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Preparation of activated carbons from walnut shells via vacuum chemical activation and their application for methylene blue removal

Juan Yang, Keqiang Qiu*

School of Chemistry and Chemical Engineering, Central South University, Changsha, Hunan 410083, China

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ABSTRACT

Activated carbons were prepared from walnut shells by vacuum chemical activation with zinc chloride as the activation agent. To optimize the preparation method, the effects of the main process parameters (such as system pressure, activation temperature, and impregnation ratio) on the properties (expressed in terms of specific surface area and pore volume) of the obtained activated carbons were studied. It was found that the optimum activated carbon obtained with system pressure of 30 kPa, activation temperature of 450 °C, and impregnation ratio of 2.0 has a BET surface area of 1800 m²/g and total pore volume of 1.176 cm³/g. The prepared activated carbons were characterized by SEM, TEM, and FTIR. Then they were used as an adsorbent for the removal of methylene blue from aqueous solutions. The results showed that the methylene blue adsorption capacity was positively correlated to the BET surface area. The highest methylene blue adsorption capacity was 315 mg/g for the optimum activated carbon. The effect of the dose of the activated carbon was evaluated and the adsorption isotherm of methylene blue was determined. Redlich–Peterson and Langmuir–Freundlich models were found to best represent the equilibrium data, suggesting heterogeneous surface adsorption of methylene blue on the activated carbon.

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1. Introduction

The wide use of dyes in textile industries has lead to a variety of environmental problems, especially water pollution. Methylene blue (MB) is the most commonly used substance for coloring among all other dyes of its category and is generally used for dying cotton and silk [1]. Due to the harmful impacts of such dye on water, it is environmentally important to remove them from waste streams before discharge to public water sources.

Sorption is generally regarded as an effective technique for the treatment of dye-containing wastewater. Activated carbons, because of their large surface area and relatively high sorption capacity for a wide variety of dyes, have become the most promising and effective adsorbent [2,3]. Nevertheless, their applications are restricted, because the most widely used carbonaceous materials for the production of commercially activated carbon are derived from natural materials such as wood or coal, which are expensive and are often imported [4]. Therefore, in the recent years, there is growing interest in the production of activated carbons from agricultural wastes because of their abundant resources and cheap prices. Several suitable agricultural wastes including coffee husks [5], rice husks [6], pistachio-nut shells [7], cotton stalks [3], coconut husks [8], cherry stones [9], corn cobs [10], and plum kernels [11] have been investigated in the last years as activated carbon precursors and are receiving renewed attention. Furthermore, converting the agricultural wastes into value-added activated carbons provides a new way for agricultural waste treatment.

Typically, the preparation of activated carbon can be divided into physical activation and chemical activation. Physical activation consists of the pyrolysis of the precursor material and activation of the resulting char in steam or carbon dioxide. Chemical activation is a single step process and is held in presence of some chemical reagents, such as KOH, NaOH, K₂CO₃, ZnCl₂, FeCl₃, H₃PO₄, and H₂SO₄. Chemical activation normally takes place at a lower temperature than that used in physical activation. In addition, the carbon yield in chemical activation is usually higher than in physical activation because the chemical agents possess dehydrogenation properties which can inhibit the formation of tar and reduce the production of other volatile substances. Among the chemical activation agents, ZnCl₂ is the most widely used since it resulted in high surface areas and high yields [12–14].

There are many studies in the literature relating to the preparation of activated carbons from agricultural wastes via chemical activation. However, most of the studies at present are carried out under atmospheric conditions. Lua and Yang have reported that activated carbons obtained under vacuum have better properties (e.g., higher specific surface area) than that prepared under atmospheric conditions [7]. Our previous studies also show that the morphology, pore size distribution, Brunauer–Emmett–Teller

^{*} Corresponding author. Tel.: +86 731 88836994; fax: +86 731 88836994. *E-mail address:* qiuwhs@sohu.com (K. Qiu).

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(BET) surface area, and adsorption properties of activated carbons are closely related to the system pressure [15]. In order to distinguish the traditional chemical activation (i.e., under atmospheric condition) from the chemical activation under vacuum condition, we call the latter vacuum chemical activation. Though the vacuum chemical activation has obvious advantages over traditional chemical activation, as far as we know, there are still very few reports on the preparation of activated carbons by vacuum chemical activation, let alone the applications of activated carbons prepared by this method.

Walnut shell, a good precursor for activated carbon production, is a major agricultural waste in China. According to statistics, there is more than 100,000 tonnes of walnut shells are produced in China annually. To make better use of the cheap and abundant agricultural waste, it is proposed to use it for activated carbon production. Therefore, the objective of this study was to prepare relatively well developed porosity activated carbons from walnut shells on a laboratory scale via vacuum chemical activation utilizing ZnCl₂ as the activation agent. To optimize the preparation method, the effects of the main process parameters (system pressure, impregnation ratio, activation temperature) on the characteristics of the prepared activated carbons were studied. The low-cost walnut shell-based activated carbons were fully characterized and subsequently used as an adsorbent for methylene blue removal. Isotherms for the adsorption of methylene blue on the obtained activated carbons were measured and fit to five different isotherm equations to determine the best isotherm model to represent the experimental adsorption data.

2. Materials and methods

2.1. Preparation of activated carbons

Walnut shells used in this study were obtained from a fruit grower. The proximate, ultimate, and component analyses of this material are shown in Table 1. This agricultural waste is considered as a good candidate for conversion to activated carbon because of its relatively high carbon content and low ash. Prior to use, the precursor was washed with distilled water for several times to remove dust and other inorganic impurities, oven-dried for 48 h at 105 °C to reduce the moisture content, crushed, and sieved to a particle size of 0.15–0.90 mm. Zinc chloride pellets were dissolved in water and then impregnated into the shells with a certain impregnation ratio (defined by the weight ratio of ZnCl₂ to walnut shell). The mixture was maintained at room temperature for 48 h to incorporate all the chemicals in the interior of the particles, and then evaporated to dryness at 105 °C.

The impregnated walnut shell was placed in a stainless steel reactor (self-manufactured) which was inserted into an electric furnace. As shown in Fig. 1, the reactor was connected to a cold trap, which was used to collect the liquid product (biomass-oil). The end of the cold trap was connected to a mechanical vacuum

Table 1

Proximate analysis (as received, wt%)		
Moisture	3.42	
Ash	0.53	
Volatile	78.44	
Fixed carbon	17.61	
Ultimate analysis (dry basis, wt%)		
C	48.07	
Н	7.11	
Ν	0.76	
O ^a	42.84	
S	1.22	
Component analysis (dry basis, wt%)		
Hemicellulose	29.28	
Lignin	37.14	
Cellulose	23.55	
Benzene-alcohol extractives	5.21	

^a Estimated by difference.

pump. In each experiment, the system was first vacuumed to a preselected system pressure, and then the sample was heated from room temperature to a final temperature (350-600 °C) at a heating rate of 5 °C/min. The sample was activated at the final temperature for a holding time of 60 min before it was cooled to room temperature again. The heating and cooling processes were conducted under the same vacuum conditions. The resulting activated carbons were thoroughly washed with 0.1 M hydrochloric acid and distilled water to remove the residual ZnCl₂ until the pH value of the washed solution was between 6 and 7. The sample was then dried at 105 °C and ground to obtain a powder for subsequent analyses and uses.

The yield of activated carbon (Y_{AC}) and chemical recovery (CR) [16] were estimated according to the following equations:

$$Y_{\rm AC}(\%) = \frac{W_{\rm AC}}{W_{\rm WS}} \times 100 \tag{1}$$

$$CR(\%) = \frac{W_{SB} - W_{AC}}{W_{IC}} \times 100$$
⁽²⁾

where W_{AC} is the weight of the obtained activated carbon, W_{WS} is the weight of walnut shell used, W_{SB} is the weight of the sample before washing, and W_{IC} is the weight of impregnated chemical.

2.2. Characterization of activated carbons

The specific surface area and pore structure characteristic of prepared activated carbons were determined by nitrogen adsorption at -196 °C (Micromeritics ASAP2020). The BET surface area was calculated using the BET equation, total pore volumes were estimated to be the liquid volumes of N₂ at a high relative pressure (~0.99), and micropore volume and micropore specific surface area were obtained using the t-plot method. The surface functional groups and structure were studied by Fourier transform infrared spectroscopy (Nicolet 380 FT-IR). The FTIR spectra of the



Fig. 1. Schematic diagram of the experimental apparatuses used in the activation process.



Fig. 2. The chemical structure of methylene blue.

raw material and the resulting activated carbons were recorded from a wavenumber of 400–4000 cm⁻¹. The morphologies of the activated carbons were examined by scanning electron microscope (SEM, JEOL JSM-6360) and transmission electron microscope (TEM, JEM-100CX II).

2.3. Adsorption of methylene blue

The adsorbate used in the experiments was methylene blue (C.I. 52015), chemical formula = $C_{16}H_{18}CIN_3S$, MW = 319.85 g/mol, λ_{max} = 660 nm [17]. Its chemical structure is shown in Fig. 2.

Adsorption of methylene blue for the prepared activated carbon was conducted at room temperature of 25 °C. The methylene blue absorption capacity of activated carbon was determined according to China national standard GB/T 12496.10-1999. The adsorption isotherm was determined over the concentration range 500-2000 mg/L of methylene blue solutions in a series of 100 mL Erlenmeyer flasks containing 25 mL solution of each concentration. Certain amounts of activated carbon (about 0.1 g) were first added into the solutions. As many studies have shown that several hours are sufficient to attain the equilibrium for methylene blue absorption [18-20], the flasks were shaken at 270 rpm in a shaker for 24 h. Then the samples were separated by filtration, and the concentrations of methylene blue at equilibrium (C_e) were determined using a UV-vis spectrometer at wavelength of 665 nm. The amount of methylene blue adsorbed onto activated carbon (i.e., q_e) was calculated according to the following equation:

$$q_{\rm e} = \frac{V(C_0 - C_{\rm e})}{W} \tag{3}$$

where C_0 and C_e are the initial and equilibrium concentrations of methylene blue (mg/L), respectively, V is the volume of the solution (L), and W is the mass of adsorbent (g).

In order to evaluate the effect of dose of adsorbent, batch experiments were carried out by adding different amounts of activated carbon (0.02–0.13 g) into each 100 mL methylene blue solution (200 mg/L). The remaining steps were the same as the adsorption isotherm measurement. The removal percentage of methylene blue was calculated according to the following equation:

$$R(\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{4}$$

3. Results and discussion

3.1. Preparation of activated carbons from walnut shell

3.1.1. Effects of processing parameters on yield of activated carbon and chemical recovery

The yields of activated carbons and the chemical recoveries in the activation process are shown in Table 2. The results showed that the system pressure has little influence on carbon yield. The activation temperature has a negative effect on carbon yield. This is expected because at a higher temperature, more volatiles are released, resulting in a lower yield. However, when the activation temperature exceeds 450 °C, most of the volatiles have been released; therefore, the yields maintain almost a constant value. A similar trend has been reported in some studies for ZnCl₂ chemical activation [14,21]. However, in those studies, the yield of activated carbon is still decreased even though the temperature is higher than 600 °C. This can be attributed to the influence of vacuum condition, which accelerates the release of volatiles, causing the volatile matter to be released completely at a relatively low temperature. With an increase in the impregnation ratio from 0.5 to 2.0, the yield of activated carbon decreased from 43.8% to 40.1%. With a higher impregnation ratio, the movement of the volatiles through the pore passages will occur more easily, leading to a lower carbon yield. Lua and Yang also reported a similar result in their research on the preparation of activated carbon by vacuum chemical activation [7].

For chemical recoveries, system pressure and activation temperature were found to be the main factors. As can be seen from Table 2, the chemical recoveries were dramatically decreased when the system pressure was lower than 30 kPa or the activation temperature was higher than 450 °C. This is because lower system pressure or higher temperature can make ZnCl₂ evaporate more easily and therefore result in a lower chemical recovery. The result is also verified by the fact that the chemical recovery of vacuum chemical activation (63.7%) in this study was lower than that of traditional chemical activation (80.16%) [22] under the same condition (activation temperature: 600 °C; impregnation ratio: 1.0). However, most of the chemical recoveries in this work are higher than 85%, which are higher than that of 74.43–81.24 wt% for traditional chemical activation [22].

3.1.2. Effects of processing parameters on surface area and pore volume of activated carbon

Within the scope of our research, an attempt has been made to optimize the process parameters which lead to an activated carbon

Table 2 Yields of activated carbons and chemical recoveries in the ZnCl_2 vacuum activation process.

System pressure (kPa)	Activation temperature (°C)	Impregnation ratio	Yield of activated carbon (wt%)	Chemical recovery (wt%)
10	450	1.0	40.7	79.9
30	450	1.0	41.1	88.4
50	450	1.0	40.1	88.7
100	450	1.0	41.4	89.4
30	350	1.0	48.7	88.3
30	400	1.0	44.8	88.0
30	500	1.0	41.4	86.4
30	550	1.0	41.3	78.0
30	600	1.0	41.7	63.7
30	450	0.5	43.8	85.1
30	450	0.75	43.9	87.0
30	450	1.5	41.5	93.7
30	450	2.0	40.1	96.1



Fig. 3. Effects of system pressure on the (a) surface areas and (b) pore volumes of activated carbons (activation temperature: 450 °C; impregnation ratio: 1.0).

with good properties. As illustrations, Figs. 3–5 show the effects of system pressure, activation temperature, and impregnation ratio on the surface area and pore volume of the prepared activated carbons. The exact surface area and pore volume values are shown in Table S1.

The effects of system pressure on the surface areas and pore volumes of activated carbon were detected as shown in Fig. 3. It is interesting to note that the porosity is closely related to the system pressure. As the system pressure decreased, the micropore surface area and volume of resulting activated carbon increased, while the mesopore surface area and volume decreased. From the figure, we can see that the maximum of the BET surface area and total pore volume of activated carbon appear at a system pressure of 30 kPa. Decreasing system pressure in a certain range can reduce the oxygen in the system, and the residence time of organic vapor formed during pyrolysis in the reactor is gradually decreased; the secondary reactions of organic vapor such as the formation of carbonaceous deposits on the surface and in the pores of activated carbon are limited [15]. Therefore, the prepared activated carbon has a more porous structure. However, when the system pressure is too low, the volatilization of pyrolysis vapor is violent. It will destroy the micropore structure. Also, the evaporation of zinc chloride increases with decreasing system pressure. Excessive evaporation of zinc chloride will decrease the activation effect and result in a decrease of the BET surface area and total pore volume. It can be clearly seen that a system pressure of 30 kPa seems to be the most suitable for the development of high surface area and large pore volume of the activated carbon.

The effects of activation temperature on the surface areas and pore volumes of activated carbon (Fig. 4) show that the BET surface area, micropore surface area, mesopore surface area, total pore volume, micropore volume and mesopore volume have the same variation trend with temperature, which begin to increase with an



Fig. 4. Effects of activation temperature on the (a) surface areas and (b) pore volumes of activated carbons (system pressure: 30 kPa; impregnation ratio: 1.0).



Fig. 5. Effects of impregnation ratio on the (a) surface areas and (b) pore volumes of activated carbons (system pressure: 30 kPa; activation temperature: 450 °C).



Fig. 6. SEM micrographs of walnut shell (a and b) and walnut shell-based activated carbon (c and d).

increase of the temperature from 350 to 450 °C, and then decrease when the temperature exceeds 450 °C. The increase in surface areas and pore volumes in the low temperature range can be attributed to the dehydration of $ZnCl_2$ and the increasing release of volatile matter. However, a continuous decrease in the BET surface area and pore volume was observed when the activation temperature was increased from 450 to 600 °C. There are two factors which can contribute to this phenomenon: (i) from Table 2 we can see that most of the volatiles have been released when the temperature is higher than 450 °C; (ii) at a higher temperature, the heat shrinkage of the carbon structure will result in a decrease in surface area and pore volume [23]. Thus, keeping the activation temperature at around 450 °C can lead to a better development of the porosity of the activated carbon.

Fig. 5 shows the effects of impregnation ratio on the surface area and pore volume of activated carbon. It can be seen that the BET surface area, mesopore surface area, total pore volume and mesopore volume are all increased with increasing impregnation ratio. However, a peak value at the impregnation ratio of 1.0 is found for the micropore surface area and micropore volume. It indicates that the activated carbons prepared with a low impregnation ratio (lower than 1.0) have more microporous structure, while for impregnation ratios higher than 1.0, the activated carbons are mostly mesoporous. The results can also be obtained from the nitrogen adsorption isotherms and the mesopore size distributions as shown in Fig. S1. The increase of micropores at low impregnation ratio can be attributed to the effect of ZnCl₂, which inhibits the formation of tar and promotes the release of volatiles to produce more micropores. But when the impregnation ratio higher than 1.0, the more swelling impregnated material and stronger release of volatiles in the activation process will lead to a widening of pores; micropores formed are subsequently converted to mesopores and even probably macropores. Our results are in good agreement with the previous reports related to ZnCl₂ chemical activation [13].

The above results show that the most efficient activated carbon is that obtained under the following optimum conditions: a system pressure of 30 kPa, an activation temperature of 450 °C, and an impregnation ratio of 2.0. The surface area and pore volume of activated carbon prepared under optimum conditions were 1800 m²/g and 1.176 m³/g, respectively.

3.2. Characterization of the optimal activated carbon

3.2.1. Morphology

The SEM technique was used to observe the surface physical morphology of the raw material and the prepared activated carbon. Fig. 6a and b presents the micrographs for walnut shell employed as the raw material for the preparation of activated carbon. The material presents a surface morphology in the form of particles, possibly with a low specific surface area. However, after activation, the compact structure of the sample turned to be crispy and porous. For the activated carbon prepared under the optimum conditions (Fig. 6c and d), its surface is smooth and different from the rough surface of the raw walnut shell. All of the pores observed by SEM are macropores. The nitrogen adsorption data showed that the activated carbon produced was mainly mesoporous. The pores would not be visible at the magnification of the SEM, since mesopores in the prepared activated carbon are characterized in the region of less than 50 nm.

With much higher magnification, TEM has been carried out to examine the microstructure of the activated carbon. Fig. 7a represents the TEM image of the walnut shell-based activated carbon. Obviously, the activated carbon has a well developed porous structure consisting of inter-connected nanochannels (white fringes), which were formed by the disordered packing of turbostratic carbon sheets and clusters (black fringes). The microstructure can be observed more clearly after the TEM image processed by ImageJ using the FFT Filter plugin (Fig. 7b). More information about the image process can be found in Supporting Information.

3.2.2. Fourier transformed infrared spectroscopy (FTIR)

The FTIR spectrum of the starting material is shown in Fig. 8. The raw walnut shell shows indications of various surface functional groups. The wide peak, which located at around 3405 cm^{-1} is typically attributed to hydroxyl groups or adsorbed water. The bands located at around 2926 and 2856 cm^{-1} correspond to C–H stretching vibrations in methyl and methylene groups [24]. The band appearing at 1744 cm^{-1} is ascribed to carbonyl (C=O) groups. The olefinic C=C stretching vibrations adsorptions cause the band at about 1624 cm^{-1} while the skeletal C=C vibrations in aromatic rings cause another two bands at about 1513 and 1428 cm^{-1}



Fig. 7. (a) Original and (b) processed TEM micrograph of walnut shell-based activated carbon; the inset of figure is an enlarged image of the selected area.

[7]. The bands at around 1455 and $1376 \,\mathrm{cm}^{-1}$ corresponded to the C–H in-plane bending vibrations in methyl and methylene groups. The appearance of a band at $1322 \,\mathrm{cm}^{-1}$ can be attributed to C–O stretching vibrations in carboxylate groups [25]. The band at $1248 \,\mathrm{cm}^{-1}$ and a relatively intense band at about $1052 \,\mathrm{cm}^{-1}$ can be assigned to C–O stretching vibrations in alcohols, phenols, or ether or ester groups. The C–H out-of-plane bending vibrations in benzene derivative cause the bands at 897 and 831 cm⁻¹. Finally, the band caused by O–H out-of-plane bending vibrations band is located at $609 \,\mathrm{cm}^{-1}$. From the band assignment, the oxygen groups present in the walnut shell include carbonyl groups, ethers, esters, alcohols, and phenol groups.



Fig. 8. Fourier transform infrared spectra of walnut shell and walnut shell-based activated carbon.



Fig. 9. Relationship between methylene blue adsorption capacity and BET surface area.

The FTIR spectra of activated carbon prepared under the optimum conditions is also shown in Fig. 8. Fewer functional groups were detected, indicating that the surface functional groups of walnut shell experienced chemical changes during pyrolysis. Compared with the walnut shell, the C–H vibrations in methyl and methylene groups (at 2921 and 2852 cm⁻¹) become much weaker after activation, suggesting the carbonization of the material is almost complete. As the release of light volatile matters in the heating process, a new band at 2362 cm⁻¹ appears that can be ascribed to C≡C stretching vibrations in alkyne groups. The peak at 1744 cm⁻¹, which is observed in the starting material, belonging to carbonyl groups, disappears with the thermal treatment. Many other bands decrease dramatically indicating the decrease in functionality in the main matrix. More detailed band assignments of the raw material and activated carbon can be found in Table S2.

3.3. Adsorption of methylene blue

3.3.1. Effect of BET surface area on adsorption of methylene blue

Methylene blue dye (MB), with a molecular size of $1.6 \text{ nm} \times 0.7 \text{ nm}$, is a widely used dye in the textile processing industry. In addition, it is also the most recognized probe molecule for assessing the ability of the sorbent to remove large molecules. Fig. 9 shows the relationship between methylene blue adsorption capacity and BET surface area. It can be seen that the methylene blue adsorption capacity is positively correlated to the BET surface area. Walnut shell-based activated carbon subjected to the optimum conditions showed the highest methylene blue adsorption capacity of activated carbon prepared by ZnCl₂ chemical activation in the literature [3,5].

3.3.2. Effect of activated carbon dose on adsorption of MB

Under the conditions of pH of 7.0, *C*₀ of 200 mg/L, and contact time of 24 h, the effect of dose of activated carbon (obtained at the optimum conditions) on the percentage removal of methylene blue is shown in Fig. 10. It is apparent that the percentage removal of methylene blue was increased by increasing the activated carbon dose. This was the reason that the number of available adsorption sites was increased by increasing the adsorbent dose [26]. When the activated carbon dose was 0.75 g/L, the removal percentage of methylene blue can reach 99%. Furthermore, increasing the carbon dose decreased the adsorption capacity. This can be attributed to that increasing the carbon dose, the adsorption sites remain unsaturated during the adsorption reaction leading to drop in adsorption capacity [27]. Additionally, the aggregation of adsorbent particles at higher mass may lead to a decrease in the surface area and an increase in the diffusional path length [28].



Fig. 10. Effect of dose of activated carbon on the removal of methylene blue.

3.3.3. Adsorption isotherm of methylene blue

The adsorption isotherm describes how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. It can provide qualitative information on the nature of the solute–surface interaction at constant temperature [29]. The original data for the determination of adsorption isotherm of methylene blue are shown in Table S3. In this study, five isotherms models were used for describing the results, namely the Langmuir isotherm, the Freundlich isotherm, the Langmuir–Freundlich isotherm, the Temkin isotherm, and the Redlich–Peterson isotherm.

The Langmuir isotherm is derived on the assumption of monolayer adsorption on a homogenous surface. It is expressed by [30]:

$$q_{\rm e} = \frac{bq_0C_{\rm e}}{1+bC_{\rm e}}\tag{5}$$

where q_e is the equilibrium adsorption capacity (mg/g), C_e is the equilibrium concentration (mg/L), b is the Langmuir adsorption constant (L/mg), and q_0 is the maximum adsorption capacity (mg/g).

The Freundlich isotherm assumes heterogeneous surface energies, which is appropriate for the description of multilayer adsorption with interaction between adsorbed molecules. The Freundlich isotherm is expressed by the following empirical equation [31]:

$$q_{\rm e} = K_{\rm F} C_{\rm e}^{1/n} \tag{6}$$

where K_F (L/mg) is the Freundlich adsorption constant and 1/n is the heterogeneity factor.

The Redlich–Peterson model may be used to represent adsorption equilibrium over a wide concentration range, and can be applied either in homogeneous or heterogeneous systems due to its versatility [32]. The Redlich–Peterson isotherm is represented by following equation:

$$q_{\rm e} = \frac{K_{\rm R}C_{\rm e}}{1 + \alpha C_{\rm e}^{\beta}} \tag{7}$$

where $K_{\rm R}$ (L/g), α (L/mg) and β are the constants of Redlich–Peterson. β is the exponent, which fluctuates between 0 and 1 and can characterize the isotherm as if β = 1, the Langmuir will be the preferable isotherm, while if β = 0, the Freundlich will be the preferable isotherm [33].

The Langmuir–Freundlich model is usually used with a heterogeneous adsorption surface. The Langmuir–Freundlich isotherm equation is given as [34]:

$$q_{\rm e} = \frac{q_0 (K_{\rm LF} C_{\rm e})^{\alpha_{\rm LF}}}{1 + (K_{\rm LF} C_{\rm e})^{\alpha_{\rm LF}}}$$
(8)



Fig. 11. Comparison of different isotherm models for methylene blue adsorption onto walnut shell-based activated carbon.

where K_{LF} is the constant of Langmuir–Freundlich (L/mg) and α_{LF} is the heterogeneity parameter.

The Temkin equation shows the effects of some indirect adsorbate/adsorbate interactions on adsorption isotherm. The heat of adsorption of all the molecules in the layer would decrease linearly with coverage. The Temkin isotherm can be expressed as [35]:

$$q_{\rm e} = \frac{RT}{b_{\rm T}} \ln(AC_{\rm e}) \tag{9}$$

where A is the Temkin isotherm constant (L/mg), b_T is the Temkin constant related to the variation of adsorption energy (J/mol), R is the universal gas constant (8.314J/(mol K)) and T is the absolute temperature (K).

Fig. 11 shows the five fitted model curves and the experimental points of the methylene blue adsorption equilibrium isotherm obtained at 25 °C with the activated carbon prepared by vacuum chemical activation (under the optimum conditions). The fitting results, i.e. isotherm parameters and the coefficient of determination, R^2 , are shown in Table 3.

For Langmuir adsorption isotherm, one of the essential characteristics could be expressed by dimensionless constant called equilibrium parameter, R_L [36]:

$$R_{\rm L} = \frac{1}{1 + bC_0} \tag{10}$$

where C_0 is the highest initial solute concentration, *b* is the Langmuir adsorption constant (L/mg). The value of R_L indicates the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). By processing the above equation, R_L value for investigated dye-adsorbent system was found to be

Table 3

Isotherm models and their parameters.

Isotherms	Parameters	Values
Langmuir	b	3.711
	q_0	355.5
	R^2	0.9113
Freundlich	K _F	238.1
	n	10.36
	R^2	0.8600
Redlich-Peterson	K _R	2228
	α	7.619
	β	0.9496
	R^2	0.9948
Langmuir–Freundlich	q_0	390.5
	K _{LF}	2.735
	$\alpha_{\rm LF}$	0.5142
	R^2	0.9734
Temkin	b_{T}	81.47
	Α	2240
	R^2	0.9201

1.5E-4, suggesting the prepared activated carbon is favourable for adsorption of methylene blue under conditions used in this study. This can also be concluded from the Freundlich model fitting results. The magnitude of the exponent, 1/n, gives an indication of the favourability of adsorption. Value of n > 1 represents favourable adsorption condition [37]. The Redlich–Peterson constant $\beta \approx 1$, indicating the Langmuir model is more preferable than Freundlich model. This can be further confirmed by the fact that the coefficient R^2 for Langmuir isotherm was higher than that for Freundlich isotherm. The Langmuir model fitted the experimental data better than Freundlich model, indicating the adsorption of methylene blue onto the adsorbent tended to monolayer adsorption. The Redlich-Peterson and Langmuir-Freundlich models were found to best represent the equilibrium data, suggesting the heterogeneous surface adsorption of methylene blue on the prepared activated carbon. The $b_{\rm T}$ obtained from the Temkin equation is positive, indicating the adsorption reaction is exothermic [38]. Furthermore, The R^2 of the five models descend in the order of: Redlich-Peterson > Langmuir-Freundlich > Temkin > Langmuir > Freundlich. The results revealed that the equilibrium data are better fitted by the three-parameter models rather than the

4. Conclusions

two-parameter models.

The results of this study showed that activated carbons prepared from walnut shells by vacuum chemical activation exhibit welldeveloped porosity and high BET surface area. The properties of the activated carbons were closely related to the system pressure, activation temperature, and impregnation ratio. The maximum surface area of $1800 \text{ m}^2/\text{g}$ and total pore volume of $1.176 \text{ cm}^3/\text{g}$ were obtained under the following optimal conditions: a system pressure of 30 kPa, an activation temperature of $450 \,^\circ\text{C}$, and an impregnation of 2.0. The FTIR results showed the presence of many oxygen groups and olefinic and aromatic carbon structures in the raw walnut shell. During the activation, the functionality in the main matrix was decreased. SEM and TEM micrographs showed that the prepared activated carbon had a well developed porous structure.

The activated carbon prepared in the present study was applied to methylene blue adsorption. The BET surface area was found to have a positive effect on the methylene blue adsorption capacity. The adsorption isotherm was determined and fit to five models. The results showed that the adsorption of methylene blue onto the prepared activated carbon was monolayer and heterogeneous surface adsorption. The removal percentage of methylene blue can reach to 99% when the activated carbon dose was 0.75 g/L, indicating that the prepared activated carbon is a good candidate for water treatment to remove some organic pollutants.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cej.2010.09.019.

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