Pore structure and adsorption performance of the KOH-activated carbons prepared from corncob

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Abstract

Carbonaceous adsorbents with controllable surface area were chemically activated with KOH at 780 °C from chars that were carbonized from corncobs at 450 °C. The pore properties, including BET surface area, pore volume, pore size distribution, and mean pore diameter of these activated carbons, were characterized by the *t*-plot method based on N₂ adsorption isotherms. Two groups are classified according to the types of adsorption/desorption isotherms. Group I corncob-derived activated carbons, with KOH/char ratios from 0.5 to 2, exhibited BET surface area ranging from 841 to 1221 m²/g. Group II corncob-derived activated carbons, with KOH/char ratios from 3 to 6, showed high BET surface areas, from 1976 to 2595 m²/g. From scanning electron microscopic (SEM) results, the surface morphology of honeycombed holes on corncob-derived activated carbons was significantly influenced by the KOH/char ratios. The adsorption kinetics of methylene blue, basic brown 1, acid blue 74, 2,4-dichlorophenol, 4-chlorophenol, and phenol from water at 30 °C were studied on the two groups of activated carbons, which were suitably described by two simplified kinetic models, pseudo-first-order and pseudo-second-order equations. The effective particle diffusivities of phenols and dyes at the corncob-derived activated carbons of group II are higher than those of ordinary activated carbons. The high-surface-area activated carbons were demonstrated to be promising adsorbents for pollution control and for other applications.

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1. Introduction

Liquid-phase adsorption has been demonstrated to be a highly efficient method for the removal of colors and odors as well as organic and inorganic matter from chemical processes or waste effluents. In general, activated carbons in both granular and powdered forms are the most widely used adsorbents because of their excellent adsorption capability for organic pollutants [1], which are usually related to their specific surface area, pore volume, and porosity [2]. In addition, the adsorption properties of activated carbons were found to depend strongly on the activation process and the nature of raw materials. Moreover, in developing the

porosity of carbons by means of both physical and chemical activation processes, an understanding of the influence of preparation variables is very important [3]. Particularly, the development of micropores and mesopores is of great importance because the adsorption of large amounts and various chemicals from gas or liquid streams on activated carbons resulted from the formation of these pores. Recent progress of industrial technologies provides a new application of activated carbons in supercapacitors, which, at the same time, requires the carbons to have a desired pore structure [4].

Recently, we prepared a series of steam-activated carbons derived from pinewood [5], corncob [6], bagasses [7], plum kernels [8], and bamboo [9]. Based on these studies, intensifying the activation, such as at an elevated temperature or a longer activation time, would increase the BET surface area (S_p) and the mesopore ratio ($V_{\text{meso}}/V_{\text{pore}}$) simultaneously. In

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addition, carbons prepared from eucalyptus wood activated in an atmosphere containing CO_2 and a small amount of O_2 showed very similar results [10]. However, the mesopore ratio was not proportionally enhanced by an increase in the chemical dosages when carbons were fabricated by chemical activation with KOH, ZnCl_2 , H_3PO_4 , etc. Accordingly, their $V_{\text{meso}}/V_{\text{pore}}$ ratios are usually smaller than 0.2, while they sometimes increased abruptly up to 0.5 [11–15]. Hence, understanding of this special phenomenon and precise control of the pore size distribution of chemically activated carbons are essential for several applications, such as pollution control and supercapacitors.

In fact, relatively few researches on the preparation and characterization of activated carbons derived from corncobs have been reported in the literature, although corncobs are a cheap and abundant agricultural waste of no economic value [16]. However, corncob-derived activated carbons have been shown to be highly porous and rich in mesopores, exhibiting high adsorption capacity for methylene blue and Pb^{2+} ions [16]. In addition, the chemical activation of corncobs with ZnCl_2 was reported to be a very suitable process for the preparation of corncob-derived activated carbons with an essentially microporous structure [17]. Note that for all previous work on the preparation and characterization of activated carbons derived from vegetation, chemical activation was performed on the precursors of vegetation. Accordingly, the intrinsic advantages of chemical activation from chars have been omitted.

Based on all the above viewpoints and our previous experience in the preparation and characterization of porous carbons [5–7,18], this work tried to demonstrate the unique structure of carbons chemically activated with KOH from chars that were carbonized from corncobs. The structural properties of these carbons (activated in various KOH/char ratios) include the BET surface area, pore size distribution, and total pore volume. In addition, merits of the structures of these activated carbons in the adsorption of methylene blue, basic brown 1, acid blue 74, 2,4-dichlorophenol, 4-chlorophenol, and phenol in aqueous media are systematically discussed. Moreover, some typical results shown in the literature are also compared to demonstrate the promising applicability of these corncob-derived activated carbons with various KOH/char ratios.

2. Materials and methods

2.1. Preparation of carbons by KOH activation

Corncobs were dried at 110°C for 24 h, placed in a sealed ceramic oven, and heated at a rate of $5^\circ\text{C}/\text{min}$ from room temperature to 450°C . In the meantime, N_2 was poured into the oven at a rate of $3\text{ dm}^3/\text{min}$ for 1.5 h. Under such oxygen-deficient conditions, corncobs were thermally decomposed to porous carbonaceous materials and hydrocarbon compounds. This is the carbonization step.

After the carbonization step, a char/corncob ratio of 35.7% was obtained. The chars were removed, crushed, and sieved to a uniform size ranging from 0.833 to 1.65 mm. These powders were well mixed with water and KOH in a stainless steel beaker with the weight ratio of KOH/char equal to 0, 0.5, 1, 2, 3, 4, and 6. Water was evaporated at 130°C for 24 h, and these dried mixtures consisting of chars and KOH (without KOH lost) was obtained. The dried mixtures were placed in a sealed ceramic oven, heated at a rate of $10^\circ\text{C}/\text{min}$ to 780°C , and kept at this temperature for 1 h. In the meantime, nitrogen gas was flowed into the oven at a rate of $3\text{ dm}^3/\text{min}$. The activated products were cooled to room temperature and washed with deionized water. These samples were poured to a beaker containing $0.1\text{ mol}/\text{dm}^3$ HCl (250 cm^3) and stirred for 1 h. Finally, they were washed with hot water until pH of the washing solution reached ca. 6–7 [19]. The dried powders were sieved in the size ranged from 0.177 to 0.42 mm.

2.2. Measurements of physical properties

The yield was defined as the weight ratio of final carbons to the initial dried raw materials. The BET surface area of carbons (S_p) was obtained from the N_2 adsorption isotherm at 77 K with a sorptometer (porous materials, BET-202A). Prior to this measurement, the samples were first dried in an oven at 130°C overnight and then, quickly placed into the sample tube. After that, the tube was heated to 230°C and evacuated for 4 h until the pressure was less than 10^{-4} Torr. The total pore volume (V_{pore}) was reduced from the adsorption data based on the manufacturer's software and the pore size distribution was derived from the BJH theory [20]. The micropore volume (V_{micro}) and external surface area (S_{ext}) were deduced using the t -plot method [21,22]. The surface area corresponding to the micropores (S_{micro}) was obtained from the difference between S_p and S_{ext} [23].

2.3. Procedures for adsorption experiments

Six adsorbates, including acid blue 74 (AB74), basic brown 1 (BB1), methylene blue (MB), 2,4-dichlorophenol (2,4-DCP), 4-chlorophenol (4-CP), and phenol, were analytical reagent grade (Merck). Molecular weights are respectively 466.4, 419.4, 284.3, 163.0, 128.6, and 94.1 g/mol . The aqueous phase for adsorption was prepared by dissolving MB, BB1, AB74, 2,4-DCP, 4-CP, and phenol in deionized water without pH adjustment. Under the investigated conditions, the initial pH was about 6.60 for $200\text{ g}/\text{m}^3$ of MB, 3.95 for $200\text{ g}/\text{m}^3$ of BB1, 6.13 for $200\text{ g}/\text{m}^3$ of AB74, and 6.10 for $1\text{ mol}/\text{dm}^3$ of phenol, 4-CP, and 2,4-DCP.

Kinetic experiments were carried out in a Pyrex glass vessel with inner diameter 100 mm, height 130 mm, and fitted with four glass baffles (10 mm in width). The aqueous solution (0.6 dm^3) with 0.3 g carbon powders was agitated at 500 rpm using a Cole–Parmer Servodyne agitator having a six-flat-blade impeller (12 mm high and 40 mm wide).

Fig. 1. Adsorption/desorption isotherms of N_2 at 77 K on KOH activated carbons derived from corncob (KOH/char ratio is 0 ($\diamond$), 0.5 ($\square$), 1.0 (∇), 2.0 ($\circ$), 3.0 ($\blacksquare$), 4.0 ($\blacktriangledown$), and 6.0 ($\bullet$), respectively).

When carbons were added into the vessel, adsorption time was recorded. The vessel was also immersed in a water bath controlled at 30 °C. During the experiment, aqueous samples (5 cm³) were taken from the solution and the concentrations were analyzed, the concentration of solutes in the aqueous phase was determined with a Hitachi UV/vis spectrophotometer (U-2001). Each experiment was repeated at least three times under identical conditions. The amount of adsorption at time t , q_t (mol/kg), was similarly calculated by

$$q_t = \frac{(C_0 - C_t)V}{W}, \quad (1)$$

where C_t is the liquid concentration at time t in mol/m³. The experiment error was within 4%.

3. Results and discussion

3.1. Physical properties of activated carbons

Identifying the pore structure of adsorbents is an essential procedure before designing the adsorption processes, which is commonly determined by the adsorption of inert gases [1,24]. Fig. 1 shows the typical adsorption/desorption isotherms of N_2 at 77 K for all activated carbons with various KOH/char values. Two different types of curves are found in Fig. 1: group I activated carbons were prepared with the KOH/char values ranging from 0 to 2 (empty circles in the figure) and group II carbons were fabricated with the KOH/char values from 3 to 6 (real circles in the figure). Note that when P/P_0 values vary from 0 to 1.0, the adsorbed volumes of group I activated carbons are nearly unchanged. For group II carbons, the initial adsorbed volumes are almost the same (488 cm³/g) at $P/P_0 = 0$, while under specified P/P_0 values, the adsorbed volume increases with increasing KOH/char value. When P/P_0 value is equal to or above 0.2, the increase in the amount of adsorption becomes very small. All the above results indicate that developing the pore structure of corncob-derived activated carbons strongly depends on the KOH/char value.

Fig. 2. Pore size distribution of the KOH activated carbons derived from corncob.

Fig. 2 shows the typical pore size distribution of all corncob-derived carbons activated from chars with KOH. For group I, one peak is clearly visible, which is located in the mesopore region with pore size between 3 and 5 nm. The above findings are similar to the pore size distribution for the corncob-derived activated carbon prepared by steam activation [6]. On the other hand, most pores of group II carbons are below 3 nm.

Typical SEM photographs of activated carbons with the KOH/char values of 1 and 4 are shown in Figs. 3a–3c and 3d–3f. From Figs. 3a–3c, many large holes (with diameters about 10 μ m) in a honeycomb shape were clearly found on the surface of group I activated carbons. In addition, these irregular cottony holes were surrounded with contracted and twisted walls. Moreover, on the basis of the results shown in Figs. 1 and 2 as well as Table 1, group I activated carbons should be highly porous. On the other hand, for group II, as found in Figs. 3d–3f, the honeycomb-shaped holes are well arranged and regular. In addition, the walls of these holes are thick and smooth without any cottony structure. Note that all the above large holes should originate from the corncob precursors, which are not detectable by the N_2 adsorption technique of the BET method.

Based on the SEM observations, the following hypotheses are proposed. When chars were soaked in a large amount of KOH, a thin film of KOH should be coated on their surface and the interior of chars should be covered with KOH completely. During the activation in an inert atmosphere, surface pyrolysis does not occur on the surface of chars, resulting in the absence of a cottony structure. Accordingly, the final activated carbons maintain the original structure of chars; i.e., holes with smooth and thick walls are not twisted or deformed. However, the soaking of KOH into the interior of holes favors the development of micropores (chemical activation), resulting in an increase in the amount of micropores [19]. On the contrary, when char is soaked in a relatively small amount of KOH, most of the KOH should be seeped deeply into the interior of chars, while the surface coating of KOH on these chars should be incomplete. If this is the case, the surface of chars, should undergo violent pyrolysis creating an irregular cottony feature on the

Fig. 3. Observations with SEM: (a), (b), (c) are KOH/char = 1, (d), (e), (f) are KOH/char = 4.

Table 1
Physical properties of carbons derived from corncob under KOH activation conditions

KOH/char ratio	S_p (m ² /g)	S_{micro}/S_p (–)	V_{pore} (cm ³ /g)	$V_{\text{micro}}/V_{\text{pore}}$ (–)	D_p (nm)	Yield (%)	ρ_b (kg/m ³)
Char	<10	–	–	–	–	35.7	263
0	309	0.851	0.20	0.677	2.6	15.0	285
0.5	841	0.929	0.49	0.821	2.3	21.0	266
1	1071	0.923	0.69	0.805	2.6	22.3	198
2	1221	0.919	0.87	0.768	2.9	19.5	135
3	1976	0.943	1.10	0.871	2.3	19.2	98
4	2402	0.930	1.29	0.844	2.1	18.1	112
6	2595	0.899	1.43	0.780	2.2	15.9	94

surface of holes. Accordingly, contracted, twisted, thin, and deformed walls of honeycomb holes are clearly found. However the soaking of KOH in the char interior still promotes the etching during the activation process, which creates micropores. Therefore, surface areas increase with increasing the KOH/char value. This indicates that both surface pyrolysis and interior etching processes occur simultaneously during the preparation of group I activated carbons.

Table 1 shows the pore properties of all activated carbons, including S_p , S_{micro}/S_p , V_{pore} , $V_{\text{micro}}/V_{\text{pore}}$, D_p , yield, and ρ_b . Note that S_p of all activated carbons are gradually in-

creased with increasing the KOH/char ratio. These results are in agreement with those in Refs. [25,26]. The S_p values of group I are ranged from 841 to 1221 m²/g meanwhile for group II activated carbons, S_p values of 1976–2595 m²/g are higher than the highest S_p value (1806 m²/g) of corncob-derived activated carbons (activated with 15 wt% KOH) reported in Ref. [2]. Since the corncob precursors were directly soaked with KOH in Ref. [2], which is different from the two-step process employed in this study, the very high S_p values of group II activated carbons are reasonably attributed to the efficient chemical activation of chars in this work.

From Table 1, the fraction of micropore area, S_{micro}/S_p , for the carbons derived from corncob with KOH activation ranges from 0.90 to 0.94, which is larger than that of the steam-activated carbon (0.87) [6]. In addition, the fraction of micropore volume, $V_{\text{micro}}/V_{\text{pore}}$, located between 0.77 and 0.87 for the KOH-activated carbons, which is larger than that of the steam-activated one (0.66) [6]. These results also indicate that KOH activation promotes the formation of micropores, as clearly observed in Fig. 2.

From Table 1, when the KOH/char ratio increased from 0.5 to 6, S_p was gradually increased from 841 to 2595 m²/g. However, the $V_{\text{micro}}/V_{\text{pore}}$ ratios equal 0.82, 0.81, 0.77, 0.87, 0.84, and 0.78, respectively, indicating an irregular dependence on the KOH/char ratios. This is probably due to the interior etching process of KOH activation. Note that for the carbons activated with chemicals (such as KOH, ZnCl₂, and H₃PO₄), S_p was found to increase with increasing chemical dosages, while the $V_{\text{micro}}/V_{\text{pore}}$ ratios did not always increase proportionally. For example, in the case of coconut shells, when ZnCl₂/shell ratios were equal to 0.25, 0.5, and 0.75, S_p values of 1017, 1355, and 1510 m²/g were obtained, while the $V_{\text{micro}}/V_{\text{pore}}$ value equaled 0.82, 0.86, and 0.86, respectively [11]. In another case, on the other hand, when the ZnCl₂/shell ratio was increased from 1 to 3, the $V_{\text{micro}}/V_{\text{pore}}$ ratio increased rapidly [11]. The former case, similar to our system, belongs to the interior etching process within chars by chemicals, which produces uniform micropores (see Fig. 2 and Table 1).

Yield is related with the economics of activated carbon manufacture. Activated carbons prepared from corncobs by steam [6], 50 wt% H₃PO₄ [16], 15 wt% KOH, and 37.5 wt% K₂CO₃ [2] had a yield value of 10.4, 18.3, 12.8, and 17.4%, respectively. From Table 1, when the KOH/char value is equal to 0 (i.e., only pyrolysis), the yield is only 15%. As the KOH/char values reach 0.5 and 1.0, yields rise to 21 and 22.3%, respectively. Note that under these conditions, surface pyrolysis and micropore formation by KOH activation occur simultaneously. However, when the KOH/char value is increased from 2 to 6, yield decreases from 19.5 to 15.9%, probably due to the increase in the advanced development in micropores since S_p rises quickly.

From Table 1, V_{pore} increases with increasing KOH/char ratio; i.e., V_{pore} increases from 0.49 to 1.43 cm³/g, while the V_{pore} values of group II carbons (1.10–1.43 cm³/g) are much higher than those of group I (0.49–0.87 cm³/g). In addition, activated carbons prepared from corncobs with activation by 15 wt% KOH were reported to have the highest V_{pore} value (0.87 cm³/g) in Ref. [2]. The above difference is attributed to the fact that the walls of honeycomb holes in our activated carbons are not contracted or twisted and many micropores (and large V_{pore} values) are created from the KOH activation in the char interior when chars are activated at high KOH/char values.

From Table 1, a larger average pore size (D_p ranging from 2.31 to 2.86 nm) is obtained for the carbons of group I in comparison with that of group II (D_p ranging from 2.15 to

2.23 nm). In addition, D_p values of group I activated carbons are higher than that of other corncob-derived activated carbons in Refs. [2,6,16,17]. On the other hand, D_p values of group II activated carbons are close to the reported values found in these literature.

The last item in Table 1 is bulk density (ρ_b). For the activated carbons of group I (i.e., KOH/char ratio from 0.5 to 2), ρ_b values decrease from 266 to 135 kg/m³. These values are compatible to the data reported in the literature; for example, ρ_b was found to be 450 kg/m³ for olive-mill waste activated by 200 wt% KOH [26] and 262 kg/m³ for macadamia nutshell activated by 100 wt% KOH [27]. On the other hand, for the carbons of group II, ρ_b values, between 94 and 112 kg/m³, are much lower than that of KOH-activated carbons prepared from ligneous matter found in Refs. [26,27]. Note the much higher S_p and V_{pore} values of group II activated carbons in comparison with that of activated carbons prepared from corncobs found in Refs. [2,6,16,17]. This unique structure of group II activated carbons is believed to decrease the diffusion resistance of organics within granular activated carbons (GAC), which is studied in Section 3.2 to demonstrate the promising application potential in several fields.

3.2. Adsorption kinetics

From Ref. [28], activated carbons prepared through chemical activation of KOH under 500–900 °C still are of many abundant functional groups. The presence of different functional groups on the carbon surface (e.g., carboxylic, carbonyl, hydroxyl, ether, quinone, lactone) implies that there exist many types of solute–adsorbent interactions [29]. In addition, any kinetic or mass transfer representation is likely to be global. Accordingly, in this work, two kinetic models are adopted to examine the mechanism of adsorption processes.

First, the kinetics of adsorption is analyzed through the pseudo-first-order equation shown as [30,31]

$$dq_t/dt = k_1(q_e - q_t), \quad (2)$$

where k_1 is the pseudo-first-order rate constant (1/min) and q_e denotes the amount of adsorption at equilibrium. After integration, by application of the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (2) becomes

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1}{2.303} \right) t, \quad (3)$$

where the value of q_e must be obtained independently from the equilibrium experiments.

The pseudo-second-order equation based on the adsorption capacity is of the form [32]

$$dq_t/dt = k_2(q_e - q_t)^2, \quad (4)$$

where k_2 is the pseudo-second-order rate constant (kg/(g min)). By integrating Eq. (4) and applying the initial con-

Table 2

Kinetic parameters and standard deviations for the adsorption of dyes on the group I corn cob activated carbon

Solute	KOH/char	First order			Second order
		$k_1 \times 10^2$ (min)	q_e (mol/kg)	Δq (%)	Δq (%)
MB	0.5	6.38	0.349	16.7	26.1
	1	6.17	0.600	3.8	11.5
	2	6.84	0.840	4.7	15.4
BB1	0.5	4.14	0.242	5.8	16.8
	1	5.42	0.456	5.3	16.6
	2	6.07	0.557	6.5	17.5
AB74	0.5	5.38	0.023	6.9	11.1
	1	6.31	0.130	4.0	16.9
	2	5.73	0.193	2.4	14.6
Average				6.2	16.3

Table 3

Kinetic parameters and standard deviations for the adsorption of dyes on the group II corn cob activated carbon

Solute	KOH/char	First order	Second order		
		Δq (%)	k_2 (kg/(mol min))	q_e (mol/kg)	Δq (%)
MB	3	5	0.217	1.08	4.7
	4	8.6	0.173	1.27	5.5
	6	10.9	0.255	1.28	1.7
BB1	3	12	0.230	0.68	2.2
	4	13.3	0.217	0.74	1.9
	6	8.5	0.310	0.75	4.3
AB74	3	11.9	0.306	0.31	4.7
	4	12.1	0.201	0.35	3.3
	6	10.5	0.149	0.38	2.8
Average		10.3			3.5

ditions, an integration equation is obtained:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \left(\frac{1}{q_e} \right) t. \quad (5)$$

It is noticed that k_2 and q_e in Eq. (5) can be obtained from the intercept beforehand.

Evidently, the validity of these models can be checked by each linear plot of $\log(q_e - q_t)$ vs t and (t/q_t) vs t . The applicability of each model is quantitatively determined from the normalized standard deviation Δq_t (%), which is defined as

$$\Delta q_t(\%) = 100 \sqrt{\frac{\sum [(q_{t,\text{exp}} - q_{t,\text{cal}})/q_{t,\text{exp}}]^2}{(N - 1)}}, \quad (6)$$

where N is the number of data points.

Table 2 lists the results for the adsorption of dyes onto group I activated carbons for all models. It is obvious that the adsorption of MB, BB1, and AB74 onto the group I carbons is best described by the pseudo-first-order equation with an average Δq_t of 6.2. The pseudo-second-order equation has an average Δq_t of 16.3, which is larger than that of the pseudo-first-order equation. This result is in compliance with those for the adsorptions of dyes BR22 and AB25 onto corn cob-derived carbons activated by steam [6].

Table 3 lists the results for the adsorption of dyes onto group II activated carbons for all models. It is obvious that

the three dyes' adsorption onto the group II carbons is best described by the pseudo-second-order equation with an average Δq_t of 3.5. Comparisons of the simulated values from these two models and the experimental results are shown in Fig. 4. Fig. 4a shows the adsorption of MB, in which curves are the simulated results calculated from the pseudo-first-order and pseudo-second-order equations. These curves show that group I activated carbons (empty symbols) are better fitted with the pseudo-first-order equation and those of group II (solid symbols) are better described by the pseudo-second-order equation. Figs. 4b and 4c show the adsorption of BB1, and AB74, respectively. The results are very similar to those found in Fig. 4a. For the shapes of two modeled curves, the curves of the pseudo-first-order equation are flatter while those of the pseudo-second-order equation is steeper. For the adsorption of larger molecule dyes, group I carbons are adequately fitted by the former models, while group II carbons are reasonably described by the latter model. In addition, group II carbons adsorb dyes more quickly.

Table 4 lists the fitting results for the adsorption of phenols for all models. It is obvious that the adsorption of phenol, 4-CP, and 2,4-DCP on all activated carbons is most suitably described by the pseudo-second-order equation with an average Δq_t of 4.4%. Figs. 5a–5c show the curves of the simulated results from two models for the adsorbates 2,4-

Table 4
Kinetic parameters and standard deviations for the adsorption of phenols on the all corncob activated carbon

Solute	KOH/char	First order	Second order		
		Δq (%)	k_2 (kg/(mol min))	q_e (mol/kg)	Δq (%)
Phenol	0.5	16.0	0.105	1.90	11.1
	1	14.7	0.062	2.48	2.6
	2	12.9	0.060	2.47	2.3
	3	13.3	0.070	2.61	2.5
	4	6.1	0.070	3.27	5.2
	6	5.8	0.081	3.47	5.6
4-CP	0.5	9.0	0.067	2.22	8.1
	1	10.9	0.073	3.49	3.2
	2	11.0	0.084	3.86	3.5
	3	12.1	0.074	4.32	2.6
	4	7.0	0.074	4.90	4.0
	6	6.2	0.074	5.16	5.7
2,4-DCP	0.5	9.7	0.105	1.54	4.8
	1	10.5	0.062	2.99	2.9
	2	8.2	0.060	3.55	5.8
	3	12.8	0.059	4.17	3.1
	4	8.8	0.064	4.56	2.8
	6	8.8	0.070	4.80	3.0
Average		10.2			4.4

Fig. 4. Comparison of the pseudo-first-order and pseudo-second-order models for adsorption of (a) MB, (b) BB1, and (c) AB74 on the corncob carbons activated with different KOH/char (KOH/char ratio 0.5 ($\square$), 1.0 (∇), 2.0 ($\circ$), 3.0 ($\blacksquare$), 4.0 ($\blacktriangledown$), and 6.0 ($\bullet$), respectively: pseudo-first-order (---) and pseudo-second-order (—)).

DCP, 4-CP, and phenol. They show that all activated carbons are excellently described by the pseudo-second-order equations.

Fig. 5. Compare of the pseudo-first-order and pseudo-second-order models for adsorption of (a) MB, (b) BB1, and (c) AB74 on the corncob carbons activated with different KOH/char (KOH/char ratio 0.5 ($\square$), 1.0 (∇), 2.0 ($\circ$), 3.0 ($\blacksquare$), 4.0 ($\blacktriangledown$), and 6.0 ($\bullet$), respectively: pseudo-first-order (---) and pseudo-second-order (—)).

The adsorption of phenols onto the corncob-derived activated carbons prepared by steam activation is better fitted by the pseudo-second-order equation; further, the adsorp-

Table 5
Effective particle diffusivity for the sorption of phenols and dyes from water at 30 °C

Activated carbon	D_s (m ² /s) × 10 ¹²					
KOH/char	Phenol	4-CP	2,4-DCP	MB	BB1	AB74
0.5	3.98	8.22	7.45	4.67	6.60	4.68
1	8.10	10.40	8.41	6.53	4.33	7.87
2	12.30	12.50	9.66	7.44	4.99	4.90
3	12.80	16.00	10.80	11.00	7.24	4.52
4	27.30	17.40	13.10	9.88	7.44	5.48
6	33.50	19.60	15.30	14.40	10.60	6.53

Table 6
Compare of literature and this work values for effective particle phase diffusivity for the sorption of phenols and dyes

Adsorbent	Solute	D_s (m ² /s) × 10 ¹²	Reference
Activated carbon	Phenol	0.124	[36]
Activated carbon	Chlorophenol	0.629	[36]
Activated carbon	Nitrophenol	0.378	[36]
Activated carbon	Pentachlorophenol	0.226	[36]
Activated carbon	Acid dye, Tectilon red 2B	0.170	[37]
Coal; Cецarbon GAC40	Phenol	1.41	[35]
Coconut shell; 208c	Phenol	2.76	[35]
Wood; Pica 103	Phenol	3.80	[35]
Straw type 5; 800/200/12	Phenol	2.21	[35]
Tyre type 6; 900/100/18	Phenol	2.63	[35]
Mixed adsorbent (fly ash and coal)	Chrome dye	2.88	[38]
Corncob-activated carbon			
Group I (KOH/char = 1)	Phenol	8.10	This work
Group II (KOH/char = 4)	Phenol	27.30	This work
Group I (KOH/char = 1)	Methylene blue	6.53	This work
Group II (KOH/char = 4)	Methylene blue	9.88	This work

tion of dyes is better fitted by the pseudo-first-order equation [8]. This work shows that adsorption kinetics of group I activated carbons is similar to that of the steam-activated carbons. However, group II activated carbons are apt to the pseudo-second-order model equation, which show steep, rapid adsorption rates; they show the characteristics of KOH-activated carbons. In addition, group I activated carbons have both physical and chemical activation characteristics.

The adsorption kinetics of organics should be functions of the size/structure of organics and the pore structure of activated carbons. From the results shown in Fig. 2 and Table 1, most pores developed in group I activated carbons should be microporous and their diameters are believed to be significantly smaller than 2 nm. The larger mean diameter of the group I carbons in comparison with that of group II is attributed to the mesopores (about 4 nm) within the former carbons (see Fig. 2). Accordingly, the size of most pores developed within the activated carbons of group II is very close to 2 nm and uniform, which favors the diffusion of organics in both small (i.e., phenols) and large (i.e., dyes) sizes. Note that for both group I and II carbons, the adsorption kinetics for phenols is suitably described by the pseudo-second-order equation (see Fig. 5). This equation is based on the equilibrium chemical adsorption, which predicts the behavior over the whole range of studies, strongly supporting the validity, and agrees with chemisorption (chemical reaction) being rate-controlling [33,34]. The reaction mechanism may

mainly result from hydrogen binding between the hydroxyl groups of phenols and the functional groups, such as carboxylic, on the activated carbon surface. On the other hand, such heterogeneous reactions may be retarded within more hindered pore environments due to structural effects. Hence, the adsorption of dyes within the group I activated carbons, obeying the pseudo-first-order equation, should be ascribed by this phenomenon due to pore structure, since most micropores within group I carbons are significantly less than 2 nm.

In order to compare the rate of uptake of dyes and phenols from water, an effective diffusion coefficient for the adsorption of adsorbates into activated carbons by the Fick's second law was proposed and calculated in this work. The fraction approaching to equilibrium, $F(t)$, depends only on the dimensionless time parameter, Dt/r_0^2 [35]:

$$F(t) = [1 - \exp(-D_s t \pi^2 / r_0^2)]^{0.5}. \quad (7)$$

The half-time for adsorption is given by substituting $F(t) = 0.5$; i.e.,

$$t_{50} = 0.030 r_0^2 / D_s, \quad (8)$$

where r_0 is the particle size radius assuming spherical geometry and D_s is the effective particle phase diffusivity. The calculated values of D_s for phenol and dye adsorption on each of the activated carbon samples (assuming $r_0 = 0.149$ mm; $T = 30$ °C) are given in Table 5. For the adsorption of phenols, effective diffusivities for all samples lie

in the range between 3.98×10^{-12} and 33.5×10^{-12} m²/s. In addition, D_s for the adsorption of dyes for all samples lies in the range from 4.67×10^{-12} to 14.4×10^{-12} m²/s.

Table 6 shows that D_s values of phenols range from 1.24×10^{-13} to 3.8×10^{-12} m²/s, which are only about 1/10 of those obtained in this study. In addition, D_s values of chrome dye and acid dye were found to be 2.82×10^{-12} and 1.7×10^{-13} m²/s, respectively, which are also lower than those of dye adsorbed by the carbons prepared in this study. All the above adsorption results reveal that the carbons chemically activated by KOH from chars carbonized from corncobs show a unique pore structure (the uniform size of most pores developed within the activated carbons of group II is very close to 2 nm) that favors the transportation of organics in both small (i.e., phenols) and large (i.e., dyes) sizes to the adsorption sites within the solid interior. Therefore, activated carbons with high D_s values are successfully developed in this work. These activated carbons should be worthy of being applied to supercapacitors since the capacitive performance of carbons was shown to be describable from the adsorption behavior of organics in our previous work [39].

4. Conclusions

From the SEM observation, corncob-derived activated carbons of group I with the KOH/char ratio from 0.5 to 2 show a cottony, twisted, and deformed surface of honeycomb holes with contracted walls. For group II activated carbons with their KOH/char ratio between 3 and 6, regular honeycomb holes with thick and smooth walls are clearly visible. The BET surface area for the group I activated carbons ranges from 841 to 1221 m²/g; meanwhile it is between 1976 and 2595 m²/g, for group II. Based on the pore characteristics ($S_{\text{micro}}/S_{\text{p}}$, $V_{\text{micro}}/V_{\text{pore}}$, D_p , ρ_b , and yield), surface pyrolysis and micropore developing by KOH activation should undergo simultaneously during the activation process of group I carbons while only the KOH interior etching process occurs for group II. For the adsorption kinetics, data from the adsorption of MB, BB1, and AB74 onto the group I activated carbons are more suitably fitted by the pseudo-first-order equation. When phenols (phenols, 4-CP, and 2,4-DCP) are used as the adsorbates, pseudo-second-order equations more adequately describe the adsorption behavior. The adsorption rate of dyes and phenols onto the group II carbons is fast and the pseudo-second-order equation is a suitable model. Effective particle diffusivity, calculated from the t_{50} method, shows that the carbons chemically activated by KOH from chars carbonized from corncobs have high D_s , which is 10 times the D_s of ordinary activated carbons. The group II activated carbons with a uniform size of most micropores (very close to 2 nm) not only have high specific surface areas but also exhibit unique high D_s values for all adsorbates.

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Appendix A. Nomenclature

C_t	solute concentration in the aqueous phase at time t (mol/m ³)
C_0	initial solute concentration in the aqueous phase (mol/m ³)
D_p	mean pore diameter (nm)
D_s	effective particle diffusivity (m ² /s)
$F(t)$	the fractional approach to equilibrium (–)
k_1	rate constant of pseudo-first-order equation defined in Eq. (2) (1/min)
k_2	rate constant of pseudo-second-order equation defined in Eq. (4) (kg/(mol min))
q_e	amount of adsorption at equilibrium (mol/kg)
q_t	amount of adsorption at time t (mol/kg)
Δq_t	normalized standard deviation defined in Eq. (6) (%)
r_0	particle size radius (m)
S_{micro}	micropore surface area (m ² /g)
S_p	total BET surface area (m ² /g)
t	adsorption time (min)
V	volume of the solution (m ³)
V_{micro}	micropore volume (cm ³ /g)
V_{pore}	total pore volume (cm ³ /g)
W	amount of dry adsorbents used (kg)
ρ_b	bulk density (kg/m ³)

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