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PREPARATION OF ACTIVATED CARBONS FROM BANANA LEAVES BY CHEMICAL ACTIVATION WITH PHOSPHORIC ACID. ADSORPTION OF METHYLENE BLUE

PREPARACIÓN DE CARBONES ACTIVADOS A PARTIR DE HOJAS DE PLATANERA MEDIANTE ACTIVACIÓN QUÍMICA CON ÁCIDO FOSFÓRICO. ADSORCIÓN DE AZUL DE METILENO

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Abstract

Banana leaves, which represent the second major residue generated in banana cultivations, were used as raw material for the preparation of six different activated carbons. The adsorbents were developed from this lignocellulosic precursor by means of chemical activation with phosphoric acid, modifying the concentration of the activating agent and the carbonization temperature during the production process. The obtained activated carbons presented slightly acid points of zero charge, high specific surface areas (798.51-1227.60 m^2/g) and large total pore volumes (0.83-1.29 cm^3/g), resulting mainly mesoporous. These adsorbents were employed for the adsorption of Methylene Blue in batch process. The dynamic experimental data were adjusted to pseudo-first and pseudo-second order kinetic models by non-linear regression, while the equilibrium experimental data were correlated to the Freundlich and Langmuir models. The monolayer adsorption capacities of this dye reached significant values, between 19.08 and 48.01 mg/g.

Keywords: activated carbon, banana leaf, methylene blue, phosphoric acid, adsorption isotherm.

Resumen

Las hojas de platanera, segundo residuo vegetal en orden de importancia del cultivo del plátano, se utilizaron como materia prima para la preparación de seis tipos de carbones activados diferentes. Los adsorbentes se fabricaron a partir de este precursor lignocelulósico mediante activación química con ácido fosfórico modificando durante el proceso de producción la concentración de activante y la temperatura de carbonización. Los diversos carbones activados obtenidos presentaron puntos de carga cero, ligeramente ácidos con considerables áreas superficiales específicas (798.51-1227.60 m^2/g) y elevados volúmenes totales de poro (0.83-1.29 cm^3/g) resultando predominantemente mesoporosos. Para determinar la capacidad adsorbente de estos tipos de carbones se realizaron pruebas batch utilizando Azul de Metileno. Los datos experimentales dinámicos fueron sometidos a los modelos cinéticos de pseudo-primer y pseudo-segundo orden mediante regresión no lineal, mientras que los datos experimentales de equilibrio se correlacionaron a los modelos de Freundlich y de Langmuir. Las capacidades de adsorción monocapa de este colorante alcanzaron valores importantes que oscilaron entre 19.08 y 48.01 mg/g.

Palabras clave: carbón activado, hoja de platanera, azul de metileno, ácido fosfórico, isoterma de adsorción.

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1 Introduction

Water has become a scarce resource, requiring its conservation of a continuous effort from the scientific and technological community, in such a way that an important part of their efforts and resources are employed in the development of new treatments and systems to facilitate both water purification and reuse.

Many industries use water, not only as raw material, but as a media for the evacuation of residues. This produces an alteration in the properties of water and therefore, its pollution. Particularly, textile companies, tanneries and pulp and paper plants, between others, employ industrial dyes in their productive processes. These dyes are serious organic pollutants due to their high molecular weights and complex structures (Gholami *et al*., 2003), which enables their persistence in aquatic media. The presence of these xenobiotic products in water ponds, lakes and rivers causes a great negative visual impact, even at concentrations below 1 ppm (Salleh *et al*., 2011). Moreover, these compounds inhibit the proper development of the photosynthesis process, as it impedes the penetration of solar radiation (Salleh *et al*., 2011), causing serious problems to the aquatic systems.

The existing methods for the elimination of dyes from liquid effluents include biological treatments, coagulation-flocculation, oxidation and adsorption processes (Amin, 2008), among others. Considering these techniques, adsorption operation represents a highly potential process for the removal of dyes from industrial effluents and provides considerable advantages in comparison to traditional treatments. Some of these benefits are flexibility of design and operation process as well as reduced space requirement for its implementation (Amin, 2008).

Activated carbon is one of the most commonly used materials among the different adsorbents currently available. This is due to its high adsorption capacity, given mainly by its high specific surface area and suitable pore size distribution (Mohanty *et al*., 2006). Nevertheless, the high acquisition cost of activated carbon together with the difficulty for its regeneration (Amin, 2008) has encouraged researchers to seek for low cost and highly available raw materials to produce activated carbon. In this sense, urban-industrial residues and agricultural residues provide a double benefit: on the one hand, the reduction of the adsorbent production cost and on the other, the decrease in the accumulation of solid wastes (Alam *et al*., 2007).

Although banana cultivations generate an important amount of vegetal residues, 1.6 kg per m^2 of cultivated surface area for *Cavendish species* (Oliveira *et al*., 2007), the exploitation of this waste for the production of activated carbon has not been sufficiently evaluated. Among these residues, the use of pseudostem has been investigated by various authors (Salman and Hameed, 2010; Salman *et al*., 2011; Sathishkumar *et al*., 2008); however, no references have been found for the use of leaves in the elaboration of activated carbons.

Therefore, considering the above, in this work we have prepared activated carbons by means of activation with phosphoric acid and employing as precursor banana leaves from the species *Dwarf* and *Giant Cavendish*. These activated carbons were texturally characterized and employed in the adsorption of Methylene Blue.

2 Materials and methods

2.1 Preparation of activated carbons

Dry leaves from banana plants of the species previously mentioned were brushed, grinded and sieved (Octagon Digital, Endecotts) for their classification according to particle size. To that effect, those particles under 300 μm were selected as starting fraction for the production of activated carbons, as the precursors with smaller particle size offer a larger superficial area that can be exposed to the activating agent, therefore improving the activation process (Khalili *et al*., 2000).

The chosen sieved fraction were washed with distilled water (Devi *et al*., 2008) during 2 hours at room temperature and with constant stirring (Agimatic-N, JP Selecta) at 1100 rpm. For every 50 g of solid, 1000 mL of water were employed. Next, the solid was dried (Conterm, JP Selecta) for 24 h at 105 ^{o}C (Devi *et al*., 2008). The resulting conditioned raw material was then subjected to the activation procedure.

Activated carbons can be generated either by physical or chemical activation, requiring this last process a unique thermal stage and lower processing temperatures (Lim *et al*., 2010). The chemical reagents generally employed in chemical activation of lignocellulosic residues are zinc chloride and phosphoric acid, although the use of zinc chloride implies a serious environmental hazard (Lim *et al*., 2010). For this reason, in this work, we chose a chemical activation procedure based on wet impregnation with phosphoric acid.

Three samples consisting of 10 g of conditioned banana leaves were impregnated with 100 mL of a 18.9% w/w phosphoric acid solution (purity 85%, PA-ACS-ISO grade, Panreac), while other three samples were prepared in the same way, but using a 27.6% w/w solution of phosphoric acid. Similar acid concentrations have been used in previous works (Amin, 2008; Shaarani and Hameed, 2010). The samples were then stirred (Shaker 685/2, Nahita) for 2 h at 100 rpm and were left to settle for a week at ambient conditions.

Once the activation had been completed, the activating solution was removed by gravitational filtration and the activated solid was dried at 105 °C for 24 h (Shaarani and Hameed, 2010). A second drying process was accomplished at 170 °C in order to remove the remaining water from the phosphoric acid solution (Kriia *et al*., 2010). The activated and dried material was then subjected to carbonization (ELF 11/14B, Carbolite) with a heating rate of 10 °C/min and a carbonization time of 2 h (Shaarani and Hameed, 2010). Three carbonization temperatures, similar to those in bibliography (Amin, 2008; Li and Wang, 2009; Shaarani and Hameed, 2010), were selected in this work: 450, 550 and 650 °C.

Wang *et al*. (2011) generated activated carbons using phosphoric acid as impregnation agent and using first a 1 M sodium hydroxide solution and later distilled water in the washing procedure. Fan *et al*. (2011) employed hot distilled water and a 0.1 M sodium hydroxide solution in the washing stage. Therefore, the activated carbons obtained in this work were washed in order to remove the remaining phosphoric acid and possible impurities generated in the thermal procedure. The methods found in literature were considered for this purpose, and, therefore, each activated carbon was washed with hot distilled water (500 mL) and several progressive doses (0.5 mL) of a 5% w/w sodium hydroxide solution (purity 98%, PA-ACS-ISO grade, Panreac). pH was continuously controlled (MM40 Crison) and the washing solution was removed, continuing with new washing stages until a constant pH over 5 was obtained in the washing effluent. This non-aggressive alkaline method was employed in order to minimize blockages in pores and adsorption centers.

Finally, the adsorbents were dried at 105 °C for 24 h (Devi *et al*., 2008), grinded and sieved, resulting in a particle size of less than 250 μm. Fig. 1 summarizes the steps of the production process for the activated carbons included in Table 1. The production yields Y (%) presented in Table 1 were determined through Eq. (1),

$$Y = \frac{W_a}{W_b} \cdot 100 \tag{1}$$

being the mass of the conditioned banana leaves and the obtained mass of activated carbon respectively, W_b (g) and W_a (g), both in dry basis.

2.2 Textural characterization and pH_{ZC}

The activated carbons were characterized by means of their points of zero charge and textural properties (specific surface area, total pore volume, mesopore volume, micropore volume, pore size distribution and pore mean size). Points of zero charge (pH_{ZC}) were determined following the procedure described in literature (Giraldo-Gutiérrez and Moreno-Piraján, 2008). The textural characterization was obtained from Nitrogen adsorption/desorption isotherms at -196 °C (Autosorb-6, Quantachrome) (Wang *et al*., 2005). The activated carbons had been previously degasified under vacuum (Autosorb degasser, Quantachrome) at around 200 °C (Wang *et al*., 2005) in order to remove possible adsorbed products that could interfere in the analysis.

2.3 Adsorption studies

The probe molecule in this study was Methylene Blue (82% purity, PA grade, Panreac), which is a cationic dye frequently used by researchers to study the adsorption of coloured substances and organic pollutants in aqueous solutions (Hameed *et al*., 2007). This product was dried in an oven at 110 °C for 2 hours (Bulut and Aydin, 2006) prior to the preparation of the solutions required in the adsorption studies. These solutions were prepared with distilled water.

The adsorption studies were carried out in batch mode at 25 °C (Macedo *et al*., 2006) and 100 rpm (Song *et al*., 2011). The initial dye concentration and solution volume, as well as the adsorbent load adopted in this work, were near to those employed by Macedo *et al*. (2006).

2.3.1 Kinetic studies

In order to study the adsorption kinetic, samples of 3.5 mg activated carbon in 25 mL of a 2.5 mg/L Methylene Blue solution at pH around 6.5 ($pH > pH_{ZC}$) were stirred during different contact times, varying from 0 to 1.5 h. After the contact time assigned to each sample, the activated carbon was separated from the solution by filtration (Hameed *et al.*, 2007). pH and absorbance at 664.5 nm (UV-Vis Lambda 2, Perkin Elmer) were determined for the filtrate. This enabled the determination of the remaining dye concentration, C (mg/L), according to the calibration curves previously developed. The specific amount of Methylene Blue removed in every instant, q_t (mg/g), was determined using the Eq. (2),

$$q_t = \frac{C_0 - C_t}{W} \cdot V \tag{2}$$

which represents the ratio between the initial C_0 (mg/L) and the remaining C_t (mg/L) concentrations of dye, considering the adsorbent load W (g) for a particular solution volume V (L).

Equilibrium studies

For the determination of the adsorption isotherms, different activated carbon loads (1.0-2.5 mg) were added to 25 mL samples of the previously described Methylene Blue solution. These samples were stirred at 100 rpm during 1.5 h and next were filtered. The remaining concentration of dye in equilibrium, C_e (mg/L), was determined following the procedure previously described. The specific amount of dye removed in the equilibrium condition, q_e (mg/L), was calculated from the Eq. (3).

$$q_e = \frac{C_0 - C_e}{W} \cdot V \tag{3}$$

3 Results and discussion

3.1 Production yields and characterization of activated carbons

The production yields are shown in Table 1. The obtained yields varied between 27 to 36%; these results were similar to those published by Reffas *et al.* (2010) in the generation of activated carbons from lignocellulosic waste with phosphoric acid activation. Matter losses along the different steps of the production process (see Fig. 1) did not enable to establish possible dependencies of this parameter with activating agent concentration and carbonization temperature.

The points of zero charge presented by the produced adsorbents are included in Table 1. These resulted near to those published in other works (Fan *et al.*, 2011; Giraldo-Gutiérrez and Moreno-Piraján, 2008; Li and Wang, 2009), in which the activation method employed was a chemical activation with phosphoric acid.

Nitrogen adsorption/desorption isotherms for the activated carbons were obtained. Adsorbed gas volume V_a (cm^3/g) vs. relative pressure (P/P_0), shown in Figs. 2a and 2b, presented IV shape with H3 hysteresis loop according to IUPAC classification. Therefore, the adsorbents can be classified as mainly mesoporous with prevalence of slit-shaped pores in their structures (Khalili *et al.*, 2000). The physisorption isotherms presented a high symmetry, and no modification was observed in their geometry with varying carbonization temperature for a constant activating agent concentration. This behaviour has been observed previously by others researchers (Kriia *et al.*, 2010). Moreover, in this study, a similar trend has been verified when modifying activating agent concentration for a constant carbonization temperature.

Table 1. Production conditions, yields, points of zero charge and textural properties

Activated carbon	C_a (% w/w)	T_c (°C)	Y (%)	pH$_{ZC}$	S$_{BET}$ (m^2/g)	V_t (cm^3/g)	W_0 (cm^3/g)	V_{mes} (cm^3/g)
CA1	18.9	450	32	4.69	1006.56	0.83	0.39	0.44
CA2	18.9	550	27	5.93	1227.60	1.01	0.46	0.54
CA3	18.9	650	30	4.40	1203.60	1.07	0.45	0.62
CA4	27.6	450	35	4.77	1206.27	1.29	0.47	0.83
CA5	27.6	550	30	3.26	798.51	0.89	0.31	0.58
CA6	27.6	650	36	3.87	1010.80	1.12	0.38	0.73

C_a concentration of phosphoric acid, T_c carbonization temperature, Y production yields, pH$_{ZC}$ points of zero charge, S_{BET} total surface area, V_t total porous volume, W_0 microporous volume, V_{mes} mesoporous volume.

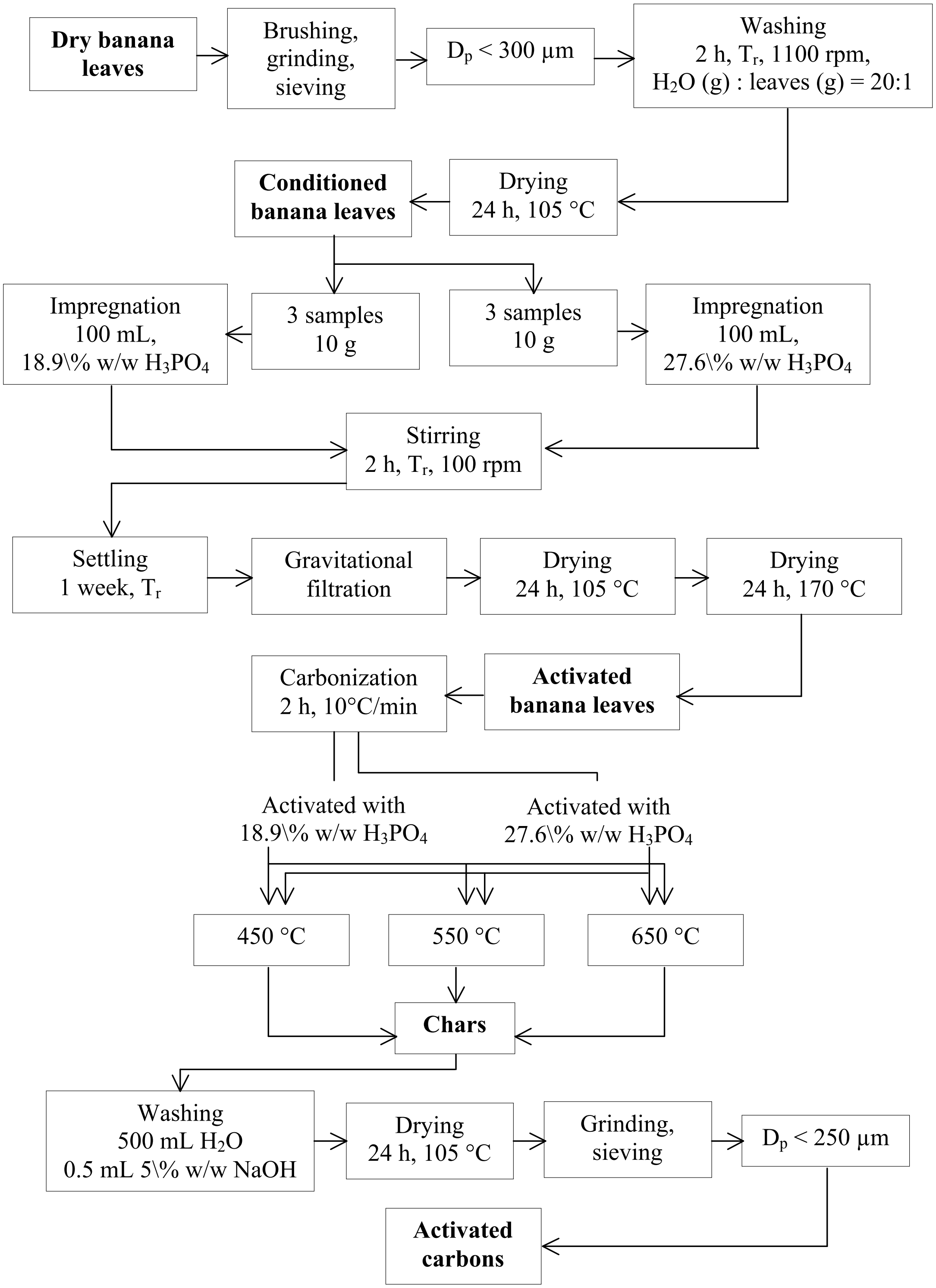

Fig. 1. Integral layout of the production process. (D_p, particle size; T_r, room temperature)

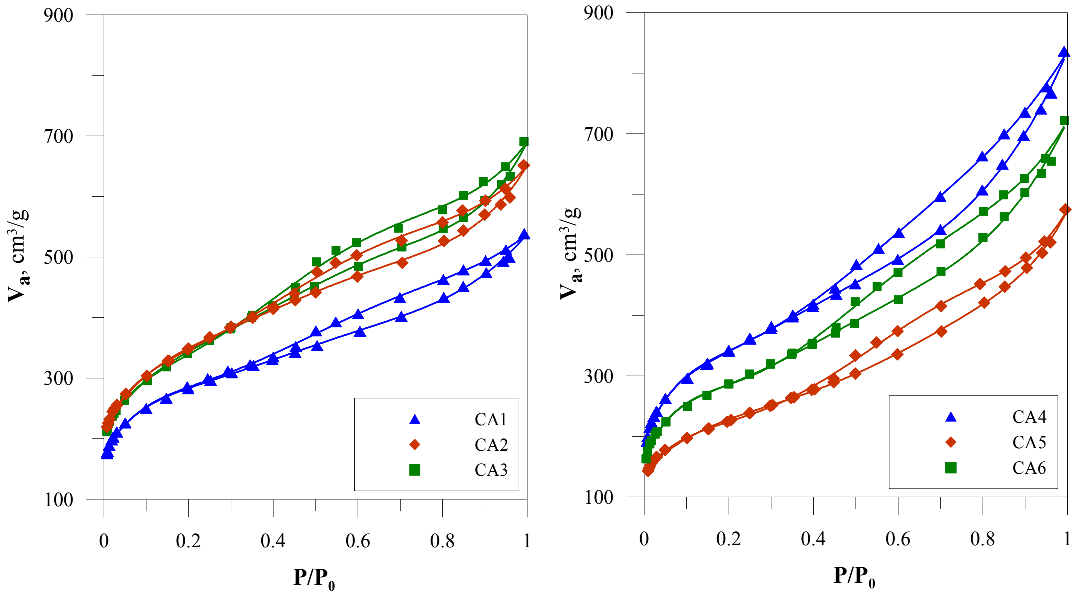

Fig. 2. Nitrogen adsorption-desorption isotherms.

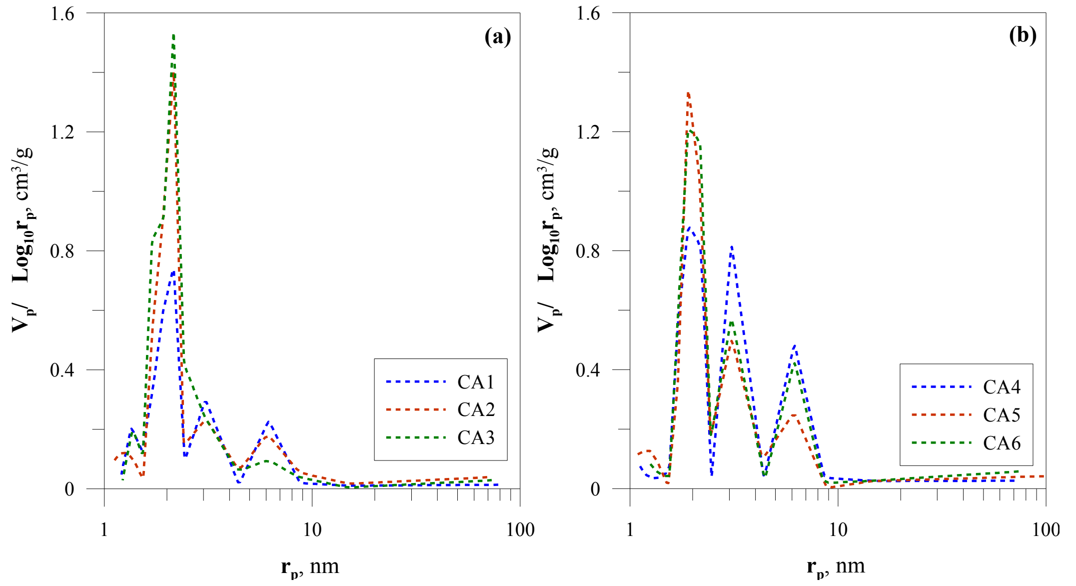

Fig. 3. Pore size distributions.

Consequently, variations in both carbonization temperature and activating agent concentration, in the ranges adopted in this work, do not seem to significantly modify the typology of the generated activated carbon.

The textural properties of the developed adsorbents are shown in Table 1 and were determined from the physisorption isotherms, following the methodology described in literature (Khalili *et al.*, 2000) by means of Brunauer-Emmett-Teller, Dubinin-Radushkevich and Barrett-Joyner-Halenda models.

Specific surface areas and total pore volumes between 524-1032 m^2/g and 0.75-1.43 cm^3/g were obtained by Girgis and Ishak (1999) for activated carbons produced from reuse of cotton stalks by impregnation with phosphoric acid. Prahas *et al.* (2008) report values of 2-1260 m^2/g and 0.525-0.733 cm^3/g for the same textural properties in activated carbons generated from jackfruit peel waste by H_3PO_4 chemical activation. The activated carbons produced in this study from banana leaves by chemical activation with phosphoric acid presented specific surface areas and total pore volumes between 798.51-1227.60 m^2/g and 0.83-1.29 cm^3/g respectively, resulting these values comparable or even higher than those of other activated carbons found in literature (Girgis and Ishak, 1999; Prahas *et al.*, 2008) and developed from agricultural precursors.

The analysis of the micropore and mesopore volumes presented in Table 1 shows a predominance of mesopores in the six adsorbents produced. This characteristic is increased for those activated carbons produced with higher concentration of phosphoric acid.

When considering the total pore volumes, including micropores and mesopores (see Table 1), we can verify the existence of dependence ratios between these textural properties and the conditions in which the activated carbons were developed. Globally, we can observe that an increase in the concentration of phosphoric acid for a constant carbonization temperature increases the pore volumes. In general terms, the same characteristic is observed when carbonization temperature is increased for a constant activating agent concentration. These results agree with those described in literature (Dastgheib and Rockstraw, 2001; Prahas *et al.*, 2008).

The pore size distributions, pore volume V_p (cm^3/g) vs. pore radius r_p (nm), of the produced adsorbents are shown in Figs. 3a and 3b. Polymodal behaviour can be observed. This distribution typology has also been obtained by other researchers for activated carbons developed from lignocellulosic residues by chemical activation with phosphoric acid (Fan *et al.*, 2011; Lim *et al.*, 2010). The predominant pore radius for the adsorbents produced with the 18.9% w/w solution of phosphoric acid was 2.15 nm (see Fig. 3a), while for the activated carbons produced with the 27.6% w/w solution this value was slightly lower: 1.91 nm (see Fig. 3b). Therefore, in this work, an increase in carbonization temperature for a constant activating agent concentration did not make difference in the predominant pore size. However, a rise in phosphoric acid concentration for a constant carbonization temperature modifies the mean pore size in a small degree.

Considering Figs. 3a and 3b we observe that an increase in the activating agent concentration for a fixed carbonization temperature generates an enlargement in the pore size distribution. A similar behaviour has been previously informed (Reffas *et al.*, 2010). Globally, it can be considered that an increase in carbonization temperature for a constant phosphoric acid concentration produces the diminishment of the peaks located at higher pore radius and a rise in the intensity of the peaks situated at lower pore sizes. This trend was specially seen for the adsorbents CA1-CA2-CA3. An analogue situation has been described by Yavuz *et al.* (2010) for carbonization temperatures above 500 ºC. The absence of peaks at pore radius over 25 nm discards the presence of macropores in the structures of the six activated carbons developed for this paper.

3.2 Adsorption of methylene blue

Kinetic of methylene blue

The effect of contact time on the reduction of Methylene Blue for the six activated carbons is shown in Figs. 4a and 4b. It can be observed that the elimination takes place in two stages for all the adsorbents. The first stage is characterized by a strong and fast adsorption in the first 20 minutes, while the second one is noted by a slower adsorption until the equilibrium is reached. This same behaviour has been described in previous works for the adsorption of Methylene Blue on activated carbons (Macedo *et al.*, 2006; Nunes *et al.*, 2009).

The fast initial adsorption, which is greater in carbons produced with higher activating agent concentration (see Fig. 4b), can be due to the migration of Methylene Blue molecules from the solution to the external surface of the adsorbents. The thereafter slow elimination can be consequence of an internal diffusion process by which the molecules enter the porous structure of the activated carbons.

Considering Figs. 4a and 4b we can verify that the time required to achieve the large amount of the maximum distribution of Methylene Blue on the adsorbents is less than 1 h. This period, needed to reach the equilibrium state, is lower than that reported in other papers with similar conditions in the adsorption studies (Macedo *et al.*, 2006).

The removal percentages varied between 40-90%, observing the presence of dependent ratios between dye removal and the conditions in which the activated carbons were developed (see Figs. 4a and 4b).

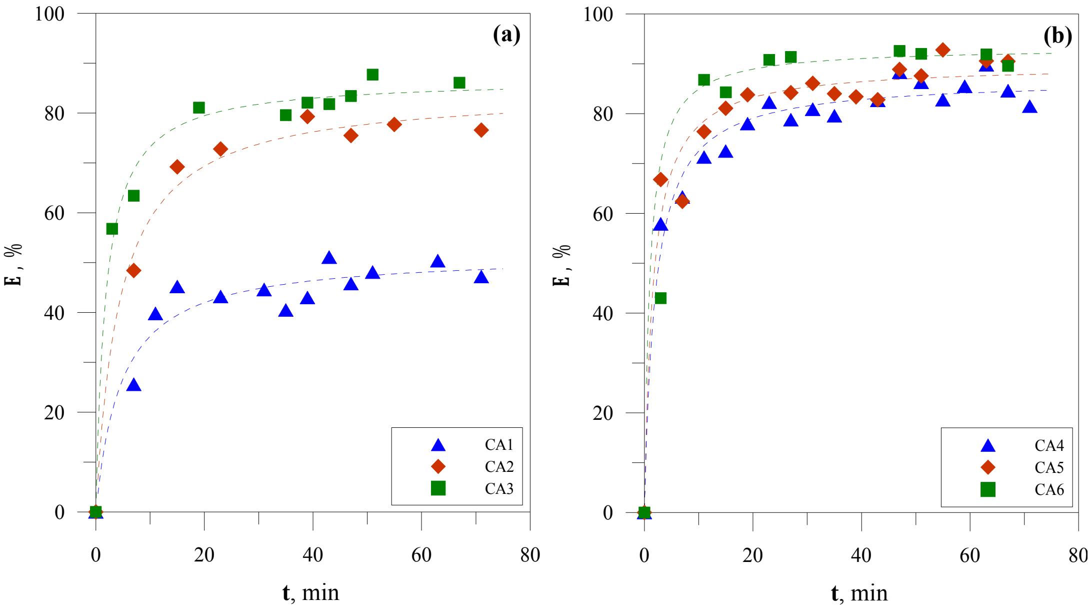

Fig. 4. Effect of contact time in the removal rate of Methylene Blue.

In this sense, an increase in carbonization temperature for a constant concentration of activating agent raises the removal rate. This was specially observed for the adsorbents CA1-CA2-CA3. Moreover, an increase in phosphoric acid concentration during the chemical activation procedure for a constant carbonization temperature produces a rise in the removal, mostly for the adsorbents CA1-CA4. This can be attributed to the increase in mesopore volumes with increasing carbonization temperature and activating agent concentration. Methylene Blue has proven to be mostly retained in the mesopores.

In order to evaluate the adsorption kinetic of Methylene Blue on the six produced activated carbons, $q_t - t$ values were correlated to the two principal kinetic models for adsorbates in aqueous solution: pseudo-first and pseudo-second order kinetic models, following the equations:

$$q_t = q_e(1 - e^{-k_1 \cdot t}) \tag{4}$$

$$q_t = \frac{k_2 \cdot q_e^2 \cdot t}{1 + k_2 \cdot q_e \cdot t} \tag{5}$$

In this work, we employed both models in their non-linear forms to determine the kinetic constants k_1 (1/min) and k_2 (g/mg·min) because in this way, the kinetic parameters are predicted better than in the linearized forms of these models (Kumar, 2006). The suitability of both models for the experimental data was verified considering statistical parameters, including the standard deviation, σ, and the mean error, em, which are determined by the following equations:

$$\sigma = \sqrt{\frac{\sum_{i=1}^{i=N}(q_{eexp,i} - q_{ecalc,i})^2}{N - p}} \tag{6}$$

$$e_m = \frac{\sum_{i=1}^{i=N}\left|\frac{q_{eexp,i} - q_{ecalc,i}}{q_{eexp,i}}\right|}{N} \cdot 100 \tag{7}$$

In Eqs. (6) and (7), the experimental and calculated values of retained Methylene Blue in equilibrium are represented by q_{eexp} and q_{ecalc} (mg/g) respectively, while N is the number of experimental data and p is the number of parameters in the models.

Pseudo-first and pseudo-second order kinetic models have demonstrated to describe adequately the adsorption of Methylene Blue on activated carbons produced by different methods from several precursors (Hameed *et al.*, 2007; Karagöz *et al.*, 2008; Kumar, 2006). This is the reason why they were applied. Furthermore, the pseudo-second order model seems to explain very well the adsorption kinetic for the entire adsorption period (Kumar, 2006).

Figs. 5a and 5b show the application of the kinetic models to the experimental data, while Table 2, in which the regression coefficient R^2 is presented, shows the parameters obtained from the correlation of the data to the mentioned models.

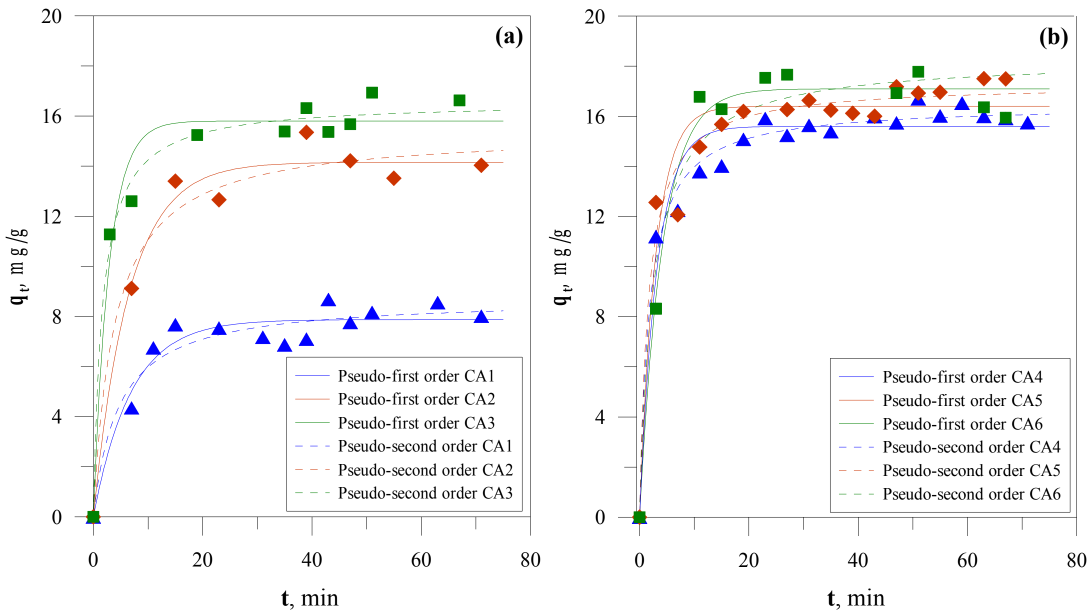

Fig. 5. Correlation to the pseudo-first and pseudo-second kinetic models in their non-linear forms.

Table 2. Parameters of the kinetic models

Activated carbon	q_{eexp} (mg/g)	Pseudo-first order model					Pseudo-second order model					
		k_1 (1/min)	q_{ecalc} (mg/g)	R^2	σ	e_m (%)	k_2 (g/mg·min)	$q_{e,cal}$ (mg/g)	R^2	σ	e_m (%)	h (mg/g·min)
CA1	8.12	0.15	7.87	0.93	0.62	7.45	0.03	8.73	0.93	0.64	7.96	2.29
CA2	14.44	0.15	14.16	0.98	0.78	4.25	0.02	15.39	0.97	0.92	5.90	4.74
CA3	16.14	0.35	15.80	0.97	0.95	5.38	0.04	16.58	0.99	0.59	3.45	11.00
CA4	16.01	0.32	15.60	0.95	0.88	4.75	0.03	16.47	0.99	0.49	2.57	8.14
CA5	16.84	0.34	16.41	0.93	1.14	5.62	0.04	17.30	0.97	0.74	3.53	11.97
CA6	16.93	0.35	16.97	0.99	0.68	3.35	1.45	16.94	0.99	0.69	3.33	416.10

From Figs. 5a and 5b we can observe that the dispersion of the experimental data is generally moderate, although reduced adsorbent loads were employed. Besides, from the results in Table 2 we can corroborate that the pseudo-second order model provides a better mathematical correlation of the experimental data and a better prediction of the dye removal by the developed adsorbents in the equilibrium condition. This agrees with that informed in literature for the adsorption of Methylene Blue on activated carbons (Hameed *et al.*, 2007; Macedo *et al.*, 2006; Wang *et al.*, 2005). Therefore, it seems obvious that the limiting stage in these adsorption systems is the chemisorption stage (Nunes *et al.*, 2009).

For the pseudo-second order model the initial adsorption rates, *h* (mg/g·min), were calculated through the Eq. (8) and were also included in Table 2. It can be observed from this table that higher initial adsorption rates are obtained when carbonization temperature is raised for a constant phosphoric acid concentration and, in the same way, this parameter is higher when activating agent concentration is increased for a particular carbonization temperature. This behaviour could be explained considering that the rise of both operation conditions lead, in general, to higher mesopore volumes that seem to facilitate the access of dye molecules into the structure of the activated carbons. This type of pore is considered as the main transport arteries for the adsorbate in adsorption processes (Hu and Srinivasan, 2001).

$$h = k_2 \cdot q_e^2 \qquad (8)$$

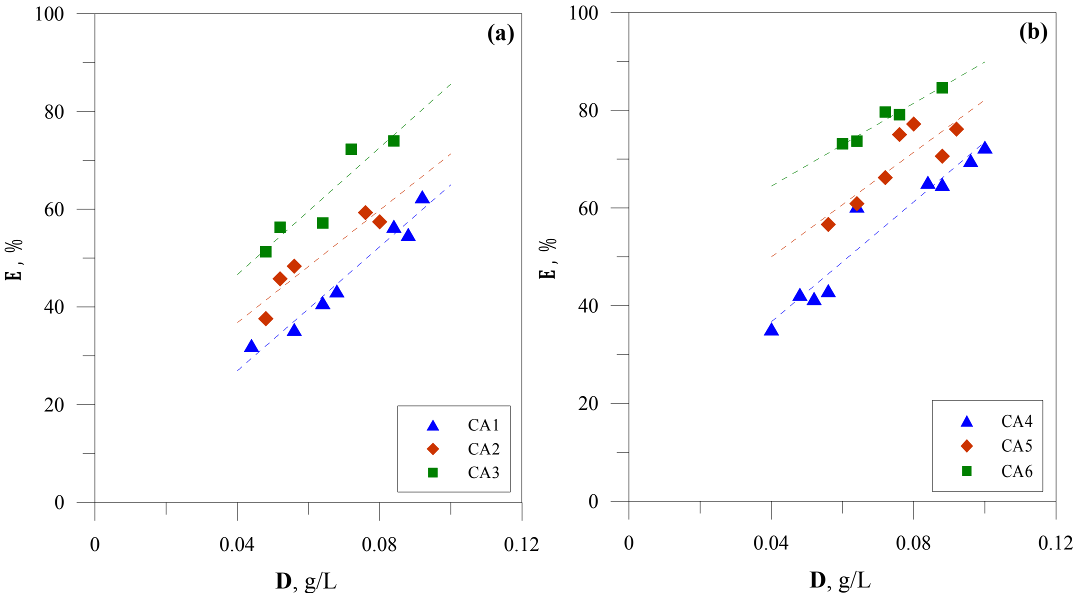

Fig. 6. Effect of the activated carbon load in the removal rate of Methylene Blue.

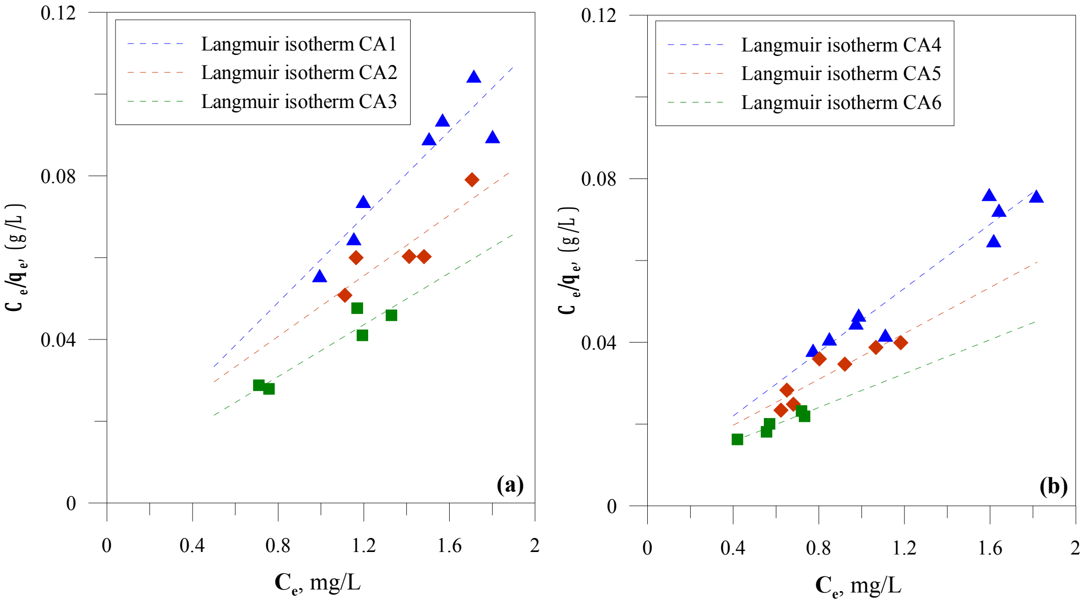

Fig. 7. Correlation to the Langmuir model in its linear form.

3.2.2 Adsorption isotherms

The adsorption isotherm data of Methylene Blue obtained by the modification of activated carbon load method, enabled the determination of the effect the adsorbent load, *D* (g/L), has on the dye removal as shown in Figs. 6a and 6b. We can observe that, for all the adsorbents, an increase in activated carbon load produces a practically linear rise in the removal of Methylene Blue. This can be due to the presence of a larger number of adsorption centers available for the retention of the dye molecules.

Table 3. Parameters of the Langmuir model

Activated carbon	Q_0 (mg/g)	b (L/mg)	R_L	R^2	σ
CA1	19.08	7.38	0.05	0.85	7.24×10^{-3}
CA2	26.95	3.34	0.10	0.76	5.81×10^{-3}
CA3	31.60	5.65	0.06	0.89	3.53×10^{-3}
CA4	25.58	6.20	0.05	0.93	4.70×10^{-3}
CA5	35.59	3.31	0.10	0.84	2.97×10^{-3}
CA6	48.01	2.79	0.12	0.92	9.39×10^{-4}

This has been similarly described in literature (Nunes *et al*., 2009) for the adsorption of this cationic dye on activated carbon.

A similar performance for those activated carbons for which the same concentration of activating agent has been used is also observed (see Figs. 6a and 6b), being the removal rate higher for those activated carbons produced at 650 °C. Then, the quantities $q_e - C_e$ were correlated to the Freundlich and Langmuir models, respectively expressed as:

$$\mathrm{Logq_e} = \mathrm{Logk_F} + \frac{1}{\mathrm{n}} \cdot \mathrm{LogC_e} \tag{9}$$

$$\frac{\mathrm{C_e}}{\mathrm{q_e}} = \frac{1}{\mathrm{Q_0} \cdot \mathrm{b}} + \frac{\mathrm{C_e}}{\mathrm{Q_0}} \tag{10}$$

The Freundlich model includes the parameters k_F [(mg/g)·(L/g)$^{1/n}$] and n, which inform of the adsorption or distribution coefficient and of the heterogeneity of the adsorbent surface (Hameed *et al*., 2007). The Langmuir model contains the parameters Q_0 (mg/g) and b (L/mg), related with the adsorption capacity and the adsorption energy, respectively (Amin, 2008). This last model includes a dimensionless factor known as equilibrium parameter R_L that informs about the nature of the adsorption process which can be not favourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) and irreversible ($R_L = 0$) (Amin, 2008). This parameter is defined by the following equation:

$$\mathrm{R_L} = \frac{1}{1 + \mathrm{C_0} \cdot \mathrm{b}} \tag{11}$$

The Freundlich model did not describe appropriately the adsorption equilibrium of Methylene Blue for the six activated carbons. This is probably due to its limited application for solutions with small concentrations of adsorbate (El-Qada *et al*., 2006), as was the concentration employed in this work ($C_0 = 2.5$ mg/L).

The application of the Langmuir model is shown in Figs. 7a and 7b, where the ordinate represents the ratio between the remaining dye concentration in the liquid phase (i.e. non-adsorbed Methylene Blue concentration) and the adsorbed quantity. It is expected that activated carbons with isotherms located towards higher ordinate values are less effective in the removal of the cationic dye. Moreover, considering Eq. (10), it is also expected that adsorbents with isotherms that present higher slopes are worse in the uptake of the selected adsorbate, as the slopes are inversely related to the monolayer adsorption capacities. Therefore, it seems that CA-3 is the best activated carbon of the series CA-1,CA-2,CA-3, while CA-6 is the best adsorbent of the series CA-4,CA-5,CA-6 and of the six produced activated carbons in terms of Methylene Blue removal.

The above is supported by the monolayer adsorption capacities listed in Table 3, where are also included the values of b, the factor R_L and the statistical parameters of the correlations. The standard deviations were calculated by means of Eq. (6) replacing adsorbed quantities by C_e/q_e in the residual sum of squares. We can observe that the regression coefficients are not high although the standard deviations are low; these results are due to the moderate dispersion of the experimental data, as a consequence of the systematic error generated when working with small loads of the adsorbent.

The Langmuir model describes the experimental data adequately (see Figs. 7a and 7b), which indicates that the surfaces of the activated carbons are homogeneous and adsorption takes place by forming monolayers (El-Qada *et al*., 2006). The adsorption process of Methylene Blue on the developed adsorbents is favourable, as can be deduced from the equilibrium parameter, which was, in all cases, between 0 and 1. Regarding the monolayer adsorption capacities, these varied between 19.08 y 48.01 mg/g, which are higher values than those in literature (Karagöz *et al*., 2008). We obtained higher adsorption capacities with increasing activating agent concentration and carbonization temperature.

Conclusions

In this work we have verified the possibility to produce activated carbons using as precursor banana leaves and as activating agent phosphoric acid. In this sense, we propose a new valorization method for this agricultural residue, which can involve an improvement in the total reuse of the waste produced by this species.

We observed that the modification of the conditions during the production of these adsorbents affects both its textural properties and the adsorption of Methylene Blue from aqueous solutions. On the one hand, increase in carbonization temperature with constant activating agent concentration increased total pore volumes, including mesopores and micropores, enlarged the peaks located at lower pore radius to the detriment of those located at larger size, and enabled higher rates of dye removal. On the other hand, an increase in the activating agent concentration at a constant carbonization temperature enabled higher pore volumes, an enlargement of the pore size distributions and higher removal rates of the cationic dye chosen for this paper.

In this work, we have produced adsorbents with high specific surface areas, important total pore volumes, mainly mesoporous and with polymodal pore size distributions. These characteristics provide these adsorbents with the capacity to remove high molecular weight compounds from aqueous solutions. In this sense, the removal of Methylene Blue, studied in this work, resulted between 40 and 90% in less than 20 minutes.

The experimental data obtained for the adsorption of Methylene Blue were applied to different kinetic models. The pseudo-second order model provided a better mathematical correlation and a better prediction than the pseudo-first order model. Therefore, the limiting stage in the adsorption kinetic of this dye seems to be the chemisorption process. When employing equilibrium models, the Langmuir model described well the experimental data, resulting the adsorption of this dye favourable on the activated carbons produced in this work. The results show adsorption capacities higher than those informed in other studies for the same type of adsorption system (Methylene Blue-activated carbon).

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