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Removal of methylene blue by carbons derived from peach stones by H_3PO_4 activation: Batch and column studies

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Abstract

Several activated carbons were obtained by H_3PO_4 at 500 °C, under increasing acid concentrations of 30–70%. Products were characterized by N_2 at 77 K, and proved to be highly microporous with high surface area and pore volume that increased with impregnation ratio. Two modified carbons were prepared by concurrently passing N_2 during pyrolysis of impregnated precursor with 50% H_3PO_4 at 500 °C, and post-heat treatment at 800 °C for one carbon. A low reduction in porosity accompanied this treatment. Equilibrium adsorption of methylene blue (MB) proved good uptake of the bulky dye, which improved considerably with impregnant concentration that was related to enhanced porosity. Dynamic removal of MB was carried out by running solutions of influent concentrations, of 100–200 mg/L, through a mini-column. Many column performance parameters were estimated at different stages on the typical S-shaped breakthrough curves: volume treated, amounts uptaken, bed service time, height of mass transfer zone, and column exhaustion characteristics. Increased impregnation ratio improved column performance, as well as forcing N_2 pyrolysis or extra heat-treatment. Activated carbon impregnated with 70% H_3PO_4 and carbonized at 500 °C exhibited the best properties which prevailed upon raising treated dye concentration to 150 and 200 mg/L, although degraded its capacity due to the limited mass of adsorbent and to the short contact time.

Keywords: Activated carbon; Batch adsorption; Porosity; Fixed-bed removal

1. Introduction

Among the different pollutants of aquatic ecosystem, dyes are a large and important group of chemicals. They are widely used in industries such as textiles, paper, rubber, plastics, cosmetics, etc., to color their products. These dyes are invariably left in the industrial wastes and consequently discharged mostly in surface water resources. Dyes even in low concentrations are visually detected and meanwhile affect the aquatic life and food web. These colored compounds are not only aesthetically displeasing but also inhibiting sunlight into the stream and reducing the photosynthetic reaction. Since many organic dyes are harmful to human beings, the removal of color from process or waste effluents becomes environmentally important. Due to the large degree of organics in these molecules and the stability of modern dyes, conventional physicochemical and biological treatment methods are ineffective for their removal [1].

The conventional methods, such as coagulation and flocculation, used for the removal of dyes from water introduce metallic impurities and produce a large amount of sludge which requires further disposal. The sludge-free treatments are, therefore, gaining importance. Activated carbon adsorption is one such method which has a great potential for the removal of dyes from wastewater [1–6].

The adsorption capacity of activated carbon depends on various factors such as surface area, pore size distribution and surface functional groups on the adsorbent; polarity, solubility and molecular size of adsorbate; solution pH and the presence of other ions in solution and so on [7]. The most widely used activated carbons are microporous and have high surface areas, and as a consequence, show high efficiency

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for the adsorption of low molecular weight compounds and low for larger molecules. The adsorption of bigger size compounds such as dyes, dextrines or natural organic compounds, requires materials with high mesopore contribution to the total pore volume of adsorbents [4,8].

Activated carbons are expensive materials for many countries and produced commercially from three main source feedstocks (unavailable, economically in many parts of the globe); these are wood, coal and coconut shells [9]. Practically any carbonaceous material, natural or synthetic, rich in carbon and low in ash is theoretically feasible for activated carbon production. However, any newly developed carbon should be characterized and tested particularly when intended for the treatment of wastewaters containing large size pollutant molecules such as dyes. A traditionally favorite dye of choice has been methylene blue (MB), and considered a probe molecule for laboratory and technical purposes. It was suggested very early by Giles et al. [10], and currently in use since this time in many research reports [2,11–18], as well as in technical brochures of industrial carbons. Its ionic formula weight (319), cross-sectional area (120 $Å^2$) and molecular size (13–15 Å) are well-recognized over the previous years.

However, most of the literature related to the MB has been dedicated to static equilibrium adsorption data, where it is generally accepted that a good decolorizing carbon should fulfill at least 200 mg/g removal capacity for the dye. This might refer to the capacity for dye uptake in batch removal processes, however, in water treatment fixed-bed (column) removal from effluent streams is the most currently performed. In this case, different conditions are maintained such as dye loading, flow rate, temperature, pH and target effluent concentration. Accordingly, a complete laboratory investigation for the removal from water would generally consist of two parts. First, preliminary isotherm tests to demonstrate the feasibility of activated carbons treatment, and second, laboratory column tests to obtain data to be used in designing the full-scale plant.

The present investigation demonstrates the color removal capacity of laboratory-prepared activated carbons towards a probe, strongly colored dye molecule, i.e. methylene blue. Tested carbons were derived from a local biomass (peach stone shells) by chemical activation with H_3PO_4 at 500 °C. Preparation variables are activant concentration, flowing of N_2 during pyrolysis and extra-heat treatment at 800 °C. Porosity was characterized by N_2 at 77 K. Adsorption capacity of MB was determined by equilibrium experiments, and dynamic removal performance evaluated in mini-column studies. A trial was advanced to correlate adsorption efficiency with the physicochemical and textural properties of the activated carbons.

2. Materials and methods

2.1. Activated carbons

Local peach stones, a by-product of food processing, was washed, depitted, crushed and finally ground in a laboratory mill to a size of 0.5–3.0 mm and afterwards dried in an air oven. A standard scheme of activation was followed: impregnation with H_3PO_4 followed by carbonization at 500 °C. Previous experience proved this temperature to be an optimum with many agricultural raw materials [19–24]. The only variable was the activant concentration, where stock H_3PO_4 (85 wt%) was diluted to 30, 40, 50 and 70 wt%; 50 g of precursor was soaked in 100 ml of diluted acid, which corresponds to impregnation ratios of I.R. = 0.22, 0.34, 0.43 and 0.68, respectively. After soaking overnight at 80 °C, the wet mass was transferred to an S.S. tube and introduced in a tube furnace and heated slowly to 500 °C where it stayed for 2 h. Produced carbonized material was washed thoroughly with hot water and dried till constant weight. These four carbons (C1 to C4) were obtained under their own atmosphere of evolving gases. One more carbon (C5) was prepared with 50 wt% H_3PO_4 and heat-treated at 500 °C, similar to C3, with forced flow of nitrogen. A sixth carbon (C6) was derived from the previously developed carbon 3 by further heating at 800 °C in air for 1 h. Carbon yield, ash content and slurry pH of the carbons were determined (Table 1).

2.2. Characterization of porosity

This was carried out by the conventional adsorption of N_2 at 77 K, by the help of Sorptometer Type Gemini 2375 V3.03 (a product of Quantachrome). Major texture parameters were evaluated: BET-equivalent surface area (S_{BET}) by applying the linear BET-equation within $P/P^o = 0.01-0.15$, total pore volume (V_P) from nitrogen held as liquid at $P/P^o = 0.95$, and average pore radius from $r_P = 2V_P/S_{BET}$. More detailed parameters were derived from the α_s-plots [25]: total surface area (S_t^α) from slope of early linear section connecting to the origin, the non-microporous surface area (S_n^α) from slope of the linear section connecting points at $\alpha \geq 1.0$ and microporous volume (V_o^α) from intersection of later line with adsorption axis (V_a).

2.3. Equilibrium adsorption of methylene blue (MB)

A stock solution of MB (BDH) was prepared by dissolving 0.8 g in 1.0 L of distilled water; desired concentrations were obtained by dilution with distilled water. For adsorption

Table 1
Physico-chemical and porosity characteristics of activated carbons

Parameter	Sample					
	C1	C2	C3	C4	C5	C6
Yield (%)	42.6	42.6	41.8	43.5	43.8	40.0
Ash (%)	2.9	2.0	2.8	2.9	4.0	2.5
pH	4.3	5.0	4.6	5.2	4.2	3.5
S_{BET} (m^2/g)	1153	1123	1393	1298	1153	1184
S_t^α (m^2/g)	1204	1120	1407	1249	1159	1249
S_n^α (m^2/g)	17	33	55	156	62	39
V_P (ml/g)	0.576	0.596	0.689	0.828	0.572	0.587
V_o^α (ml/g)	0.551	0.566	0.634	0.645	0.498	0.538
r_P (Å)	10.0	10.6	9.9	12.8	9.9	9.9

experiments, 0.1 g of the powdered pre-dried carbon was mixed with 100 ml of increased concentrations (80–800 mg/L). The stoppered glass bottles were agitated occasionally in a shaker for 72 h at ambient, to attain equilibrium. Supernatant solution was filtered and analyzed spectrophotometrically at 664 nm by the help of a Shimadzu UV–Vis spectrophotometer (Type UV-2401 PC). Adsorbed dye in mg/g was calculated from the mass balance equation: $q_e = (C_i - C_e)\ V/m$, where C_i and C_e are the initial and equilibrium dye concentrations, V is the volume of liquid phase and m, mass of adsorbent.

Obtained adsorption isotherm data were plotted in the linear Langmuir-isotherm model [26]

$$\frac{C_e}{q_e} = (1/q_o)K_L + (1/q_o)C_e$$

where q_o is the monolayer capacity (mg/g) and K_L (L^{-1}) is a constant related to the free energy of adsorption ($K_L \alpha\ e^{-\Delta G/RT}$) [27]. An essential characteristic of a Langmuir model can be expressed in a dimensionless constant termed as separation factor, R_L, which is defined as [28], $R_L = 1/(1 + K_L C_o)$, where K_L is the Langmuir constant and C_o highest initial solute concentration. A value of $0 < R_L < 1$ indicates a favorable isotherm adsorbate/adsorbent.

2.4. Fixed-bed (dynamic) adsorption of MB

For this purpose a mini-column was employed (8 mm in diameter and length of 20 cm), packed with a layer of washed sand, 1.0 g activated carbon (size of 0.5–1.5 mm) with bed height around 20 mm, and another layer of sand. Flow rate of dye was adjusted to 2 ml/min throughout the experiments. Effluent concentrations of MB were monitored by measuring their absorbance at 664 nm, using the same spectrophotometer. Successive measurements were estimated (C_t) until maximum color dye intensity is reached ($C_t/C_i \geq 0.8$). Breakthrough curves were constructed as C_t/C_i vs. treated volume. A standard initial dye concentration of $C_i = 100$ mg/L was maintained,

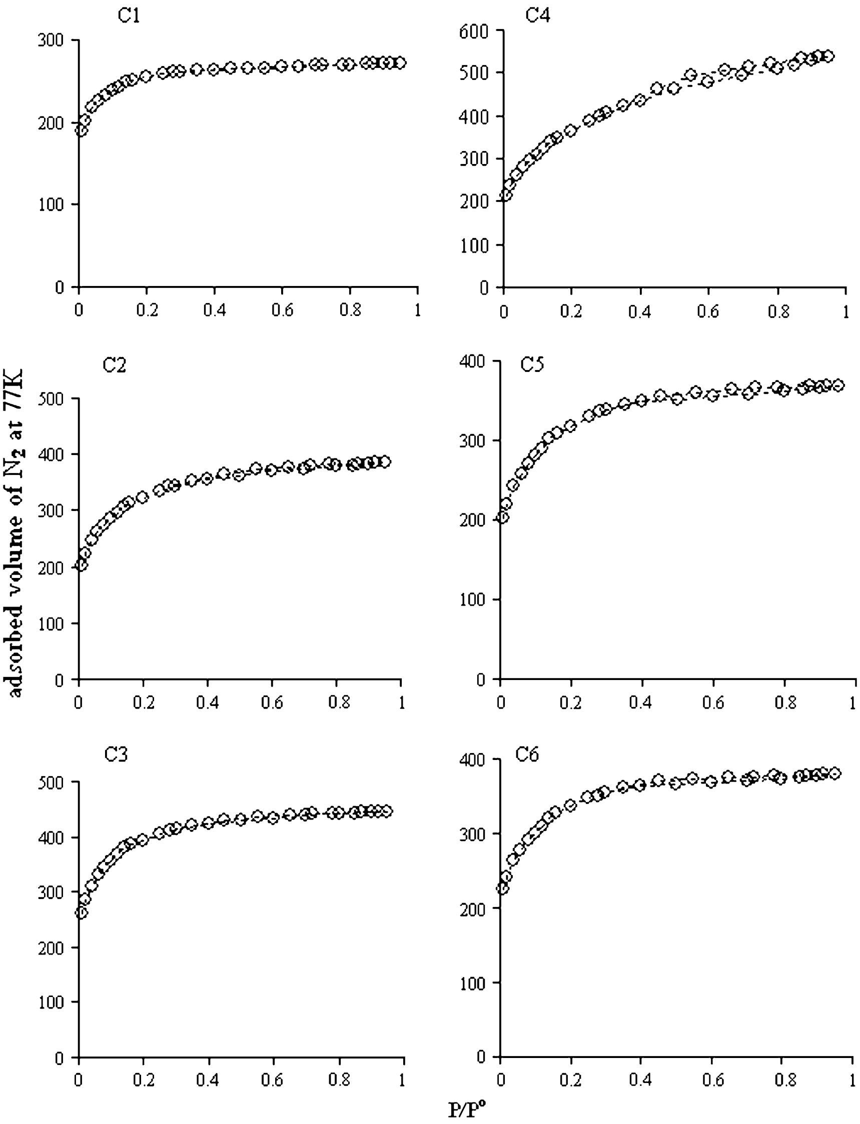

Fig. 1. Adsorption isotherms of N_2/77 K activated carbons at 500 °C.

however, for two experiments it was raised to 150 and 200 mg/L to demonstrate its effect on the breakthrough curves.

Several bed characteristics were determined for each column: (1) volume of effluent treated at different stages (at breakthrough, V_B, at 0.5 and 0.9 loading, $V_{0.5}$ and $V_{0.9}$ (taken as exhaustion points)); (2) amounts of dye adsorbed at the previous stages, X_B, $X_{0.5}$ and $X_{0.9}$; (3) time to reach breakthrough (T_B) and exhaustion (T_{ex}); (4) bed service time (BST, at an effluent rate of 50%); and (5) height of mass transfer zone (H_{MTZ} = (length of adsorbent bed × time to exhaustion)/(time to attain $C_i/2$)) [29–31].

3. Results and discussion

3.1. Characteristics of activated carbons

The obtained N_2/77 K isotherms and their corresponding α_s-plots are shown in Figs. 1 and 2, respectively. Chemical activation of peach stones with H_3PO_4 produces high carbon yields (41.8–43.8% of raw material), and low ash content (2.0–4.0%) and acidic in nature (pH = 4.0–5.0). Extra thermal treatment at 800 °C is accompanied by a negligible weight loss (1.8%) and small increase in acidity; from pH 4.6 to 3.5.

Carbons developed at 500 °C by activation with H_3PO_4 are good adsorbents with developed porosity, where their S_{BET} and V_P are enhanced by acid concentration (or impregnation ratio). Total surface area estimates (S_{BET} and S_t^{α}) are generally concordant with small differences, indicating that the BET-equation is still reliable for estimating the surface area of microporous solids. The present carbons exhibit high degree of microporosity as indicated by their content of microporosity ($V_o^{\alpha}/V_P \geq 80\%$) and low mesoporosity ($S_n^{\alpha}/S_t^{\alpha} = 1.5–12.5\%$). A 70% H_3PO_4-impregnation (C4) increases considerably the pore volume with small reduction in surface area, as compared with the previous 50% H_3PO_4 – carbon (C3). This treatment actually promotes

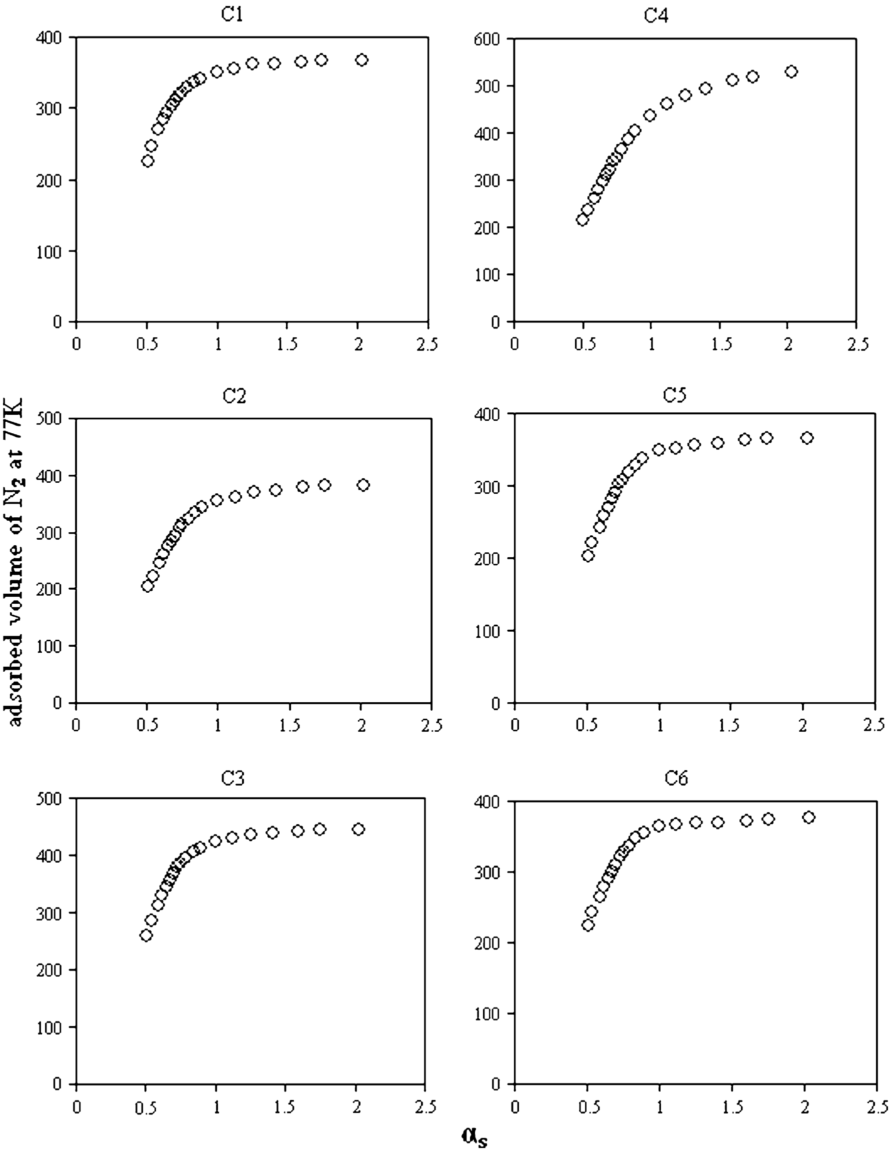

Fig. 2. α_s-Plots for activated carbons prepared at 500 °C.

mesoporosity which constitute around 20% of total porosity (as S_n^α or $V_{\rm meso}^\alpha$), and consequently enhances the average pore dimension (r_P). Passing nitrogen during pyrolysis (C5) reduces partially the internal porosity (both $S_{\rm BET}$ and V_P). Post-heating of C3 to get C6 is associated (probably) with shrinkage or collapse in micropores, as revealed by reduction in the internal porosity (surface area or pore volume). Generally, all carbons are microporous with mean average pore radii of 10 Å, only slightly widened under action of the highest impregnant concentration.

3.2. Equilibrium adsorption of methylene blue (MB)

Application of the Langmuir model to the adsorption isotherms (Fig. 3) provided satisfactory linearization of the data. The estimated parameters q_o, K_L, ΔG and R_L are shown in Table 2. Adopting the value of 120 nm^2 for the molecular area of MB [2], estimates for the areas occupied by the adsorbed MB are calculated ($S_{\rm MB}$) and the fractions covered by MB compared to the BET-surface areas are determined ($S_{\rm MB}/S_{\rm BET}$) as cited in Table 2.

Raising the impregnation ratio (or %H_3PO_4) improves the adsorption capacity, from 198 to 412 mg/g, which means an increase in accessible sites suitable for the accommodation of the dye molecules (i.e. with dimensions ≥15 Å). A parallel similar increase in accessible fraction of surface area is also evident (from 39 to 72%). Thus, raised amounts of the impregnant incorporated inside the precursor favor the pore development with generation of relatively wide micropores suitable for uptake of the bulky dye molecules. It should be reminded that MB molecules are bulky with a large cross-sectional area which is almost 7-fold that of a nitrogen

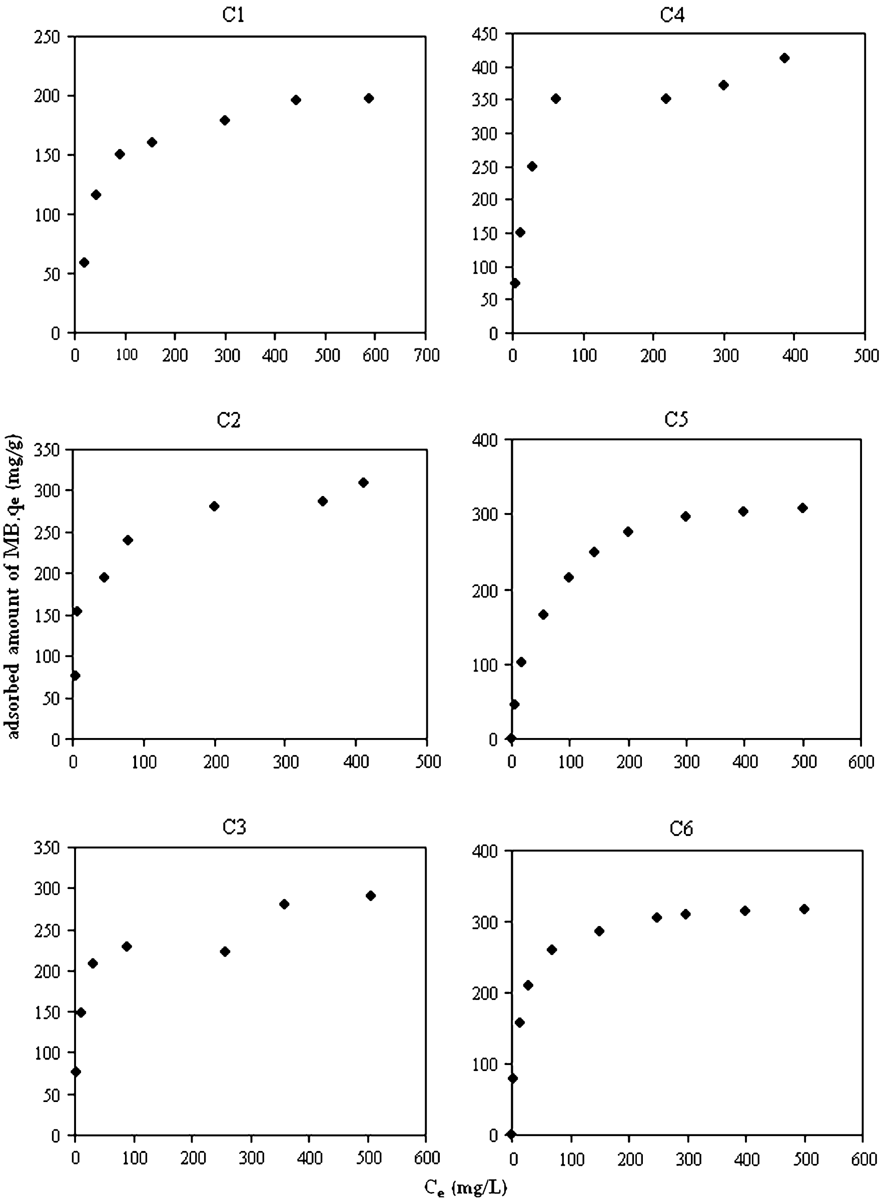

Fig. 3. Adsorption isotherms of MB onto activated carbons prepared at 500 °C.

Table 2
Equilibrium adsorption of methylene blue onto tested activated carbons

Parameter	Sample					
	C1	C2	C3	C4	C5	C6
q_o (mg/g)	198	309	362	412	306	316
K_L (L^{-1})	0.032	0.032	0.046	0.017	0.082	0.079
ΔG_a (kJ/mol)	−23.0	−23.0	−23.9	−21.4	−25.4	−25.3
R_L	0.037	0.037	0.026	0.068	0.015	0.016
$S_{MB}/S_{BET} \times 100$	39	62	59	72	60	60

molecule. A high surface area carbon ($C4 = 1300\ m^2/g$) exhibits, meanwhile, a high uptake of the moderate size organic molecule (MB) from aqueous medium attaining a value of 412 mg/g. In general, developed carbons exhibit a favorable solute/sorbent adsorption process ($R_L \ll 1.0$), with adsorption free energy around 21–25 kJ/mol, indicating a typical physical adsorption process.

Modification of C3 by either flowing nitrogen during pyrolysis or post-heat treated degrades its dye removal capacity (from 362 to 310 mg/g). Forcing nitrogen during thermal decomposition at 500 °C (C5) is thus not recommended as it reduces both the internal porosity and dye removal capacity by around 20%. Post-heat treatment of C3 at 800 °C (C6) is not accompanied by a large collapse or shrinkage of the carbon particles. Around 20% loss in either S_{BET} or q_o indicates that peach stone carbon (derived at 500 °C by 50% phosphoric acid) is thermally stable due to its physically inherited natural hardness. Occasionally, thermal regeneration of this carbon is anticipated to recover its original adsorption capacity with small quality degradation.

3.3. Fixed-bed adsorption studies

In the dynamic adsorption studies, the adsorbent (activated carbon) is loaded in columns which form a bed through which the aqueous solution of the adsorbate is passed. During its passage through the bed, the solution continuously meets a fresh part of the adsorbent and tends to establish a new equilibrium. However, as the time of contact with a given part of the adsorbent is limited, a true equilibrium is never attained [2]. As solution is passed continuously, the adsorption zone moves downwards, and at a time T_B, the adsorption zone has just reached the bottom of the bed and concentration has suddenly risen to an appreciable value for the first time. The system is said to have reached the breakpoint (BT), usually taken at $C_t/C_i = 0.02–0.05$ (in our case it is considered at 0.05) [32]. The solute concentration in the effluent now rises rapidly as the adsorption zone passes through the bottom of the bed until it eventually reaches the initial concentration ($C_t/C_i = 1.0$). In the latter stages ($C_t/C_i \geq 0.9$), little adsorption takes place since the bed is for all practical purposes entirely in equilibrium with the feed solution. The shape and time of appearance of the breakthrough curve greatly influence the method of operating a fixed-bed adsorbent. The curves generally have an S-shape but they may be steep or relatively flat and in some cases considerably distorted.

As clear from the obtained BT-curves (Figs. 4 and 5), S-shaped forms are exhibited but with different degrees and trends. Several bed characteristics are given in Table 3, as already described. The amounts of sorbate per unit weight of sorbent (X, mg/g) were calculated by [32].

$$X = \frac{\left(t_e - \int_{t_b}^{t_e} f(t)\,dt\right) Q C_o}{W}$$

where Q, C_o and W represent volumetric flow rate (ml/min), influent concentration (mg/L) and weight of sorbent applied (g); $t_e - \int_{t_b}^{t_e} f(t)\,dt$ represents the area under the BT-curve which can be estimated through integration; $f(t)$, t_b and t_e are the function representing effluent profile, time to breakthrough (t_b) and

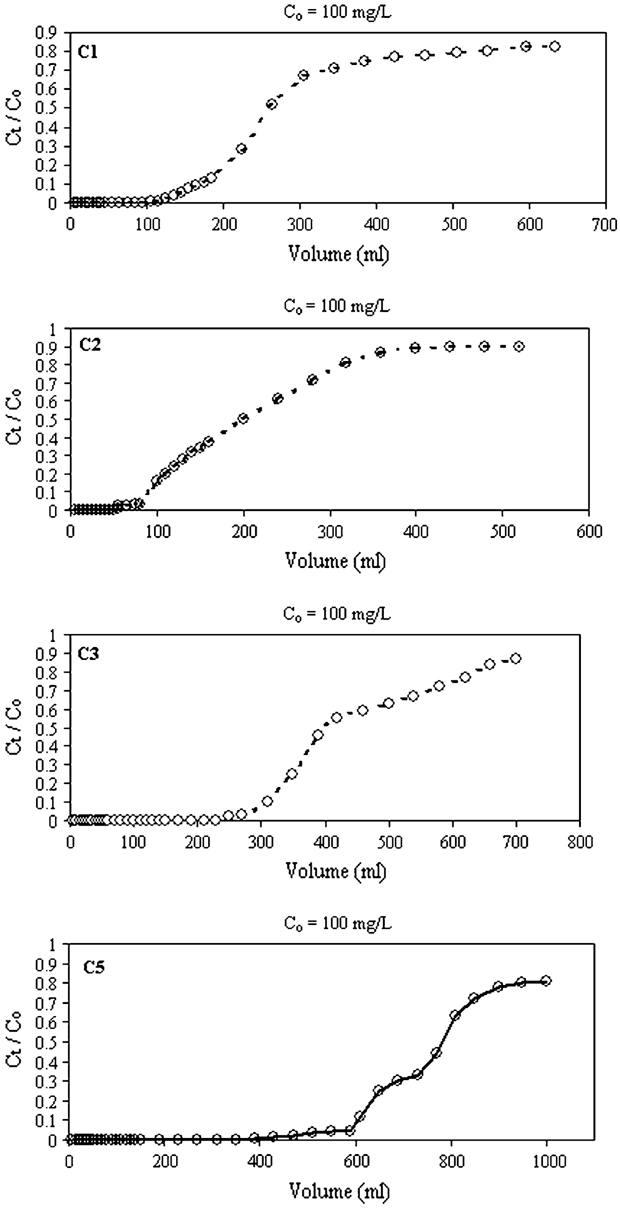

Fig. 4. Breakthrough curve of column removal of MB ($C_o = 100$ mg/L) onto activated carbons prepared at 500 °C.

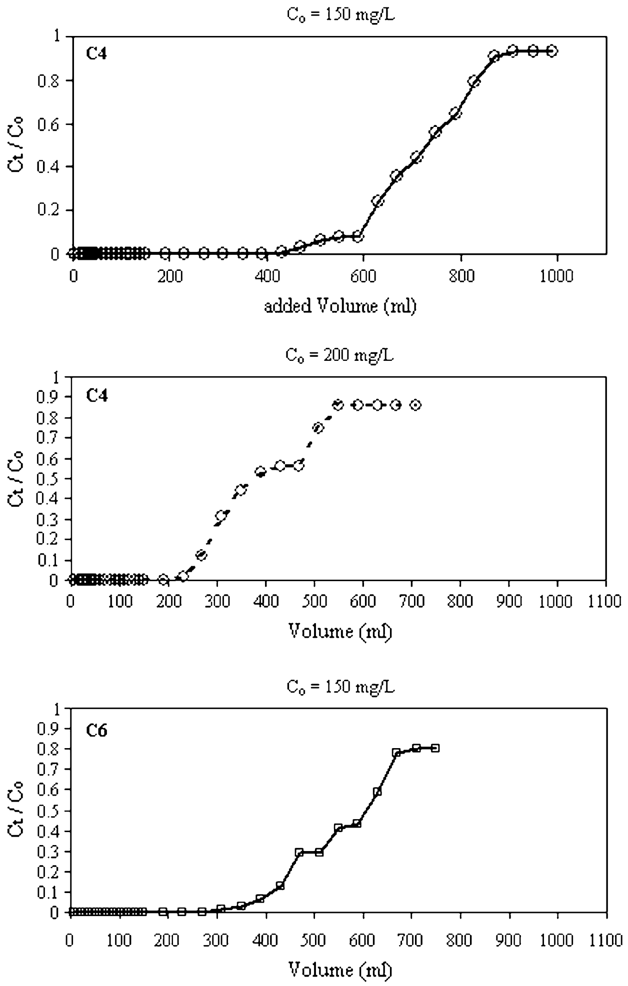

Fig. 5. Breakthrough curve of column removal of MB ($C_o = 150$ and 200 mg/L) onto activated carbons prepared at 500 °C.

time at exhaustion (t_e). Treatment of the present data to estimate the amount of dye adsorbed per unit weight of AC, was obtained by graphical integration to definite fractional loading values of BT, 0.5 and 0.9 (or sometimes to 0.8). As column exhaustion was not reached under tested conditions, the maximum (or exhaustion) value was taken at $C_t/C_o = 0.9$ or 0.8, although the column bed was still uptaking dye amounting to 10–20% of feed concentration at a very slow rate.

Upon considering the increased impregnant concentration (from 30 through 70%), there is a clear trend of improved performance as evident from all the bed characteristics (Table 3). Thus, there is a one direction increase in volumes treated, weights uptaken, duration to reach specific loadings, in addition to the BST, and decrease in H_{MTZ}. The 40%-treated carbon (C2) presents an odd exceptional case such that we represent the order of efficiency of dynamic dye removal as C4 > C3 > C1 > C2, where C4 exhibited no features of breakthrough under the experimental tested conditions of $C_o = 100$ mg/L. Such a trend could be associated with relative increase in wide microporosity as noticed from Table 1.

The modified carbons (C5 and 6) indicate an improved column performance in comparison to the standard C3-carbon ($V_{0.9}$, $X_{0.9}$, t_{ex}, BST, H_{MTZ}). It is noticeable that C6 (post-heat treated at 800 °C) is equivalent to C4, in treating 1000 ml of the 100 mg/g dye flow with no appearance of any breakthrough. Enhanced performance in this case cannot be related to any apparent porosity features but probably due to the formation of surface favorable sites for the uptake of the dye molecules. Such a small modification in the preparation conditions appears, thus, to be advantageous for producing a better adsorbent in fixed-bed treatments. It is remarkable that these carbons (C5 and C6) have already exhibited lower uptake capacity under the time-extended equilibrium conditions than C3 (Table 3).

Upon raising the influent concentration to $C_o = 150$ and 200 mg/L, in case of C4, it is noticeable that this carbon performs good removal of the dye solution with still typically S-shaped BT-curves. However, due to the high color loading (150–200 ppm), fast flow (short contact time) and the relatively small amount of adsorbent, the column performance becomes lower. For example, volume treated around exhaustion decreases from 1000 to 950 and then to 585 ml, amounts

Table 3
Fixed-bed performance in the uptake of methylene blue (MB) at $C_o = 100$, 150 and 200 mg/L

Parameters	$C_o = 100$ mg/L				$C_o = 150$ mg/L		$C_o = 200$ mg/L
	C1	C2	C3	C5	C4	C6	C4
V_{BT} (ml)	150	85	275	545	525	390	242
$V_{0.5}$ (ml)	260	210	390	770	725	365	358
$V_{0.9}$ (ml)	720	405	680	970	950	720	585
X_{BT} (mg/g)	14.8	8.5	28.3	46.9	71.8	58.2	48.1
$X_{0.5}$ (mg/g)	23.4	16.7	36.6	61.5	91.6	76.9	63.2
$X_{0.9}$ (mg/g)	28.1	19.8	44.4	63.7	95.0	85.0	71.3
BT (min)	75	43	138	275	265	195	121
BST (min)	130	103	203	365	365	285	285
H_{MTZ} (cm)	5.36	5.07	3.50	2.70	2.50	2.40	2.40
Vol_{ex} (ml)	720	405	680	970	950	720	585
T_{ex} (min)	360	202	340	485	475	358	292
$\frac{X_{Column}\ (6\ h)}{X_{eqm.}\ (72\ h)}$	0.142	0.064	0.122	0.208	0.230	0.269	0.173

removed from >100 to 95, and then to 71 mg/g, and time for exhaustion reduced from >500 to 475, and then to 292 min (at $C_o = 100$, 150 and 200 ppm, respectively). Nevertheless, this specific carbon still exhibits better performance properties than C3; higher dye loading at 150 mg/L and even at 200 mg/L.

4. Conclusions

Activated carbons derived from peach stone shells under chemical activation with H_3PO_4 at 500 °C proved to be good-quality adsorbent carbons. Increased impregnant concentration enhanced, generally the porosity characteristics to high values of surface area, around 1400 m^2/g, and pore volume up to 0.83 ml/g. Excellent adsorption capacity for methylene blue (MB) appears, under equilibrium conditions, attaining values of ≥ 400 mg/g associated with the texture properties. Fixed-bed treatment, in a mini-column, of dye solution at a loading of 100 mg/L proved promoted performance with raised activant concentration to 70% H_3PO_4. This latter carbon exhibited good color removal capacity at higher feed concentration, although to lower extent due to the limited adsorbent mass, and short contact time at the relatively fast solution rate. A carbon obtained by 50% H_3PO_4 was modified by either flowing N_2 during pyrolysis or subjecting to extra-heat treatment at 800 °C. Both factors appreciably degraded carbon porosity and equilibrium uptake of MB, although column removal was enhanced which might recommend these techniques for applications involving fixed-bed operations.

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