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Preparation, characterization, and dye removal study of activated carbon prepared from palm kernel shell

Juan Rafael García¹ · Ulises Sedran¹ · Muhammad Abbas Ahmad Zaini² · Zainul Akmar Zakaria³

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Abstract Palm oil mill wastes (palm kernel shell (PKS)) were used to prepare activated carbons, which were tested in the removal of colorants from water. The adsorbents were prepared by 1-h impregnation of PKS with ZnCl₂ as the activating agent (PKS:ZnCl₂ mass ratios of 1:1 and 2:1), followed by carbonization in autogenous atmosphere at 500 and 550 °C during 1 h. The characterization of the activated carbons included textural properties (porosity), surface chemistry (functional groups), and surface morphology. The dye removal performance of the different activated carbons was investigated by means of the uptake of methylene blue (MB) in solutions with various initial concentrations (25–400 mg/L of MB) at 30 °C, using a 0.05-g carbon/50-mL solution relationship. The sample prepared with 1:1 PKS:ZnCl₂ and carbonized at 550 °C showed the highest MB adsorption capacity (maximum uptake at the equilibrium, $q_{\max} = 225.3$ mg MB / g adsorbent), resulting from its elevated specific surface area (BET, 1058 m²/g) and microporosity (micropore surface area, 721 m²/g). The kinetic experiments showed that removals over 90% of the equilibrium adsorptions were achieved after 4-h contact time in all the cases. The study showed that palm

oil mill waste biomass could be used in the preparation of adsorbents efficient in the removal of colorants in wastewaters.

Keywords Waste biomass · Palm kernel shell · Activated carbon · Adsorption · Dye removal

Introduction

Colorant materials are widely used in different industrial activities, in areas such as paper, plastics, photography and ink manufacturing, and particularly in textile (wool, silk, cotton) production. After the continuous growth in world population, the demand for these products increased significantly (Robinson et al. 2001; Aoudj et al. 2010; Aljeboree et al. 2014). As a consequence of the significant impact of the use of dyes in an important number of industries with strong growth, it is absolutely necessary to have highly efficient systems for the removal of pollutants from wastewaters (Chowdhury et al. 2015). Otherwise, serious environmental (visual pollution, scarce penetration of light, and limit the photosynthetic zone in waterbodies) and health (potentially mutagenic and/or carcinogenic) problems are to occur (Kumar et al. 2011; Ong et al. 2011; Ratna and Padhi 2012).

Among the various techniques appropriated to remove pollutants from wastewaters (Robinson et al. 2001; Hung et al. 2011; Chowdhury et al. 2015), the adsorption on porous solids has arisen particular interest, given that it is a low-cost option, with reduced energy consumption and relatively simple technologies. Moreover, the disposal of wastes is simple (Acharya et al. 2009; Das et al. 2015). Activated carbons (ACs), being cheap materials with good adsorption capacity due to their large microporous volume and specific surface areas, are extensively used as adsorbent (Sahu et al. 2010). As

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environmental pollution became an issue with a great impact on social commitment in the last years, the need and demand for activated carbons is growing continuously. Besides its normal use in water purification systems and wastewater treatment facilities, given their adsorptive properties, the ACs are also employed in gas purification, air filters in gas masks, filters in compressed air, therapeutic methods for diarrhea and poisoning, sewage treatment, metal recovering, and adsorption of heavy metal, among others (Dias et al. 2007). Activated carbons can be prepared by either physical or chemical methods (Guo and Lua 1998), their textural (mainly their microporosity), and surface (occurrence of functional groups) properties depending on the raw material and the method used for their activation (Olivares-Marín et al. 2006). Various carbonaceous raw materials can be used in the preparation of AC, among which mineral carbon, woods (Mohanty et al. 2005; Sahu et al. 2009a), agriculture wastes (i.e., nutshell (Ahmadpour and Do 1997), coconut shell (Dwivedi et al. 2008; Aljeboree et al. 2014; Das et al. 2015), pineapple leaves (Mahamad et al. 2015)), and industrial waste products such as rice husk (Mohanty et al. 2006; Sahu et al. 2009b) and sugarcane bagasse (Cronje et al. 2011) can be mentioned.

Palm oil is the edible oil with the largest production in the world, Malaysia being the second largest producer of this product. The area destined to oil palm cultivation in that country has been estimated to be about 4.9 million hectares, and the annual production of fresh fruit bunches is about 88.3 million tons (Hoe et al. 2016). Moreover, a surplus of by-products in the palm oil value chain, which have a low rate of utilization even though their potential is very large, can be noticed (Zafar 2015). Palm oil mills produce important amounts of different wastes such as palm oil mill effluent (POME), empty fruit bunches (EFBs), and palm kernel shell (PKS) (Singh et al. 2013), which annually amount to 59 million tons in Malaysia (Chen et al. 2011). Some valorization routes have been proposed for these wastes with the combined aim of reducing pollution and producing useful goods from very low cost raw materials. For example, POME and EFB were used in compost manufacturing for agricultural applications (Nor Fadilah et al. 2009; Zahrim and Asis 2010; Kavitha et al. 2013) or in fermentation processes to produce bio-ethanol (Sudiyani et al. 2013) or succinic acid (Akhtar et al. 2014), among other industrially important compounds.

The shell fraction left once the nuts have been recovered after crushing in the mills is called PKS. After greenhouse gas emission reduction policies were implemented, PKS has been extensively used as a renewable fuel in Malaysia in the past 20 years (Zafar 2015; Abdullah and Sulaiman 2013). As a consequence, most palm oil mills are energetically self-sufficient; that is, they are typically able to generate more energy than that needed to meet their energy demands. Thus, the availability of palm kernel shells increased significantly in Malaysia and neighboring countries in the last years, and it has

been postulated that PKS and other oil palm wastes, e.g., empty fruit bunches and oil palm trunks and fronds, can be gasified in order to obtain producer gas (Abdullah and Sulaiman 2013). Moreover, PKS can be used in replacement of fossil resources, such as oil and natural gas, to obtain chemicals of broad use in the industry or fuels. Recently, the cement industry started using PKS in replacement of coal, mainly because of the benefits from the achievement of Certified Emission Reduction units (CERs), after the Kyoto Protocol (Zafar 2015). On the other hand, the utilization of bio-oil derived from PKS pyrolysis to substitute synthetic phenol and formaldehyde in phenol-formaldehyde resins is possible, while the carbonaceous residues in the process can be used as a charcoal source or as an adsorbent (Abdullah and Sulaiman 2013). Phenol has many other applications, such as the manufacture of automotive parts, household appliances, electrical components, adhesive resins, and insulation materials, among others.

As previously described, the large availability of palm oil mill wastes and, consequently, the opportunity of using residual, low-cost carbonaceous raw materials to prepare activated carbons for the removal of contaminants in wastewaters are evident. In this sense, it is the objective of this work to prepare activated carbons from palm kernel shells, as well as to characterize and test them in the removal of methylene blue (MB) model colorant in water.

Experiment

Preparation of activated carbons

The residual lignocellulosic biomass (PKS) was obtained from a palm oil mill in Johor, Malaysia (Kulai Palm Oil Mill). The composition of the PKS was lignin 42.97 wt.%, cellulose 35.64 wt.%, and hemicellulose 21.36 wt.%, on a dry basis. Its contents of moisture, ash, and ethanol extractives were 9.5 wt.%, 2.5 wt.%, and 3.19 wt.%, respectively. The elemental composition was 47.70 wt.% C, 45.61 wt.% O, 5.75 wt.% H, 0.90 wt.% N, and 0.04 wt.% S. The PKS sample was washed with tap water in order to remove soil, dust, and other unwanted materials prior to sunlight drying during 1 day to remove the part of the moisture and prevent the growth of fungi during storage. The dried sample was ground and sieved to obtain particles with approximately 2 to 4 mm size. Before performing the activation, the PKS sample was dried again in an oven at 110 °C for 24 h to remove the excess of moisture.

The activated carbons were prepared using zinc chloride ($ZnCl_2$) as the activating agent by means of the following method (Mahamad et al. 2015). Different samples of dried PKS were impregnated using $ZnCl_2$ (QR&C, AR grade) to achieve PKS: $ZnCl_2$ mass ratios of 1:1 and 2:1, using 11.4 and 4.7 M solutions, respectively. The impregnated biomass

was immersed during 1 h at room temperature with manual stirring. Then, the samples were dried overnight at 110 °C and submitted to carbonization in autogenous atmosphere at 500 and 550 °C during 1 h. Table 1 shows the preparation conditions and the nomenclature assigned to the different samples. The different samples were washed at room temperature with enough amount of distilled water in order to remove residual activating agent. The activated carbons were finally dried during 24 h at 110 °C and then grounded and sieved to the 0.5–1.0-mm particle size range.

Physicochemical characterization

The adsorption-desorption isotherms of nitrogen at −196 °C were used in order to determine the textural properties of the activated carbons. The measurements were performed by using a Thermo Scientific Surfer sorptometer (Thermo Fisher Scientific Inc.). Previous to analysis, the samples were degassed under vacuum (absolute pressure less than 10^{-3} torr) for 3 h at 300 °C. The Brunauer-Emmet-Teller (BET) model was applied in the $0.15 < P/P_o < 0.30$ range to determine the BET specific surface area. The amount of nitrogen adsorbed until $P/P_o \sim 0.98$ determined the total pore volume, while the t -plot method ($3.5 \text{ \AA} < t < 5.0 \text{ \AA}$) was used to estimate the micropore volume and the specific surface area of the mesopores.

The functional groups existing on the surface of the carbons were characterized using Fourier transform infrared (FTIR) spectroscopy. Each sample of the activated carbons was grounded in a mortar using KBr (carbon:KBr mass relationship of 1:100), and 10-mm-diameter wafers were pressed under 7.6 t/cm^2 prior to analysis. The spectra were recorded with a resolution of 4 cm^{-1} in the $500\text{--}4000\text{-cm}^{-1}$ range at room temperature.

The morphological characteristics of the activated carbons were determined using a scanning electron microscope (SEM; Zeiss Supra 35 VP). The samples were placed into a SEM holder and coated with a 20-nm-thick layer of gold prior to observation.

Batch adsorption studies

The adsorptive properties of the different samples of as-prepared activated carbons were evaluated by means of batch adsorption studies using MB ($\text{C}_{16}\text{H}_{18}\text{N}_3\text{SCl}$, QR $\ddot{\text{C}}$, AR grade) as a test dye molecule. Methylene blue was dissolved

in 1 L of distilled water at 1000 mg/L in order to prepare a stock MB solution, which was then kept in a dark environment at 30 °C.

In order to perform the equilibrium adsorption experiments, 0.05 g of each activated carbon sample was added to a series of 250-mL conical flasks, each one containing 50 mL of solutions with 25–400 mg/L of MB, which were prepared by diluting the stock solution. Then, the AC suspensions were shaken during 24 h in an orbital shaking cabinet (Certomat-R, Sartorius) at 100 rpm and 30 °C without any pH adjustment. The residual MB concentration in the solution at the equilibrium was measured by using a double-beam UV-Vis spectrophotometer (Lambda 45, Perkin Elmer) at 660 nm. The extent of MB uptake by the different activated carbons once the equilibrium was reached (q_e ; mg/g) was determined by means of a simple mass balance:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 (mg/L) is the initial concentration of MB and C_e is the concentration of MB once the equilibrium was reached. V (L) is the volume of MB solution in the flask and W (g) is the mass of activated carbon used in each experiment.

Moreover, kinetic studies of MB adsorption were performed by adding 0.25 g of adsorbent activated carbon into 500-mL Erlenmeyer flasks containing 250 mL of MB solutions (100 and 200 mg/L) under magnetic stirring at 30 °C. The residual concentration of MB, $C_{(t)}$, was measured as a function of time in the range of 5–240 min, and the uptake ($q_{(t)}$) was calculated using the following mass balance:

$$q_{(t)} = \frac{(C_0 - C_{(t)})V}{W} \quad (2)$$

Results and discussion

Physicochemical properties of the activated carbons

Figure 1 shows the nitrogen adsorption-desorption isotherms of the different activated carbons, and Table 2 summarizes the textural properties of the different samples. According to the classification of the International Union of Pure and Applied Chemistry (IUPAC), all activated carbons have type I hybrid-shape isotherms, with the adsorbed volume increasing sharply at low P/P_o , followed by a plateau extending up to high relative pressures. This is typical of highly microporous materials, with a narrow pore size distribution and a relatively small external specific surface area (Sing 1985).

As it can be seen in Table 2, all the activated carbons showed micropore specific surface areas representing from 70 to 80% of the total BET specific surface area. Only sample C1-550, which has a mesopore volume ($0.258 \text{ cm}^3/\text{g}$) significantly

Table 1 Activation and carbonization conditions

	C1-500	C1-550	C2-500	C2-550
PKS:ZnCl ₂ mass relationship	1	1	2	2
Carbonization temperature (°C)	500	550	500	550

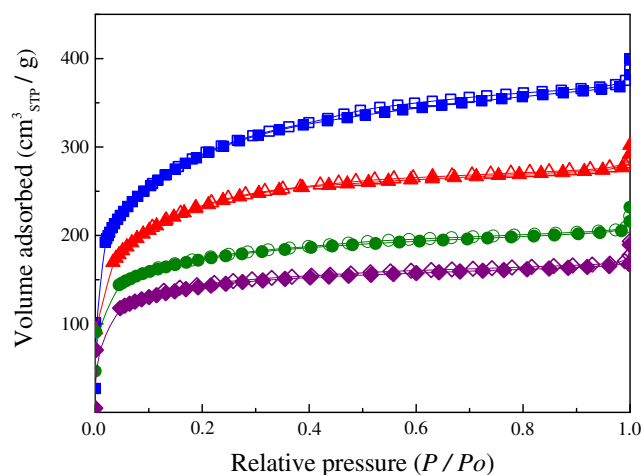


Fig. 1 Nitrogen adsorption-desorption isotherms of the different activated carbons. Red triangle C1-500, blue square C1-550, purple diamond C2-500, green circle C2-550

larger than those of the other samples in the series (between 0.075 and 0.136 cm^3/g), showed a small hysteresis loop. The simultaneous occurrence of micropore and mesopore was also observed in previous works, where activated carbons were prepared from different waste biomasses, such as, for example, jackfruit peel (Prahas et al. 2008), cattle manure compost (Zaini et al. 2008), globe artichoke leaves (Benadjemia et al. 2011), and pineapple leaves (Mahamad et al. 2015).

In the comparison of the textural properties of the various carbons, certain effects of the activation conditions can be noticed. For example, it can be seen that with both PKS:ZnCl₂ relationships, the higher the carbonization temperature is, the higher both the microporosity and mesoporosity in the carbons are, as reflected in the larger specific surface areas and volumes (see Table 2). This is probably because higher temperatures induce a more extended production of pyrolytic vapors, leading to higher yields of liquid and gas products (Bertero et al. 2011; Ahmad and Alrozi 2011), in turn producing more pores in the carbon structure. Liquid and gaseous products from the carbonization process were not

Table 2 Textural properties of the different samples of activated carbons

	C1-500	C1-550	C2-500	C2-550
BET specific surface area (m^2/g)	857	1058	511	628
Micropore specific surface area (m^2/g) ^a	682	721	415	503
Mesopore specific surface area (m^2/g)	175	337	96	125
Total pore volume (cm^3/g)	0.429	0.571	0.257	0.318
Micropore volume (cm^3/g)	0.293	0.313	0.181	0.217
Mesopore volume (cm^3/g) ^b	0.136	0.258	0.075	0.102

^a Micropore surface area = BET specific surface area – mesopore surface area

^b Mesopore volume = total pore volume – micropore volume

recovered, but, however, the yields of the AC, calculated based on the mass of dry biomass used, were approximately 54% at 550 °C and 58–60% at 500 °C.

If the effect of the biomass:activating agent mass relationship is analyzed, it can be observed that, whichever the carbonization temperature, the carbons prepared with PKS:ZnCl₂ 1:1 show a BET specific surface area, which is 68% larger than that of the carbons prepared with PKS:ZnCl₂ 2:1. When Mahamad et al. (2015) used ZnCl₂ in the preparation of activated carbon from pineapple leaves, a similar behavior was observed, a fact that has been attributed to higher ZnCl₂ loads increasing porosity due to a stronger dehydrating effect.

Surface functional groups containing oxygen play a major role in activated carbon properties such as surface hydrophobicity and charges (Fletcher et al. 2007). Surface functional groups in the various activated carbons were characterized by FTIR spectroscopy, Fig. 2 showing the different FTIR spectra. All the samples showed four well-defined signals. The broad-band at 3460 cm^{-1} is due to the O–H stretching mode of hydroxyl groups and adsorbed water (Yang and Lua 2003; Puziy et al. 2003; Das et al. 2015; Mahamad et al. 2015). The band at 1625 cm^{-1} can be assigned to the C = O axial deformation of aldehydes, ketones, and carboxyl groups (Das et al. 2015). A band with lower definition at 1393 cm^{-1} can be attributed to –CH₂ and –CH₃ twisting, while the band at 1060 cm^{-1} can be associated to symmetrical angular deformation of esters (Lapuenta et al. 1998).

The analysis of the morphological characteristics of the activated carbon was performed by using SEM imaging. Figure 3 shows the SEM micrographs of the different activated carbons. It can be seen in all the cases that a rough appearance was originated by the dehydrating effect of ZnCl₂ during the carbonization, in addition to the oxidation of organic compounds (Mahamad et al. 2015).

It can be seen that the samples prepared with 1:1 PKS:ZnCl₂ mass relationship (C1-500 and C1-550) showed a rough surface with a honeycomb-like structure and well-

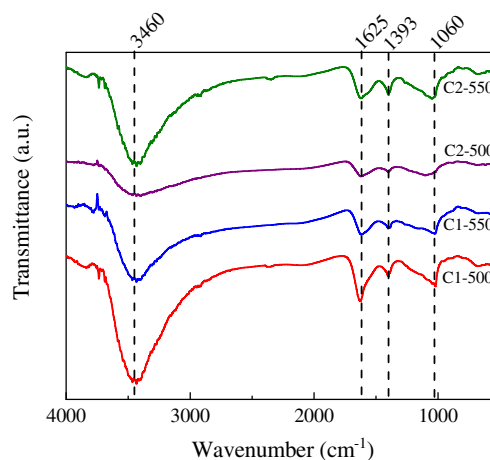
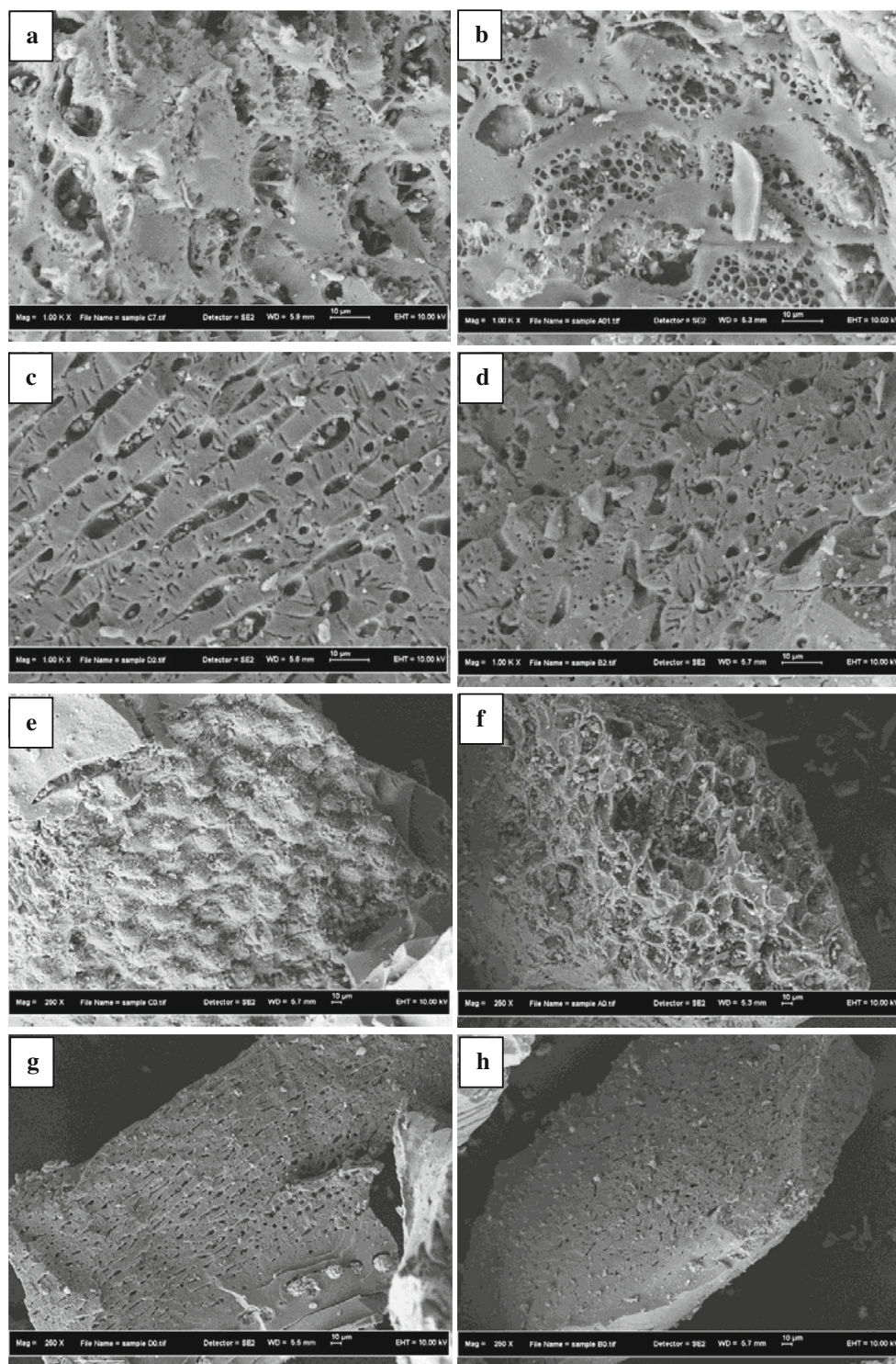


Fig. 2 FTIR spectra of the different activated carbons

Fig. 3 SEM micrographs of the different activated carbons with magnifications of $\times 1000$ (a C1-500, b C1-550, c C2-500, d C2-550) and $\times 250$ (e C1-500, f C1-550, g C2-500, h C2-550)



developed porosity (wide pores with openings which look circular; refer to Fig. 3a, b). On the contrary, the samples activated with a 2:1 PKS:ZnCl₂ mass relationship (C2-500 and C2-550) showed a smoother surface with cracks which were more oblong (see Fig. 3c, d). Then, it can be seen that the higher proportion of activating agent also impacts on the macropore domain.

Dye removal batch experiments

Some studies about the effect of the temperature on the performance of activated carbons prepared from different raw materials showed that, in the 25–40 °C range, the temperature may play not a significant role in determining the extent of methylene blue removal (Payne and Abdel-Fattah

2004; Yazdani et al. 2014; Mahamad 2015). A similar behavior in relation to the effect of the pH in the dye solution had been observed by Inbaraj and Sulochana (2002), Payne and Abdel-Fattah (2004), and Mahamad (2015) in the very ample range between 2 and 12. However, it is to be expected that extreme pH values could induce the generation of electrical charges on the surface functional groups in the activated carbons. These facts could interfere in the adsorbate-adsorbent interactions, thus conditioning the adsorption mechanism (Bulut and Aydin 2006; Kavitha and Namasivayam 2007; Prahas et al. 2008). In this work, the performance of the various activated carbons in removing dyes from water was evaluated by means of methylene blue equilibrium adsorption isotherms at 30 °C without any pH adjustment. Those conditions were selected after being considered typical in wastewater treatments.

The batch equilibrium adsorption experiments were performed by adding the same amount of activated carbon to the same volume of MB solutions with different initial concentrations. The experimental adsorption data at the equilibrium condition (q_e vs C_e) for the removal of methylene blue by different activated carbons are shown in Fig. 4.

The isotherms showed a characteristic profile, with a sharp slope at low C_e values, which decreased to reach a flat evolution in some cases, when MB concentrations at the equilibrium were higher. This is typically observed in the experiments of colorant removal using activated carbons (Kumar et al. 2011; Aljeboree et al. 2014; Mahamad et al. 2015). Moreover, adsorption isotherms can be adequately represented by Langmuir-type isotherms, the model assuming that the coverage of dye molecules until a monolayer is formed over a homogeneous adsorbent surface and that no further adsorption occurs at the already occupied sites. The Langmuir equilibrium equation is

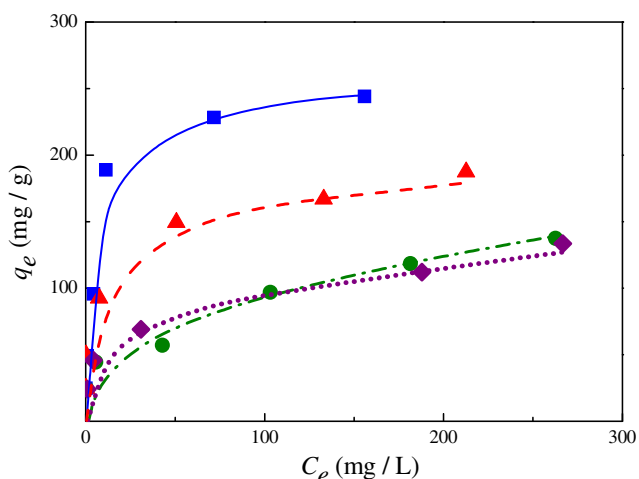


Fig. 4 Adsorption isotherm profiles for the removal of methylene blue by different activated carbons. Red triangle C1-500, blue square C1-550, purple diamond C2-500, green circle C2-550

Table 3 Parameters of Langmuir adsorption isotherm for the methylene blue adsorption at 30 °C

	C1-500	C1-550	C2-500	C2-550
q_{\max} (mg/g)	183.4	225.3	132.0	165.9
K_L (L/mg)	0.141	0.192	0.065	0.015
R^2	0.960	0.990	0.959	0.952

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

where q_{\max} is the mass of colorant adsorbed per mass of adsorbent when the monolayer is complete, while K_L is the Langmuir equilibrium constant. For each activated carbon, the adsorption data at the equilibrium condition (q_e vs C_e ; experimental points are shown in Fig. 4) gathered for different initial concentrations were fitted to the Langmuir model using a generalized reduced gradient (GRG) algorithm for solving nonlinear optimization problems (Lasdon et al. 1978), thus determining the model parameters q_{\max} and K_L . Table 3 shows the optimum parameter values for the model. These results suggest that adsorption equilibrium data can be adequately represented by a Langmuir isotherm, thus implying adsorption of the dye at homogenous sites of the activated carbon and constant adsorption enthalpy (Kundu and Gupta 2006; Pérez-Marín et al. 2007; Mahfud et al. 2008).

The comparison of the adsorption performances of the various carbons reveals that those that were prepared at the highest temperature (C1-550 and C2-550) showed better adsorptive properties (higher q_{\max} values) than the corresponding ones prepared at 500 °C (C1-500 and C2-500). For a given carbonization temperature, the lower the PKS:ZnCl₂ relationship is, the higher the q_{\max} value is. As it can be seen in Tables 2 and 3, the adsorption capacity is directly related to the specific surface area, particularly that of microporous. In fact, the relationship between q_{\max} and micropore specific surface area was essentially the same (0.31 ± 0.03 mg/m²) for all the samples. These results suggest that, in the range of activation conditions used, both the higher carbonization temperatures and the lower PKS:ZnCl₂ relationships are positive in the sense of producing carbons with increased colorant removal capacities. It should be noted that other models besides Langmuir's, such as Freundlich's or Redlich-Peterson's, could be considered to describe methylene blue adsorption equilibrium on activated carbons (Inbaraj and Sulochana 2002; Payne and Abdel-Fattah 2004; Mahamad et al. 2015). Nevertheless, the discrimination between models is out of the scope of this work. In this sense, the model by Langmuir was chosen considering that, besides being widely used in the related literature (Rozada et al. 2005; Prahas et al. 2008; Sharma et al. 2011; Kumar et al. 2011; Ahmed and Dhedan 2012; Pezoti et al. 2014; Mahamad et al. 2015), the fitted parameters q_{\max} and K_L could be adequately correlated to the conditions used to prepare the carbons and to their physicochemical properties.

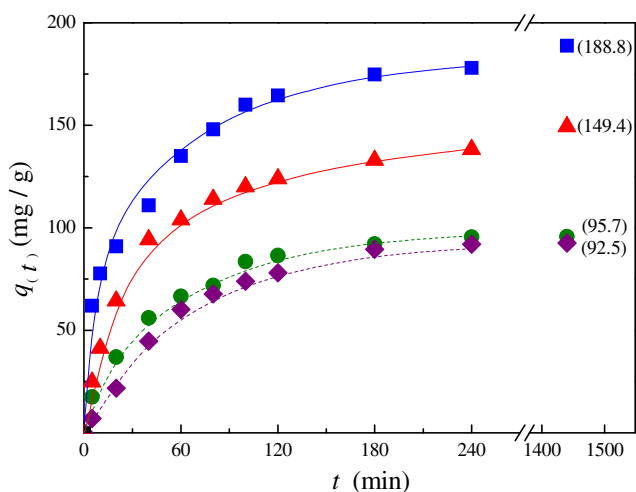


Fig. 5 Methylene blue ($V = 250$ mL) uptake curves at $C_0 = 200$ mg/L (red triangle C1-500; blue square C1-550) and $C_0 = 100$ mg/L (purple diamond C1-500; green circle C1-550). Equilibrium uptakes are shown between parentheses

If the concentration of colorant is low ($C_e \rightarrow 0$), then $K_L C_e < < 1$ and, consequently, Eq. (3) can be rewritten considering a Henry law linear equilibrium $q_e \cong (K_L q_{max}) C_e = K_H C_e$. Moreover, under these conditions, the higher the $K_H = K_L q_{max}$ value is, the higher the adsorption capacity in the solid is. It can be noticed in Table 3 that the samples prepared with the lowest PKS:ZnCl₂ relationship (C1-550 and C1-500) showed the highest K_H values (43.3 and 25.9 L/g, respectively), while in those prepared with PKS:ZnCl₂ relationship 2:1, the K_H values were 8.6 L/g (C2-500) and 2.5 L/g (C2-550). The higher dye affinity for the AC prepared with a higher proportion of ZnCl₂ activating agent, which is also confirmed by the initial slopes in Fig. 4, is probably a consequence of the higher micropore specific surface area.

If the performances of these carbons in the adsorption of colorants are compared against those of activated carbons obtained from other residual lignocellulosic biomasses under similar conditions, the values shown in Table 3 indicate that they had the same order of magnitude. Among others, sewage sludge ($q_{max} = 137.0$ mg/g, $K_L = 0.15$ L/mg (Rozada et al. 2005)),

jackfruit peel ($q_{max} = 280.3$ mg/g, $K_L = 0.52$ L/mg (Prahas et al. 2008)), cashew nut shell ($q_{max} = 68.7$ mg/g, $K_L = 0.20$ L/mg (Kumar et al. 2011)), date stones ($q_{max} = 398.2$ mg/g, $K_L = 0.04$ L/mg (Ahmed and Dhedan 2012)), and pineapple leaves ($q_{max} = 288.3$ mg/g, $K_L = 0.08$ L/mg (Mahamad et al. 2015)) can be mentioned.

The knowledge of the kinetics of the process is necessary to design adsorbers at different scales, including contact times and load of adsorbing material. As mentioned, carbons prepared with 1:1 PKS:ZnCl₂ relationship (C1-500 and C1-550) were those with the highest adsorption capacity (see Table 3), which were selected to perform kinetic experiments at 30 °C, determining the concentration of MB in the solutions as a function of time. Figure 5 shows the uptakes curves for both carbons with two initial MB concentrations (100 and 200 mg/L).

For all the experiments, the rates of adsorption, as indicated by the slopes of the uptake curves, were fast at short contact times and became slower and tended to stagnate following the gradual removal of methylene blue due to the smaller driving force for adsorption. It can be seen that the adsorption rate was faster provided that the concentration of MB in solution was higher; moreover, for given initial conditions, the uptake was faster on sample C1-550. The equilibrium uptakes, as determined in independent MB adsorption experiments (Fig. 4), are also included in Fig. 5, which show that after 4-h contact time, it was possible to reach 92.5% (C1-500) and 94.3% (C1-550) of the corresponding equilibrium uptakes when the initial MB concentration was 200 mg/L. In the case of 100 mg/L initial concentration, the removal was essentially complete. Similar trends, i.e., more extensive MB removal at lower initial concentrations, were also reported by researchers who used activated carbons prepared from other lignocellulosic sources (Yasin et al. 2007; Prahas et al. 2008; Zaini et al. 2013; Pezoti et al. 2014; Mahamad et al. 2015).

The dynamics of the colorant adsorption process can be described with the help of different kinetic models (Ho and McKay 1999; Kumar et al. 2011; Mahamad 2015), such as pseudo-first-order and pseudo-second-order models. The pseudo-first-order kinetic model (Ho and McKay 1999) is expressed as

Table 4 Fitted parameters (significance level of 95%) for both pseudo-first-order and pseudo-second-order kinetic models for adsorption of methylene blue at 30 °C

	q_e^a (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
		q_e (mg/g)	$k_1 \times 10^3$ (1/min)	R^2	q_e (mg/g)	$k_2 \times 10^3$ (g/mg/min)	R^2
C1-500 (100 mg/L)	92.5	95.2 ± 3.7	15.4 ± 1.5	0.990	124.2 ± 10.2	0.114 ± 0.032	0.980
C1-500 (200 mg/L)	149.4	129.2 ± 6.5	32.1 ± 6.0	0.984	151.9 ± 2.4	0.249 ± 0.018	0.999
C1-550 (100 mg/L)	95.7	93.6 ± 6.5	22.4 ± 4.8	0.971	113.0 ± 6.4	0.223 ± 0.051	0.990
C1-550 (200 mg/L)	188.8	163.3 ± 18.4	41.7 ± 19.4	0.915	184.1 ± 18.0	0.315 ± 0.161	0.964

^a From equilibrium experiments (see Fig. 4)

$$q(t) = q_e (1 - e^{-k_1 t}) \quad (4)$$

where k_1 (1/min) is the rate constant of pseudo-first-order adsorption. The pseudo-second-order kinetic model is (Ho and McKay 1999)

$$q(t) = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (5)$$

where k_2 (g/mg/min) is the pseudo-second-order rate adsorption constant.

The experimental results shown in Fig. 5 were fitted to the two models to determine the values of the corresponding parameters, according to Eqs. (4) and (5), using the method of least squares (Lasdon et al. 1978). The resulting parameters are shown in Table 4, together with some statistical information. It can be seen that when the initial concentration of methylene blue was relatively higher (200 mg/L), the pseudo-second-order model could best represent the rate of adsorption (considering the higher R^2 coefficient). Moreover, the q_e values from this model are closer to the equilibrium uptakes determined in independent experiments; that is, they show higher physical significance. Conversely, the rate of adsorption was best described by a pseudo-first-order model when the initial concentration of methylene blue was lower (100 mg/L). Mahamad (2015) observed a similar behavior in MB removal experiments with activated carbons obtained from pineapple leaves. The initial slopes of the uptake curves (see Fig. 5) indicate that the AC prepared by carbonization at 550 °C (C1-550) is the fastest in the removal of colorant, for both initial methylene blue concentrations. This is also confirmed by data shown in Table 4, independently from the kinetic model (higher k_1 and k_2 for sample C1-550), a fact that can be the consequence of C1-550 AC having an elevated mesoporosity, if compared against C1-500 AC (see discussion about Table 2). This would allow for a faster diffusion of methylene blue, which has a critical diameter of 1.4 nm, through the porous system. Values in Table 4 are in the same range as those observed by various authors using different waste biomasses (Rozada et al. 2005; Kumar et al. 2011; Pezoti et al. 2014), thus suggesting a high potential for using activated carbons prepared from palm kernel shell in the removal of dyes from wastewaters.

Conclusions

Different activated carbons were prepared from palm kernel shell using $ZnCl_2$ as the activating agent at two activation temperatures. The resulting activated carbons were more porous as the activation conditions were more severe, that is, lower PKS: $ZnCl_2$ relationship and higher carbonization temperature. Moreover, SEM micrographs showed that the

carbons prepared with more activating agent had a rough surface with a honeycomb-like structure and well-developed porosity. This effect was due to the more significant surface attack by $ZnCl_2$ by means of dehydration and oxidation reactions during the carbonization step, thus resulting into a higher porosity.

The carbon with a better performance in dye removal experiments was the one prepared with a PKS: $ZnCl_2$ mass ratio of 1:1 and carbonization temperature 550 °C, showing an uptake capacity comparable to those of activated carbons obtained from other residual lignocellulosic biomasses under similar conditions.

The results of this study show that oil palm mill waste biomass can be used in the preparation of alternative sustainable adsorbents that could be used with high efficiency for dye removal in wastewaters.

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