

Optimization of Mesoporous Activated Carbon from Coconut Shells by Chemical Activation with Phosphoric Acid

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Mesoporous activated carbons were prepared from coconut shells by the method of chemical activation with H₃PO₄. Effects of main influence factors on the yield and adsorption properties of activated carbon were studied via orthogonal experiments. Experimental results under the optimum conditions were as follows: the yield of the activated carbon was 36.90%; methylene blue adsorption was 21.5 mL/0.1 g; and the iodine number was 889.36 mg/g. The surface area of the activated carbon prepared was 891 m²/g, as determined by the BET method. Horvath-Kawazoe equations (H-K) and density functional theory (DFT) were introduced to analyze the porous structures of the activated carbon. It was shown that the activated carbon was mesoporous, with a total pore volume of 0.7233 mL/g, a micropore volume of 37.06%, a mesopore volume of 62.85%, and a macropore volume of 0.07%. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) studies demonstrated the results of the pore structure analysis.

Keywords: Activated carbon; Coconut shells; Phosphoric acid; Pore structure; Microstructure

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INTRODUCTION

Activated carbons are a highly porous form of solid carbon produced from carbonaceous raw materials using chemical or physical activation methods. They have been employed over the last few decades in a wide number of applications on an industrial scale, including technologies for the purification of gases, the removal of organic pollutants from water, as a catalyst or a catalyst support in catalytic processes, and as electrode materials in electrochemical devices and processes. The application of activated carbon in adsorption processes mainly depends on the surface chemistry and pore structure of porous carbons (Bhatnagar *et al.* 2013; Lorenc-Grabowska and Gryglewicz 2005; Frackowiak and Beguin 2001; Gryglewicz *et al.* 2005; Santiago *et al.* 2005).

As environmental pollution is becoming an increasingly serious problem, the worldwide demand for activated carbon is growing. Some of the raw materials being used are non-renewable. Therefore, all possible sources should be investigated. It has been reviewed and documented that lignocellulosic agricultural wastes with high carbon contents and low levels of inorganic compounds are effective precursors for the produc-

tion of activated carbons (Bhatnagar *et al.* 2013; Peláez-Cid and Teutli-León 2012; Ioannidou and Zabaniotou 2007).

Chemical activation of carbonaceous materials by H_3PO_4 is a useful technique for obtaining activated carbons with desired pore size distributions from low-cost precursors at low temperatures (Ma and Quyang 2013; Kaouah *et al.* 2013; Guo *et al.* 2009; Gratuito *et al.* 2008; Jagtoyen and Derbyshire 1993; Laine *et al.* 1989; Molina-Sabio *et al.* 1995). During phosphoric acid activation, the activation temperature is relatively low (usually around 400 to 500 °C). This reagent induces important changes in the pyrolytic decomposition of the lignocellulosic materials because it promotes depolymerization, dehydration, and redistribution of constituent biopolymers, favoring the conversion of aliphatic compounds to aromatic compounds at temperatures lower than when heating in the absence of additives, thus increasing the yield (Montané *et al.* 2005; Díaz-Díez *et al.* 2004; Gómez-Serrano *et al.* 2005; Teng *et al.* 1998). Thus, it is a material-, energy-, and time-saving scheme for the production of activated carbons.

Generally, activated carbon is mainly a microporous solid but, in addition to micropores, it contains meso- and macropores, which are very important pores in facilitating access of the adsorbate molecules to the interior of carbon particles (Marsh and Rodriguez-Reinoso 2006). Gas-adsorbing carbons usually have more micropores, while liquid-adsorbing carbons have significant mesopores, which is important due to the generally larger size of liquid molecules. Because activated carbons from the liquid phase are mostly employed in purification purposes, it is of importance to investigate the preparation of mesoporous activated carbon (Peláez-Cid and Teutli-León 2012; Ioannidou and Zabaniotou 2007). Although microporous activated carbons prepared from coconut shells have been investigated (Guo *et al.* 2009; Gratuito *et al.* 2008; Jagtoyen and Derbyshire 1993; Laine *et al.* 1989), there has been relatively little information regarding coconut shell based mesoporous activated carbons. Hu and Srinivasan (2001) reported the mesoporous activated carbon from coconut shell and palm seeds by chemical activation using $ZnCl_2$. Prauchner and Rodriguez-Reinoso (2012) carried out a comparative study of coconut shells activation by using chemical and physical methods; results indicated that chemical activation with $ZnCl_2$ or H_3PO_4 can elevate proportion of mesopores of prepared carbons.

The objective of this study was to prepare mesoporous activated carbons with relatively well-developed porosity from coconut shells by chemical activation with H_3PO_4 . Optimum conditions for the preparation of mesoporous activated carbons were obtained by orthogonal experimental design. Additionally, the nitrogen adsorption isotherm of the activated carbon prepared under optimum conditions was analyzed to characterize the porous structures. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques were used to characterize the microstructures of the activated carbons.

EXPERIMENTAL

Materials

Coconut shells were obtained from Vietnam. The proximate analysis was conducted according to ASTM D 3172-3175 standards (1999). The relative contents of air-dried coconut shells were as follows: moisture content, 8.83%; volatile solids, 68.54%; fixed carbon, 18.99%; and ash, 3.64%. Phosphoric acid (Shanghai Chemical

Reagent, China) with a purity of 85% was used as the activating agent. High-purity nitrogen (99.9999% from Kuming, China) was used to provide an inert atmosphere.

Preparation of Activated Carbon

Prior to use, coconut shells were crushed and sieved to obtain particles with sizes less than 2 mm. Fifteen-gram portions of the crushed samples were mixed thoroughly in a glass beaker with 53-gram H₃PO₄ solutions of various concentrations (20, 30, 40, or 50 wt%), and then the samples were held in the air for various impregnation times (12, 24, 36, or 48 h). Subsequently, the impregnated coconut shells were loaded on a ceramics boat that was placed inside a stainless steel tube reactor with an internal diameter of 38 mm. The impregnated coconut shells were heated to the carbonization temperature at a heating rate of 30 K/min and were held for at least 30 min at the carbonization temperature under N₂ gas flow. The carbonization temperature varied from 673 to 973 K. After carbonization, the samples were cooled to room temperature under N₂ atmosphere. The carbonized samples were washed with hot distilled water and finally with cold distilled water to remove residual chemicals. The washed samples were dried at 393 K for 2 h to yield activated carbon products. The yield was calculated by the equation

$$Y = M/M_0 \times 100 \quad (1)$$

where M is the mass of activated carbon and M_0 is the mass of air-dried coconut shells.

Characterization of Activated Carbons

Characterization of the activated carbons included adsorption properties and pore structures. The iodine (mg of iodine adsorbed/g of carbon) and methylene blue numbers (mL of methylene blue adsorbed/g of carbon) were determined according to ASTM 4607-86 (1994) and GB/T12496.10-1999 (1999) (testing standard for activated carbon in China) standards, respectively.

The N₂ adsorption-desorption isotherms were measured with an accelerated surface area and porosimetry system (ASAP2000, Micromeritics) to determine the surface areas and total pore volumes. Prior to the measurements, the samples were outgassed at 300 °C under nitrogen flow for at least 2 h. The nitrogen adsorption-desorption data were recorded at liquid nitrogen temperature (77 K). The nitrogen adsorption isotherm was measured over a relative pressure (p/p_0) range from approximately 10⁻⁶ to 1. The BET surface area was calculated using the BET (Brunauer, Emmett, and Teller) equation from selected N₂ adsorption data within the range of relative pressure from 0.1 to 0.3 (Gregg and Sing 1982). The total pore volume, V , was estimated by converting the amount of N₂ gas adsorbed (expressed in cm³/g STP) at a relative pressure of 0.99 to liquid volume of the nitrogen adsorbate (Guo and Lua 2000). The pore size distribution in the micropore range was obtained using the Horvath-Kawazoe (HK) method (Ustinov and Do 2002). According to this method, the cumulative pore volume distribution was first calculated using points from the isotherm at relative pressures corresponding to previously calculated pore sizes. Then, the cumulative distribution was differentiated to give the pore size distributions (PSDs). In the present work, for comparison purposes with the micropore volume (V_{mi}), we have obtained a V_{mi} -HK micropore volume by reading the cumulative volume at a pore diameter of 2 nm. Obviously, the V_{mi} -HK value was equal to that calculated from the area under the PSD curve (*i.e.*, the definite integral). PSD was computed using the DFT (density functional

theory) method by minimizing the grand potential as a function of the fluid density profile. The volume fractions of micropores, mesopores, and macropores were calculated based on the tabular PSD data (Ismadji and Bhatia 2001; Kowalczyk *et al.* 2003; McCallum *et al.* 1999; Valladares *et al.* 1998).

A scanning electron microscope (SEM, EMPA-1600) and a transmission electron microscope (TEM, JEM 2010) were used to observe the surface pore structure of the activated carbons. For SEM measurements, the samples were coated with a thin layer of gold and mounted on a copper stab using a double stick carbon tape. For TEM measurements, the powder samples were dispersed in ethanol and dried on a carbon film with multiple holes on a Cu grid for measurements.

Method of Orthogonal Experiments

Orthogonal experimental design is one way to qualitatively analyze the correlations among the relevant variables at different levels by designing orthogonal tables and statistical analysis (Fan and Chen 1996; Cui *et al.* 2007). Regressive analysis can be used to obtain the parameters optimized. The effects of impregnating time, concentration of phosphoric acid solution, carbonization temperature, and holding time on the adsorption properties of activated carbon were systematically investigated *via* orthogonal experiments. Four levels were chosen in each of the factors. Orthogonal experiments ($L_{16}(4^5)$) were used to design experimental tables, as illustrated in Table 1. In total, there were 16 groups of experiments, and average values were obtained after completing each group of experiments three times.

Table 1. Factors and Levels of Orthogonal Test

Levels \ Factors	H ₃ PO ₄ acid concentration (%)	Impregnating time (h)	Carbonization temperature (K)	Holding temperature time (min)
1	20	12	673	10
2	30	24	773	20
3	40	36	873	30
4	50	48	973	40

RESULTS AND DISCUSSION

Experimental Results for Activated Carbons

Effects of various parameters on the properties of activated carbon are listed in Table 2. Activated carbon specimens were found to have different properties (iodine number, methylene blue, and yield) under various conditions. With the range analysis results in Table 3, the adsorption properties and yields of activated carbons with the different effect factors can be compared. There are two important parameters in a range analysis: K_{ji} and R_j . K_{ji} is defined as the sum of the evaluation indexes of all levels ($i, i = 1, 2, 3, 4$) in each factor ($j, j = A, B, C, D$) and \bar{K}_{ji} (mean value of K_{ji}) is used to determine the optimal level and the optimal combination of factors. The optimal level for each factor could be obtained when \bar{K}_{ji} is the largest. R_j is defined as the range between the maximum and minimum value of \bar{K}_{ji} and is used for evaluating the importance of the

factors, *i.e.* a larger R_j means a greater importance of the factor. For iodine number, the R values of the four factors were in the order $B > C > A > D$; for methylene blue adsorption, the R values of the four factors were in the order $C > D > A > B$; for yield, the R values of the four factors were in the order $C > D > B > A$. The optimum conditions of the four parameters for the iodine number, the methylene blue adsorption, and the yield were $A_2 > B_1 > C_4 > D_4$, $A_2 > B_3 > C_4 > D_4$, and $A_3 > B_3 > C_1 > D_1$, respectively. As a result, the optimum conditions for this procedure could be expressed as $A_2B_1C_4D_4$, where A_2 , B_1 , C_4 , and D_4 denote the concentration of phosphoric acid solution, impregnating time, carbonization temperature, and holding time, respectively. A_2 , B_1 , C_4 , and D_4 are 30%, 12 h, 700 °C, and 40 min, respectively. Under the optimum conditions, activated carbons were prepared, and the iodine number, methylene blue adsorption, and yield were 889.36 mg/g, 21.5 mL/0.1 g, and 36.90%, respectively.

Table 2. Results of Orthogonal Test

No.	H ₃ PO ₄ acid concentration (%)	Impregnating time (h)	Carbonization temperature (°C)	Holding temperature (min)	Iodine number (mg/g)	Methylene blue adsorption (mL/0.1g)	Yield (%)
1	20	12	400	10	832.04	12	43.37
2	20	24	500	20	832.54	13	41.37
3	20	36	600	30	765.51	16	38.42
4	20	48	700	40	825	20	35.64
5	30	12	500	30	888.29	17	34.89
6	30	24	400	40	922.49	19	38.66
7	30	36	700	10	886.11	17.5	41.52
8	30	48	600	20	844.15	14	41.35
9	40	12	600	40	882.65	16	40.87
10	40	24	700	30	861.36	18	35.75
11	40	36	400	20	706.82	8	45.54
12	40	48	500	10	809.56	10	39.74
13	50	12	700	20	907.14	18	33.42
14	50	24	600	10	770.69	11	45.06
15	50	36	500	40	860.67	17	35.54
16	50	48	400	30	722.89	11	39.72

Table 3. Range Analysis Results

Level	Factors											
	H ₃ PO ₄ acid concentration (%) (A)			Impregnating time (h) (B)			Carbonization temperature (°C) (C)			Holding temperature time (min) (D)		
	1	2	3	1	2	3	1	2	3	1	2	3
K _I	3255.09	61.0	158.80	3510.12	152.55	152.55	3184.24	50.0	167.29	3298.40	50.5	169.69
K _{II}	3541.04	67.5	156.42	3387.08	160.84	160.84	3391.06	57.0	151.54	3290.65	53.0	161.68
K _{III}	3260.39	52.0	161.90	3219.11	161.02	161.02	3263.00	57.0	165.7	3238.05	62.0	148.78
K _{IV}	3261.39	57.0	153.74	3201.60	156.45	156.45	3479.61	73.5	146.33	3490.81	72.0	150.71
K _I	813.77	15.3	39.70	877.53	38.14	38.14	796.06	12.5	41.82	824.60	12.6	42.42
K _{II}	885.26	16.9	39.11	846.77	40.21	40.21	847.77	14.3	37.89	822.66	13.3	40.42
K _{III}	815.10	13.9	40.48	804.78	40.26	40.26	815.75	14.3	41.43	809.51	15.5	37.20
K _{IV}	815.35	14.3	38.44	800.40	39.11	39.11	869.90	18.4	36.58	872.70	18.0	37.68
R	71.49	3.9	2.04	77.13	2.12	2.12	73.84	5.9	5.24	63.19	5.4	5.22

*1: Iodine number; 2: Methylene blue adsorption; 3: Yield

Iodine number usually gives an estimation of the relative surface area of two samples and is used to measure the porosity for pores greater than 1.0 nm in diameter (Bansal *et al.* 1988). Thus, the iodine number was measured to evaluate the adsorptive capacity of the activated carbon. Haimour and Emeish (2006) reported that the maximum value of the iodine number of activated carbon produced from waste date stones using H_3PO_4 as an activation agent was about 495 mg/g under the following conditions: impregnation ratio, 0.4; activation time, 60 min; activation temperature, 800 °C; and particle size, 0.60 mm; these values of iodine number are much lower than that of the present study. The iodine number of activated carbon prepared from woody biomass (birch) by impregnation with phosphoric acid followed by steam pyrolysis was 1280 mg/g (Budinova *et al.* 2006), which is higher than that of the present study.

The results of the present study demonstrated that highly microporous/mesoporous activated carbon with a high surface area can be prepared from coconut shells by H_3PO_4 activation under appropriate process conditions.

Pore Structure Characterization

Nitrogen adsorption is a standard procedure for determination of the porosity of carbonaceous adsorbents. The adsorption isotherm is the information source for the porous structure of the adsorbent, heat of adsorption, physical and chemical characteristics, and so on. The N_2 -adsorption isotherm obtained for the sample prepared under the optimum conditions is shown in Fig. 1.

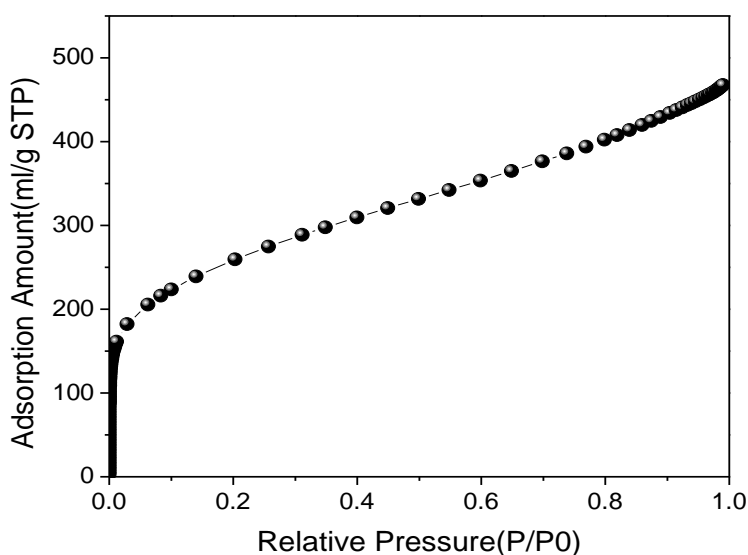


Fig. 1. Adsorption isotherm of N_2 at 77 K on activated carbon prepared under the optimum conditions

The isotherms belong to type IV, as defined by the International Union of Pure and Applied Chemistry (IUPAC), and provide an approximate assessment of the pore size distribution. As shown in Fig. 1, the initial part of the type-IV isotherm for carbon represents micropore filling, and the slope of the plateau at high relative pressure is due to multilayer adsorption on non-microporous surfaces, *i.e.*, in mesopores, in macropores, and on the external surface (Rouquerol *et al.* 1999). This indicated that the sample had a mesoporous structure that contained plenty of mesopores and micropores and a few

macropores. The PSD (pore size distribution) was broad. The point at $p/p_0 = 0.02$ indicated that monolayer coverage was completed and that multilayer adsorption began at this stage. From the nitrogen adsorption isotherm analysis results, the BET surface area and total pore volume of the carbon were $891 \text{ m}^2/\text{g}$ and 0.7233 mL/g , respectively. The BET surface area of activated carbon derived from woody biomass (birch) using H_3PO_4 and water vapor activation was $1360 \text{ m}^2/\text{g}$ (Budinova *et al.* 2006), and the BET surface area of activated carbon prepared from pecan shells with phosphoric acid was $861 \text{ m}^2/\text{g}$ (Guo and Rockstraw 2007).

In accordance with the classification adopted by IUPAC (1982), adsorbent pores are classified into three groups: micropores ($< 2 \text{ nm}$), mesopores (2 to 50 nm), and macropores ($> 50 \text{ nm}$). Micropores can be divided into ultramicropores (width less than 0.5 nm) and supermicropores (width from 1 to 2 nm). This distinction is important because most molecules of gaseous pollutants range in diameter from about 0.4 to 0.9 nm . Therefore, gas-adsorbing carbons usually have more micropores, while liquid-adsorbing carbons have significant mesopores due to the generally larger size of liquid molecules. An alternative method for determining PSD proposed by Horvath and Kawazoe was to calculate an average potential function inside the micropore, relating the fluid-fluid and solid-fluid interactions of an adsorbed molecule to its free energy change upon adsorption.

The Horvath-Kawazoe method is an improvement over the Kelvin approach in that it acknowledges the strong adsorbent-adsorbate attractive forces in micropores and is effective for calculating micropore size distribution.

The micropore size distribution for activated carbon according to the Horvath-Kawazoe method is shown in Fig. 2. From the differential pore volume plots, ultramicropores less than 0.7 nm were present, which leads to the selectivity of adsorption (molecular sieve effect). A heterogeneous micropore size distribution was obtained, with two different peaks at 0.55 and 0.59 nm . The average micropore size was 0.65 nm .

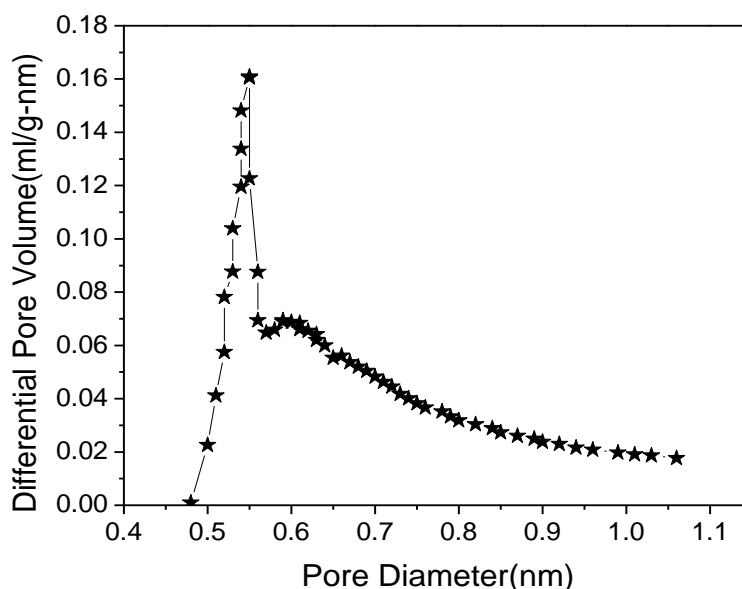


Fig. 2. Micropore size distribution of activated carbon prepared under the optimum conditions as determined by the H-K equation

The PSD obtained by DFT analysis of the nitrogen adsorption isotherm is shown in Fig. 3 and was consistent with the isotherm trend discussed earlier. From Fig. 3, the activated carbon contains 37.06% micropores, 62.85% mesopores, and 0.07% macropores. The PSD was broad, with four different peaks at 0.73, 1.18, 2.73, and 3.43 nm.

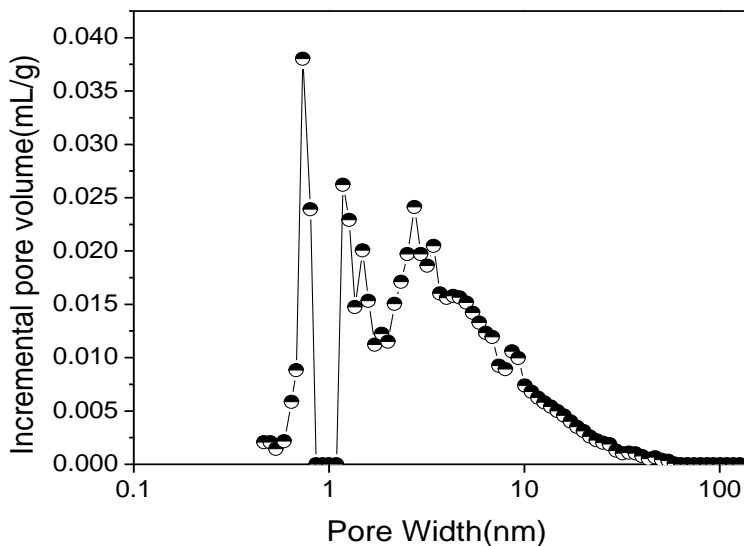


Fig. 3. Pore size distribution of the activated carbon prepared under the optimum conditions as determined by DFT

Microstructural Analysis

The SEM technique was used to observe the surface physical morphology of the activated carbon. Results, as shown in Fig. 4, indicated that the activated carbon contained open and homogeneous macropores on the external surfaces and had an irregular, highly porous surface.

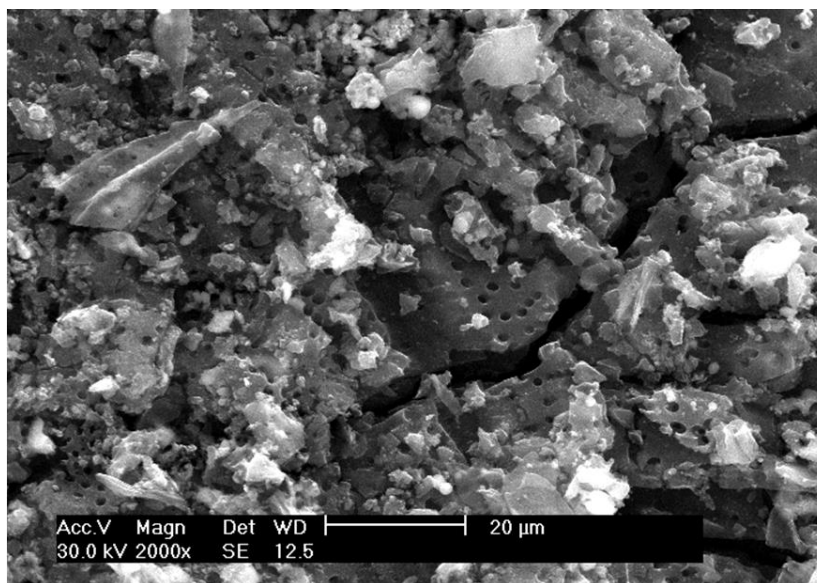


Fig. 4. Scanning electron micrograph of the activated carbon prepared under the optimum conditions

TEM is a vital characterization tool to examine the microstructure of activated carbon. In the TEM image shown in Fig. 5, the carbon frame in the sample was visualized as black particles and the pores are shown as white areas. There are both mesopores and micropores present in the activated carbon. The results of SEM and TEM analysis were consistent with the results of nitrogen adsorption isotherm analysis.

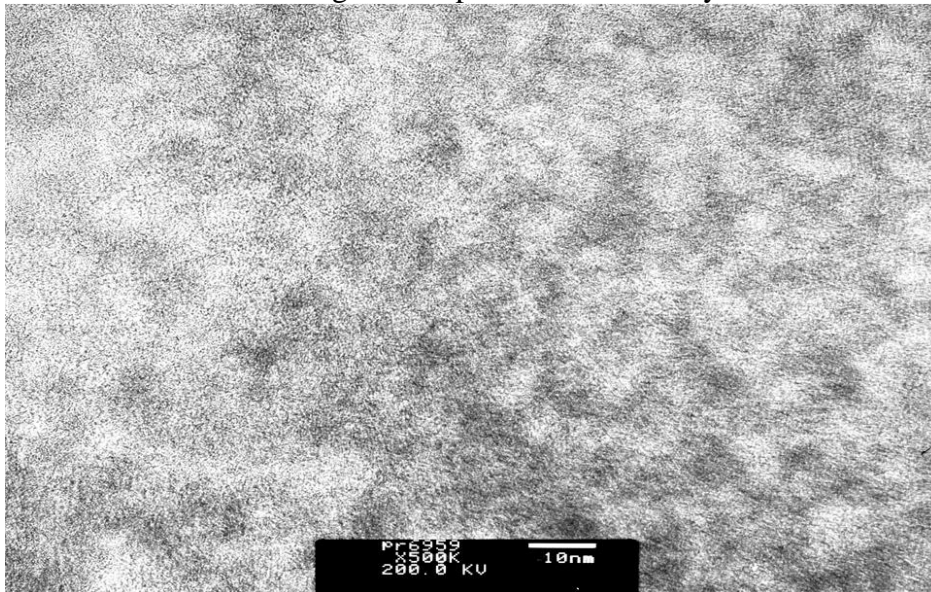


Fig. 5. Transmission electron micrograph of the activated carbon prepared under the optimum conditions

CONCLUSIONS

1. This study indicates that H_3PO_4 is a suitable activating agent for the preparation of mesoporous activated carbons from coconut shells under appropriate process conditions.
2. Experimental results under the optimum conditions, as determined through orthogonal experiments, were as follows: the yield of the activated carbon was 36.90%; methylene blue adsorption was 21.5 mL/0.1 g; and the iodine number was 889.36 mg/g.
3. The microstructures of the activated carbon, observed by SEM and TEM, agreed with the pore structure results from the analysis of the nitrogen adsorption isotherm.
4. The activated carbon was shown to be a mesoporous structure with a total pore volume of 0.7233 mL/g, a micropore volume of 37.06%, a mesopore volume of 62.85%, and a macropore volume of 0.07%. The surface area of the activated carbon prepared was 891 m^2/g , as determined by the BET method.

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