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Effect of preparation conditions on the characteristics of activated carbon produced by $ZnCl_2$ activation

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The effect of preparation conditions Carbonization Temperature (CT), Carbonization time (Ct) and, weight ratio of activator ($ZnCl_2$) to dry stones (R)) on the structural and adsorptive characteristics of Activated Carbon (AC) produced from Talh tree trunks (Acacia Asak) was investigated. Adsorption data for Methylene Blue (MB) and benzene were fitted to a Freundlich-type isotherm ($X = k C_e^n$). The unit capacity (k) and the heterogeneity factor (n) were determined. The most influential factor was found to be R where high values of R produced AC with abundant mesoporous structure especially at high CT and low Ct. A combination of low R, high CT and large Ct produces AC with lower surface area most probably due to pore widening which results from the collapse of the walls of the micropres. For benzene, n did not change significantly with preparation conditions and its adsorption strongly depended on the available surface area associated with meso and micropore volumes. For MB, n changed with preparation conditions. This may indicate a change in the affinity between MB and the carbon surface resulting from a change in the surface chemistry of the carbon and/or a change in the pore size distribution with preparation conditions.

في هذا التقرير يتم أستعراض تاثير ظروف التحضير(درجة حرارة الكربنة و زمن الكربنة و نسبة المنشط (كلوريد الزنك) الى النوى الجاف) على تركيب وخواص الأدمصاص للكربون النشط المنتج من جذوع شجر الطلح. وفي ضوء هذه الدراسة تبين ان أدمصاص أزرق الميثيلين والبنزين يمكن تمثيله بأستخدام معادلة فروندليتش ($X = k C_e^n$) وتم استخدام هذه المعادلة لحساب سعة الوحدة (k) وعامل عدم التجانس (n). وقد وجد أن أهم العوام المؤثرة على خواص الكربون هي نسبة المنشط (كلوريد الزنك) الى النوى الجاف. حيث لوحظ أن إستخدام نسبة عالية من المنشط بالنسبة الى نوى التمرالجاف ينتج عنه كربون يحتوي نسبة عالية من المسامات دون المجهرية وبالخصوص أذا تم التحضير عند درجات حرارة مرتفعة وأوقات كربنة قصيرة. كما وجد أن الجمع بين نسبة منخفضة من المنشط مع درجات حرارة منخفضة ووقت كربنة طويل يؤدي الى إنخفاض المساحة السطحية للكربون و يمكن تعليل ذالك بحصول أنهيار في جدران المسامات دون المجهرية وتكون مسامات أكبر. وبالنسبة للبنزين فأن قيمة n لم تتغير كثيرا مع ظروف التحضير وأعتمد أدمصاص البنزين بشكل رئيسي على المساحة السطحية المتوفرة. ومن جهة أخرى فان n بالنسبة أزرق المثيلين تتغير بشكل كبير مع ظروف التحضيرمما يعني تغير طبيعة التجاذب بين سطح الكربون و أزرق المثيلين نتيجة لتغير كيمياء السطح للكربون أوتغير في توزيع حجم المسامات مع أختلاف ظروف التحضير.

Key words: Activated carbon, Activation, Adsorption, Carbonization

1. Introduction

Activated Carbon (AC) is an amorphous form of carbon that is specially treated to produce a highly developed internal pore structure and a large surface area, thus, producing cheap and excellent adsorbent capable of adsorbing gases and vapors, and removing dissolved substances from liquids. [1-3]. AC is used in diverse applications such as decolorization, purification and deodorization of vegetable oils and fats, sugars refining and other food industries. Other uses of AC include treatment of process-water, pollution control and in wastewater treatment for water reuse, where it can be employed as a point source treatment or as a final polish operation [1, 4].

Two distinct methods for production of AC are described in the literature, namely, chemical activation (activation with mineral salts) and physical activation (activation using oxidizing agents such as steam or CO_2). In chemical activation, the precursor is impregnated with an activating agent such as zinc chloride followed by carbonization in an inert atmosphere at high temperatures. After cooling, the carbonized product is leached to remove the activation agent. $ZnCl_2$ has long been the preferred activating agent. Other

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salts and acids are also used as activating agents [1- 2]. Chemical activation is used almost exclusively with botanical precursors of recent origin such as sawdust. Ample studies are available in the literature about the production of AC from various agricultural precursors including dates stones [5, 8-9], corncob [10-12], coconuts shells [7, 13-14], nuts shells and stones [15 -29], oil palm stones and shells [30-37], apple pulp [38-39], chickpea husks [40], rice straw [41] and palm tree branches [6].

Although the characteristics of the produced AC depend to some extent on the precursor used, the most influential factors are those related to preparation conditions, namely, the impregnation Ratio (R), Carbonization time (Ct) and, Carbonization Temperature (CT). R, that is, the weight ratio of the anhydrous activator to the dry precursor seems to influence the porosity of the resulting products. The activation agent seems to influence the chemistry of pyrolytic processes (acting as a catalyst) so that the formation of tar is restricted to a minimum and the pyrolysis temperature is lowered. This in urn seems to promote the development of a porous structure [1-3]. Usually micropores predominate at low values of R whereas at higher values wide micropores and mesopores predominate [38-39]. The speed and extent of the pyrolysis reaction taking place will depend primarily on the temperature and time of carbonization respectively. These three factors are interrelated in a complex manner and play a crucial rule in determining the characteristics of the final product [1-3, 38-39].

Many investigators [7, 15-16] found that zinc chloride is the best amongst other activators studied. Alhamed and Abdulsalam [6] and Alhamed [5] investigated the properties of activated carbon from palm tree branches and from date's stones, respectively, using zinc chloride as an activator. Optimum values reported are R = 2 and CT = 600 ^{o}C for 1 to 2 hours based methylene blue removal. Gergis et al. [8] used phosphoric acid as an activator and carbonization time of two hours only. Best-developed porosity was at 700 ^{o}C. Banat et al. [9] found that physical activation of date pits reduced the adsorption capacity for MB compared to raw pits. Optimum conditions reported by Tsai et al. [14] were CT = 500 ^{o}C and Ct = 0.5 hours using corn cob as a precursor and Zinc chloride as an activator.

$ZnCl_2$ activation of peanut hulls yields essentially microporous AC with a moderate adsorbing capacity for MB and surface area of 420 m^2/g while H_3PO_4 creates an abundant microporosity with attaining a maximum surface area of 1177 m^2/g at R = 1.0, however, it should be noted that in this study the comparison between these two activators is unfair due different preparation conditions used (see table 1). Low value of R were used for $ZnCl_2$ (R = 0.5), while for H_3PO_4, R ranged from 0.5 to 1.6. Furthermore, Ct higher than 2 hours (see table 1) was used in this study [21]. Higher temperatures, a longer activation times and a higher KOH content increased the adsorption capacity and resulted in a widening of the pores of AC produced from walnut shells. A milder activation favored the production of AC with small micropores. Depending on the synthesis conditions, the size of the pores in the adsorbent could be controlled in the ultramicropore (pore diameter < 0.6 nm) to supermicropore (from 0.6 to 1.6 nm) range [27].

AC produced from oil-palm stone and shells using H_3PO_4 contained acidic surface groups such as phenols and carboxylic acids, whereas AC produced using KOH as an activator contained basic surface groups. On the other hand AC produced by $ZnCl_2$ activation produced a neutral carbon [31]. The amount of phosphoric acid used in the impregnation step strongly influenced the porous texture of AC obtained by pyrolysis of apple pulp. Micropores were predominant at low impregnation ratios whereas larger amounts of phosphoric acid produced wide micropores and mesopores [38-39]. AC prepared from chickpea was using K_2CO_3 as an activator had a maximum specific surface area of 1778 m^2/g at 1073 K and impregnation ratio of 1.0 [40].

Table 1 summarizes some recent literature on AC production from various agricultural precursors using chemical activation. In this table the ranges of parameters studied and the optimum preparation conditions are presented. We can notice from this table the following points:

- Most of these studies did not cover a wide range of the parameters Ct, CT and R and in many cases only a single level of these variables was investigated.
- The wide range of the optimum values for CT reported in the literature (500 to 800 °C) reflects the strong effect of the activator and precursor used for the production of AC.
- In most of the studies reported in literature, only a single level of Ct was used.
- Large carbonization times, (e.g. ref. 22) were sometimes used.

The aim of this study therefore, is to bring about more understanding on the influence of preparation conditions on the physical (e.g. surface area and pore-size distribution) and adsorptive characteristics (using benzene and methylene blue as a model adsorbate) of activated carbon prepared by $ZnCl_2$ activation.

Table1
Summary of recent literature on production of activated carbon from various agricultural precursors

SN	Precursors	Activator	Range of preparation conditions			Optimum values			Ads.	SA	Ref.
			R	CT (°C)	Ct (h)	R	CT (°C)	Ct (h)			
1	DP	H_3PO_4	0.7 – 1.7	300 - 700	2	1.4	700	??		945	8
	DTB	$Zn Cl_2$	1-3	500- 700	0.5 - 3	2	600	1-2	MB B		6
2	DP	$Zn Cl_2$	0.5 - 2	500- 700	0.5 - 3	2 2	600 700	0.5 1.5	MB Ph	1100	5
3	Corn cob	$Zn Cl_2$	0.2 – 2.0	400 to 800	0.5 - 4	1.75	500	0.5	None	1563	10
4	Peanut hulls	H_3PO_4	0.5 – 1.6	500	3 - 6	1	NA	3	MB	1177	21
		$ZnCl_2$	0.5	300, 750	6	NA	NA	NA	MB	420	
		KOH	1	500	3	NA	NA	NA	MB	228	
5	Shells and stones	$Zn Cl_2$	0.42	750 - 850	6 – 24	NA	NA	NA		905	22
6	Oil palm stones	None	0	400 – 900	1 – 4	NA	800	3	NA	320	30
7	Chickpea husk	K_2CO_3	1	500 – 900	1		800			1778	40
8(1)	Rice straw	KOH	4	500 – 900	1	4	700/ 900	1		2410	41
9	lignin	$ZnCl_2$ H_3PO_4	1 1	500 – 900 500 – 900	1 1		600 600			1700 1000	42
10(2)	Grain sorghum	H_3PO_4	0.1 – 0.6	450 – 700	0.1 – 0.6	0.4	500	0.25		1522	43
11	Olive seeds	H_3PO_4	0.3(2)	400, 600, 800	1		800	1			44

DP = date's pits, DTB = Date's Tree Branches, CT = Carbonization Temperature (°C), Ct = Carbonization time (hours), R=impregnation ratio (gram activator per gram dry precursor). SA = Specific Surface area (m^2/g) Ads. = adsorbent, B = benzene, Ph = phenol, MB = Methylene Blue, (1) precursor first charred then activated with KOH, (2) carbonization at 300 °C for 15 min. then impregnating with H_3PO_4 followed activation

2. Materials and methods

2.1. Preparation of activated carbon

A botanic precursor was selected for this study that is Talh tree trunks (Acacia Asak) . Talh trees are common in the southern parts of Saudi Arabia. The trunks of the tree have long been used as fire-wood. Charcoal produced from Talh tree is characterized by its high density and energy content. These characteristics make this precursor a suitable source for AC.

The wood was first dried in an oven at 100 °C for 24 hours, grinded, and sieved. Fractions with size ranging from 1 to 2 mm were used. The selected fraction was further dried for two hours at 120 °C. Zinc chloride was dissolved in water and added to the wood. The amount of solution was adjusted to obtain the desired ratio of zinc chloride (dry basis) to dry wood. Excess water was then evaporated by heating on a hot plate while stirring, followed by drying in an oven at 120 °C for 2 hours to remove the last traces of water.

The impregnated wood was packed into a 2.5 cm ID, 30 cm long Pyrex tubes. The tubes were nearly filled with the dry impregnated mixture then sealed leaving an opening of 0.5 mm at the end of the tube. The desired number of tubes containing samples impregnated with various ratios of zinc chloride to dry wood (R), namely 2:1, 1:1 and 0.5:1, were placed inside a muffle furnace and heated to the desired temperature. At a given temperature one sample of each ratio was withdrawn at predetermined time intervals, namely after 0.5, 1, 1.5, and 2 hours. Some samples were also carbonized for 3 hours. After cooling, carbonization products were grinded into a fine powder, washed thoroughly using distilled water, then, 100 ml of diluted hydrochloric acid was added to each sample in 250 ml conical flask and the samples were left overnight under continuous shaking. Excess acid was neutralized by adding 100 ml of 20% sodium carbonate. After that the samples were filtered and washed with distilled water thoroughly. Complete removal of chloride ions was confirmed using silver nitrate test of the washing liquid. Finally, the samples were dried at 120 °C for two hours, cooled and stored in closed containers for further use.

2.2. Adsorption measurements

2.2.1. Single bottle point test

Rapid screening for comparing different ACs is usually accomplished using single bottle point uptake of certain adsorbate such as *MB* from its aqueous solution [5, 6, 21]. For this purpose, 0.25 g of each of the AC powdered samples was added to 50 ml of *MB* solution (0.35 g/L) in 200 ml conical flask and allowed to equilibrate at room temperature (23±1 °C) for 24 hours under continuous shaking. The carbon was then filtered and the concentration of *MB* in the filtrate was determined using a spectrophotometer. The percentage removal of *MB* (% *MBR*) was calculated using the formula:

$$\% MBR = [(C_{MB})_0 - (C_{MB})_e / (C_{MB})_0) x \, 100. \qquad (1)$$

Where; $(C_{MB})_0$ and $(C_{MB})_e$ are the initial and equilibrium concentrations of *MB*.

2.2.2. Adsorption isotherms

Adsorption data for *MB* and benzene were collected by contacting a given weight of AC (0.125 g for *MB* and 0.05 g for benzene) powder with 25 ml of an aqueous solution of each adsorbate (50 to 500 PPM). Adsorption measurements were made at room temperature (23 ± 1°C) without adjustment of the pH. The samples were placed in shaker for 24 hours before analysis of the residual concentration of the adsorbate.

The adsorption data were fitted to a Freundlich isotherm described by the equation.

$$X = k \, C_e^n . \qquad (2)$$

Were; C_e is the equilibrium concentration of the sorbet in Parts Per Million (PPM), X is the amount adsorbed in mg per gram of AC. The constant k is the so-called unit capacity factor and n is an empirical parameter that represents the heterogeneity of the site energies [45] or the affinity of the adsorbate to the carbon surface [46].

2.3. Characterization

Surface area of selected samples was determined by applying the BET method to nitrogen adsorption data collected using Quanta Sorb Jr apparatus (Qauntchrom Corporation USA). The porosity and pore-size distribution was determined using Autoscan - 33 mercury porosometer (Qauntchrom Corporation USA) capable of attaining pressures up to 32,000 psia. Mercury porosimetry data was also exploited to calculate surface area contributions for pores greater than 6 nm (SHg) according to the procedure reported in ref. [3].

3. Results and discussion

3.1. Effect of preparation conditions on % MBR

Fig. 1 shows the % *MBR* by AC prepared at various conditions as a function of Ct. For AC prepared using R = 2 fig. 1-a, the %MBR did not change significantly with carbonization time nor with CT and it attains a constant value around 97%. For AC prepared using R=1 fig. 1-b, the %MBR versus time curve depended on CT. A gradual increase in % MBR with Ct is evident for CT = 500 ^{o}C with a maximum value of 97% is reached at Ct = 2 hours. On the other hand, for CT = 600 and 700 ^{o}C, % MBR attained a constant value of 97% within half an hour and remained constant with the increase in Ct. For AC prepared using R = 0.5 fig. 1-c, the % MBR depended strongly on both CT and Ct. Generally, a longer carbonization time is required to attain the highest value of %MBR at lower carbonization temperatures, e.g. Ct = 1.5 hr for CT = 500 ^{o}C and Ct = 1 hr for CT = 600 ^{o}C. For AC prepared using R =0.5, and CT = 700 ^{o}C, further increase in Ct above 1 hour adversely affected the %MBR. It is clear from these figures that this test is not conclusive regarding the quality of AC obtained. Except for few samples, especially for R > 0.5, the %MBR varied within a narrow range between 95 and 97% which is make it difficult to really distinguish the good from the bad using %MBR. Further insight on the effect of preparation conditions on the quality of the obtained AC can be obtained by physical characterization and adsorption measurements.

3.2. Porosity development

The pore volumes (V_p) reported in this study were obtained using a mercury porosimeter capable of measuring pore sizes down to 6 nm, and hence it only shows the contribution of macropore volume (V_{ma}) plus mesopore volume (V_{mes}) greater than 6 nm in width (mesopores cover the range from 2 to 50 nm). Fig. 2 shows the pore size distribution for AC prepared at CT = 500 ^{o}C and R =1 for different carbonization times. As can be seen from this figure, most of the measured pore volume (not including pores less than 6 nm) is macro-porous with only about one fourth of the pore volume in the mesoporous region. Increasing the carbonization time from 0.5 to 1.5 hour mainly brings about a slight increase in mesoporosity. The influence of R on the nature of porosity and pore size distribution is depicted in fig. 3 for AC samples prepared at CT = 700^{o}C and Ct = 0.5 hr. Increasing R from 1 to 2 almost double the total pore volume from 0.58 cm^3/g for R =1 to 1.11 cm^3/g for R = 2. It is evident from this Figure that R shows a much stronger effect on porosity compared to Ct. It also can be noted from this figure that for both values of R, V_{ma} is almost the same (about 0.4 cm^3/g). The increase in the pore volume for R = 2 is primarily due to the increase in V_{mes}. It is not possible to follow the change in micropore volume (V_{mic}) using mercury porosimetry, nonetheless, further insight on the development of porosity can be gauged from the measurement of the BET surface area.

The effect of carbonization time, Ct, on various characteristic parameters of AC (BET, SHg, kB and Vp) is depicted in fig. 4. kB is the unit capacity for benzene adsorption obtained from fitting the benzene adsorption data to Fruendlich isotherm. It is evident from this figure that there is a gradual increase in BET surface area from 435 m^2/g to 908 m^2/g with carbonization time. The slow development of the surface area at this temperature can be attributed to the low rate of the pyrolysis reaction taking place at this temperature. It is also evident from this figure that kB increases (from 0.6 to 1.4 mg /g AC) in parallel with the increase in the surface area. In fact, kB is directly proportional to BET surface area under these conditions as shown in fig. 5 where kB is plotted versus the BET surface area. This may be taken as an evidence that benzene adsorption is physically adsorbed and it is not affect by the surface heterogeneity of the AC.

Again referring to fig. 4 it can be seen that V_p, and SHg are slightly affected by increase in Ct at these conditions. This indicates that these characteristics of carbon depend primarily on R which is kept constant in this case. This conclusion can be tested by investigating the effect of R on these parameters as depicted in fig. 6. As can be seen from this figure, BET, V_p and SHg depends strongly on R. Extrapolating the surface area versus R curve using a second degree polynomial, it was found that the maximum value of the BET surface area which could be obtained is about 1528 m^2/g at R = 2.5. Any additional increase in R above 2.5 seems to have little effect on the surface area.

3.3. Adsorption of benzene

The effect of carbonization time on the adsorption of benzene was studied using three groups of activated carbons AC1 (R = 0.5 and CT = 600 ^oC), AC2 (R = 1.0 and CT = 500 ^oC) and AC3 (R = 2.0 and CT = 500 ^oC). The values of the Freundlich isotherm parameters for the adsorption of benzene (nB and kB) using these carbons are summarized in Table 2 along with the correlation coefficient (R^2). In most cases R^2 higher than 0.96 was obtained. A representative sample for the adsorption isotherms of benzene is shown in Fig. 7. It is clear that the adsorption data of benzene can be represented by a Freundlich isotherm within the range of concentrations investigated.

Inspecting the values of nB for AC2 (table 2 and fig. 9), it is obvious that nB fluctuate within a narrow range from 0.677 to 0.775 with increase in Ct from 0.5 to 3 hr. The average value of nB is 0.723 and the standard deviation is 0.039. There is no clear trend in the variation of nB with carbonization time. Noting the small value of the coefficient of variation of (5%), nB can be considered constant within the experimental error encountered in these measurements.

Considering the adsorption of benzene by AC1, it is clear from table 2 and fig. 9 that nB was high (nB = 2.07) at Ct = 0.5 hour. For Ct ≥ 1 hr, however, the average value of nB is 0.744 and the standard deviation is 0.079 which corresponds to a coefficient of variation of only 10.6%. Wider variation for nB is observed in this case compared to adsorption on AC2. Nonetheless, the average values are remarkably similar (compare average values for nB of 0.723 for AC2 and 0.744 for AC1). Similar argument can also be presented for benzene adsorption on AC3 and in this case the average value of nB is 0.693 with and the coefficient of variation is 12.1%. Therefore, it can be said that for carbonization times equal to or greater than 1 hour, nB is the same for AC1, AC2 and AC3. The high values of nB at Ct = 0.5 is explained by the fact at such low reaction time the pyrolysis process is far from complete and the adsorption of benzene is essentially taking place on the biomass not a carbon surface.

The significance of nB is that it reflects the affinity of the adsorbate to the carbon surface [46] or the heterogeneity of the site energies [45]. It is expected that long pyrolysis times (high Ct) should produce a carbon surface with less site heterogeneity due to development of the porous structure and the elimination of surface functional groups. Therefore, any change in surface heterogeneity should be also associated with a change in nB. The fairly constant value of nB (excluding data for carbonization times equal 0.5 hours) shows that R, Ct and CT did not affect the affinity between benzene and the carbon surface significantly. The nature of the interaction between benzene and the surface of the carbon occurs most probably through physical adsorption and thus benzene adsorption is not affected by the change in the surface chemistry of the carbon with the progress of the pyrolysis reaction with time or change in either R or CT.

Referring to fig. 10 and table 2, we can see that kB is greatly influenced by various preparation parameters in a complex manner. For benzene adsorption on AC2, and AC3, kB increases progressively with increasing carbonization time. The difference between AC2 and AC3 is the higher R used in the later which produced carbon with higher kB (kB = 7.5). The increase in kB is associated with the increase in surface area as it was shown earlier (see fig. 5) and the increase in the surface area can be attributed to the increase in micropores and mesopores volume at high value of R [38-39].

On the other hand, we can see from table 2 and figure10 that for AC1, kB increases with increasing Ct from 3.99 mg/g (excluding the data for Ct = 0.5 as discussed earlier) to reach a maximum value of 6.166 mg/g at Ct = 2 hours. Increasing the carbonization time to 3 hours resulted in a decrease in kB to 3.11 mg/g AC. This behavior was not observed for AC2 and AC3. It seems that for AC1 a combination of low R (R = 0.5) and high carbonization temperature (CT = 600°C) and long carbonization time (3 hours) produces AC with low surface area most probably through pore widening as a result of the collapse of the walls of the micropres. The size of benzene molecule is about 0.7 nm [45] and thus it can be accommodated in the micropores greater than 1 nm as well as mesopores and therefore their should be a direct correlation between kB for benzene and the BET surface as it was shown earlier (fig. 5). The behavior of benzene adsorption clearly shows that benzene adsorption is not affected by the surface chemistry of the carbon and rather it is strongly dependent on the available surface area associated with meso and micropore volumes.

3.4. Adsorption of methylene blue

The effect of carbonization time on the adsorption of MB was studied using two groups of activated carbons AC1 (R = 0.5 and CT = 600 °C) and AC3 (R = 2.0 and CT = 500 °C). The values of the Freundlich isotherm parameters for MB (nMB and kMB) adsorption are summarized in table 3 along with the correlation coefficient (R^2). In most cases R^2 higher than 0.96 was obtained. A representative sample for the adsorption isotherms of MB is shown in fig. 8.

Referring to table 3 and fig. 9 we can see that nMB decreased gradually with increasing carbonization time for both AC1 (nMB = 1.677 to 0.377) and AC3 (nMB = 0.542 to 0.253). As discussed earlier, it is expected that long pyrolysis times (high Ct) should produce a carbon surface with less site heterogeneity. The decrease in nMB with increasing carbonization times thus indicates a change in the affinity between MB and the carbon surface due to change in surface chemistry. MB adsorption seems to be strongly affected by the surface chemistry of the carbon [47] which depends on the preparation conditions. Salame and Bandosz [45] found a good correlation between unit capacity (k) and heterogeneity parameter (n) with the concentration of carboxylic and acidic groups on the AC.

Referring to table 3 and fig. 10 we can see that kMB increased gradually with increasing carbonization time for both AC1 and AC3. The effect of Ct on adsorption of MB by AC1 was completely different than that observed for benzene. MB and benzene differ considerably in their molecular size and structure. Due to its large molecular size MB can only enter pores greater than 1.3 to 1.5 nm [3 and 51]. Adsorption of MB in micropores is improbable since it requires very long adsorption time in excess of 180 hours [47]. This is much longer than that used in this study (24 hours). Thus it can be assumed that the increase in kMB with carbonization time (Ct) is associated with the increase mesopore volume.

4. Conclusions

This study showed that structural and adsorptive characteristics of AC prepared by chemical activation depended on CT, Ct and R in a complex manner. The most influential factor is R where high values of R produced AC with abundant mesoporous structure especially at high temperature and low carbonization times. A combination of low R, high CT and large Ct eventually lead to a reduction of surface area most probably through pore widening as a result of the collapse of the walls of the micropres.

The heterogeneity factor (n) for benzene did not change significantly with preparation conditions. Benzene adsorption strongly depended on the available surface area associated with meso and micropore volumes.

MB adsorption on AC produced at different conditions showed that the heterogeneity factor (n) for MB changed significantly with preparation conditions which thus indicate a change in the affinity between MB and the carbon surface and/or shift in pore size distribution towards higher mesopores.

Using the %MBR test is not sensitive enough to effectively discriminate AC produced at different preparation conditions, especially at high carbonization times and high R.

Table 2
Summary of Freundlich isotherm parameters for benzene adsorption on AC prepared at various carbonization times and two different carbonization temperatures (500 and 600 OC) and two different ratios (0.5 and 1.0)

Ct (hr)	AC1			AC2			AC3		
	(R = 0.5 and CT = 600 °C)			(R = 1.0 and CT = 500 °C)			(R = 2.0 and CT = 500 °C)		
	kB	nB	R²	kB	nB	R²	kB	nB	R²
0.5	0.07	2.07	0.998	0.615	0.775	0.972	0.068	1.65	0.964
1	3.99	0.757	0.967	1.225	0.677	0.998	3.46	0.650	0.970
1.5	6.17	0.633	0.982	1.326	0.741	0.996	4.07	0.639	0.982
2	6.1	0.765	0.996	1.429	0.693	0.995	7.5	0.790	0.891
3	3.11	0.820	0.993	2.491	0.731	0.959			
Average value of n*		0.743*			0.723			0.693**	
Standard deviation*		0.079			0.039			0.084	
Coefficient of variation, %*		10.6			5.4			12.1	

R² is correlation coefficient, * average not including nB = 2.07. ** average not including nB =1.65.

Table 3
Summary of Langmuir isotherm parameters for benzene adsorption on AC prepared at various carbonization times and two different carbonization temperatures (500 and 600 OC) and two different ratios (0.5 and 1.0)

Ct (hr)	AC1			AC2			AC3		
	(R = 0.5 and CT = 600 °C)			(R = 1.0 and CT = 500 °C)			(R = 2.0 and CT = 500 °C)		
	(q_m)B	(K_L)B	R²	(q_m)B	(K_L)B	R²	(q_m)B	(K_L)B	R²
0.5	2512.0	0.0006	0.757	167.13	0.0015	0.907	2697	0.00005	0.794
1	512.3	0.0035	0.905	124.6	0.0029	0.993	283.3	0.00429	0.948
1.5	277.2	0.0075	0.953	367.9	0.0011	0.982	209.7	0.00640	0.993
2	6.93.6	0.0068	0.995	101.	0.0059	0.869	1010.9	0.0040	0.827
3	727.2	0.0023	0.992	289.0	0.00351	0.964			

Table 4
Summary of Freundlich isotherm parameters for *MB* adsorption on AC prepared at various carbonization times and two different carbonization temperatures and two different ratios

Ct (hr)	AC1			AC3		
	(R = 0.5 and CT = 600 ^{o}C)			(R = 2.0 and CT = 500 ^{o}C)		
	kMB	nMB	R^2	kMB	nMB	R^2
0.5	0.918	1.677	0.966	4.477	0.542	0.996
1	2.699	1.021	0.997			
1.5	4.491	0.910	0.992	7.747	0.254	0.961
2	4.391	0.666	0.956	7.950	0.253	0.980
3	8.690	0.377	0.997			

Table 5
Summary of Langmuir isotherm parameters for benzene adsorption on AC prepared at various carbonization times and two different carbonization temperatures two different ratios

Ct (hr)	AC1			AC3		
	(R = 0.5 and CT = 600 ^{o}C)			(R = 2.0 and CT = 500 ^{o}C)		
	$(q_m)_{MB}$	$(K_L)_{MB}$	R^2	$(q_m)_{MB}$	$(K_L)_{MB}$	R^2
0.5	1478.0	0.00035	0.907	99.0	0.013	0.974
1	1011.0	0.0031	0.996			
1.5	644.8	0.0061	0.986	32.8	0.0547	0.756
2	119.9	0.02013	0.954	33.5	0.0567	0.801
3	65.4	0.038	0.939			

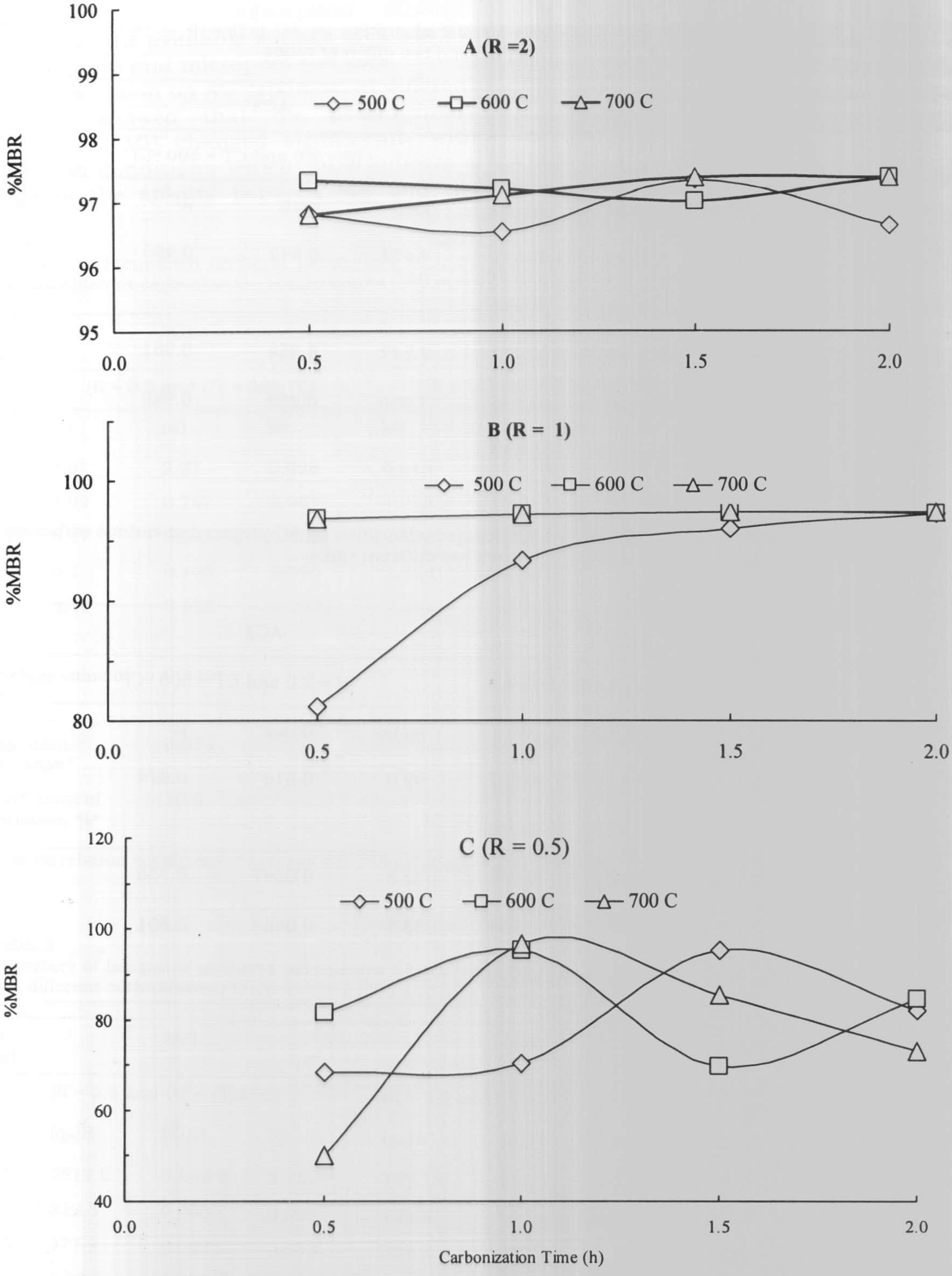

Fig. 1. Effect of carbonization time on methylene blue removal (%MBR) by activated carbons prepared at various carbonization temperatures and weight of zinc chloride to dry date's stones (R). A:R = 2:1, B: R = 1 and C: R = 0.5:1.

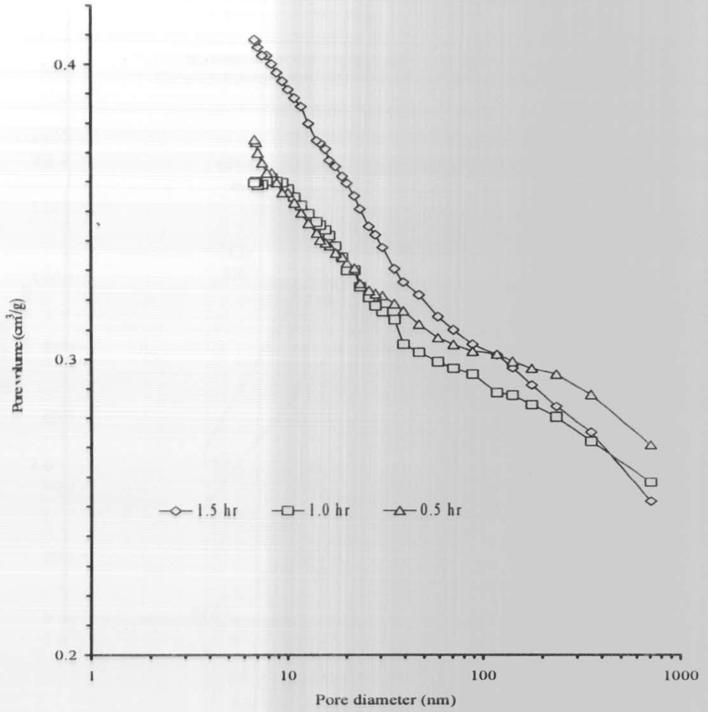

Fig. 2. Effect of carbonization time on pore volume development for carbons prepared at CT = 500 °C and R = 1

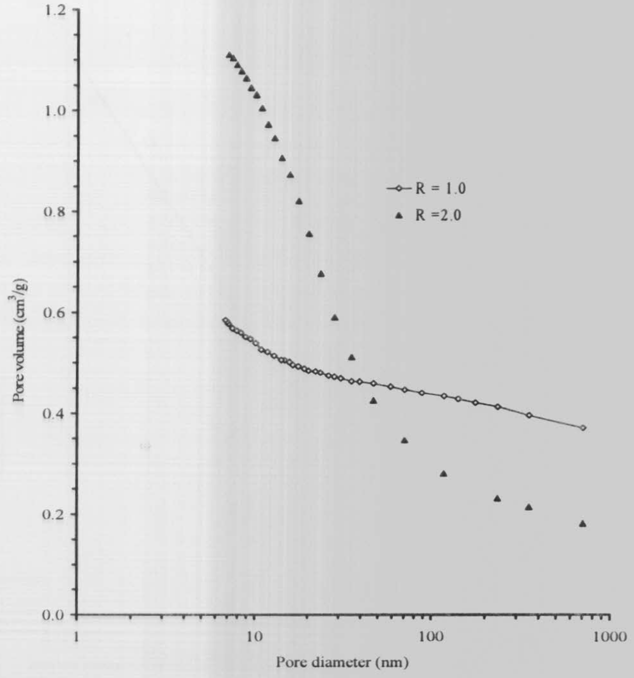

Fig. 3. Effect of R on pore volume development for carbons prepared at CT = 700 °C and CT = 0.5 hr.

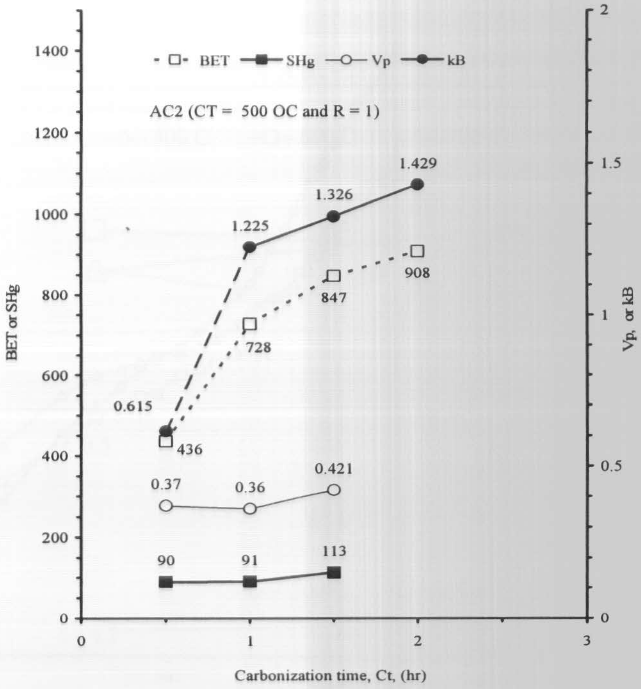

Fig. 4. Effect of Carbonization time, Ct, on BET surface area (m²/g), SHg (Surface area obtained from mercury porosometry in m²/g), V_p (pore volume in cm³/h), and kB.

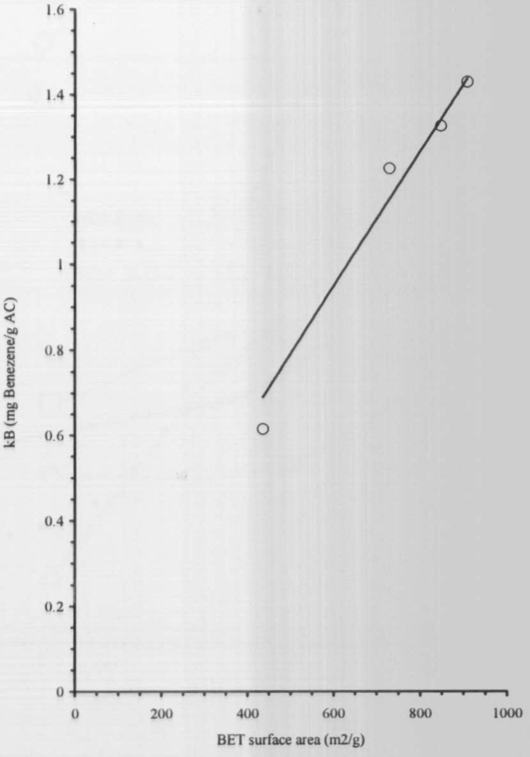

Fig. 5. kB versus BET surface area for benzene adsorption on AC2 (CT = 500 °C and R = 1) prepared at various Carbonization times.

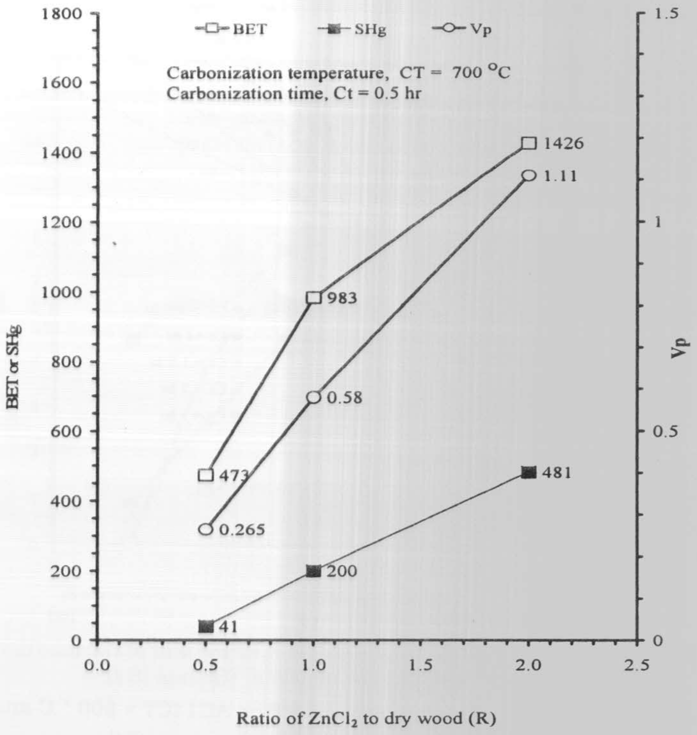

Fig. 6. Effect of ratio of $ZnCl_2$ to dry wood, R on BET surface area (m^2/g), SHg (surface area obtained from mercury porosometry in m^2/h), and V_p (pore volume in cm^3/g).

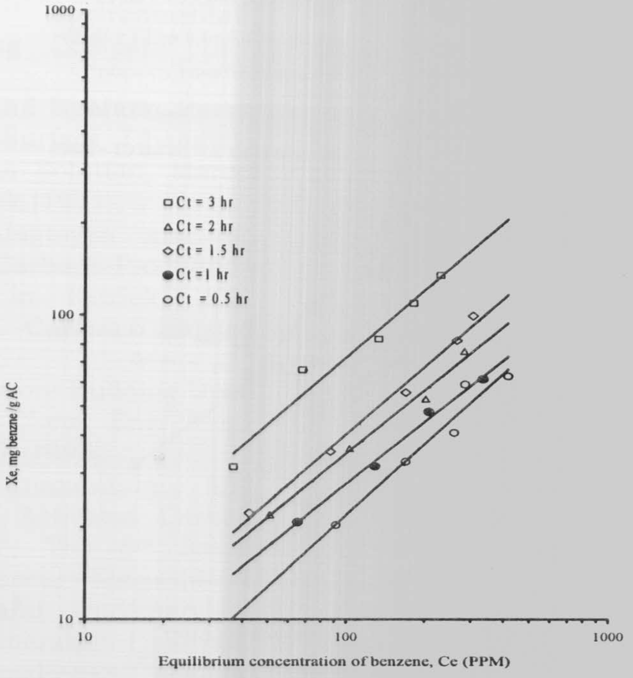

Fig. 7. Effect of carbonization time (Ct) on the Freundlich isotherm for benzene adsorption by AC2 prepared at carbon temperature (CT) = 500 ° C and zinc chloride to wood ratio (R) = 1.

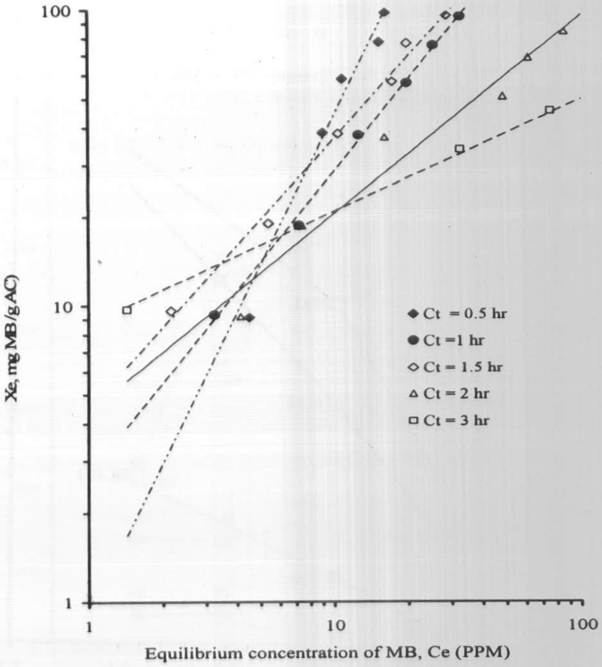

Fig. 8. Freundlich isotherm for adsorption of *MB* on AC1 (CT = 600 ° C and R = 0.5) Prepared at various Carbonization times (Ct).

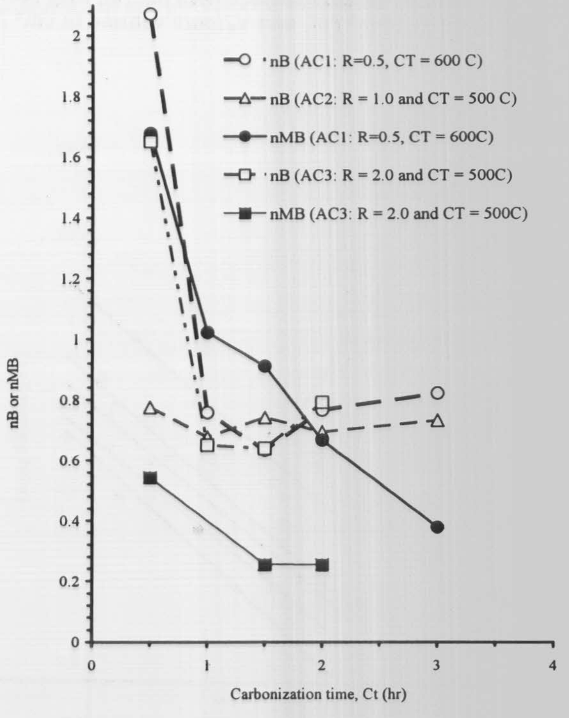

Fig. 9. Effect of Cabonization time of heterogeneity factor n, for the adsorption of benzene (nB) and MB (nMB) on AC1, AC2 and AC3.

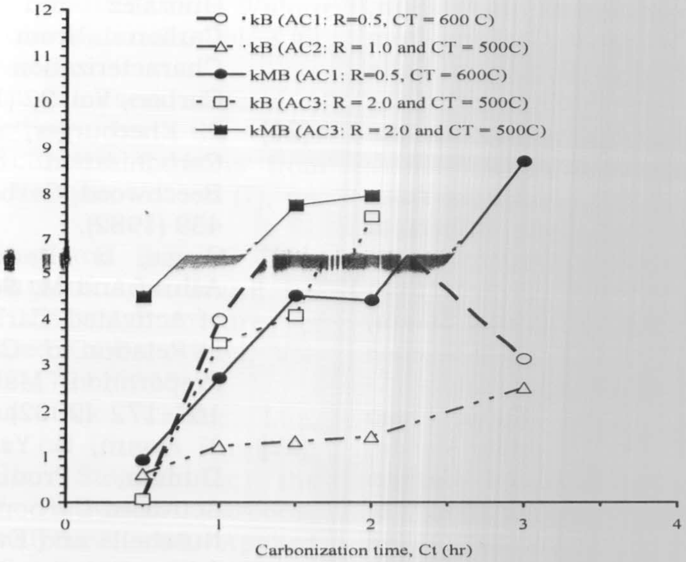

Fig. 10. Effect of carbonization time on unit capacity parameter, k, for the asorption of benzene (kB) and MB (kMB) on Ac1, AC2 and AC3.

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