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Preparation of activated carbons from cotton stalk by microwave assisted KOH and K_2CO_3 activation

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ABSTRACT

The activated carbons prepared from cotton stalk with different activation agents (KOH and K_2CO_3) under microwave radiation were investigated. The effects of different activation conditions on the adsorption capacities of activated carbons were studied. The frequency test (*F*-test) was utilized in statistics to analyze the significant effects of the factors. The properties of activated carbons prepared under optimum conditions were investigated using the following measurement: N_2 adsorption isotherms at $-196\,^\circ C$, SEM and FTIR. Finally, the samples were used in removal of methylene blue. The results showed that radiation time and radiation power were the greatest impact factor on adsorption capacities of the activated carbon prepared with KOH and K_2CO_3, respectively. Optimum conditions were different in the two prepared process. Compared with cotton stalk, different functionalities on the carbon surfaces were formed. In addition, chemical activation could develop both microporosity and mesoporosity. KOH generated a greater micropore volume than K_2CO_3 did. Compared with conventional heating method, microwave heating method could shorten the processing time and reduce the consumption of KOH. The equilibrium data of the adsorption was well fitted to the Langmuir isotherm for both activated carbons.

1. Introduction

Waste biomass is getting increasing attention all over the world as it is a kind of renewable, widely available, cheap and environmental friendly resource. One effective use of waste biomass is to produce activated carbon (AC) by thermochemical conversion. AC is a carbonaceous material with highly developed porosity. The main concern is the removal of chemical component by adsorption from the liquid or gas phase [1]. To day, AC has been produced from various biomass i.e., corncob [2], rice husk [3], cherry stones [4], coconut shells and palm shells [5].

To prepare AC, conventional heating method is usually adopted, in which the energy is produced by electrical furnace (EF). However, in some cases, the thermal process may take several hours, even up to a week to reach the desired level of activation [6]. Another problem related to the furnace is that the surface heating does not ensure a uniform temperature for different shapes and sizes of samples. This generates a thermal gradient from the hot surface to the kernel of the sample particle, blocks the effective diffusions of gaseous products to its surroundings and finally results in AC quality decrease [7,8]. Furthermore, there is a considerable risk of overheating or even thermal runaway (exothermic process) of portion of sample, leading to the complete combustion of the carbon [9].

Recently, microwave (MW) has been widely used in preparation and regeneration of AC. The main difference between MW devices and conventional heating systems is heating pattern. In MW device, the energy is directly supplied to the carbon bed. The conversion of microwave energy is not by conduction or convection as in conventional heating, but by dipole rotation and ionic conduction inside the particles [10–12]. Therefore, the treatment time can be significantly reduced through microwave heating.

The work presented in this paper focused on the AC production by using cotton stalk (CS) collected from a local farm in Xinjiang Province, China. During the past decades, cotton had been considered as the widest crop in Xinjiang. According to the latest data issued by Xinjiang Statistical Center Bureau, it is found that the production of cotton products was increasing, around 218, 290 and 302 million tones by the year of 2006, 2007 and 2008, respectively. The high output of cotton automatically resulted in the high output of byproduct, CS. A large quantity of stalk became an environmental problem, especially after CS had lost their importance as fuel. Therefore, there is an urgent need to explore new applications of CS and solve the environmental problem. Recently, a few studies

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have been reported in the literature concerning the production of AC from CS [13–18]. CS was proved to be a potential raw material to prepare AC. ACs prepared from CS were efficient adsorbents for the removal of *p*-nitroaniline [13], 2-nitroaniline [14], Pb(II) [17] and methylene blue [18] from aqueous solutions. However, most of the researches were more focused on the using of EF heating method rather than MW heating method.

In our previous work, we have prepared AC from CS using MW heating assisted $ZnCl_2$ activation in a few minutes [18]. However, the carbons obtaining remnant zinc chloride cannot be used in pharmaceutical and food industries as it may pollute the product [19]. KOH and K_2CO_3 have increasingly been used as the activation reagent turning out high specific surface area of the prepared ACs [20–22]. Furthermore, K_2CO_3 is not deleterious used as food additives [22]. Nevertheless, there was no study regarding activated carbon prepared from cotton stalk treated with microwave energy in the presence of KOH or K_2CO_3. In this work, the mixture of CS and activation agency (KOH or K_2CO_3) was heated using microwave radiation. The influences of some parameters such as radiation power, radiation time and activation agent/precursor ratios on the adsorption capacities of ACs were investigated. Then, the data were analyzed with Analysis of Variance (ANOVA). The frequency test (*F*-test) was utilized in statistics to analyze the significant effects of the factors. Finally, the properties of activated carbons were investigated and compared.

2. Experimental

2.1. Material

CS was collected from a local farm in Shihezi city, Xinjiang Province, China. It was washed with distilled water to remove dust and dried by heating at 80 °C overnight. Then the raw material was crushed, sieved into a uniform size of less than 2.0 mm. The contents of C, H, N, and S of the CS were measured by using a LECO CHNS 932 Elemental Analyzer. The contents of moisture and total ash were determined by the standard procedures [19]. The results were as follows: C, 41.43%; N, 1.160%; S, 1.063%; H, 6.158%; total ash, 3.68%; moisture, 3.42%.

KOH and K_2CO_3 (Xi'an chemicals reagent, China) with analytical grade were used as the activation agent.

2.2. Preparation of ACs

Approximately, 6 g of dried CS was mixed with 30 mL of KOH or K_2CO_3 solution of vary concentrations for 24 h at ambient temperature. After mixing, the slurries were placed in a microwave heating apparatus. The experimental apparatus is similar to that described elsewhere [18]. After a certain radiation power and time, all activated samples were washed with 0.1 M HCl, hot water and cold distilled water to remove residual organic matters and alkalis, until the pH of the filtrating solution was neutral. Finally, the clean samples were dried at 105 °C for 24 h. ACs obtained from chemical activation with K_2CO_3 and KOH were denoted as KCAC and KAC, respectively.

2.3. Characterization of ACs

Adsorptive properties were measured by using iodine and methylene blue (MB) as adsorbates. Adsorption capacities of iodine and MB were normally listed as specification parameters for commercial ACs. Iodine and MB were considered as probe molecules for assessing the adsorption capacity of adsorbent for solutes of molecular sizes <10 and >15 Å, respectively. Therefore, iodine number and MB number were selected as responses to optimizing preparation conditions in our research. Iodine number (q_{iodine}, mg/g carbon) and MB number (q_{MB}, mg/g carbon) of AC were measured according to standard accepted methods [19]. The concentration of MB was measured by using a double beam UV–vis spectrophotometer (Hitachi Co., Japan) at 665 nm.

Textural properties were deduced from the adsorption isotherms of N_2 at −196 °C by using a porosimeter (Micromeritices, ASAP-2010). Prior to measurement, the samples were degassed under vacuum at 350 °C and pressure 10^{-5} Torr for 4 h. About 0.10 g of samples was used in each adsorption experiment. Analysis of the adsorption isotherms was carried out by applying Langmuir and BET equations to get S_L, S_{BET} and total pore volume, V_t. An average pore diameter was also estimated from the relation:

$$D_p(nm) = \frac{4V_t \times 1000}{S_{BET}} \tag{1}$$

The micropore volumes (V_{mic}) and micropore specific surfaces (S_{mic}) of samples were evaluated by the *t*-plot method, V_t was estimated from nitrogen adsorption at a relative pressure of 0.98, the external surface area (S_{ext}) was calculated by subtracting S_{mic} from S_{BET}, and pore size distribution (PSD) was determined by using the BJH model [23].

The surface physical morphology was identified by using scanning electron microscopy (SEM) technique. A JSM-6390LV (JEOL Ltd., Japan) with a 3 kV accelerating voltage was used to characterize the morphology of ACs which was dried overnight at approximately 105 °C under vacuum before SEM analysis.

The Fourier transform infrared spectroscopy (FTIR) was used to qualitatively identify the chemical functionality of ACs prepared from CS. FTIR spectra were recorded between 4000 and 400 cm^{-1} by using AVATAR 360 (Thermo Nicolet Co., USA) Spectrophotometer. The transmission spectra of the samples were recorded by using the KBr pallet containing 0.1% of sample.

2.4. Batch equilibrium

The 30-mL samples of MB solution with known concentration and the samples of the produced ACs with the mass of 0.10 g were added to Erlenmeyer flasks. The flasks were shaken in a shaker incubator in an isothermal condition of 30 ± 1 °C and shaking speed of 160 rpm for 2 h to reach adsorption equilibrium conditions. Then the samples were filtered and the residual concentration of MB in the filtrate was analyzed. The amount of MB adsorbed per unit mass of adsorbent at equilibrium conditions, q_e (mg/g), was calculated by [24]:

$$q_e = \frac{(C_0 - c_e)}{M} \times V \tag{2}$$

where C_0 (mg/L) and C_e (mg/L) were the initial and the equilibrium concentrations of MB at solutions, respectively. *V* (L) was the volume of solution and *M* (g) was the mass of AC. We used Langmuir and Freundlich models to investigate the equilibrium behavior of MB adsorption on the prepared AC samples. They are described in Table 1.

Another characteristic parameter of the Langmuir isotherm is the dimensionless factor R_L (separation factor), related to the shape of the isotherm. Its value indicated either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) adsorption and it was evaluated as [25]:

$$R_L = \frac{1}{b + C_0} \tag{3}$$

where *b* was the Langmuir constant and C_0 (mg/L) was the highest concentration of the adsorbate.

Table 1
Adsorption isotherm models adopted in this work and their parameters.

Isotherm	Equation	Parameters
Freundlich isotherm	$q_e = K_F C_e^{1/n}$	K_F (L mg^{-1}): the Freundlich adsorption constant n: the empirical parameter representing the energetic heterogeneity of the adsorption sites (dimensionless) q_e (mg g^{-1}): the amount of dye adsorbed
Langmuir isotherm	$q_e = \frac{q_m K_L C_e}{1+K_L C_e}$	C_e (mg L^{-1}): the equilibrium concentration q_m (mg g^{-1}): complete monolayer adsorption capacity K_L (L mg^{-1}): the equilibrium adsorption constant

3. Results and discussion

3.1. Preparation of ACs from CS

3.1.1. Effects of activation agency/CS ratios on adsorption capacities of ACs

Effects of activation agency/CS ratios on iodine number and MB number of AC prepared from CS were evaluated. The experimental conditions and the results are shown in Fig. 1. Enhancing ratios of KOH/CS from 0.4 to 0.6, iodine number and MB number of AC sample were increased. Augmenting ratios of KOH/CS from 0.6 to 1.4, the adsorbed amounts of iodine and MB molecule on KAC surface were decreased gradually. Similarly, the amounts of MB and iodine adsorption of KCAC also increased with enhancing ratios of K_2CO_3/C from 0.6 to 0.8, and then decreased gradually with augmenting ratios of K_2CO_3/CS from 0.8 to 1.4.

It is believed that adsorption of matter onto activated carbon depends on both the pore structure and the surface chemical properties of carbon as well as the adsorbate. Kasaoka et al. found that when micropores were present, adsorption occurred only when the average micropore diameter increased to about 1.7 times the molecule's second widest dimension [26]. From an adsorption free energy standpoint, compounds are preferentially adsorbed into pores that are similar in size to the adsorbate because of the greater number of contact points between the molecule and the adsorbent [27]. The methylene blue molecule has a minimum molecular cross-section of about 0.8 nm and it has been estimated that the minimum pore diameter it can enter is 1.3 nm [28]. Therefore, it can only enter the largest micropores, but most of it is likely to be adsorbed in mesopores. In contrast, the iodine molecule is greatly adsorbed due to its smaller size (= 0.27 nm) permitting its penetration into micropores (larger than 1 nm) [29].

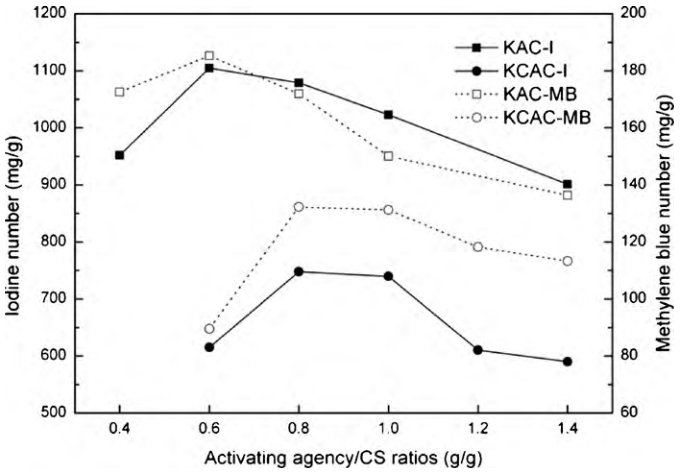

Fig. 1. Effect of activation agent/CS ratios on adsorption capacities of ACs (KCAC preparing conditions: radiation power = 720 W, radiation time = 8 min; KAC preparing conditions: radiation power = 680 W, radiation time = 10 min).

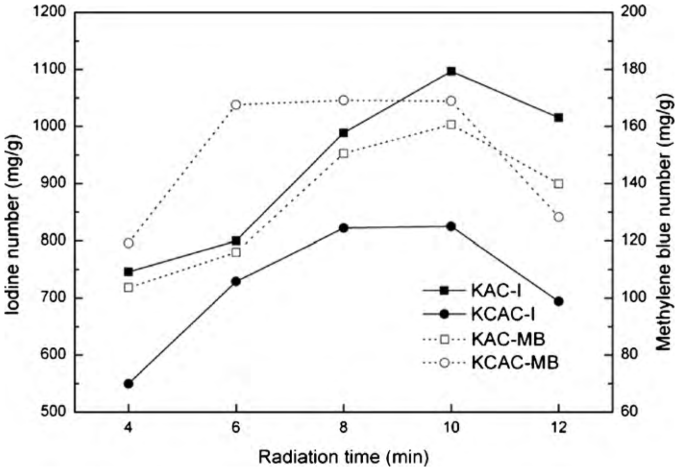

Fig. 2. Effect of radiation time on adsorption capacities of activated carbons (KCAC preparing conditions: radiation power = 720 W, K_2CO_3/CS = 0.8; KAC preparing conditions: radiation power = 680 W, KOH/CS = 0.6).

The development of porosity of AC by KOH activation was associated with gasification reaction. It was assumed that KOH was reduced to metallic potassium during the carbonization process. The reaction between KOH and carbon occurs according to the following reaction [30,31]:

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3$$

McKee [32] and Lillo-Ródenas et al. [31] studied the gasification of graphite by alkali metal and found that K_2CO_3 was reduced in inert atmosphere by carbon as follows:

$$K_2CO_3 + 2C \rightarrow 2K + 3CO$$

$$K_2CO_3 \rightarrow K_2O + CO_2$$

Meanwhile K_2CO_3 was reduced by carbons to form K, K_2O, CO and CO_2 so that more pores were formed. Furthermore, when activation temperature reached the boiling point of potassium 800 °C, potassium would diffuse into the layer of carbon, also causing the formation of pores of ACs. Therefore, by increasing the ratios of activation agency/CS, the activation reaction would be strengthened and a large number of pores would be formed. Correspondingly, the adsorption capacity of carbons was enhanced. When the ratios reached optimum value, the active sites on the carbons had reacted completely and the adsorption capacity reached the maximum amount. However, the pores would be widened and burnt off when the ratios arrived at a certain value [7], lowering the adsorption capacity of ACs.

3.1.2. Effects of radiation time on adsorption capacities of ACs

The effects of radiation time on adsorption capacities are demonstrated in Fig. 2. The experimental conditions are also shown in Fig. 2. As can be seen, the activation time had a great influence on the adsorption capacities of KCAC and KAC. During the preparation of KCAC, both iodine number and MB number were increased significantly at the initial stage. It was indicated that the pores were formed and enlarged in this period. With radiation time going on, the increase of adsorption amount gradually became slow. A slight drop was observed at 10 min. The phenomenon implied that the formation of new pores became less significant with the

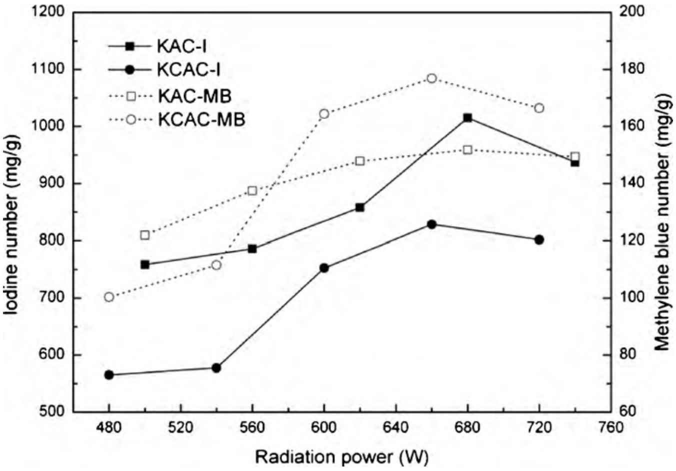

Fig. 3. Effect of radiation power on adsorption capacities of activated carbons (KCAC preparing conditions: radiation time = 8 min, K_2CO_3/CS = 0.8; KAC preparing conditions: radiation time = 10 min, KOH/CS = 0.6).

activation proceeding, and the micropores or mesopores were continuously widened into larger ones. Furthermore, they might also be destroyed after long time exposure to the microwave radiation. Similar tendency had been observed in the preparation of KAC, the maximal iodine number and MB number were obtained at radiation time of 10 min.

3.1.3. Effects of radiation power on adsorption capacities of ACs

The effects of microwave power levels on adsorption capacities of ACs prepared by different activation agency were investigated. The experiment conditions and the results are presented in Fig. 3. During the preparation of KCAC, the iodine number and MB number of the KCAC were increased gradually with the enhancing of microwave power lever from 480 to 660 W, and then decreased with the increasing of the lever to 720 W. There were similar tendencies found in the preparation of KAC. As suggested by the results, microwave power played an important role in the activation process. Wang et al. [33] found that the carbon precursor could hardly be heated without the impregnation of the activation agent, indicating that activation agency acted as the main microwave absorber at the initial stage. With the development of the pore structure, the AC itself could also receive microwave energy. At low microwave power, the pore structure was not adequately developed, which got better with the increasing of the microwave power. Therefore, the adsorption capacities of KCAC and KAC were increased with the increasing of radiation power. However, at high radiation lever, adsorbed microwave energy exceeded a certain lever, so that the overfull energy could make a small quantity of carbon burnt, the structure of pores was destroyed, and adsorption capacities were decreased.

3.1.4. Analysis of variance

Analysis of variance (ANOVA) is a method of portioning variability into identifiable sources of variation and associated degree of freedom in an experiment. The collected data were analyzed by the statistical analysis software, SPSS, version 16.0 (SPSS Inc., Chicago, IL, USA); the ANOVA was done at 95% confidence level, and it was established based on the sum of the square (*SS*), the degree of freedom (*df*), the mean square, *F* value and *P* value. The frequency test (*F*-test) was utilized in statistics to analyze the significant effects of the factors, which form the adsorption capacities.

Usually, the larger the *F* value, the greater the effect on the result value due to the change of the process parameter [34]. The results of the ANOVA are presented in Tables 2 and 3. From the analysis of Table 2, it is found that radiation time with the biggest *F* value of 16.046 was the most important factor affecting iodine number of KAC, followed by radiation power and KOH/CS ratios. The factor affecting iodine number of KCAC was followed as in the order: radiation power, K_2CO_3/CS ratios and radiation time. As shown in Table 3, the greatest factor effect on MB number of KAC was radiation time which had the highest *F* value, followed by KOH/CS ratios and radiation power. Also analyzed from Table 3, radiation power was found to have the greatest effect on MB number of KCAC with the highest *F* value. Then, K_2CO_3/CS ratios and radiation time followed.

Table 2
ANOVA of iodine number.

Type of AC	Source	Sum of squares	*df*	Mean square	*F*	*P*
KAC	KOH/CS ratios	32395.782	4	8098.946	5.314	0.165
	Radiation power	56324.429	4	14081.107	9.239	0.100
	Radiation time	97821.608	4	24455.402	16.046	0.060
	Error	3048.113	2	1524.056		
	Total	1.340×10^7	14			
KCAC	K_2CO_3/CS ratios	53456.713	4	13364.178	9.108	0.101
	Radiation power	71524.194	4	17881.048	12.187	0.077
	Radiation time	53221.675	4	13305.419	9.068	0.102
	Error	2934.508	2	1467.254		
	Total	7424911.188	14			

Table 3
ANOVA of methylene blue number.

Type of AC	Source	Sum of squares	*df*	Mean square	*F*	*P*
KAC	KOH/CS ratios	1491.118	4	372.779	13.051	0.072
	Radiation power	672.266	4	168.067	5.884	0.151
	Radiation time	2613.145	4	653.286	22.872	0.042
	Error	57.125	2	28.563		
	Total	327967.821	14			
KCAC	K_2CO_3/CS ratios	4065.159	4	1016.290	2.395	0.316
	Radiation power	4859.546	4	1214.887	2.863	0.275
	Radiation time	2197.252	4	549.313	1.294	0.480
	Error	848.738	2	424.369		
	Total	293985.210	14			

Table 4
Main characteristic of pore structure of KAC and KCAC.

Typical parameters	KCAC	KAC
S_{BET} (m^2/g)	621.47	729.33
S_L (m^2/g)	869.70	1015.46
S_{ext} (m^2/g)	236.80	199.88
S_{mic} (m^2/g)	384.67	529.46
V_t (cm^3/g)	0.38	0.38
V_{mic} (cm^3/g)	0.11	0.26
D_p (nm)	2.43	2.08

3.2. Characterization of prepared ACs from CS

From the discussions mentioned above, radiation power, radiation time and the impregnation ratios of activation agency had effects on the adsorption capacities of ACs prepared from CS with chemical activation by microwave heating. Therefore, ACs used in the characterization analysis were prepared under optimum conditions as follows: the ratios of K_2CO_3/CS of 0.8, radiation time of 8 min, microwave power of 660 W; the ratios of KOH/CS of 0.6, radiation time of 10 min, microwave power of 680 W.

3.2.1. Surface morphology of ACs

Scanning electron microscopy (SEM) technique was employed to observe the surface physical morphology of samples. SEM images of the microstructures of the raw CS, KCAC and KAC are shown in Fig. 4. A significant difference of the surface topography between raw material and ACs was observed. Some occasional cracks were relatively organized on the surface of raw CS. Nevertheless, it could be seen from the micrographs that the external surface of the chemically ACs was full of cavities. Those pores resulted from the evaporation of the chemical reagent during carbonization, leaving the space being previously occupied by the reagents. In addition, since in KOH activation, K_2CO_3 and other related compounds were formed after the pyrolysis process, these salts would be leached out by 0.1 M HCl to form micropores within the carbon matrix [35,36]. It also could be seen from Fig. 4, the micrograph of KAC and KCAC were similar. However, there was a significant difference between KAC (KCAC) and the AC prepared with $ZnCl_2$ activating (ZAC) in our previous work [18]. The diameters of cavity of KAC and KCAC were smaller than that of ZAC. It suggested that the surface morphology of the ACs prepared from CS were dependent on the kind of activation agency.

3.2.2. Specific surface area and pore structure of ACs

The corresponding nitrogen isotherms at −196 °C were used to compare the specific surface area and pore structure of samples. Data for KCAC and KAC are shown in Fig. 5. As could be seen, according to the IUPAC classification, both of the isotherms corresponded to a mixture of 1–4 types associated with the presence of both micropores and mesopores. Once micropores were filled ($P_0 < 0.03$), the adsorption of the non-microporous surface began. The presence of a hysteresis loop indicated that large quantities of non-micropores were present (due to capillary condensation in mesopores, macropores or on the external surface). On the other hand, it seemed clearly that the adsorbed amount of N_2 of the KAC samples increased both in the micropore and the mesopore zone compared with that of the KCAC. These results could also be proved in Table 4, in which the main characteristic of pore structure of the ACs was list.

From Table 4, it could be seen that the BET surface area, micropore surface area and micropore volume of the KCAC were all lower than those of the KAC. In the mechanism showed previously and demonstrated by Marsh and Rodriguez-Reinoso [30] and Lillo-Ródenas et al. [31], K_2CO_3 was formed in the reaction between KOH and CS, obtaining metallic K and H_2. Then, the reaction between carbons and K_2CO_3 took place producing CO, CO_2 and K_2O which will continue with the activation reaction. Therefore, the lack of reactivity of carbonate-based precursors had been attributed to the fact that the first reaction was not produced. Consequently, results exposed that the first reaction that took place between CS and KOH was the responsible to the development of a large porosity.

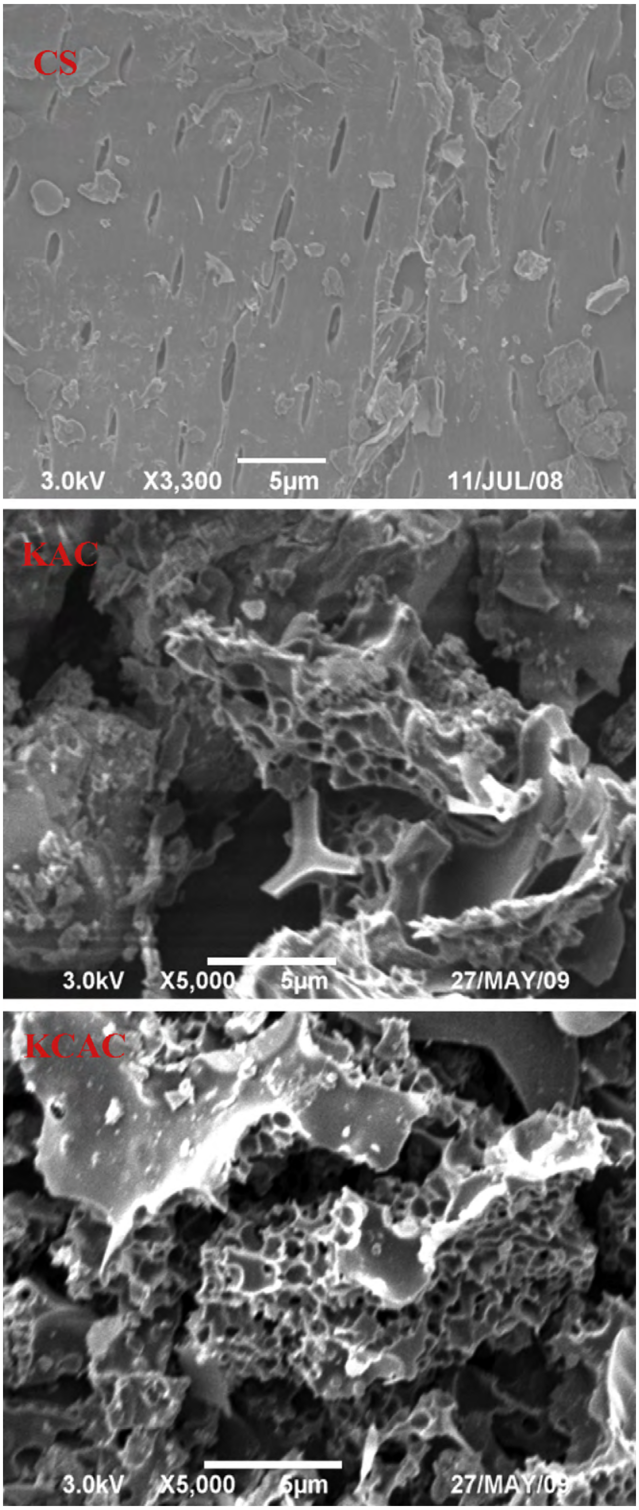

Fig. 4. SEM micrographs of the CS, KAC and KCAC.

Pore size distribution (PSD), a very important property of adsorbents, determines the fraction of the total pore volume accessible to molecules of a given size and shape. According to the classification

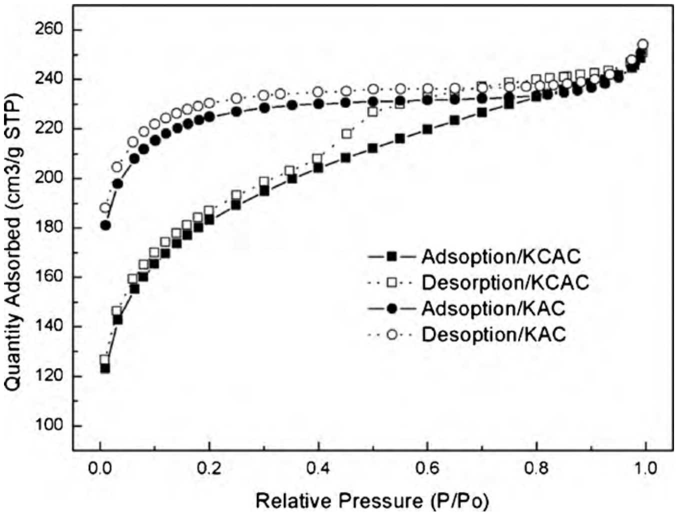

Fig. 5. Volume of N_2 adsorbed/desorbed versus relative pressure for activated carbons prepared by various activating agency.

of IUPAC-pore dimensions, the pores of absorbers could be grouped into micropores ($d < 2$ nm), mesopore ($d = 2–50$ nm) and macropore ($d > 50$ nm). Fig. 6 shows the pore size distribution calculated in the standard manner by using BJH method [23]. It seems that the pore volume of the activated samples increased markedly in the micropore region. Higher increase in the micropore volume took place when KOH was used as activation agent. Moreover, the evidences of mesopores development were showed in both of the samples. In this work, percentages of micropores area were 72.6% (KAC) and 38.10% (KCAC), respectively. The strong interaction between K and raw CS took place when KOH used as activation agency. It produced a large quantity of micropores. Nevertheless, the mild interaction related to K_2CO_3 produced fewer micropores. Furthermore, the micropore percent of ZAC was 13.2% [18]. It was possible demonstrated that the porosity of activated materials could be controlled by using different activation agents. Similar phenomenon was reported by Ryu et al. [37] and Jiménez et al. [38].

Three ACs were prepared from CS by using EF heating KOH activation by Abdel-Nasser et al. [15]. Among these, one kind of ACs had similar specific surface area (613 m^2/g) and micropore percent (75.9%) to the KAC prepared in this work. The prepared conditions of the AC were as follows: KOH-to-stalks ratios of 2:1, carbonization temperature of 700 °C and carbonization time of 1 h. The consumption of KOH in EF heating process was about 3.6 times of that in this work. Activation time spent in the MW heating process was only one-sixth of that in the EF heating. Microwave heating based on the direct interaction of matter with electromagnetic energy [9]. Therefore, the tremendous thermal gradient from the interior of the char particle to its cool surface allowed the microwave-induced reaction to proceed more quickly and effectively at a lower bulk temperature, resulting in shortening the processing time and reducing the consumption of activation agent used in the treatment.

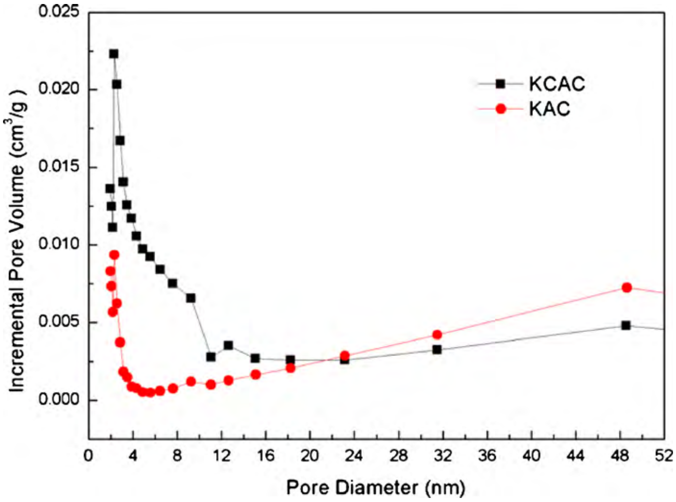

Fig. 6. Pore size distribution of activated carbon prepared by various activating agency.

3.2.3. Function groups of ACs

To characterize surface groups on CS, KCAC and KAC, Fourier transform infrared (FTIR) transmission spectra were obtained. Three main components of CS were cellulose, hemicellulose and lignin. The expected oxygen groups in CS were hydroxyl, ether, carbonyl acetoxy, etc. According to FTIR spectra (Fig. 7), CS displayed the following bands: the band at 3421 cm^{-1} was attributed to O–H stretching in hydroxyl functional groups. The band at 2914 cm^{-1} and its shoulder at 2859 cm^{-1} were ascribed to νC–H and δC–H (ν = stretching and δ = bending) absorption bands that might be present in methyl and methylene groups in the precursor. The relatively band at 1738 and 1651 cm^{-1} was ascribed to C=O stretching from ketones, aldehydes or carboxyls groups. The bands in the region 1640–1430 cm^{-1} were ascribed to the C=C stretching vibrations in the aromatic rings bands. The band at 1025 cm^{-1} was attributed to C–O–C stretching in ethers and the later band at 772 and 669 cm^{-1} were attributed to out-of-plane bending in benzene derivatives.

Fig. 7 also depicted the FTIR spectra of the AC samples. It was found that KAC and KCAC samples had similar absorbance bands. According to the FTIR spectra of the studied carbons and the literature [39–43], one could assume that they had surface functionalities with C=O (carboxylic, anhydride, lactone, and ketene groups having IR bands at 1750–1630 cm^{-1}), C–O (lactonic, ether, phenol, etc., with a very intensive band at 1300–1000 cm^{-1}) and C=C (1640–1430 cm^{-1}). In addition, weak bands at 2649 and 1154 cm^{-1} in KAC and might be ascribed to the traces of potassium carbonates active centres beside metallic potassium that could be produced at 873 K [44,45]. This indicated that in spite of the extremely prolonged washing, a trace amount of potassium remained chemical bound inside the pore structure. An intensive band at 3700–3200 cm^{-1} of adsorbed water, which was observed in both samples, could mask a band of νOH in different groups of CO–H. Notice that the diffuse reflection FTIR spectra of both samples depicted only low-intensity bands over the ranges of 1100–660 and 1650–1400 cm^{-1} against an intensive background absorbance. Thus, the chemical structure of the ACs surface was relatively combined with different CO, COC, CC, and C–H bonds.

Significant changes in the spectra of CS, KAC and KCAC are observed which, in particular, concerned the bands located in a range between 2920 and 2840 cm^{-1} where a sharp decrease in the bands intensities is noticed in the regions for both the carbon products. It suggested that many weak bonds disappeared under carbonization and activation conditions. Similar phenomena had appeared in the AC prepared from CS using EF heating [15]. In addition, the significant difference appeared in the spectra of ZAC, KAC and KCAC. Sharp bands were located in a range between 1627 and 1604 cm^{-1} for ZAC [18], but they disappeared in the spectra of KAC and KCAC. It suggested that various surface groups formed on carbons could be influenced by the activation agency.

3.3. Equilibrium adsorption isotherms

The experimental data were fitted into the Langmuir and Freundlich models. The results are shown in Table 5. The values of

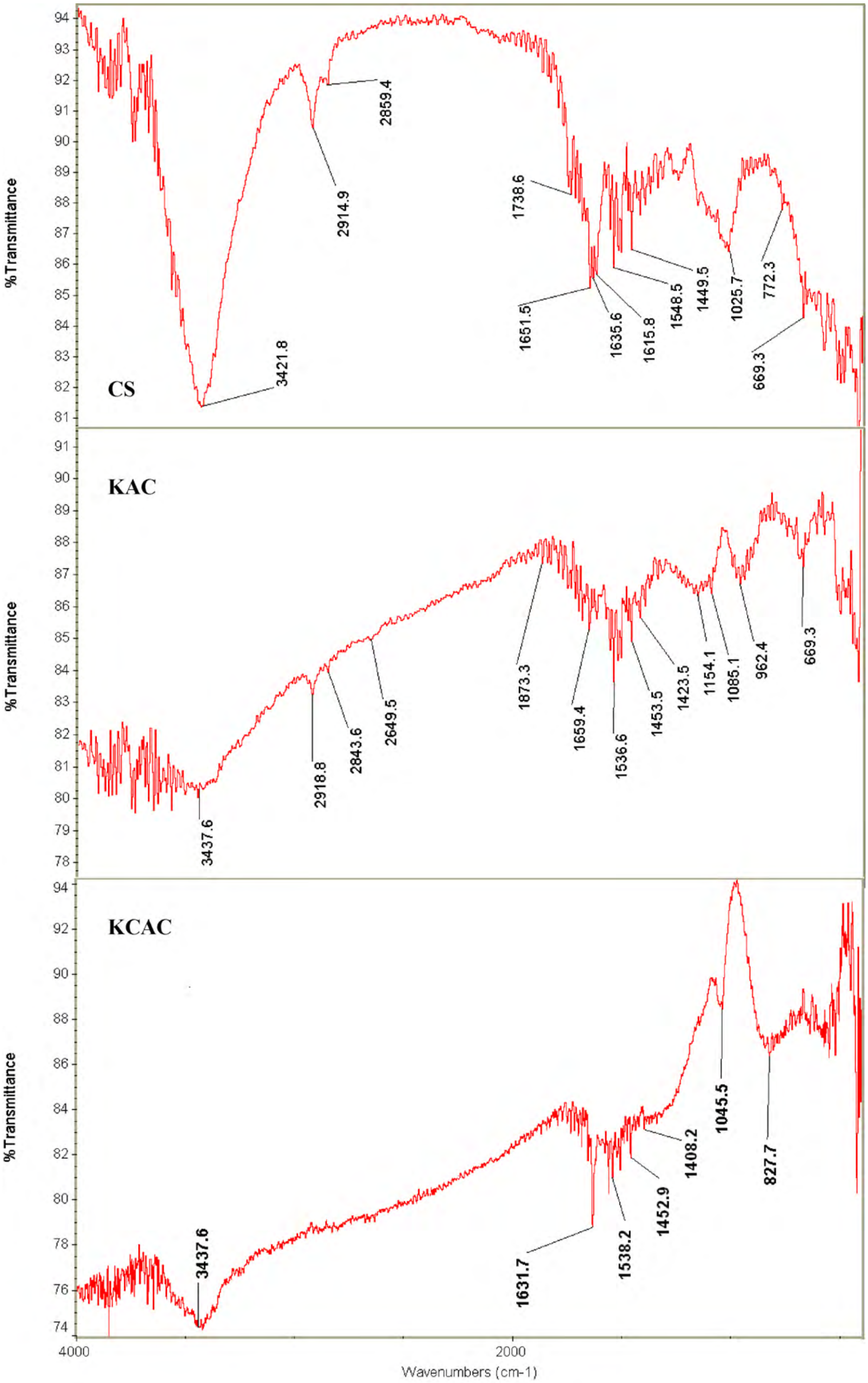

Fig. 7. Fourier transform infrared spectra of cotton stalk and activated carbons.

Table 5
Isotherm parameters for MB adsorption onto KAC and KCAC.

Isotherms	Parameters	Adsorbent	
		KCAC	KAC
Freundlich	K_F (L mg^{-1})	195.29	227.15
	n	16.34	24.27
	R^2	0.8434	0.9268
Langmuir	q_m (mg g^{-1})	285.71	294.12
	K_L (L mg^{-1})	1.029	0.7083
	R_L	0.0012	0.0018
	R^2	0.9991	0.9992

Table 6
Comparison of the maximum monolayer capacities of MB on various adsorbents.

Adsorbent	q_m (mg/g)	Reference
Anaerobically sewage sludge	114.943	[46]
Sewage sludge from agrofood industrial wastewater	86.957	[46]
activated carbon prepared waste apricot	102.04	[47]
Hazelnut shell-based activated carbon	8.82	[48]
Almond shell-activated carbon	1.33	[48]
Walnut shell-activated carbon	3.53	[48]
Apricot stones-activated carbon	4.11	[48]
Coconut shell	277.90	[49]
Groundnut shell carbon	164.90	[49]
Bamboo dust carbon	143.20	[49]
Sulphuric acid treated Parthenium (an agricultural waste) carbon (SWC)	39.68	[50]
Phosphoric acid treated Parthenium (an agricultural waste) carbon (PWC)	88.49	[50]

correlation coefficients showed that the experimental data of MB adsorption fitted the Langmuir isotherm ($R > 0.9990$) better than the others for all ACs. This implied the homogeneous and the monolayer coverage of MB on the surface of ACs. The maximum MB adsorption capacity (q_m) on the KAC and KCAC were 294.12 and 285.71 mg/g, respectively. The dimensionless separation factors for MB adsorption was calculated equal to zero which showed the MB adsorption was favorable. The similar phenomenon has also been observed in our previous work [18]. Though the maximum MB adsorption capacities of KAC and KCAC were smaller than that of ZAC, they were higher than those of many adsorbents prepared by other researchers (Table 6).

4. Conclusions

Cotton stalk was chemically activated with KOH and K_2CO_3 by using microwave as heating energy. The effects of impregnation ratios of activation agency, radiation power and radiation time on iodine number and MB adsorption number of ACs were investigated systematically. Radiation time was the greatest impact factor on adsorption capacities of the KAC, radiation power was the most significant impact factor on adsorption capacities of the KCAC. Optimum conditions were different in two prepared process. The AC samples prepared under optimum conditions were characterized. The external surfaces of the chemical ACs were full of cavities against that of raw CS. Chemical activation could develop both microporosity and mesoporosity. When KOH was used as the activation agent, a large quantity of micropores and some mesopores were generated. Nevertheless, when K_2CO_3 was used, a larger number of mesopores were produced. The porosity and surface groups of the activated materials could be controlled by using different activation agent. The equilibrium data of the adsorption was well fitted to the Langmuir isotherm for both activated carbons. The maximum MB adsorption capacity (q_m) on the KAC and KCAC were 294.12 mg/g and 285.71 mg/g, respectively. Compared to conventional heating, microwave heating could shorten the processing time and reduce the consumption of KOH. Chemical activation could form different functionalities on the carbon surfaces compared with CS in both heating process.

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