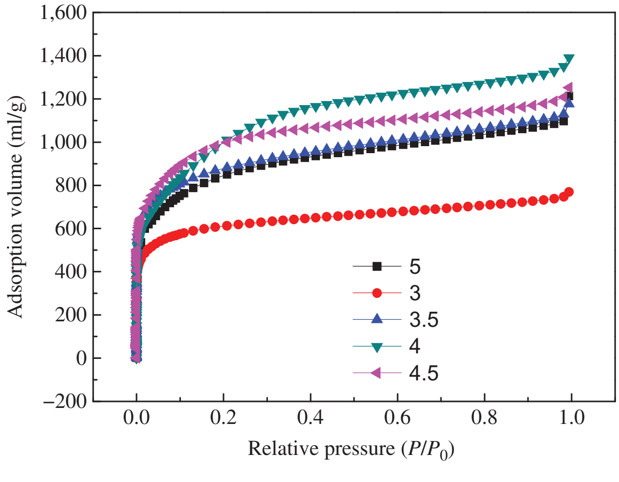

Figure 4: Nitrogen adsorption isotherm of the activated carbon with different KOH/C ratio.

convex shape which indicates that adsorption is transitioned from monolayer to multi-molecular layer. The adsorption capacity continues to increase and shows a tailing at a relative pressure close to 1. It also can be ascertained from Figure 4 that the isotherms except impregnation ratio of 3 is found to possess significant proportion of mesopores, typical of type IV isotherms as referred to IUPAC classification. Table 2 summarizes the pore characteristics which show an increase surface area and total pore volume with increase in the KOH/C ratio. An optimal mixture ratio was observed at an KOH/C ratio of 4, which accounts for a surface area of 3,441 m^2/g. A drop in surface area as well as pore volume is observed with KOH/C ratio beyond 4. The optimal mixture ratio in terms of pore volume and surface area could be attributed to the pore merger phenomena at higher impregnation ratios.

Table 3 compares the surface area of various activated carbons prepared using different activating agents utilizing different precursors as reported in literature. Although it is a small sample from the large number of activated carbon reported in literature, it clearly evidence the high surface area of the activated carbon prepared in the present work as compared with the literature. A surface as high as 3,441 m^2/g is very rarely reported in literature which could form the basis for additional work on exploring the combination of bamboo precursor with the KOH activating agent.

FTIR analysis

The Fourier transformed infrared spectra of the activated carbon is prepared using microwave heating at different KOH/C ratio are shown in Figure 5. It can be observed from the Figure 5 that irrespective of KOH/C ratio utilized the overall shapes of the spectra looks similar, with the major peaks observed at 3,432, 1,710, 1,630 and 1,100 cm^{-1}. An increase in the width of the peak was observed with increase in mixture ratio. At a KOH/C ratio of 3–5, the intensity of peak is weak relatively in the range 1,200–1,600 cm^{-1}, which could be attributed to lower oxygen content. The band at around 3,432 cm^{-1} can be assigned to the O–H stretching vibration mode of hydroxyl functional groups [34]. The band at 1,710 cm^{-1} indicates that there may exist C = O functional group [35, 36] and the band at around 1,630 cm^{-1} can be assigned to C = C symmetrical stretching of pyrone and C = O of carboxylic groups [37] and the band at

Table 2: Details of pore structure of activated carbon with different KOH/C ratio.

Sample	S_{BET}(m^2/g)	S_{mic}(m^2/g)	$S_{External}$ (m^2/g)	V_{tot} (ml/g)	V_{mic} (ml/g)	V_{mic}/V_{tot} (%)
AC3.0	1,823	1,503	320.8	1.158	0.8194	70.76
AC3.5	2,691	2,082	608.6	1.752	1.127	64.33
AC4.0	3,441	2,591	850.1	2.093	1.304	62.30
AC4.5	3,055	2,627	427.7	1.873	1.403	74.91
AC5.0	2,782	2,188	593.7	1.700	1.100	64.71

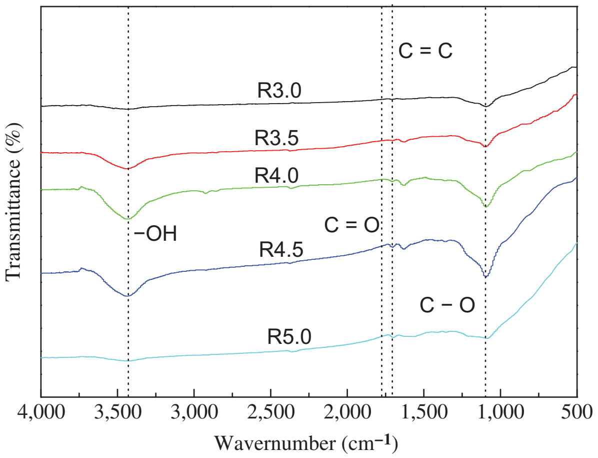

Figure 5: FTIR spectra of activated carbon: KOH/C ratio is from 3.0 to 5.0.

1,100 cm^{-1} is assigned to be C–O stretching vibration mode [38, 39].

SEM analysis

Figure 6(A) is a SEM image of the activated carbon at KOH/C ratio is 4 while Figure 6(B) is a partial enlarged view of (A). As can be seen from Figure 6, the activated carbon surface has abundant pores characterized by thick pore walls and circular pores. The pores on the surface could be macro pores which leads to the branching micropores in the interiors of the activated carbon. The macropores lead the way to the tributaries that are micropores.

Conclusions

Bamboo-based activated carbon which was prepared with KOH presenting surface area to 3,441 m^2/g and total pore volume of 2.093 ml/g were obtained. Prepared with different kinds of activating agents such as KOH, NaOH, K_2CO_3 and Na_2CO_3, it was found that KOH had an excellent effective. When KOH/C ratio was 4, surface area and total pore volume have presented maximum value. The characterization of FTIR illustrated that surface of activated carbon had abundant functional groups. Position and intensity of adsorption peak were changed with KOH/C ratio changes. SEM results showed that activated carbon had more developed pore structure.

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Table 3: Comparison of surface area of activated carbon using different activating agents.

Activating agent	Precursors	Heating method	S_{BET} (m^2/g)	References
KOH	Bamboo	Microwave heating	3,441	Present study
	Coconut husks	Microwave heating	1,356	[19]
	Isotropic petroleum pitch	Conventional heating	2,992	[20]
K_2CO_3	Sisal waste	Conventional heating	1,038	[21]
	Edible fungi residue	Microwave heating	684	[22]
$ZnCl_2$	Coffee husks	Conventional heating	1,522	[23]
H_3PO_4	*Acacia mangium* wood	Conventional heating	1,040	[24]
	Olive waste cakes	Conventional heating	1,020	[25]

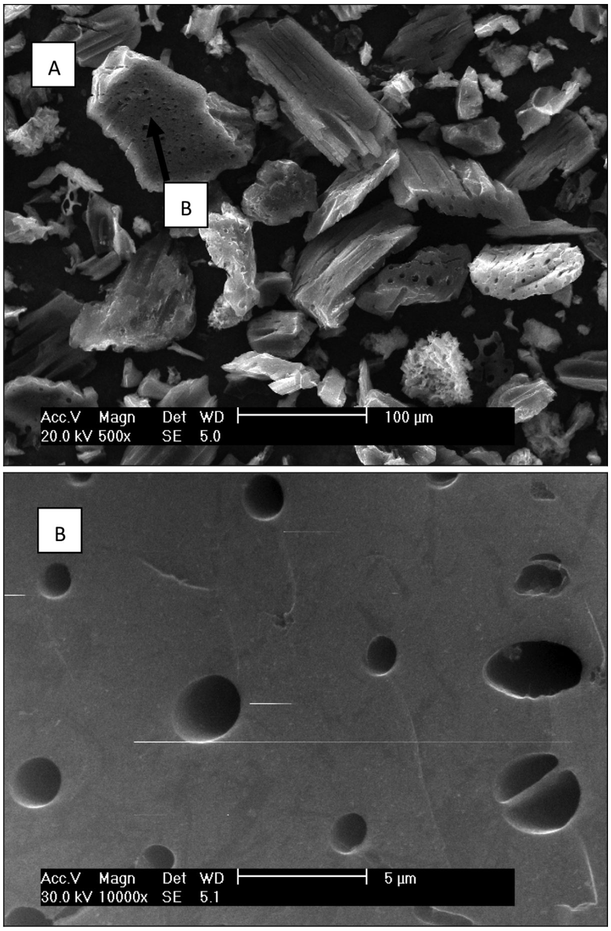

Figure 6: SEM images of activated carbon ((B) is a partial enlarged view of (A)).

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