

Textural Characteristics of Activated Carbons Prepared from Oil Palm Shells Activated with $ZnCl_2$ and Pyrolysis Under Nitrogen and Carbon Dioxide

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Abstract: The textural characteristics of activated carbon prepared from oil palm shells activated with zinc chloride ($ZnCl_2$) and pyrolysis under nitrogen and carbon dioxide were studied in this paper. The pyrolysis was carried out at different activation temperatures in the range of $400^\circ C$ – $800^\circ C$. The BET surface areas obtained were in the range of 1429.71 – $1134.74\text{ m}^2\text{ g}^{-1}$. The difference of values between micropore surface area and external surface area showed that the activated carbons were predominantly microporous adsorbents. The Dubinin-Astakhov (D-A) approach was used to study the pore size diameter of activated carbon. The pore size diameters of activated carbons obtained were in the range of 1.76 – 1.84 nm and the exponent (n) parameter in the range of 1.2 to 1.6 indicated predominantly micropores. The Dubinin-Radushkevich (D-R) method was used to evaluate the micropore volume of activated carbon. The micropore volumes found were in the range of 0.74 – $0.619\text{ cm}^3\text{ g}^{-1}$. The structural morphology and composition of activated carbons were evaluated by SEM-EDX. It was clearly seen that the activated carbons were full of cavities, and some of Zn metals were still trapped at the surface of activated carbons. In general, the heterogeneous and predominantly microporous activated carbon was produced.

Keywords: activated carbon, nitrogen, carbon dioxide, activation, impregnation, zinc chloride

1. INTRODUCTION

The two largest producer countries of palm oil in the world are Malaysia and Indonesia. In Malaysia, oil palm shells containing high carbonaceous materials are generated in large quantity as a major by-product of the oil palm milling industry. Oil palm shells are usually burned as a low-value energy resource or discarded in the field, both of which are unfavorable to the environment. Due to high carbonaceous materials, oil palm shells are used as the precursor in the production preparation of activated carbon.¹

Activated carbons are widely used as adsorbents. They represent extremely versatile adsorbents of industrial significance and are widely used in many applications which concern principally with the removal of undesirable

species from liquids or gases. They are also used as catalysts or catalyst supports or gas storages.

For these applications, activated carbons are required to possess a high specific surface area and controllable pore size distribution. These properties are very important in the field of activated carbon design. They can be produced by either physical or chemical activation process. Chemical activation is the most commonly used process for preparing activated carbon due to its lower activation temperature and excellent properties for the product compared to physical activation process. Normally, phosphoric acid and $ZnCl_2$ are widely used as chemical agents in the chemical activation process.²⁻⁵

Analysis of physical properties of the activated carbon involves the determination of the total surface area, the extent of microporosity and the pore size distribution. These are very important indicators for the suitability of activated carbon as an adsorbent. The nitrogen adsorption-desorption isotherm at low temperature ($-196^\circ C$) is commonly used for the analysis of the physical properties. Determination of total surface area is commonly based on the theory of multilayer adsorption developed by Brunauer, Emmett and Teller with the relative pressure (p/p^0) in range of 0.05–0.30.⁶⁻⁸ The extent of microporosity is commonly evaluated by applying t-method involving micropore surface area and external surface area within the relative pressure in the range of 0.2–0.5.⁹ The micropore volume is evaluated using the D-R method. The pore size distribution with respect to mesopore is measured by the Barrett, Joyner and Helenda (BJH) method.¹⁰⁻¹² The micropore size distribution is measured by the D-A method by applying low relative pressure region of adsorption isotherm.

The aim of this work was to prepare and study the effect of different pyrolysis temperatures on the development of the porosity of activated carbon derived from oil palm shells activated with $ZnCl_2$. The activated carbon was prepared from solid waste of oil palm shell by two-stage methods in order to obtain the maximal adsorptive capacities.

2. EXPERIMENTAL

2.1 Reactor

The stainless steel reactor for the pyrolysis of oil palm shells with 12 cm in diameter, 25 cm in height and 5 mm in thickness. The size of reactor was suitable to be placed inside the Nabertherm graphite furnace. The gas inlet and outlet were designed at the bottom and top of the reactor, respectively, using

stainless steel pipes. Figure 1 shows the schematic diagram of the set-up for the pyrolysis of oil palm shell.

2.2 Material

The raw material for the preparation of activated carbon was the oil palm shells collected from an oil palm mill at Nibong Tebal, Malaysia. The oil palm shells as received were washed with water to reduce oily impurities and dried in the oven at 110°C. The dried oil palm shells were ground in a blender and sieved to a particle size of 0.5–1.5 mm.

2.3 Chemical Activation with ZnCl₂

About 250 g of oil palm shells with particle size of 0.5–1.5 mm was added into 500 ml of 65% ZnCl₂ solution. The mixture was refluxed in water bath at 85°C for 24 h. Thereafter, the mixture was filtered and the residue was washed with hot distilled water and dried in oven at 110°C for 24 h. The impregnated sample was pyrolyzed in two stages. First, the reactor was loaded with impregnated sample and then placed into the graphite furnace. Purified nitrogen was allowed to flow into the reactor at a constant flow rate of 200 cm³ min⁻¹. At the same time, the furnace was gradually heated at the constant heating rate 5°C min⁻¹ from the ambient temperature to the pyrolysis temperature. The temperatures were set at 400°C, 500°C, 600°C, 700°C and 800°C with the contact time of 3 h at each of the activation temperatures. After cooling to the ambient temperature, the sample was washed with hot distilled water for several times until pH 6–7 and then dried in the oven at 110°C.

In the second stages of pyrolysis, purified carbon dioxide gas was used instead of nitrogen with the contact time of 90 min at each of the activation temperatures. The activated carbon produced was washed with distilled water and then dried in the oven at 110°C for 24 h.

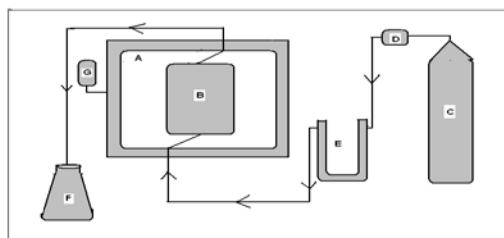


Figure 1: Schematic diagram for pyrolysis. (A) Electrical graphite furnace; (B) rector; (C) gas tank; (D) flow meter; (E) inlet gas trap silicate; (F) outlet gas trap water; (G) temperature controller.

2.4 Characterization of the Activated Carbons

2.4.1 Nitrogen adsorption studies

The determination of the adsorption-desorption nitrogen isotherms was carried out at the temperature of -196°C and the relative pressure in the range of 0.005–0.99 using a surface area analyzer (Quanthachrome Nova 2200e). Data was analyzed for the BET surface area, micropore surface area, external surface area, micropore and total pore volume, and pore size distribution. The specific surface areas were analyzed according to the BET method at the relative pressure in the range of 0.05–0.30.^{15–17} Micropore surface area and external surface area were obtained from the t-plot method whereas total pore volume was directly calculated from the volume of nitrogen held at the highest relative pressure ($p/p^0 = 0.99$). The micropore volume was estimated from the D-R plots at the relative pressure of < 0.1 . Pore size diameters were determined by the D-A method at the relative pressure in the range of 0.1–0.005. All calculations were performed using the program of Quanhachrome Nova 2200e surface area analyzer.

2.4.2 Structural morphology

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis (EDX) were used to observe the structural morphology and composition of activated carbon.

3. RESULTS AND DISCUSSION

3.1 BET Surface Area of Activated Carbon

Some studies concerning the preparation of activated carbon from oil palm shells with chemical activation had been reported.^{18–20} The textural characteristics of the activated carbon prepared from oil palm shells pyrolyzed at different activation temperatures under nitrogen and carbon dioxide are reported in Table 1. The textural characteristics of activated carbon involving BET surface area, micropore surface area, external surface area, micropore volume, total pore volume, average pore size diameter and pore size diameter are very important because they are closely related to the adsorptive capacities.²¹ The pyrolysis at the activation temperature of 500°C was found to provide the highest BET surface area, $1429.71 \text{ m}^2 \text{ g}^{-1}$. In general, activated carbon activated with ZnCl_2 produced high surface area in the range of $1148.18\text{--}1429.71 \text{ m}^2 \text{ g}^{-1}$.

Table1: Textural characteristics of activated carbon at different activation temperatures.

Temp. (°C)	BET surface area (m ² g ⁻¹)	Micropore surface area (m ² g ⁻¹)	External surface area (m ² g ⁻¹)	D-R micropore volume (cm ³ g ⁻¹)	Total pore volume (p/p ^o = 0.99) (cm ³ g ⁻¹)	Average pore size diameter (nm)	D-A pore size diameter (nm)
400	1148.18	973.1	175.1	0.54	0.62	2.16	1.76 (n = 1.6)
500	1429.71	1024.3	404.4	0.74	0.77	2.16	1.84 (n = 1.2)
600	1297.09	842.2	454.9	0.53	0.71	2.18	1.84 (n = 1.2)
700	1317.22	975.1	342.1	0.58	0.71	2.14	1.80 (n = 1.4)
800	1134.74	694.2	440.6	0.46	0.63	2.22	1.82 (n = 1.3)

Table 1 shows that the BET surface area of activated carbon increased from 1148.18 to 1428.71 m² g⁻¹ with increasing of the activation temperatures from 400°C to 500°C; thereafter, decreased at higher activation temperatures. At the activation temperature of 400°C, the developing rudimentary pores of activated carbon were formed by removing the low-molecular-weight volatile compounds from the matrix structure. Increasing the activation temperature to 500°C enhanced the removal of molecular weight volatile compounds and further created new pores, resulting in the acceleration of porosity development of the activated carbon. The presence of ZnCl₂ as an impregnation agent would increase the heat energy on the pyrolysis process, and thus initiate to develop the porosity of activated carbon.²² However, when the activation temperature was increased to 600°C, excessive heat energy was given to the carbon resulting in the knocking and breaking of some of porous wall, thus blocking the porosity formation. Hence, the pyrolysis at this activation temperature would yield decreasing BET surface area, micropore surface area, external surface area, micropore volume, total pore volume but increasing average pore size distribution.

3.2 Other Textural Characteristics of Activated Carbon

Figure 2 shows the nitrogen adsorption-desorption isotherms at -196°C on the activated carbon prepared at different activation temperatures in the range of 400°C–800°C. All of the plots exhibit typical Type I isotherm with a well-developed sharp "knee" at the low relative pressure that tend to become almost a plateau at higher relative pressure. The type I isotherm indicated the presence of microporous adsorbents with relatively small external surface at low relative pressure of < 0.1.²³

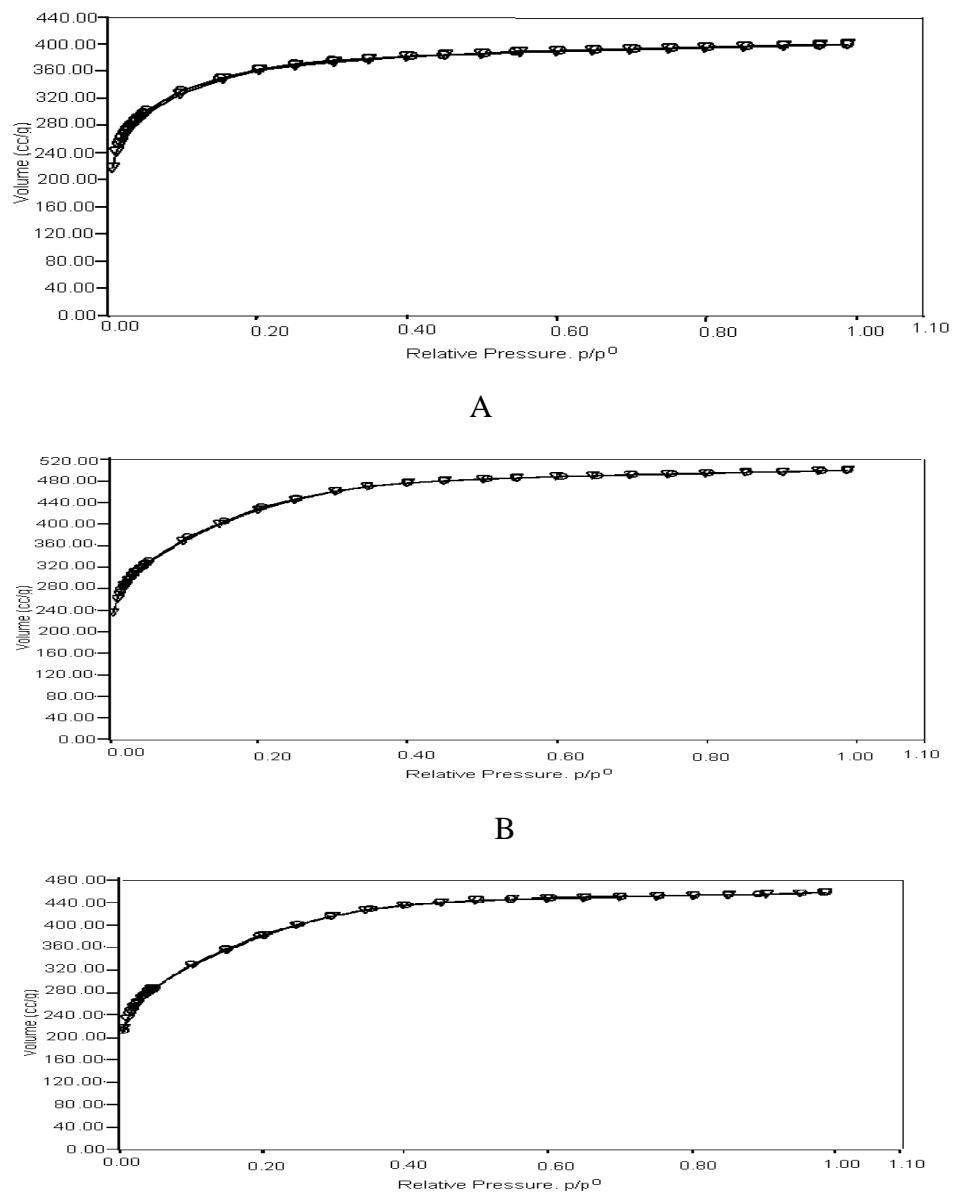


Figure 2: Nitrogen adsorption-desorption isotherms at -196°C on the activated carbon prepared from oil palm shells activated with ZnCl_2 and at various pyrolysis temperatures. (A) 400°C ; (B) 500°C ; (C) 600°C (D) 700°C ; (E) 800°C .

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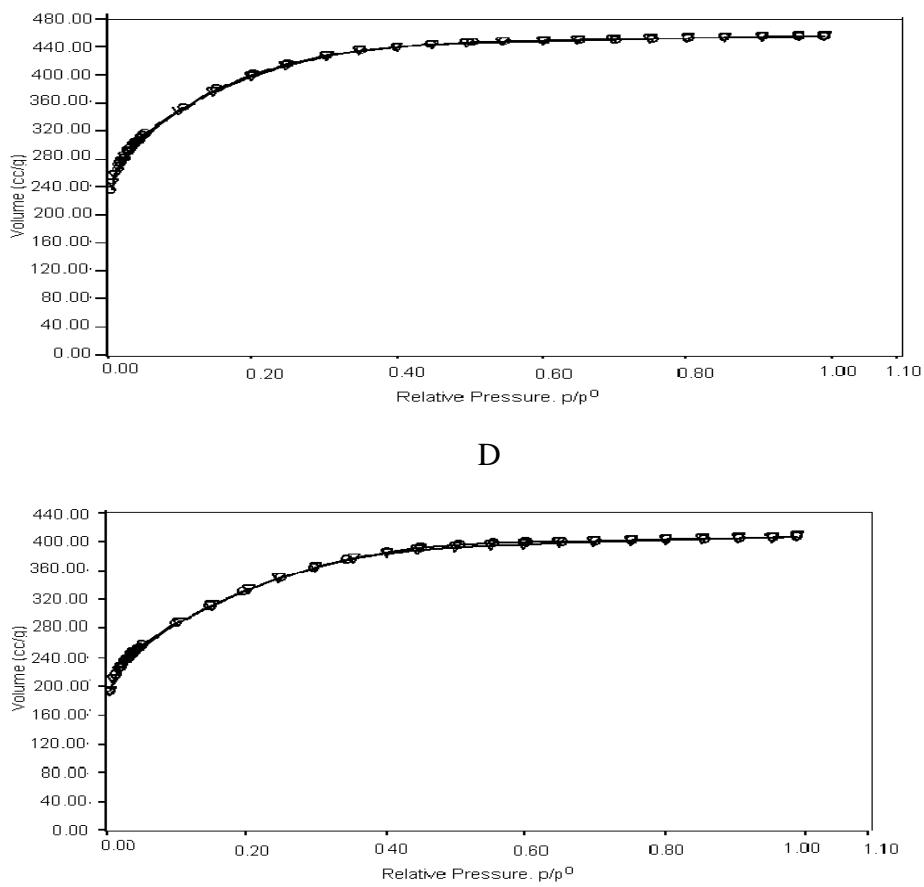


Figure 2: (continued)

Figure 3 shows the various curves of pore size distributions of activated carbon prepared at different pyrolysis temperatures. All of the pore size distribution curves of activated carbon have their maxima at the pore diameter less than 2 nm indicating the presence of micropores. The micropore diameters were determined to be in the range of 1.76–1.84 nm. Micropore volumes were evaluated using the D-R equation at the relative pressure in the range of 0.1–0.005 and the results are shown in Table 1. The micropore volume increased with increasing activation temperature from 400°C to 500°C, but thereafter, decreased with further activation temperature increase. At the activation of 500°C, the maximum micropore volume was $0.74 \text{ cm}^3 \text{ g}^{-1}$. At the lower pyrolysis

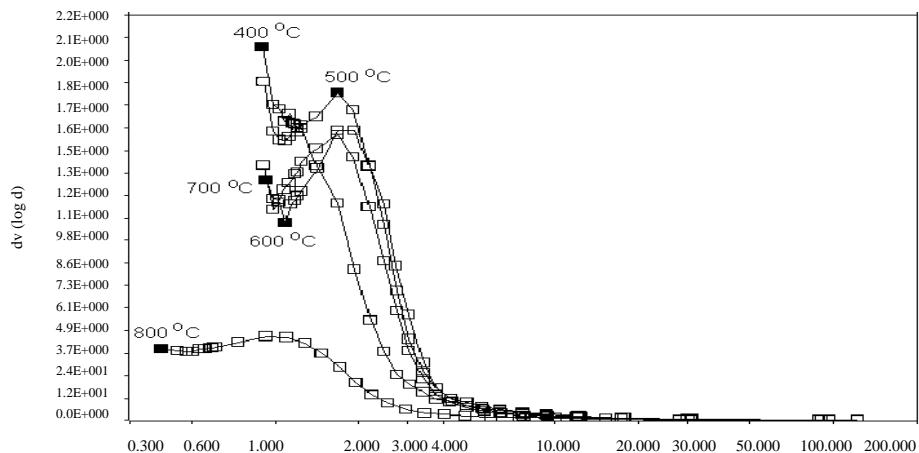


Figure 3: Pore size distributions of activated carbon prepared by chemical activation with 65% ZnCl_2 at different pyrolysis temperatures.

temperature of 400°C , the heat energy of pyrolysis was not enough to develop porosity and produced low micropore volume of activated carbon. However, the decrease of micropore volume at higher pyrolysis temperatures in the range of 600°C – 800°C was caused by a contraction or breaking of some of the porous wall of activated carbon, thus blocking the pores.

It was noticed that D-A method was usually used to evaluate the micropores of activated carbon. The D-A equation required the characteristic energy (E_0) and n parameter distributions. In this approach, n reflects the width of the energy distribution, which is related to the pore size distribution. Values of n between 1 and 4 have been obtained for large carbon adsorbents. Values of $n > 2$ provide homogeneous micropores with narrow micropore of small size range, while values of < 2 are found for heterogeneous carbon with a wide range of pore size such as conversion of micropore to mesopores and macropores. As showed in Table 1, the values of n for activated carbon prepared by chemical activation with ZnCl_2 ranged from 1.6 to 1.2 which indicated to heterogeneous activated carbon with wide size range of micropores.

3.3 Surface Morphology of Activated Carbon

Scanning electron macrographs for the external morphology of the activated carbon at the pyrolysis temperature of 500°C are displayed in Figure 4. It can be seen that the external surface of activated carbon is full of cavities.

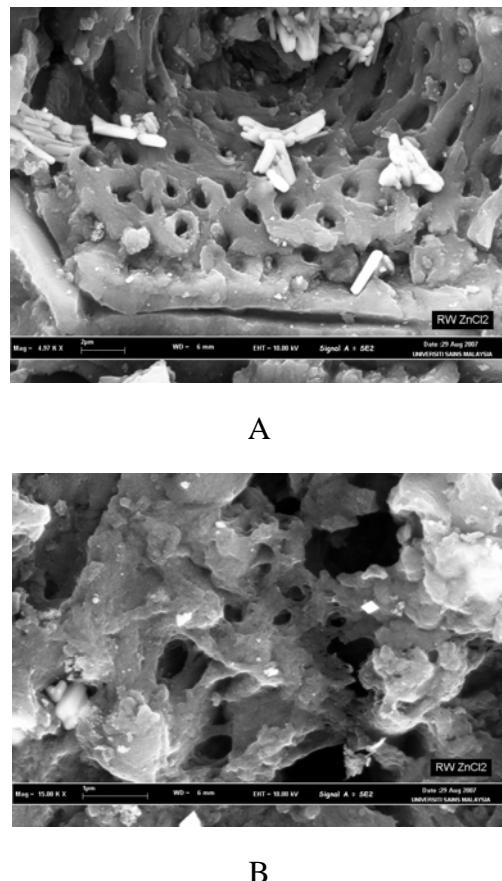


Figure 4: Structural morphology of activated carbon prepared by chemical activation with ZnCl_2 at 500°C . (A) Magnitude of 4980x; (B) magnitude of 15000x.

The composition of resulted activated carbon was determined by the EDX analysis. Some Zn metals found to be trapped at the surface of the activated carbon are shown in Figure 5.

3. CONCLUSION

Oil palm shell, a waste from oil palm milling industry, is a good material to prepare activated carbon which possesses high adsorptive capacities. Development of the porosity of activated carbon was affected by the activation temperature and the presence of ZnCl_2 for impregnation. The maximum surface

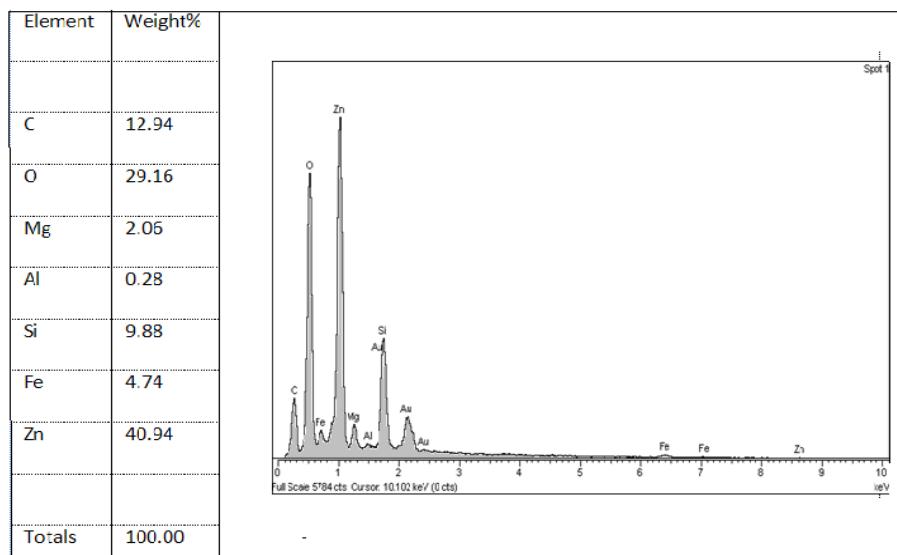


Figure 5: Composition of activated carbon prepared by chemical activation with 65% solution of ZnCl_2 at the pyrolysis temperature of 500°C.

area of $1429.71 \text{ m}^2 \text{ g}^{-1}$ was obtained at the activation temperature of 500°C. The value of micropore surface area was much higher than the value of external micropore area, indicating that the activated carbon consisted of predominantly micropores. Nitrogen adsorption-desorption isotherm showed Type I indicating the presence of micropore activated carbon. The micropore volume and pore diameter were evaluated by the D-R and D-A methods, respectively, yielding the maximum micropore volume ($0.74 \text{ cm}^3 \text{ g}^{-1}$) and small pore diameter ($< 2 \text{ nm}$). Textural morphology of activated carbon determined by the SEM-EDX clearly showed that the activated carbon was full of cavities. Some Zn metals were found at the surface of the activated carbon.

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