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Methylene blue number as useful indicator to evaluate the adsorptive capacity of granular activated carbon in batch mode: Influence of adsorbate/adsorbent mass ratio and particle size

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ABSTRACT

The adsorption of methylene blue (MB) on three commercial granular activated carbons (GACs), 12 × 40 mesh size, namely Filtrasorb 400, Norit and Picacarb has been researched. A comparative study of adsorptive capacity using the proposed single-point test and the traditional multi-point isotherm test was carried out. For the single-point test, the influence of some parameters such as MB/GACs mass ratio and contact time were evaluated. For this test the adsorptive capacities of the three GACs studied were 319 ± 14, 280 ± 7 and 260 ± 6 mg g^{-1} for Filtrasorb 400, Norit and Picacarb, respectively. For multi-point isotherm adsorption test the Langmuir model was used. The parameters involved were obtained by linear and non-linear regression methods. The maximum adsorptive capacity values obtained for both methods were similar and statistically not different than those obtained with the single-point tests. This experimental work also aimed at establishing a relationship between the adsorbent particle size and the adsorptive capacity which could be used complementarily to evaluate the quality of GACs as adsorbents. For a mean particle diameter of 1 mm and after 24 h of contact time the adsorptive capacity values were 255 ± 7, 222 ± 7 and 160 ± 7 mg g^{-1} for Filtrasorb 400, Norit and Picacarb, respectively.

1. Introduction

Most parameters that characterize an activated carbon are standardized by different organizations worldwide such as the American Society for Testing and Materials (ASTM), the American Water Works Association (AWWA), the Food and Drug Administration (FDA) codex in the USA, the Japanese Industrial Standards (JIS) in Japan, and the European Council of Chemical Manufacturers Federation (CEFIC) in Europe. Activated carbon products can be characterized by physical and activity properties. Both kinds of properties become important factors in the specification of commercial carbons. Important physical properties are surface area, density, mesh size, abrasion resistance and ash content. Activity characterizations are key indicators of a carbon's potential performance for removing contaminants from water. Inexpensive tests have been used to approximate the distribution of pores available for a carbon. These tests include the adsorption of a single standard reference adsorbate, and help to distinguish activity characteristics in different carbons. The most common standard parameters for measuring carbon adsorptive capacity are: iodine number (ASTM D4607), which defines the small pore (<2 nm) of an activated carbon and therefore reflects its ability to adsorb small substances, and the molasses number, which defines the large pore (>50 nm) and is used as a relative guideline for measuring the capacity of an activated carbon for larger molecules. Another indicator of the adsorptive capacity of activated carbon is the methylene blue number (MB_N). This parameter is related to the macro- and mesopore capacity of activated carbon [1]. Unfortunately, there is no standardized testing procedure to assess or compare the adsorptive capacity of granular activated carbons (GACs), although two general methods are described in the literature. The first one, which is the Chemviron Carbon Company method [2], involves adding a measured amount of activated carbon to a standard MB solution and is defined as the mg of dye adsorbed by one gram of carbon in equilibrium with a solution of MB with a concentration of 1 mg L^{-1}. The second one is the CEFIC method [3], and it involves the addition of a standard MB solution to a sample of activated carbon until no further discoloration occurs. The result is reported as mL g^{-1}. On the other hand, a lot of the research reported in the literature in which the amount of MB removed from aqueous solution by unit of mass of activated carbon was obtained by using the traditional multi-point isotherm adsorption tests and applying the Langmuir model to fit the experimental data [4–6].

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The present experimental work also includes the use of raw adsorbent material to evaluate how the adsorbent particle size influences the adsorptive capacity of GACs, with the purpose of establishing a relationship between them.

Therefore, the aims of this paper were: (i) to evaluate the adsorption behaviour of MB onto GAC, suggesting general rules for studying some of the experimental parameters that influence the determination, (ii) to compare the results of the adsorptive capacity obtained with the proposed single-point method with the traditional multi-points Langmuir isotherm, (iii) to evaluate the real adsorptive capacity of GACs in batch mode.

For this purpose, the experimental work includes a comparative study of three 12 × 40 mesh size GACs, one of the most popular aqueous phase carbons used for the treatment of drinking water, because they have a good balance between size, surface area and headloss characteristics.

2. Materials and methods

2.1. Adsorbate = MB

MB is a synthetic cationic thiazine dye of an amorphous nature with a molecular formula $C_{16}H_{18}ClN_3S{\cdot}xH_2O$. It is also called basic blue 9, tetramethylthionine chloride and colour index (CI) number 52015. It is a dark green powder, with a characteristic deep blue colour in aqueous solution where it dissociates into an MB cation and a chloride anion. The MB dehydrated properties are: molecular weight (320 g mol^{-1}), width (14.3 Å), depth (6.1 Å), thickness (4 Å), molecular volume (241.9 cm^3 mol^{-1}) and molecular diameter 0.8 nm [7].

The reagent MB used was analytical grade and supplied by Panreac (Spain). The certificate analysis showed that it loses 14.4% in weight after heating for 2 h at 110 °C, the dehydrated dye pure content being 94.5%. Due to the fact that MB is heat sensitive (it smells bad and is foam-forming in water solution), the use of the hydrated dye is recommended as is the correction for water and pure content to prepare the stock solution of 2000 mg L^{-1}. All the MB solutions used in the study were prepared by the dilution of the above-mentioned solution with distilled water.

2.2. Adsorbents = GACs

The three different commercial GACs 12 × 40 mesh size used in this study to determine the MB_N were Filtrasorb 400 (F_{GAC}), Norit (N_{GAC}) and Picacarb (P_{GAC}). They were supplied by Calgon Corporation, Fluka and Picacarbon, respectively.

The mean particle diameter (MPD) of the three GACs used was 1.0 mm. This value was checked by experimental determinations from the average sieve opening and the amount of carbon passing through each one [8]. For this purpose a mechanical sieve shaker (Retsch AS 200 basic, Germany) and a set of sieves E11 ASTM specification (Neward, USA) with 1.8, 1.4, 1.0, 0.710, 0.500 and 0.355 mm of particle size were used to screen the GACs. To determine the real adsorptive capacity in batch mode, the different fractions and corresponding mean particle diameter used were: F I (1.6 mm), F II (1.2 mm), F III (0.855 mm), F IV (0.605 mm) and F V (0.428 mm). In all the experiments, the moisture of GACs was previously removed by drying the adsorbent material at 150 °C for 1 h. For the rest of determinations the GACs were ground and sieved to obtain a fraction lower than 66 μm. This uniform fraction was used as a reference particle size in powdered adsorption tests.

2.3. Batch adsorption experiments

A lot of research has been previously carried out on the adsorptive capacity of MB on different adsorbents, including novel materials [9,10]. The main experimental variables that influenced the process should be divided into three groups: (1) MB solution: pH, concentration and volume; (2) adsorbent: dose and particle size; (3) others: contact time and temperature. The possible combinations of variables are innumerable, with the consequent lack of a MB_N understood worldwide. Pavan et al. [11] used a factorial design to determine which factors have important effects on a response as well as how the effect of one factor varies with the level of the

Table 1
Experimental conditions for the trial adsorption experiments carried out.

Run number	MB		GAC		MB/GAC	Time
	Volume (mL)	Concentration (mg L^{-1})	Weight (mg)	Size (μm)	Mass ratio (mg MB/mg GAC)	(min)
I. Single-point isotherm studies						
1	50	1000	100	<66	0.5	5–180
2	100	500	100	<66	0.5	5–180
3	200	250	100	<66	0.5	5–180
4	50	1500	100	<66	0.75	5–180
5	100	750	100	<66	0.75	5–180
6	200	375	100	<66	0.75	5–180
7	50	2000	100	<66	1.0	5–180
8	100	1000	100	<66	1.0	5–180
9	200	500	100	<66	1.0	5–180
II. Multi-point isotherm studies						
1	100	200	100	<66	0.20	30
2	100	250	100	<66	0.25	30
3	100	300	100	<66	0.30	30
4	100	350	100	<66	0.35	30
5	100	400	100	<66	0.40	30
6	100	500	100	<66	0.50	30
III. Influence of particle size studies						
1	100	500	100	1800–1400	0.5	60–2880
2	100	500	100	1400–1000	0.5	60–2880
3	100	500	100	1000–710	0.5	60–2880
4	100	500	100	710–500	0.5	60–2880
5	100	500	100	500–355	0.5	60–2880

other factors. Unfortunately, the number of experiments necessary to carry out the earlier study made the implantation difficult as a routine for this analytical determination. In the present research the only premise was to easily obtain a value of MB_N that could be used as a tool to evaluate the adsorptive capacity of GAC. For this reason, the tests were carried out at the original pH solution, without any adjustment. Table 1 summarizes the experimental conditions for the different tests performed.

For each experiment three independent adsorption tests were run and the final results expressed as mean values. The adsorbent was introduced into an Erlenmeyer flask of 250 mL working volume. The dye solution was added and the content of the flask was mixed at 300 rpm with a magnetic bar using a multi-stirrer system (SBS 9001, Spain). The tests were performed at a constant temperature of $25 \pm 2^{\circ}$C by means of a thermostatically regulated bath. Two main parameters were evaluated:

1. Methylene blue number (MB_N), defined as the maximum amount of dye adsorbed by 1 g of adsorbent. Therefore, it is the concentration of dye in the solid phase. It is also described in the literature as q. This value was obtained using the following equation:

$$MB_N\,(\mathrm{mg\,g^{-1}}) = \frac{(C_o - C_e) \times V}{M} \quad (1)$$

2. Methylene blue removal (MB_R), defined as the percentage of initial concentration removed. This value was obtained using the following equation:

$$MB_R\,(\%) = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

where C_o ($\mathrm{mg\,L^{-1}}$) is the concentration in the MB solution at time $t = 0$, C_e ($\mathrm{mg\,L^{-1}}$) is the concentration in the MB solution at equilibrium time, V (L) is the volume of solution treated, and M (g) is the amount of adsorbent added.

Taking into account that one of the aims of the research was to obtain the MB_N of GACs with a single-point batch test, this parameter must always be jointly analyzed with MB_R, and when a high value in the range of 90%–100% is obtained, a new attempt with an increased dosage of dye must be carried out. Ozer et al. [12] showed the evolution of both parameters in the study of the effect of initial MB concentration on temperature dependent adsorption using dehydrated peanut hull as adsorbent.

2.3.1. Single-point isotherm adsorption studies

The capacity of an adsorbent for a particular adsorbate in liquid system involves the interaction among three properties: the concentration of the adsorbate in the liquid phase, the concentration of the adsorbate in the solid phase and the temperature of the system. If the temperature is kept constant, an adsorption isotherm is obtained, which shows the relationship between the concentration in the liquid and the solid phases [13].

In the present study two parameters, such as MB/GAC mass ratio and contact time were evaluated to find out their effect on the adsorption of MB onto GACs. For these tests a constant weight of 100 ± 2 mg of GACs (with a particle size under 66 μm) was used as adsorbent. The experiments were programmed to evaluate the influence of three MB/GAC mass ratios (0.5, 0.75 and 1.0) which were given by different MB solution volumes (50, 100 and 200 mL) and concentrations (ranging from 250 to 2000 $\mathrm{mg\,L^{-1}}$). Samples were taken at predetermined contact time intervals of 5, 15, 30, 45, 60, 120 and 180 min (Table 1-I).

2.3.2. Multi-points isotherm adsorption studies

An adsorption isotherm is characterized by certain constants whose values express the surface properties and affinity of the adsorbent. The Langmuir isotherm is the best known and most frequently used equation applied for the adsorption of a solute from a liquid solution and has been used to evaluate the adsorptive capacity of many adsorbents [14,15]. This model can be described by the following equation:

$$q_e = \frac{q_{max} \cdot b \cdot C_e}{1 + b \cdot C_e} \quad (3)$$

where q_e ($\mathrm{mg\,g^{-1}}$) is the solid phase equilibrium concentration, q_{max} ($\mathrm{mg\,g^{-1}}$) is the Langmuir maximum monolayer adsorptive capacity, C_e ($\mathrm{mg\,L^{-1}}$) is the liquid phase equilibrium concentration and b ($\mathrm{L\,mg^{-1}}$) is the Langmuir equilibrium constant (ratio of adsorption/desorption rates and related to the energy of adsorption or affinity of the binding sites).

There are different possibilities for the linearization of the Langmuir model; the two most used are given by the following equations:

- According to Stumm and Morgan [16]:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{q_{max} \cdot b \cdot C_e} \quad (4)$$

- According to Weber [17]:

$$\frac{C_e}{q_e} = \frac{1}{b \cdot q_{max}} + \frac{C_e}{q_{max}} \quad (5)$$

Eq. (5) is the most frequently used to estimate the Langmuir maximum adsorptive capacity and Langmuir constant of adsorbents due to their better goodness-of-fit [18]. When C_e/q_e is plotted against C_e, a straight line with slope $1/q_{max}$ and intercept $1/b{\cdot}q_{max}$ are obtained when adsorption follows the proposed model.

The favourable nature of adsorption can be expressed in terms of the dimensionless separation factor of the equilibrium parameter, which is defined by [19]:

$$R_L = \frac{1}{1 + b \cdot C_o} \quad (6)$$

The value of R_L indicates the type of isotherm: irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$).

For these studies, the experimental conditions selected were 100 mL of MB solution volume, a contact time of 30 min, a temperature of 25 °C and the same weight and particle size of GACs as in previous experiments. These experimental conditions were selected with the aim of obtaining values comparable with those obtained in the single-point experiment. Therefore, in these batch tests the isotherm parameters were obtained varying the initial dye concentration from 200 to 500 $\mathrm{mg\,L^{-1}}$ (Table 1-II) in order to cover a broad range of MB/GAC ratios.

2.3.3. Real adsorptive capacity studies

Although most literature related to MB has focused on static equilibrium, the real adsorptive capacity of a GAC should only be obtained by dynamic operation testing such as fixed-bed column, where the concentration of adsorbate never reaches equilibrium because dye is constantly entering the column [20]. Further research of the batch mode to look for a relationship between MB_N and the adsorbent particle size was also carried out. In this way, the preliminary results obtained in the batch mode could be used as a basis for establishing the column design and operational parameters in continuous mode.

Table 2
Variation of MB_N and MB_R with the increased values of different experimental variables that influenced the adsorption process.

	MB solution		GAC adsorbent		System conditions	
	pH	Dose	Dose	Particle size	Temperature	Time
MB_N	+	+	–	–	+	+
MB_R	+	–	+	–	+	+

(+): Increase; (–): Decrease.

For these studies, the GACs were sieved into five fractions with the desired mean particle diameter. The MB solution volume, adsorbent mass and MB/GAC mass ratio used were 100 mL, 0.1 g and 0.5 mg MB/mg GAC, respectively. Samples were taken at predetermined contact time intervals of 1, 5, 10, 24, 30 and 48 h (Table 1-III).

2.4. Dye analysis

A volume of 1.0 mL of sample was pipetted out from mixed flasks at predetermined time intervals. The collected samples were centrifuged for 10 min at 10,000 rpm, using a centrifuge (Eppendorf Minispin, Germany) and the MB residual from the supernatant solutions was measured by a Vis Spectrofotometer (Spectronic 20 Genesis, USA) at a maximum wavelength of 665 nm. Previously, the relationship between the concentration of MB and the absorbance was determined using a 7-point calibration curve in the range of 0–5 mg MB L^{-1}. Replication measurements of the calibration curve performed over short (days) and long periods (months) from the same initial stock solution yielded perfectly coincident data. The dye concentrations for unknown samples were determined from the calibration curve, using the absorbance values. Samples were diluted with distilled water if absorbance values exceeded 1500 units of optical density. The MB adsorption on the glassware was negligible.

2.5. Statistical analysis

The replicate values of absorbance obtained for each assay were related to the concentration of MB by a calibration curve. Therefore, the uncertainties of concentration were calculated by linear estimation as proposed by Miller and Miller [21], and these values were used to calculate the uncertainties in MB_N and MB_R.

For linear regression, the method of least squares has been used to find the uncertainties and parameters of the models applied. For the non-linear regression method, the solver add-in function of Microsoft Excel was used to obtain the isotherm parameters by minimizing the error distributions between theoretical and experimental data.

3. Results and discussion

The literature includes plenty of research where the influence of some experimental parameters in the adsorption tests has been studied. To understand their influence, it is important to know that the general mechanism of colour removal from effluent involved four steps: (i) migration of dye molecules from the bulk solution to the surface of the adsorbent; (ii) diffusion of dye through the boundary layer to the surface of the adsorbent; (iii) intra-particle diffusion of dye into the interior pores of the adsorbent; (iv) adsorption. Table 2 summarizes the expected trends of MB_N and MB_R with the increase value of the main experimental parameters, the detailed explanation being as follows:

(i) MB solution pH: it is to be expected that MB_N and MB_R will increment with the increase in the initial pH. The results can be explained by the electrostatic interaction of dye cationic species with the negatively charged adsorbent surface at basic pH values.

(ii) MB dose: the increase in MB solution volume or initial concentration decreased MB_R, and increased MB_N until a plateau is achieved. This trend is expected due to the increase in the driving force by the gradient of concentration. Therefore, when no adsorbent sites are available, the increase in dye concentration does not affect the process.

(iii) GAC dose: the increase in adsorbent dose decreased the MB_N but increased the MB_R. The increase of MB_R can be attributed to an increased carbon surface area and availability of more adsorption sites, resulting from the increased dose of GAC. On the other hand, the MB_N decreased with the increase in adsor-

Table 3
Results for MB_N and MB_R in the single-point experiments using Filtrasorb 400.

Run	MB/GAC	MB_N		MB_R	
	Mass ratio (mg MB/mg GAC)	Average (mg g^{-1})	SD (mg g^{-1})	Average (%)	SD (%)
1	0.5	315	8	64	2
2	0.5	323	29	65	6
3	0.5	308	19	62	4
4	0.75	323	4	43	1
5	0.75	315	14	42	1
6	0.75	312	6	42	1
7	1.0	326	4	33	1
8	1.0	316	8	32	1
9	1.0	333	8	34	1

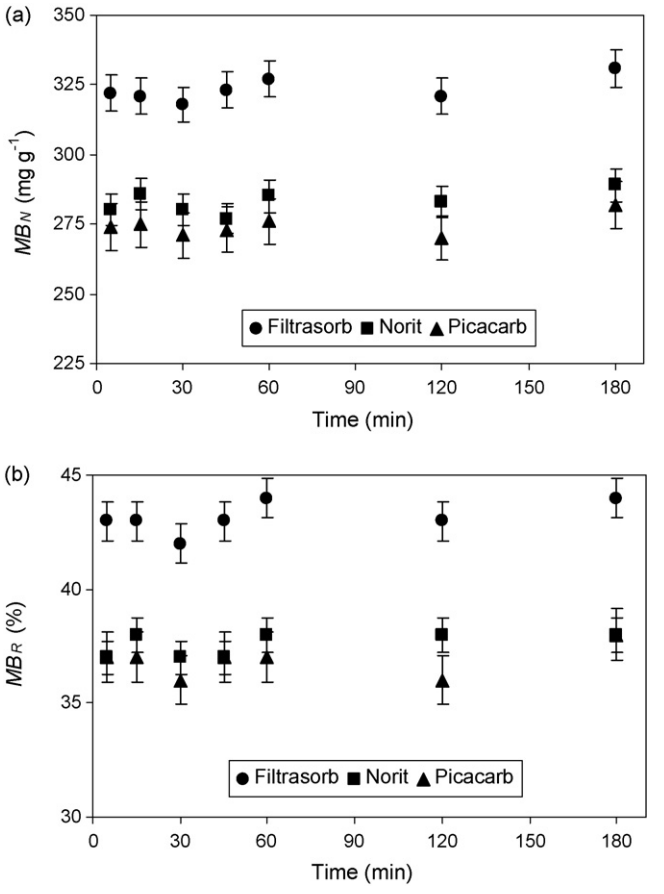

Fig. 1. Influence of contact time in (a) MB_N and (b) MB_R of the three GACs assayed. Experimental conditions: 0.75 mg MB/mg GAC; MB volume = 50 mL; MB concentration = 1500 mg L^{-1}.

bent dosage due to the split in the flux or the concentration gradient between solute concentrations in the solution and in the adsorbent surface [22].

(iv) GAC particle size: the MB_N and MB_R increase with the decrease in particle size of the adsorbent. When the particle size decreases, more surface area is available for the adsorption process.

(v) Temperature: the temperature has two major effects on the adsorption process. Firstly, it increases the rate of diffusion of the adsorbate molecules across the external boundary layer and secondly, it changes the equilibrium capacity of the adsorbent. The MB_N and MB_R increase by raising the temperature, indicating that the process is endothermic.

(vi) Contact time: the MB_N and MB_R increased with time until a constant value was achieved. Obviously, the adsorption phenomenon requires a certain contact time to complete the four steps previously described.

3.1. Single-point isotherm studies

The joint effect of volume and concentration of MB solution versus time was evaluated as a factor with a possible influence in the adsorption systems.

3.1.1. Influence of contact time

The effect of contact time on the amount of dye adsorbed was researched. As an example of all the tests performed, Fig. 1 shows the MB_N and MB_R evolution with the contact time for the three GACs assayed, for defined experimental conditions of 0.75 mg MB/mg GAC mass ratio and 50 mL MB solution volume. It was found that the removal of MB from aqueous solutions by adsorption onto GAC achieved the equilibrium state very quickly (5 min) for all the adsorbents and MB/GAC mass ratios studied. Therefore, taking into account the experimental conditions and the results obtained in the present study, the influence of contact time in the amount of MB removed is totally rejected. For this reason, the 7 points of MB_N and MB_R registered for each replica test of MB/GAC mass ratio assayed were processed as an average value. Tables 3–5 summarize the results obtained for F_{GAC}, N_{GAC} and P_{GAC}, respectively. A previous study with various powdered activated carbons showed a similar trend of a rapid increase in MB_N with contact time reaching a maximum and constant value thereafter [23].

3.1.2. Influence of MB/GAC mass ratio

The dose of MB is given by the volume and concentration of MB solution used. The influence of both parameters was studied.

3.1.2.1. MB solution volume (MB_{vol}). The MB_{vol} is a variable in the isotherm experiments, ranging in the literature from 30 to 1500 mL. So far no research has been reported regarding the effect of the MB volume as a factor in the adsorption experiments. They have been frequently focused on finding out the total amount and/or volume of dye treated by the adsorbent system [24]. In this study, the influence of MB_{vol} at fixed MB/GAC mass ratios was evaluated. Fig. 2 shows the values corresponding to MB_N and MB_R for the three GACs assayed to a mass ratio of 0.75 mg MB/mg GAC, although this trend was similar for all the MB/GAC mass ratios studied. As can be seen in Fig. 2, an increase in MB_{vol} had no repercussion in MB_N and MB_R, whose values were not significantly different for the three GACs assayed.

3.1.2.2. MB solution concentration (MB_{conc}). The increase in the initial MB solution concentration is the most commonly used system for carrying out isotherm adsorption studies. Fig. 3 shows the values corresponding to MB_N and MB_R for the three GACs assayed to a fixed MB_{vol} of 100 mL, although this trend was similar for all the volumes used. The results obtained for MB_R showed that the larger the concentration, the lower the MB_R; whereas for the MB_N, the initial dye concentration had no effect, reaching a constant value.

To sum up, the effects of MB_{vol}/GAC mass ratio and MB_{conc}/GAC mass ratio in the adsorption process were also negligible. The extensive experimental work carried out demonstrated that for experiments with an excess of dye (MB_R different of 100%), the single batch system proposed gives an extremely accurate MB_N, and it is independent of the experimental variables studied. For the three GACs studied the order of the adsorptive capacity was as follows: $F_{GAC} > N_{GAC} > P_{GAC}$; with average values of 319 ± 14, 280 ± 7, and $260 \pm 6\ mg\ g^{-1}$; and relative values of 100%, 88% and 81%, respectively.

3.2. Multi-point isotherm studies

Results obtained for each GAC, where the initial dye concentrations varied against residual adsorbate concentration in the equilibrium, were fit to the Langmuir isotherm model. The adsorption behaviour of MB onto GACs was evaluated using both linear and

Table 5
Results for MB_N and MB_R in the single-point experiments using Picacarb.

Run	MB/GAC	MB_N		MB_R	
	Mass ratio (mg MB/mg GAC)	Average ($mg\ g^{-1}$)	SD ($mg\ g^{-1}$)	Average (%)	SD (%)
1	0.5	270	3	56	1
2	0.5	269	9	54	2
3	0.5	263	4	52	1
4	0.75	264	4	37	1
5	0.75	254	8	33	1
6	0.75	245	7	33	1
7	1.0	270	10	28	1
8	1.0	266	9	27	1
9	1.0	269	4	27	1

Table 4
Results for MB_N and MB_R in the single-point experiments using Norit.

Run	MB/GAC	MB_N		MB_R	
	Mass ratio (mg MB/mg GAC)	Average ($mg\ g^{-1}$)	SD ($mg\ g^{-1}$)	Average (%)	SD (%)
1	0.5	280	3	56	1
2	0.5	286	6	58	1
3	0.5	282	3	56	1
4	0.75	283	4	38	1
5	0.75	279	6	38	1
6	0.75	286	2	38	1
7	1.0	272	6	33	1
8	1.0	277	12	32	1
9	1.0	279	8	34	1

non-linear regression methods, and the results were summarized in Fig. 4.

Linear regression analysis is commonly used as the best fit model, and the least squares method has been widely used for obtaining the isotherm parameters of the Langmuir model. The goodness-of-fit of the model is often evaluated based on the value of the R^2 (determination coefficient). In this study, the application of the Langmuir model to the adsorption isotherm provided a satisfactory linearization of the data and a very good mathematical fit, as confirmed by the R^2 values, which were higher than 0.99 for the three GACs studied.

The non-linear regression plots show that the amount of MB adsorbed incremented as the concentration increased up to a saturation value, beyond which any increase in the MB concentration causes no further adsorption. Moreover, the plots showed that their initial slopes lie very close to the *y*-axis. It is well known that obtaining parameters from a non-linear equation using its linear form may cause serious errors, but problems due to linearization can be avoided if the experimental data are fitted by a non-linear regression method, which involves minimizing the error distribution between the experimental data and the predicted isotherm by error functions. Five different non-linear error functions, such as the sum of the squares of the errors (ERRSQ), the hybrid error function (HYBRID), Marquardtïs percent standard deviation (MPSD), the average relative error (ARE), and the sum of absolute errors (EABS) can be used to fit the isotherm data and to obtain the model parameters involved. These error functions are defined elsewhere [25]. In order to simplify the discussion, only the ARE error function was used and considered in the present study.

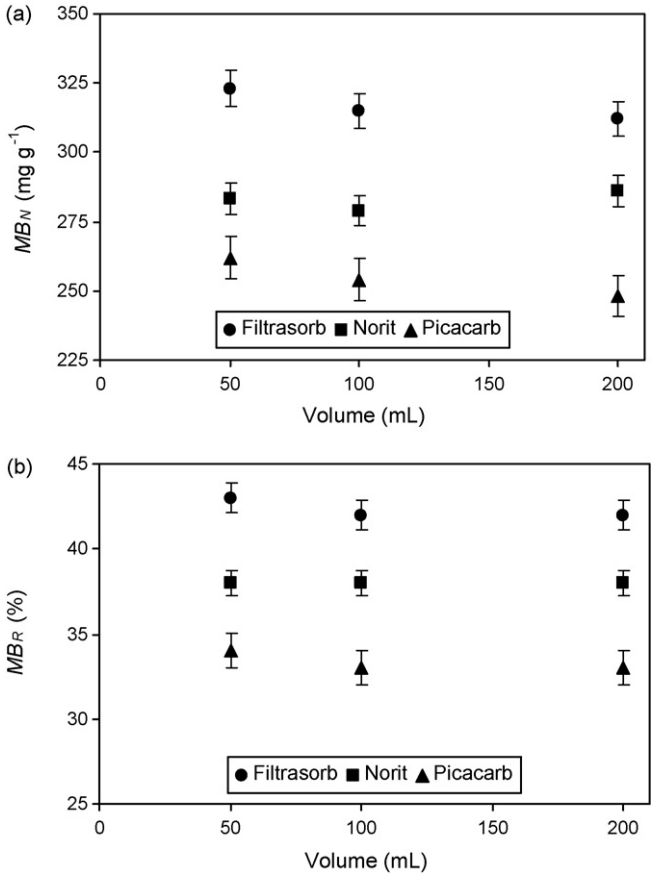

Fig. 2. Influence of MB solution volume in (a) MB_N and (b) MB_R of the three GACs assayed. Experimental conditions: MB/GAC = 0.75; MB concentration = 1500, 750 and 375 mg L^{-1}.

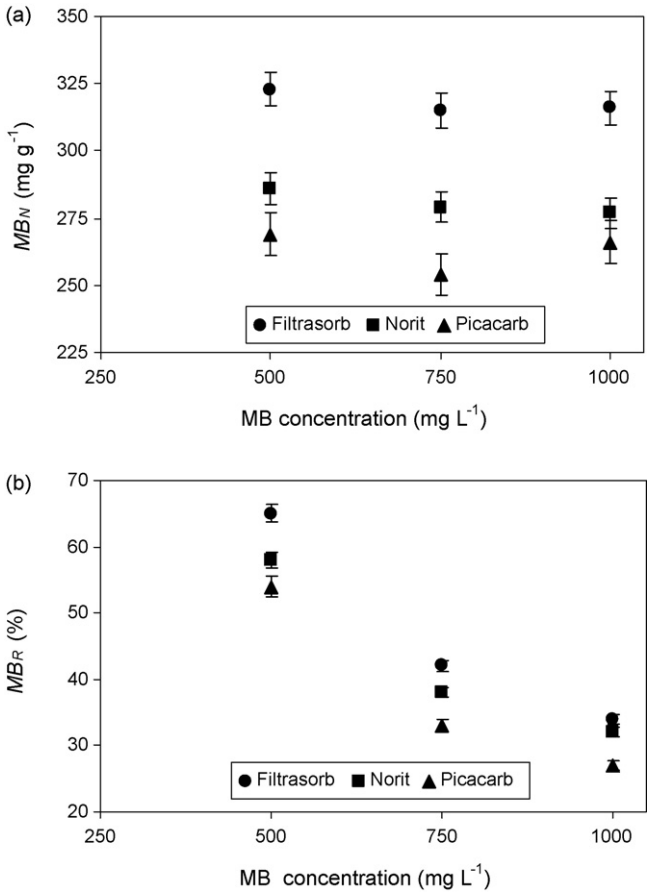

Fig. 3. Influence of MB initial solution concentration in (a) MB_N and (b) MB_R of the three GACs assayed. Experimental conditions: MB volume = 100 mL.

To ensure accurate results, the adsorption behaviour of MB onto GACs was analyzed using both linear and non-linear regression methods, and the results are summarized in Table 6. The main results obtained can be discussed as follows: firstly, in all cases R_L values were in the range of 0–1, indicating a favourable dye-adsorption process; secondly, the Langmuir isotherm parameters calculated from linear and non-linear methods are similar in the three GACs studied. A similar trend was previously obtained by Kumar et al. [26] using commercial powered activated carbon, however, a different trend was observed by Jumasiah et al. [27] using palm kernel shell activated carbon, where the parameters obtained differed substantially, and the use of the values derived from linear regression as initial guesses for the non-linear regression method was recommended.

On the other hand, when comparing the results of the maximum monolayer capacities of GACs given by single-point (MB_N) and multi-point (q_{max}) isotherm experiments, it can be concluded that they were similar. Therefore, the proposed method could be used as an analytical technique for GAC quality control. In previous research works, Hameed et al. [4,5] obtained the same values for MB_N and q_{max}, but lower MB_N values against q_{max} in the studies of the effect of dye concentration using activated carbon prepared from rattan sawdust and bamboo, respectively.

3.3. Real adsorptive capacity studies

The adsorbent particle size is one of most important factors influencing the adsorption process, although a literature survey showed that in a lot of adsorption research this parameter was

Table 6
Langmuir isotherm parameters obtained by linear and non-linear regressions.

	Adsorbent		
	Filtrasorb	Norit	Picacarb
Linear form			
q_{max} (mg g^{-1})	299 ± 3	276 ± 3	246 ± 2
b (L mg^{-1})	0.92	1.07	4.56
R^2	0.9997	0.9997	0.9998
R_L	0.0022–0.0043	0.0019–0.0037	0.0004–0.0009
Non-linear form			
q_{max} (mg g^{-1})	295 ± 3	276 ± 3	248 ± 2
b (L mg^{-1})	0.93	1.68	4.94
ARE	7.3	1.3	0.8
R_L	0.0021–0.0043	0.0012–0.0024	0.0004–0.0008

not evaluated. The GACs used as adsorbents are a mix of granules with different particle sizes. Therefore, a detailed study focusing on establishing a relationship between MB_N and MPD was also carried out in the present research work.

Fig. 5 illustrates a plot of MB_N versus contact time for the five particle size fractions considered. This plot demonstrated the important role played by the adsorbent particle size in the adsorption properties of GACs. The results obtained confirmed that adsorption is basically a surface phenomenon, where the amount of dye adsorbed increases with the decrease in adsorbent particle size. For this reason, the GAC particle size must be described in detail and provided in all the studies related to MB adsorption. Obviously, the adsorptive capacity was also influenced by the con-

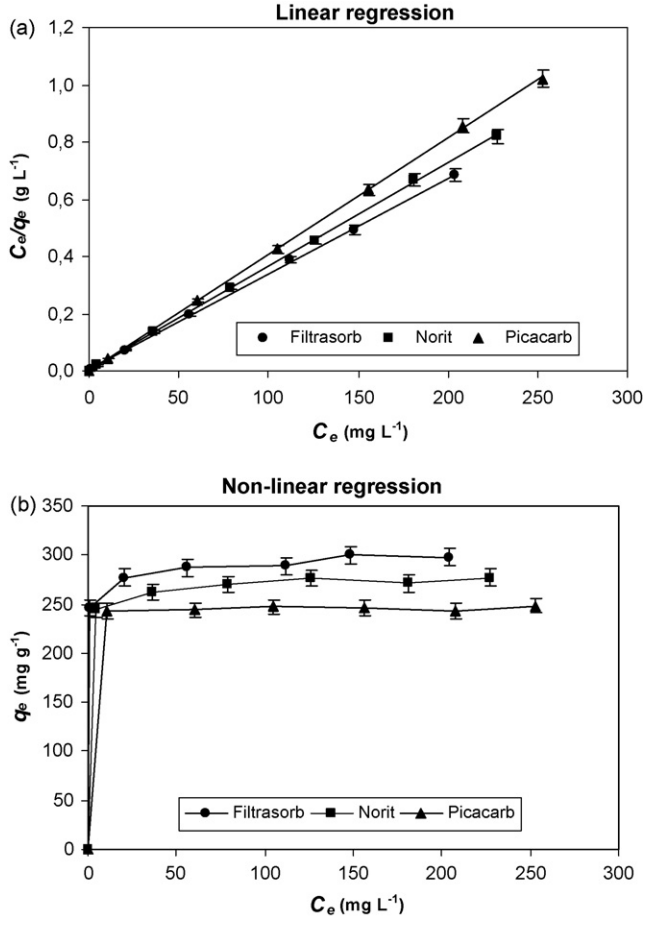

Fig. 4. Langmuir isotherms for MB adsorption onto the three GACs assayed.

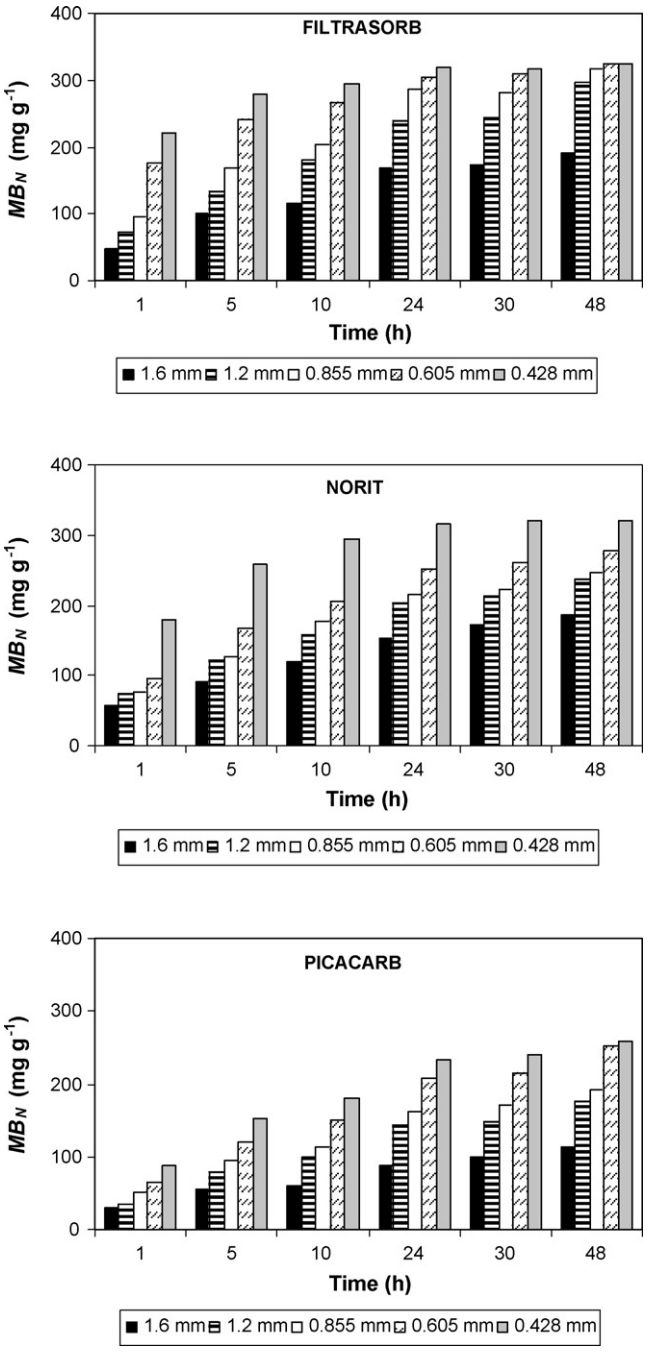

Fig. 5. Influence of particle size on MB adsorption onto the three GACs assayed.

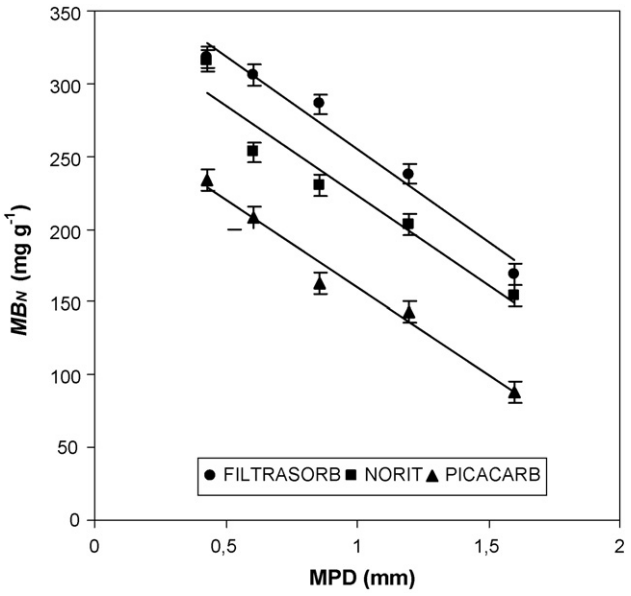

Fig. 6. Relationship between MB_N and MPD for the three GACs assayed.

tact time, with progressively increased values with increased time. Although the general trends were very similar for the three GACs assayed, F_{GAC} showed the best properties of adsorption, the total amount adsorbed being higher and the process being quicker. For example, the MB_N values of F_{GAC}, N_{GAC} and P_{GAC} for the 0.428 mm particle size fraction at 1 h compared to 48 h of contact time were 68%, 56%, and 34%, respectively. On the other hand, for F_{GAC} the influence of the particle size in MB_N at 48 h of contact time was not significant, except for the largest fraction (1.6 mm). It can be seen that for N_{GAC} and P_{GAC} only the smallest fraction (0.428 mm) reached the adsorption equilibrium at the end of the contact time evaluated.

To improve the practical applicability of the determination, reducing the necessary time to have available results, a standardized contact time of 24 h was chosen to measure the isotherm adsorption of all samples. Fig. 6 plots MB_N versus MPD for the three GACs studied. As can be seen, there is a linear relationship, as was also evident in the R^2 values obtained (F_{GAC}: 0.972; N_{GAC}: 0.929; P_{GAC}: 0.978). A similar observation was reported by Kannan and Sundaram [23] for powdered activated carbons with a particle size ranging from 90 to 250 μm. For a MPD of 1 mm, the order of the adsorptive capacity was as previously mentioned: $F_{GAC} > N_{GAC} > P_{GAC}$; with average values of 255 ± 7, 222 ± 7 and 160 ± 7 mg g^{-1}. These values were lower than those obtained in powdered form, but while F_{GAC} and N_{GAC} decreased by 20%, P_{GAC} decreased by 39%. For $F_{GAC,}$ N_{GAC} and P_{GAC} the relative adsorption values obtained in granular form were 100%, 87% and 63%, respectively. Therefore, the proposed complementary analysis of GACs should avoid the advantageous values of adsorptive capacities in powdered against granular forms which should mask a bad quality GAC.

4. Conclusions

The adsorptive capacity can be used as a useful tool to characterize GACs. This value should be obtained by a single-point isotherm study. It was demonstrated that the contact time and MB/GAC mass ratio did not show any significant effect. Therefore, with the experimental conditions established in this research work, the values obtained for the adsorptive capacity were independent of the MB concentration and volume. The traditional multi-point isotherm study showed that the Langmuir model fitted the experimental data well, and no influence of linear or non-linear regression methods appeared on the parameters involved. Both methods gave values similar and moreover statistically no different than those obtained with the single-point method. The complementary analysis of GAC confirmed the great influence of particle size on the adsorption process, making it possible to establish a linear relationship between MB_N and MPD. Furthermore, these results indicated the advantageous values proportioned by analysis with powdered as against granular form to characterize a GAC. Filtrasorb (F_{GAC}) was found to be the adsorbent with the highest adsorptive capacity both in granular and powdered forms.

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References

[1] M.G. Lussier, J.C. Shull, D.J. Miller, Activated carbon from cherry stones, Carbon 32 (8) (1994) 1493–1498.
[2] Calgon Carbon Corporation, Determination of the Methylene Blue Number of Activated Carbon (TM 11), Calgon Carbon Corporation, USA, 1971.
[3] European Council of Chemical Manufacturers' Federation (CEFIC), Test Methods for Activated Carbon, European Council of Chemical Manufacturers' Federation (CEFIC), Belgium, 1986.
[4] B.H. Hameed, A.L. Ahmad, K.N.A. Latiff, Adsorption of basic dye (methylene blue) onto activated carbon prepared from rattan sawdust, Dyes Pigments 75 (2007) 143–149.
[5] B.H. Hameed, A.T.M. Din, A.L. Ahmad, Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies, J. Hazard. Mater. 141 (2007) 819–825.
[6] I.A.W. Tan, A.L. Ahmad, B.H. Hameed, Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies, Desalination 225 (2008) 13–28.
[7] C. Pelekani, V.L. Snoeyink, Competitive adsorption between atrazine and methylene blue on activated carbon: the importance of pore size distribution, Carbon 38 (2000) 1423–1436.
[8] AWWA B604-74, Standard of the American Water Work Association. Specifications for Granular Activated Carbon used in Treatment of Potable Water, 1997.
[9] B.H. Hameed, M.I. El-Khaiary, Removal of basic dye rom aqueous medium using a novel agricultural waste material: pumpkin seed hull, J. Hazard. Mater. 155 (2008) 601–609.
[10] B.H. Hameed, M.I. El-Khaiary, A novel agricultural waste adsorbent for the removal of cationic dye from aqueous solution, J. Hazard. Mater. 162 (2009) 305–311.
[11] F.A. Pavan, Y. Gushikem, A.C. Mazzocato, S.L.P. Dias, E.C. Lima, Statistical design of experiments as a tool for optimizing the batch conditions to methylene blue biosorption on yellow passion fruit and mandarin peels, Dyes Pigments 72 (2007) 256–266.
[12] D. Ozer, G. Dursun, A. Ozer, Methylene blue adsorption from aqueous solution by dehydrated peanut hull, J. Hazard. Mater. 144 (2007) 171–179.
[13] J.F. Richardson, J.H. Harper, J.R. Backhurst, Chemical Engineering: Particle Technology and Separation Processes, vol. II, fifth edition, Butterworth-Heinemann, Oxford, 2002.
[14] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (9) (1918) 1361–1403.
[15] G. McKay, J.F. Porter, G.R. Prasad, The removal of dye colours from aqueous solutions by adsorption on low-cost materials, Water Air Soil Poll. 114 (1999) 423–438.
[16] W. Stumm, J.J. Morgan, Aquatic Chemistry, second edition, Wiley Interscience, John Wiley and Sons, 1981.
[17] J. Weber, in: R.L. Metcalf, J.N. Pitts (Eds.), Adsorption in Physical–Chemical Processes for Water Quality Control, Wiley Interscience, John Wiley and Sons, 1972.
[18] O. Hamdaoui, Batch study of liquid-phase adsorption of methylene blue using cedar-sawdust and crushed brick, J. Hazard. Mater. 135 (2006) 264–273.
[19] K.R. Hall, L.C. Eagleton, A. Acrivos, T. Vermeulen, Pore and solid diffusion kinetics in fixed-bed adsorption under constant pattern conditions, Ind. Eng. Chem. Fundam. 5 (2) (1966) 212–223.
[20] F. Rozada, L.F. Calvo, A.I. García, J. Martín-Villacorta, M. Otero, Dye adsorption by sewage sludge-based activated carbons in batch and fixed-bed systems, Bioresour. Technol. 87 (2003) 221–230.
[21] J.C. Miller, J.N. Miller, Statistics for Analytical Chemistry, second edition, Wiley, London, 1988.

[22] I. Ghodbane, L. Nouri, O. Hamdaoui, M. Chiha, Kinetic and equilibrium study for the sorption of cadmium(II) ions from aqueous phase by eucalyptus bark, J. Hazard. Mater. 152 (2008) 148–158.
[23] N. Kannan, M.M. Sundaram, Kinetics and mechanism of removal of methylene blue by adsorption on various carbons—a comparative study, Dyes Pigments 51 (2001) 25–40.
[24] K.V. Kumar, K. Porkodi, Batch adsorber design for different solution volume/adsorbent mass ratios using the experimental equilibrium data with fixed solution volume/adsorbent mass ratio of malachite green onto orange peel, Dyes Pigments 74 (2007) 590–594.
[25] J.C.Y. Ng, W.H. Cheung, G. McKay, Equilibrium studies of the sorption of Cu(II) ions onto Chitosan, J. Colloid. Interf. Sci. 255 (2002) 64–74.
[26] K.V. Kumar, K. Porkodi, F. Rocha, Isotherms and thermodynamics by linear and non-linear regression analysis for the sorption of methylene blue onto activated carbon: comparison of various error functions, J. Hazard. Mater. 151 (2008) 794–804.
[27] A. Jumasiah, T.G. Chuah, J. Gimbon, T.S.Y. Choong, I. Azni, Adsorption of basic dye onto palm kernel shell activated carbon: sorption equilibrium and kinetics studies, Desalination 186 (2005) 57–64.