Preparation of high surface area carbons from Corncob with KOH etching plus CO₂ gasification for the adsorption of dyes and phenols from water

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Abstract

Carbonaceous adsorbents with controllable surface area and the microporous volume ratio ($V_{\text{micro}}/V_{\text{pore}}$) were activated from carbonized corncobs (i.e., char) with KOH etching plus CO₂ gasification in this work. Activated carbons derived from KOH/char ratio equal to 1 and CO₂ gasification time from 0 to 60 min exhibited BET surface area increasing from 1071 to 1991 m² g^{−1} and the $V_{\text{micro}}/V_{\text{pore}}$ values decreasing rapidly from 0.805 to 0.565. And those derived from KOH/char ratio of 4 and CO₂ gasification time from 0 to 30 min exhibited high BET surface area from 2402 to 2844 m² g^{−1}. Scanning electron microscopic (SEM) results revealed that violent reactions took place on the surfaces of honeycombed holes in these carbons when the KOH/char ratio was equal to 1 and CO₂ gasification was used. The adsorption of three dyes (MB, BB1, and AB74) and three phenols (phenol, 4-CP, and 2,4-CP) from water on all activated carbons at 30 °C were investigated. Adsorption kinetics was in agreement with the Elovich equation, and the values of the Elovich parameter ($1/b$) of the carbons with different CO₂ gasification time were compared. The equilibrium isotherms were in agreement with the Langmuir equation, and they were used for comparing the amounts of adsorption corresponding to the monolayer coverage of the different carbons.

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1. Introduction

In general, the physicochemical properties of activated carbons (ACs) have been found to strongly depend on the activation process as well as the nature of the raw material. Moreover, an understanding of the influence of activation variables on the physicochemical properties of ACs is very important in developing the structure of carbons in both physical and chemical activation processes [1]. The high adsorption capacity of ACs is attributed to surface area, pore volume, and porosity. These characteristics are functions of the type of raw material employed as well as the method of activation [2]. This is especially important in the development of micro- and mesopores, which are related to the adsorption capability and ability of carbons to various types of chemicals either from gas or liquid. Accordingly, recent research has focused on the development of ACs with desired

pore structures as well as with new application possibilities in different fields [3].

Besides, activated carbons can also be applied to supercapacitors [4–7], catalyst supports of fuel cells [8], safe storage of large quantities of CH₄ [9] or H₂, and to the field of biomedical engineering. Activated carbons used in these fields not only have high specific surface area but also high ratio of mesopores and macropores providing the main transport channels for adsorbates.

In previous studies, peach stone was activated with H₃PO₄ with a weight ratio of peach stone/H₃PO₄ equal to 1:0.91 to form activated carbon, which was then under CO₂ gasification for 9 h. Activated carbon with a total pore volume of 2 cm³ g^{−1} and a mesoporous volume ratio of 67.5% was obtained [10]. Coconut shell was activated with ZnCl₂ with a weight ratio of coconut shell/ZnCl₂ ratio equal to 1:1. The obtained activated carbon was further under 6 h of CO₂ gasification. Activated carbon with a BET surface area of 2634 m² g^{−1} and a mesoporous volume ratio of 62% was obtained [11]. When coconut shell was activated with KOH with a weight ratio of coconut shell/KOH equal

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Nomenclature

C_e	solute concentration in the aqueous phase at equilibrium (mol m^{-3})
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	average diameter of pores (nm)
K_L	Langmuir constant defined in Eq. (6) ($\text{m}^3 \text{mol}$)
q_e	amount of adsorption at equilibrium (mol kg^{-1})
q_t	amount of adsorption at time t (mol kg^{-1})
q_{mon}	amount of adsorption corresponding to monolayer coverage (mol kg^{-1})
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)

to 1:0.5 and was further under 6 h CO_2 gasification, activated carbon with a BET surface area of $2390 \text{ m}^2 \text{ g}^{-1}$ and a mesoporous volume ratio of 47% was obtained [12]. The abovementioned studies revealed that CO_2 gasification did enhance high mesopore volume ratio as well as surface area in activated carbons.

Not much research on the preparation and characterization of ACs derived from corncob has been reported although corncob is a cheap and abundant agricultural waste of no economical value [13]. In addition, corncob-derived ACs have been proven to be highly porous and rich in mesopores, exhibiting high adsorption capacity to methylene blue and Pb^{2+} ions [13]. However, ZnCl_2 activation was reported to be a very suitable process for the preparation of corncob-derived ACs with an essentially microporous structure [14].

In general, ACs with different pore size distributions usually result from the differences in precursors and treatments [10,15]. In our laboratory, a series of studies were conducted to prepare porous carbons from various wood wastes and fruit shells by physical activation method (steam) and chemical activation method (KOH), in which these carbons were evaluated for the possibility of applications to industrial pollution control and supercapacitors [16–21].

According to previous report, high surface area micropore activated carbon of BET surface area of $2595 \text{ m}^2 \text{ g}^{-1}$ and S_{micro}/S_p ratio of 0.899 was obtained from corncob activated with KOH [22]. Furthermore, CO_2 will be utilized to develop ACs of high surface area and higher ratio mesopore for wider applications in this study. In this work comparisons were made for the physicochemical properties of the corncob carbon activated by KOH followed by CO_2 gasification for different time duration. The physical properties studied included the BET surface area, pore size distribution, and total pore

volume. The kinetics and equilibrium of the adsorption to methylene blue, basic brown 1, acid blue 74, 2,4-dichlorophenol, 4-chlorophenol, and phenol in aqueous media were systematically discussed.

2. Materials and methods

2.1. Preparation of carbons by KOH etching plus CO_2 gasification

According to previous report [22], the ACs activated with KOH/char ratios of 0.5, 1.0, and 2 were classified as Type I, the activation reaction being surface activation and micropore etching. And those with KOH/char ratios equal to 3, 4, 6 were classified as Type II, the activation reactions being only micropore etching. The AC activated with KOH/char ratio equal to 1 (Type I) and that with KOH/char ratio equal to 4 (Type II) were selected to study the effects of the combined CO_2 gasification in this research. The effects on both ACs from various CO_2 gasification times were compared.

Activated chars were prepared from corncob by carbonization in nitrogen. The apparatus and procedures were described in detail elsewhere [22]. These chars were well mixed with water and KOH in a stainless steel beaker with the weight ratios of KOH/char equal to 1 and 4. Water was evaporated at 130°C for 24 h, and these dried mixtures consisting of chars and KOH (without KOH lost) were 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 flowed into the oven at a rate of $3 \times 10^{-3} \text{ m}^3 \text{ min}^{-1}$. When the time was up, the nitrogen gas was shut off and CO_2 immediately flowed into the oven at a rate of $2 \times 10^{-3} \text{ m}^3 \text{ min}^{-1}$. The total duration of nitrogen and CO_2 flows to the oven kept at 780°C was 60 min. The activated products were cooled to room temperature and washed with deionized water [22]. The samples were classified according to the KOH/char ratio and the CO_2 gasification time and denoted as Cob1000, Cob1015, Cob1030, Cob1060, Cob4000, Cob4015, and Cob4030, respectively. The first three letters, Cob, represent the material, corncob; the fourth digit represents the KOH/char ratio; and the last three digits represent the CO_2 gasification time (minutes).

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 the carbon (S_p) was obtained from the N_2 adsorption isotherm at 77 K with a sorptiometer (Porous Materials, BET-202A). Prior to this measurement, the samples were first dried in an oven at 130°C overnight and then, quickly placed in the sample tube. After that, the tube was heated at 230°C and evacuated for 4 h until the pressure was less than $1.33 \times 10^{-4} \text{ mbar}$. The total pore volume (V_{pore}) was deduced from the adsorption data based on the manufacturer's software, and the pore size distribution was derived from the BJH theory [23]. The micropore volume (V_{micro}) and external surface area (S_{ext}) were deduced by using the t-plot

Fig. 1. Adsorption/desorption isotherms of N_2 at 77 K on activated carbons derived from corn cob using KOH with CO_2 gasification (carbons is Cob1000 (○), Cob1015 (▽), Cob1030 (□), Cob1060 (◇), Cob4000 (●), Cob4015 (▼), and Cob4030 (■), respectively).

method [24,25]. The surface area corresponding to the micropores (S_{micro}) was obtained from the difference between S_p and S_{ext} [26].

2.3. Procedures for adsorption experiments

Six solutes including acid blue74 (AB74), basic brown 1 (BB1), methylene blue (MB), 2,4-dichloropenol (2,4-DCP), 4-chloropenol (4-CP), and phenol are analytical reagent grade (Merck). Molecular weights are, respectively, 466.4, 419.4, 284.3, 163.0, 128.6, and 94.1 g mol⁻¹. The molecular structures of MB, BB1, and AB74, and the characteristics of the phenols and dyes are from the previous study [27].

The kinetic experiments were carried out in a Pyrex glass vessel 100 mm in inner diameter, 130 mm in height, and fitted with four glass baffles (10 mm in width). The aqueous solution (0.6 dm³) with 0.3 g carbon powder was agitated at 500 rpm using a Cole-Parmer Servodyne agitator having a six-flat-blade impeller (12 mm high and 40 mm wide). When carbons were added to 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, and the concentrations of solutes in the aqueous phase were determined with a Hitachi UV–vis spectrophotometer (U-2001). The amount of

Fig. 2. Pore size distribution of the activated carbons derived from corn cob using KOH with CO_2 gasification.

adsorption at time t , q_t (mol/kg), was calculated by

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

where C_0 and C_t are the liquid concentrations (mol m⁻³) at the beginning and time t , respectively, and W/V is the dose of dried carbons (kg m⁻³). The experiment error was mostly within 4%.

In the adsorption equilibrium experiments, 0.1 g carbon was well dispersed in 0.1 dm³ aqueous solution in a 0.25-dm³ flask and stirred for 5 days in a water bath (Haake Model K-F3) at 30 °C. Preliminary tests showed that adsorption was complete after 3 days. After filtration with glass fibers, the concentrations were analyzed. Each experiment was repeated at least three times under identical conditions. The amount of adsorption at equilibrium, q_e (mol kg⁻¹), was calculated according to Eq. (2):

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (2)$$

where C_e is the equilibrium liquid concentrations (mol m⁻³).

3. Results and discussion

3.1. Physical properties of activated carbon

Identifying the pore structure of adsorbents is an essential procedure before designing the adsorption process, which is commonly determined by the adsorption of inert gases [28,29]. Fig. 1 shows the typical adsorption/desorption isotherms of N_2

Table 1
Physical properties of carbons derived from corn cob using KOH and CO_2 activation

Carbons	KOH/char ratio (–)	Gasification time (min)	S_p (m ² /g)	S_{micro}/S_p (–)	V_{pore} (cm ³ /g)	$V_{\text{micro}}/V_{\text{pore}}$ (–)	ρ_b (kg/m ³)
Cob1000	1	0	1071	0.923	0.691	0.805	198
Cob1015	1	15	1383	0.886	0.875	0.721	157
Cob1030	1	30	1625	0.859	0.991	0.679	155
Cob1060	1	60	1991	0.790	1.270	0.565	108
Cob4000	4	0	2402	0.930	1.290	0.844	112
Cob4015	4	15	2510	0.905	1.369	0.796	92
Cob4030	4	30	2844	0.894	1.533	0.772	91

at 77 K for all ACs with different CO₂ gasification times. Two different types of curves are found in Fig. 1: one group of corn-cob ACs were prepared with KOH/char ratio equal to 1 (empty circles in the figure), and another group of ACs were prepared with KOH/char ratio equal to 4 (solid circles in the figure). Note that, when P/P_0 values vary from 0 to 1.0, the initial adsorbed volumes of the group with KOH/char ratio equal to 1 are almost the same ($327\text{--}369\text{ cm}^3\text{ g}^{-1}$) at P/P_0 approaching zero, while under specified P/P_0 values, the adsorbed volume increases with increased CO₂ gasification time. For the group with KOH/char ratio equal to 4 the initial adsorbed volumes are almost the same ($488\text{ cm}^3\text{ g}^{-1}$) at P/P_0 approaching zero, while under specified P/P_0 values, the adsorbed volume increases with increased CO₂ gasification time, the same as the group with KOH/char ratio equal to 1. But, when the P/P_0 value equaled to or was above 0.2, these three curves approach horizontal. All the above results indicated that developing the pore structure of corn-cob ACs strongly depended on the CO₂ gasification time.

Fig. 2 shows a typical pore size distribution of all ACs activated with KOH etching combined with CO₂ gasification. For the group with KOH/char ratio equal to 1, one peak is visible. The peak is in the mesopore region with pore sizes between 3 and 5 nm. On the other hand, most pores of the AC group with a KOH/char equal to 4 are below 3 nm. Fig. 2 shows that very wide pore distributions were produced in the activated carbons with KOH/char ratio equal to 1 because of the additional CO₂ gasification, while microporous type was still maintained for the activated carbons with KOH/char ratio equal to 4 in spite of the additional CO₂ gasification. It appears that the process of KOH etching plus CO₂ gasification has two different reaction mechanisms on carbon. These two graphs together with SEM observations are used to present and explain this result.

Table 1 shows the pore properties of all ACs, including S_p , S_{micro}/S_p , V_{pore} , $V_{\text{micro}}/V_{\text{pore}}$, and ρ_b . Note that the S_p values of all ACs gradually increase with increased gasification time. These results are in agreement with those in other literatures [11,12]. The S_p values of the group with KOH/char ratio equal

Fig. 3. Micropore volume (V_{micro}), mesopore volume (V_{meso}), mean pore size (D_p), and yield of activated carbons using KOH with CO₂ gasification with different BET surface-areas: (a) KOH/char = 1 (●) (△); KOH/char = 4 (■) (◇); (b) KOH/char = 1 (○) (▲); KOH/char = 4 (□) (◆).

Fig. 4. Observations with SEM, (a) Cob1060 and (b) Cob4030.

to 1 ($1071\text{--}1991\text{ m}^2\text{ g}^{-1}$) and the group with KOH/char ratio equal to 4 ($2402\text{--}2844\text{ m}^2\text{ g}^{-1}$) are comparable to those of the ACs prepared from corncobs activated with steam [17], 50 wt% H_3PO_4 [13], 200 wt% ZnCl_2 [14], 15 wt% KOH, and 37.5 wt% K_2CO_3 [2], having the S_p values of 943, 960, 1563, 1806, and $1541\text{ m}^2\text{ g}^{-1}$, respectively. The raw materials in the above mentioned studies were directly soaked in chemicals to activate them, which is different from the two step process of KOH etching plus CO_2 gasification for activated carbon preparations in this study.

This is why the S_p values of the group with KOH/char ratio equal to 4 of this study are higher than those in the other studies. In this paper BET surface area ($1991\text{ m}^2/\text{g}$) of the activated carbon with KOH/char ratio equal to 1 plus 60 min of CO_2 gasification is approximately equal to that ($1976\text{ m}^2/\text{g}$) with KOH/char ratio equal to 3 without CO_2 gasification [22]. Less chemical dose is required for the preparation of higher surface activated carbons.

The fraction of micropore area, S_{micro}/S_p , of the group with KOH/char ratio equal to 1 show that prolonged CO_2 gasification

Fig. 5. Test of the Elovich equation for the adsorption of dyes and phenols on the activated carbons using KOH combined with CO_2 gasification (a) phenol, (b) 4-CP, (c) 2,4-DCP, (d) MB, (e) BB1, and (f) AB74 (carbons is Cob1000 (○), Cob1015 (▽), Cob1030 (□), Cob1060 (◇), Cob4000 (●), Cob4015 (▼), and Cob4030 (■), respectively).

leads to a decrease in $S_{\text{micro}}/S_{\text{p}}$ (0.923–0.790). In addition, the fraction of micropore volume, $V_{\text{micro}}/V_{\text{pore}}$, of the group with KOH/char ratio equal to 1 shows that prolonged CO_2 gasification leads to a decrease in $V_{\text{micro}}/V_{\text{pore}}$ (0.805–0.565). Porous, high surface area activated carbons are gradually, widely applied to the field like supercapacitors. KOH activation can only produce microporous activated carbon, and the process of KOH plus CO_2 gasification can produce activated carbon of higher ratio mesopores ($V_{\text{micro}}/V_{\text{pore}} = 0.565$ of Cob1060), which improves mass transfer within the activated carbon.

These results also indicate that CO_2 gasification promotes the formation of mesopores within the activated carbon, as can be seen in Fig. 2. Table 1 shows that V_{pore} values increase with prolonged CO_2 gasification. The V_{pore} values of the group

Table 2
Kinetic parameters for the adsorption of phenols and dyes at 30 °C

Solute	Carbon	$1/b$ (mol kg ⁻¹)	t_0 (10 ⁻³ h)	r^2 (-)
Phenol	Cob1000	0.529	8.79	0.987
	Cob1015	0.488	3.69	0.994
	Cob1030	0.429	3.02	0.997
	Cob1060	0.417	1.99	0.998
	Cob4000	0.525	1.21	0.989
	Cob4015	0.370	3.24	0.980
	Cob4030	0.412	0.78	0.981
4-CP	Cob1000	0.719	6.29	0.991
	Cob1015	0.599	2.18	0.994
	Cob1030	0.695	2.99	0.992
	Cob1060	0.584	1.01	0.988
	Cob4000	0.889	2.70	0.995
	Cob4015	0.733	1.68	0.997
	Cob4030	0.779	2.49	0.993
2,4-DCP	Cob1000	0.621	7.96	0.996
	Cob1015	0.657	7.31	0.996
	Cob1030	0.662	6.34	0.995
	Cob1060	0.582	2.66	0.996
	Cob4000	0.898	4.48	0.992
	Cob4015	0.694	3.41	0.992
	Cob4030	0.689	2.74	0.992
MB	Cob1000	0.115	6.14	0.969
	Cob1015	0.152	5.31	0.983
	Cob1030	0.181	5.64	0.992
	Cob1060	0.226	6.00	0.989
	Cob4000	0.256	6.34	0.989
	Cob4015	0.225	2.59	0.999
	Cob4030	0.253	3.52	0.995
BB1	Cob1000	0.086	9.35	0.975
	Cob1015	0.122	10.7	0.987
	Cob1030	0.126	7.08	0.996
	Cob1060	0.154	8.06	0.998
	Cob4000	0.153	9.06	0.999
	Cob4015	0.154	6.38	0.997
	Cob4030	0.161	6.09	0.990
AB74	Cob1000	0.025	5.90	0.970
	Cob1015	0.041	3.08	0.993
	Cob1030	0.055	4.15	0.997
	Cob1060	0.065	4.53	0.990
	Cob4000	0.072	11.6	0.996
	Cob4015	0.081	4.96	0.995
	Cob4030	0.080	3.49	0.992

with KOH/char ratio equal to 4 (1.29–1.53 cm³ g⁻¹) are much higher than those prepared from corncobs in the other studies [2,13,14,18]. This is attributed to the fact that the holes walls were not contracted or twisted and large V_{pore} values were created from the KOH etching in the char interior when the corncob was activated at high KOH/char values [22]. The last item in Table 1 is bulk density (ρ_b). For the ACs of the group with KOH/char ratio equal to 1, the ρ_b values significantly decreased from 198 to 108 kg m⁻³. For the group with KOH/char ratio equal to 4 the ρ_b values decreased from 112 to 91 kg m⁻³ without significant variation. The ρ_b values of the ACs in this work are obviously lower than those prepared from lignocellulosic materials in other studies [13,30,31], probably due to the porous honeycomb structure of corncob ACs [22]. This unique structure is believed to decrease the resistance of liquid phase mass transfer within GAC (granular activated carbon).

The dependence of V_{micro} , V_{meso} , D_p , and yield of AC on S_p is shown in Fig. 3a and b. Fig. 3a shows V_{micro} as well as the relationship between S_p and V_{ext} . Note that V_{micro} and V_{meso} increase proportionally with the S_p values. But when the S_p values are in the range of 1071–1991 m² g⁻¹ (the group with KOH/char equal to 1), the slope of V_{meso} to S_p (4.47×10^{-4} cm³ m⁻²) is larger than that of V_{micro} to S_p (1.75×10^{-4} cm³ m⁻²). This proves that V_{meso} of ACs of the group with KOH/char ratio

Fig. 6. Relationships of the Elovich parameter $1/b$ and CO_2 gasification time.

equal to 1 increases swiftly with CO_2 gasification time while V_{micro} increases slowly, thus facilitating the development of mesoporous carbons. When the S_p values are in the range of $2402\text{--}2844\text{ m}^2\text{ g}^{-1}$ (the group with KOH/char equal to 4), both V_{meso} and V_{micro} increase, but the V_{micro} values are about four times the V_{meso} values. These carbons belong to microporous carbons.

The D_p (average diameter of pores, $4V_{\text{pore}}/S_p$) values of ACs provide important data for various applications (adsorption, supercapacitors, catalyst-support). They are related to the rate of mass transfer and effective surface area. Fig. 3b shows that although the yield might decrease, the D_p values are nearly constant with the S_p increasing. But when the S_p are in the range of $1071\text{--}1991\text{ m}^2\text{ g}^{-1}$ (the group with KOH/char ratio equal to 1), the average D_p is 2.53 nm, larger than that of 2.16 nm when the S_p are in the range of $2402\text{--}2844\text{ m}^2\text{ g}^{-1}$ (the group with KOH/char ratio equal to 4).

Yield is related to the economics of activated carbon manufacture. Fig. 3b shows that yields of the group with KOH/char ratio equal to 1 (from 22.3% to 6.4%) decreased higher than those of the group with KOH/char ratio equal to 4 (from 18.1% to 13.7%).

In the case of the group with KOH/char ratio equal to 1, the distortion of surfaces caused by CO_2 gasification was obvious (it was discovered that the oven temperature rose rapidly right after the introduction of CO_2). However, the group with KOH/char ratio equal to 4 the surface were not significantly changed. This is because the activation reactions were the surface activation and micropore etching for the group with KOH/char ratio equal to 1. Thus, exothermic reactions between CO_2 and C_f of carbons occurred after the introduction of CO_2 , and caused the CO production and temperature rise. However, the CO_2 effect was not significant for the group with KOH/char ratio equal to 4. This is because large amount of KOH enveloped the carbons, thus lowered the reactions between CO_2 and carbons.

3.2. SEM observations

Typical SEM photographs of ACs activated with KOH etching plus CO_2 gasification are shown in Fig. 4a and b. The group with KOH/char ratio equal to 1 (Cob1000) are highly porous with honeycomb shaped, irregular, cottony holes, and with contracted and twisted walls (Fig. 3b in literature [22]).

Fig. 7. Adsorption isotherms of phenols and dyes at $30\text{ }^{\circ}\text{C}$ on the activated carbons using KOH combined with CO_2 gasification (a) phenol, (b) 4-CP, (c) MB, and (d) BB1 (carbons is Cob1000 ($\circ$), Cob1015 (∇), Cob1030 ($\square$), Cob1060 ($\diamond$), Cob4000 ($\bullet$), Cob4015 ($\blacktriangledown$), and Cob4030 ($\blacksquare$), respectively). The solid curves were calculated with the Langmuir equation.

After being gasified with CO₂ for 60 min (Cob1060), the cottony outsides of holes are transformed into plain surfaces (Fig. 4a). On the other hand, the group with KOH/char ratio equal to 4 (Cob4000) had a regular arrangement of the porous honeycombs with well-arranged holes and with thick and smooth walls without a cottony structure (Fig. 3e in literature [22]). Changes in holes appearances of Cob4030 are not significant (Fig. 4b).

Based on the SEM observations, the following hypotheses are proposed. When char is soaked in KOH, it should be a large amount of KOH surrounding it completely (including the interior of the holes). Activation does not happen on the char surface, resulting in the absence of a cottony structure. Accordingly, the char maintains its original structure, i.e., holes are not twisted or deformed because of the contraction of the walls. However, KOH soaking through the interior of the holes favors the development of micropores, resulting in an increase in the number of micropores [32]. Because a large quantity of KOH surrounds these holes, changes of these holes are not significant after 30 min of CO₂ gasification. In contrast, when char is soaked in a relatively small amount of KOH, most of the KOH seeped deeply into the interior of char. If this is the case, the exterior surface of the holes should undergo violent activation, thus creating irregular cottony features on the surface of the holes. Because only a small amount of KOH protects the hole surfaces, the cottony outsides of the holes are gasified into plain surfaces.

3.3. Adsorption kinetics

Porous, high surface area activated carbons gradually have wider applications to fields such as supercapacitors. KOH activation can only produce microporous activated carbon, and the process of KOH etching plus CO₂ gasification can produce activated carbon of higher ratio mesopores ($V_{\text{micro}}/V_{\text{pore}} = 0.565$ of Cob1060), which improves mass transfer within the interior of the activated carbon. The section of adsorption kinetics in this paper proved this fact. The Elovich equation was adopted to examine the mechanism of the adsorption process.

According to the literature [16], the Elovich equation after arrangement can be expressed as:

$$q_t = \left(\frac{1}{b}\right) \ln(ab) + \left(\frac{1}{b}\right) \ln t \quad (3)$$

where a and b are constants for any experiment. The validity of Eq. (3) is checked by the linear plot of q_t versus $\ln t$ (Fig. 5). The modeled results well agree with the measured ones as shown in Fig. 5. Table 2 lists the results. The fit is quite good under the time ranges studied (correlation coefficient, $r^2 > 0.970$), and agrees with the assumption that $t \gg t_0$. Fig. 6(a) shows that the $1/b$ values of all dye solutes (MB, BB1, and AB74) on the ACs of the group with KOH/char ratio equal to 1 increase with the increased CO₂ gasification time. Their slopes are 1.82×10^{-3}

Table 3
Parameters of the Langmuir equation and covered area for the adsorption of phenols and dyes at 30 °C

Solute	Adsorbent	Langmuir			Covered		
		q_{mon} (mol kg ⁻¹)	K_L (m ³ mol ⁻¹)	r^2 (—)	S_c (m ² g ⁻¹)	S_c/S_p (—)	Avg. S_c/S_p (—) (%)
Phenol	Cob1000	2.48	5.10	0.997	653	0.610	0.476 ± 15.4
	Cob1015	2.56	5.31	0.997	674	0.487	
	Cob1030	2.74	4.97	0.996	721	0.444	
	Cob1060	2.73	8.28	0.999	719	0.361	
	Cob4000	3.83	2.34	0.994	1008	0.420	
	Cob4015	4.20	1.52	0.997	1105	0.416	
	Cob4030	4.50	1.81	0.997	1184	0.555	
4-CP	Cob1000	2.26	9.54	1.000	656	0.613	0.579 ± 5.2
	Cob1015	2.74	8.44	1.000	795	0.575	
	Cob1030	3.39	5.60	0.998	983	0.605	
	Cob1060	3.59	5.69	0.998	1041	0.523	
	Cob4000	4.69	5.32	0.999	1362	0.567	
	Cob4015	6.25	3.03	0.989	1813	0.722	
	Cob4030	6.71	3.63	0.984	1946	0.684	
MB	Cob1000	0.44	54.6	1.000	167	0.156	0.137 ± 6.4
	Cob1015	1.24	70.4	0.999	182	0.132	
	Cob1030	1.48	118	1.000	218	0.134	
	Cob1060	1.71	76.9	1.000	251	0.126	
	Cob4000	2.49	60.4	1.000	366	0.152	
	Cob4015	2.59	216	1.000	381	0.152	
	Cob4030	2.98	273	1.000	438	0.154	
BB1	Cob1000	1.80	11.8	0.996	319	0.298	0.305 ± 4.5
	Cob1015	2.22	19.3	0.996	393	0.284	
	Cob1030	2.88	20.9	1.000	510	0.314	
	Cob1060	3.63	21.7	0.999	643	0.323	
	Cob4000	3.16	10.6	0.993	560	0.233	
	Cob4015	3.72	22.8	0.998	659	0.263	
	Cob4030	3.98	15.9	0.999	705	0.248	

(MB), 1.04×10^{-3} (BB1), and 6.51×10^{-4} (mol kg⁻¹)(min)⁻¹ (AB74). Fig. 6(b) shows that the $1/b$ values of all dye solutes on the ACs of the group with KOH/char ratio equal to 4 are unchanged with respect to the CO₂ gasification time, with the average $1/b$ values of 0.245 (MB), 0.156 (BB1), and 0.078 (mol kg⁻¹)(AB74), higher than those of the ACs of the group with KOH/char ratio equal to 1, meaning higher mass transfer. Besides, increased CO₂ gasification time has little effect on the $1/b$ values of all phenols solutes on the ACs of both groups. Here, it was proved that increased CO₂ gasification time was beneficial to the mass transfer of larger molecular materials, such as dyes, for the ACs of the group with KOH/char ratio equal to 1. And the ACs of the group with KOH/char ratio equal to 4 all could maintain good mass transfer in the range of the CO₂ gasification time studied.

3.4. Equilibrium adsorption

Fig. 7 shows the typical equilibrium adsorption of (a) phenol, (b) 4-CP, (c) MB, and (d) BB1 at 30 °C on the ACs prepared under different CO₂ gasification time. The correlation of isotherm data by theoretical or empirical equations is essential to practical operation. The widely used Langmuir equation is given as:

$$\frac{C_e}{q_e} = \left(\frac{1}{K_L q_{\text{mon}}} \right) + \left(\frac{1}{q_{\text{mon}}} \right) C_e \quad (4)$$

where q_{mon} is the amount of adsorption (in mol kg⁻¹) corresponding to complete monolayer coverage and K_L is the Langmuir constant. Linear plots of (C_e/q_e) against C_e give K_L and q_{mon} (not shown). In addition, the parameters (listed in Table 3) estimated from Fig. 7 are reliable since the fittings for BB1, MB, 4-CP and phenol adsorption on all ACs in the concentration range of study are excellent (correlation coefficient, $r^2 > 0.984$). Table 3 shows that the adsorption capacity (q_{mon}) for all solutions increases with increased S_p except BB1. For Cob4030, the values of q_{mon} for BB1, MB, 4-CP, and phenol are 3.98, 2.98, 6.71 and 4.5 mol kg⁻¹, respectively, which are larger than those obtained earlier in similar solute-adsorbent systems [17,33–35]. Fig. 8(a) shows that in case of the group with KOH/char equal to 1, q_{mon} values increase with increased S_p except phenol. Fig. 8(b) shows that in the case of the group with KOH/char equal to 4, q_{mon} values slowly increase with increased S_p except 4-CP. These indicate that increased CO₂ gasification time increases both S_p and q_{mon} .

3.5. Surface coverage

An adsorbate forms the monolayer coverage on the surface of AC. Based on the covered mass (q_{mon}) obtained from the Langmuir equation and the projected area of an adsorbate molecule, adsorbate coverage per unit gram of activated carbon (S_c , m² g⁻¹) can be obtained using the following equation:

$$S_c = \frac{6.023 \times 10^{23} \times A_m \times q_{\text{mon}}}{1000} \quad (5)$$

Fig. 8. Adsorption capacity (q_{mon}) of phenol, 4-CP, MB, and BB1 at 30 °C on the activated carbons using KOH combined with CO₂ gasification.

where A_m is the projected area of a molecule (defined in [27]). In addition, the surface coverage is defined as the ratio of S_c to BET surface area of the AC (S_c/S_p), and the calculated results are listed in Table 3. The S_c/S_p values of both groups of ACs do not largely fluctuate except those of phenol, and their average values are listed in Table 3. These averages are 0.579, 0.305, and 0.137 for 4-CP, BB1, and MB adsorbed on the group with KOH/char ratio equal to 1, respectively; and are 0.658, 0.248, and 0.153 for 4-CP, BB1, and MB adsorbed on the group with KOH/char ratio equal to 4, respectively. The error is less than 9.2%. This result proves that additional CO₂ gasification increases the surface area of the activated carbon, while the activated carbon still maintaining the same unit area adsorption capability. This fully proves the value of the process of KOH etching plus CO₂ gasification for preparing activated carbon.

In the adsorption described by the Langmuir model the process can be expressed as:

where A represents the adsorbate molecule in the liquid phase, C^* the available adsorptive site, and $C^*(A)$ the sites occupied by adsorbate. Now, if the S_c/S_p values are the same, it means that,

those ACs (derived from different activated conditions) would have the same ratio of the sites occupied by adsorbate and the available adsorptive site. In this research, S_c/S_p values are about the same for the adsorptions of phenols and dyes on ACs activated with the same KOH/char ratio combined with different CO_2 gasification time. This is in agreement with the theory of Langmuir model.

4. Conclusions

SEM observations revealed that the corncob-derived activated carbons of the group with KOH/char equal ratio to 1 were highly porous with honeycomb shaped, cottony holes, which were transformed into plain surfaces after being gasified with CO_2 for 60 min. When the CO_2 gasification time of the group with KOH/char ratio equal to 1 was increased from 0 to 60 min, their micropore ratios decreased rapidly from 0.805 to 0.565 and their BET surface areas rapidly increased from 1071 to 1991 $\text{m}^2 \text{g}^{-1}$; while, in the case of the group with KOH/char ratio equal to 4 the micropore ratios decreased slowly from 0.844 to 0.772 and the BET surface area increased slowly from 2402 to 2844 $\text{m}^2 \text{g}^{-1}$. The BET surface area (2844 m^2/g) of cob4030 is one of the highest among the activated carbons prepared from the plant materials found so far. Based on their physical characteristics (S_{micro}/S_p , $V_{\text{micro}}/V_{\text{pore}}$, D_p , ρ_b , and yield), “surface activation” with CO_2 gasification was clearly obvious during the activation process for the preparation of the group with KOH/char equal to 1; while “surface activation” was not obvious and a KOH etching process occurred for the group with KOH/char equal to 4. For the adsorption kinetics, data from the adsorption of solution onto activated carbons were suitably fitted to the Elovich equation. It was proved that ACs with prolonged CO_2 gasification time was beneficial to mass transfer of larger molecular materials (such as dyes). For the adsorption equilibrium, the q_{mon} values of Cob4030 carbon are larger than those obtained earlier in similar solute-adsorbent systems. Besides, the average surface coverage ratios for phenols and dyes are in agreement with the theory of Langmuir model. It was proved that the activated carbons activated with KOH etching plus CO_2 gasification had good adsorption capability.

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