Journal of Zhejiang University-SCIENCE B (Biomedicine & Biotechnology)
ISSN 1673-1581 (Print); ISSN 1862-1783 (Online)
www.zju.edu.cn/jzus; www.springerlink.com
E-mail: jzus@zju.edu.cn

Adsorption of methylene blue onto activated carbon produced from tea (*Camellia sinensis* L.) seed shells: kinetics, equilibrium, and thermodynamics studies[*]

Jun-jie GAO[1], Ye-bo QIN[2], Tao ZHOU[1], Dong-dong CAO[3],
Ping XU[†‡1], Danielle HOCHSTETTER[1], Yue-fei WANG[†‡1,4]
(*[1]Department of Tea Science, Zhejiang University, Hangzhou 310058, China*)
(*[2]Crop Management Bureau, Agricultural Department of Zhejiang Province, Hangzhou 310029, China*)
(*[3]Zhejiang Academy of Agricultural Sciences, Hangzhou 310021, China*)
(*[4]Key Laboratory of Horticultural Plant Growth, Development and Quality Improvement, Ministry of Agriculture, Hangzhou 310029, China*)
[†]E-mail: zdxp@zju.edu.cn; tyfwang@gmail.com

Received Sept. 10, 2012; Revision accepted Apr. 1, 2013; Crosschecked June 17, 2013

Abstract: Tea (*Camellia sinensis* L.) seed shells, the main byproduct of the manufacture of tea seed oil, were used as precursors for the preparation of tea activated carbon (TAC) in the present study. A high yield (44.1%) of TAC was obtained from tea seed shells via a one-step chemical method using $ZnCl_2$ as an agent. The Brunauer-Emmett-Teller (BET) surface area and the total pore volumes of the obtained TAC were found to be 1 530.67 mg^2/g and 0.782 6 cm^3/g, respectively. The equilibrium adsorption results were complied with Langmuir isotherm model and its maximum monolayer adsorption capacity was 324.7 mg/g for methylene blue. Adsorption kinetics studies indicated that the pseudo-second-order model yielded the best fit for the kinetic data. An intraparticle diffusion model suggested that the intraparticle diffusion was not the only rate-controlling step. Thermodynamics studies revealed the spontaneous and exothermic nature of the sorption process. These results indicate that tea seed shells could be utilized as a renewable resource to develop activated carbon which is a potential adsorbent for methylene blue.

Key words: Activated carbon, Adsorption, Tea seed shells, Methylene blue
doi:10.1631/jzus.B12a0225 **Document code:** A **CLC number:** X712

1 Introduction

Synthetic dyestuffs used extensively in textile, paper, printing industries and dye houses are mostly discharged into surface water resources as industrial wastes. This has turned out to be a significant source of aquatic ecosystem pollutants (Aksu, 2005; Attia *et al.*, 2008). Dyeing industry effluents constitute one of the most problematic wastewaters to be treated not only for their high chemical and biological oxygen demands, suspended solids, and content in toxic compounds but also for colour, which are the first contaminant to be recognized by the human eye (Aksu, 2005). Thus, dye wastewater needs to be treated for the sake of the protection of human health and environmental safety. However, the treatment of dyes in industrial wastewater presents several problems since dyes usually have a synthetic origin and complex aromatic molecular structures which make them very stable and generally difficult to be biodegraded and photodegraded (Lorenc-Grabowska and Gryglewicz, 2007; Gupta, 2009).

[‡] Corresponding authors

[*] Project supported by the Science and Technology Department of Zhejiang Province (No. 2010C32051) and the Ministry of Science and Technology (No. 2011BAD01B03-5-1), China

Recently, the removal of dyes from wastewater through adsorption techniques has proven promising due to its simplicity, inexpensiveness, and efficiency (Wang *et al.*, 2005; Baccar *et al.*, 2010; Dural *et al.*, 2011; Kyzas *et al.*, 2012). Adsorption is the process by which a solid adsorbent can attract a component in water to its surface and form an attachment via a physical or chemical bond, thus removing the component from the fluid phase (Demirbas *et al.*, 2008). A successful adsorption process not only depends on dye adsorption performance of the adsorbents, but also on the constant supply of the materials for the process (Han *et al.*, 2008). Activated carbon is known for its unique properties including porous structure, high specific surface areas, and large sorption capacities (Dural *et al.*, 2011). It is also an excellent adsorbent, and can be used for a variety of purposes, such as purification and separation, in the abatement of hazardous contaminants, in municipal and industrial wastewater treatment, as a catalyst or catalyst support in medicine, and in the recovery of valuable metals, etc. (Sun and Jiang, 2010).

However, the costs of preparing activated carbon have historically been high. Currently agro-industrial waste, a renewable resource, is considered to be a promising candidate for the production of activated carbon and would make activated carbon widely available for adsorption. Previously, many activated carbons have been prepared from agro-industrial waste biomasses, including coconut shell (Azevedo *et al.*, 2007), waste apricot (Nal, 2006), olive stone (Kula *et al.*, 2008), coffee residue (Boudrahem *et al.*, 2011), piassava fiber (Avelar *et al.*, 2010), rice husk (Kalderis *et al.*, 2008), and pomegranate seed (Uçar *et al.*, 2009).

It is estimated that over a million tons of tea seed shells are produced annually in China. Driving the popularity of tea seed oil in recent years is the fact that it is an edible oil of high quality, containing more than 84% unsaturated fatty acid while the predominant fatty acids are oleic acid and linoleic acid (Sahari *et al.*, 2004; Demirbas, 2009). As the popularity of tea seed oil has increased, the amount of tea seed shells, the main byproduct during manufacture of seed oil, has greatly increased as well. However, tea seed shells are not typically utilized and the majorities are discarded as agro-industrial waste. Due to the large quantities of material available and the consistent accumulation of tea seed shells, there is a need for efficient management of them.

Therefore, the aim of this research was to prepare activated carbon from tea seed shells by using a $ZnCl_2$ activation method, to investigate its textural and chemical surface characterization, and to study its adsorption of methylene blue (MB) including kinetics, equilibrium, and thermodynamics studies.

2 Materials and methods

2.1 Raw materials

Tea seed used for the preparation of activated carbon was collected from the Panban tea garden (Zhejiang, China). The seed shell was removed from the seed, dried at 110 °C for 12 h, ground and sieved to a particle size range of 40–60 meshes, and then stored in sealed containers for experimentation.

2.2 Adsorbate

A cationic dye MB was chosen for the adsorption experiments. Stock solutions of 500 mg/L dye were prepared with distilled water and the required concentrations were obtained by diluting.

2.3 Preparation of the activated carbon

A one-step method of preparation of the activated carbon was selected in this paper. The processed raw material was soaked in $ZnCl_2$ solution with an impregnation ratio of 1:1 for 24 h and then dried at 110 °C for 6 h. The dried mixture was put into a furnace and heated to 500 °C at the rate of 20 °C/min under a constant N_2 (99.99%) flow of 120 cm^3/min. The activation process was maintained for 1 h. Then, the activated substance was repeatedly washed with 0.1 mol/L HCl followed by distilled water until the pH reached 7. Finally, the product was dried at 110 °C for 8 h, ground and sieved to a particle size of 180 meshes for further studies. The yield of activated carbon is defined as the weight after activation, washing, and drying. The percent yield was calculated by

$$\text{Yield} = \frac{m}{M} \times 100\%, \tag{1}$$

where m and M are the dry weights (g) of the activated carbon and the precursor, respectively.

2.4 Preparation of the activated carbon

Textural characterization of the activated carbon was measured by N_2 adsorption at 77 K (AUTOSORB-1-C QUANTACHROME, America). Surface functional groups were examined using Fourier transform infrared analysis (AVA TAR370, America) with a scanning range of 4000–400 cm^{-1}. The surface morphology was detected by a scanning electron microscope (SEM; HITACHI S-3000N, Japan). The point of zero charge (pH_{pzc}) was determined according to the method described by Foo and Hameed (2011a).

2.5 Batch adsorption studies

MB kinetic and isotherm adsorption experiments were carried out to evaluate the adsorption performance. The equilibrium adsorption research was completed by adding a fixed amount of activated carbon into 25 ml different initial concentrations of MB. The kinetic adsorption studies were performed by adding 0.2 g activated carbon into 200 ml different initial concentrations of MB. The aqueous samples were taken at pre-set time intervals and their concentrations were determined. Concentration determination of all the samples was filtered before they were measured by UV-6100A spectrophotometer at the maximum absorption wavelength of 664 nm. The amount of MB adsorption at equilibrium was calculated by

$$q_e = (C_o - C_e)V / W, \qquad (2)$$

where C_o and C_e (mg/L) are the initial and equilibrium concentrations of MB, respectively, V (L) is the volume of the solution, and W (g) is the mass of adsorbents used. The uptake of MB at time t, q_t (mg/g) was calculated by

$$q_t = (C_o - C_t)V / W, \qquad (3)$$

where C_t is the concentration of MB at any time.

3 Results and discussion

3.1 Yield

As can be seen from Table 1, a high yield of tea activated carbon (TAC) was obtained with a desiring characteristic, this should be attributed to the lower temperature used in the chemical activation, which reduced the amount of compounds liberated by volatilization (Avelar *et al.*, 2010).

Table 1 Textural characteristics, yield, and pH_{pzc} of tea activated carbon (TAC)

Parameter	Value
S_{BET} (m^2/g)	1530
V_T (cm^3/g)	0.7826
V_{mic} (cm^3/g)	0.5989
V_{mes} (cm^3/g)	0.1837
D_{ap} (nm)	2.045
Yield (%)	44.10
pH_{pzc}	6.30

S_{BET}: Brunauer-Emmett-Teller (BET) surface area; V_T: total pore volume; V_{mic}: micropore volume; V_{mes}: mesopore volume; D_{ap}: average pore diameter

3.2 Characterization of TAC

3.2.1 Textural characterization

Fig. 1 shows the N_2 adsorption and desorption at 77 K of TAC, from which it can be seen that a sharp increase of adsorption volume occurred at low relative pressure, and at high relative pressure the adsorption volume reached a plateau. According to the International Union of Pure and Applied Chemistry (IUPAC) classification for adsorption isotherm, the isotherm is classified as type I, indicating the presence of large fractions of micropores and in some cases mesopores (Dural *et al.*, 2011).

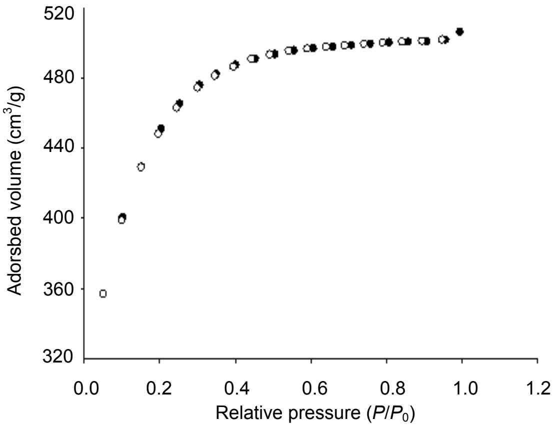

Fig. 1 N_2 adsorption and desorption isotherms of tea activated carbon (TAC) at 77 K

Pore size distribution is a very important property of adsorbents because the difference in the pore size affects the adsorption capacity for molecules of different sizes and shapes, and also this is one of the criteria by which carbon adsorbents are selected for a particular application (Xiao *et al.*, 2012). The pore size distribution of the TAC inillustrates that the sizes of the pores are smaller than 4.0 nm, in which pores less than 2.0 nm account for a large percentage (Fig. 2). From the data presented in Table 1, it can be seen that the D_{ap} value is 2.045 nm which is very near 2.0 nm indicating a great development of micropores based on the classification adopted by IUPAC: micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm). Table 2 sums up activated carbon samples prepared from various agriculture waste biomass with $ZnCl_2$ as an agent. Though the Brunauer-Emmett-Teller (BET) surface areas of activated carbons produced from sugar beet bagasse and *Enteromorpha prolifera* are higher than that in the present work, the BET surface area of the TAC is much higher than others listed in Table 2, from which it can be detected that it is a good choice to utilize tea seed shells for producing activated carbons of high specific surface area with the modification of $ZnCl_2$.

SEM micrographs of TAC under different magnifications are given in Fig. 3. It can be observed that the rough surface is filled with cavities and irregular holes, which resulted from the evaporation of $ZnCl_2$ during carbonization, leaving the space previously occupied by the reagent (Demiral and Gündüzoğlu, 2010).

3.2.2 Chemical surface characterization

Surface functional groups within activated carbon contribute significantly to its adsorption ability, as ion exchangers, adsorbents, catalysts, and catalyst supports (Ren *et al.*, 2011). Fourier transform infrared spectroscopy (FTIR) spectra of the precursor and TAC are presented in Fig. 4. The bands located at 3420–3385 cm^{-1} in both of spectra were typically attributed to O–H stretching vibration of hydroxyl functional groups. The precursor had a peak at 2925 cm^{-1} which was attributed to the C–H, yet there was a decrease in the spectrum of TAC. Significant differences occurred at the bands from 1700–1000 cm^{-1}. For the spectrum of the precursor, the band at 1739 cm^{-1} is ascribed to C=O. The band at

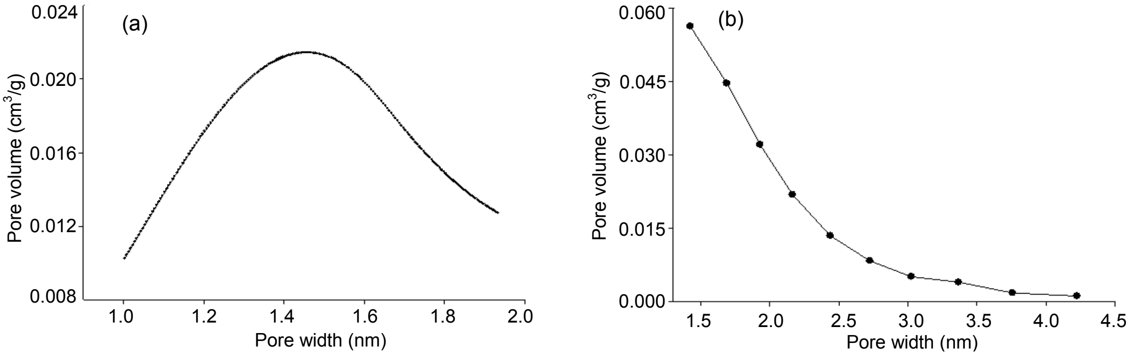

Fig. 2 Pore size distributions of TAC

(a) Micropore size distribution by Horvath-Kawazoe (HK) method; (b) Mesopore size distribution by Barrett-Joyner-Halenda (BJH) method

Table 2 Activated carbons from agriculture residues by chemical activation with $ZnCl_2$

Precursor	Activation temperature (°C)	Activation time (min)	BET surface area (m^2/g)	Reference
Terminalia arjuna nut	500	60	1260	Mohanty *et al.* (2005)
Coconut shell	500	180	1266	Azevedo *et al.* (2007)
Rice husk	700	30	750	Kalderis *et al.* (2008)
Olive stone	650	120	790	Kula *et al.* (2008)
Pomegranate seed	600	60	979	Uçar *et al.* (2009)
Piassava fiber	500	240	1190	Avelar *et al.* (2010)
Sugar beet bagasse	700	90	1826	Demiral and Gündüzoğlu (2010)
Enteromorpha prolifera	500	60	1688	Li *et al.* (2010)
Coffee residue	600	60	889	Boudrahem *et al.* (2011)
Tea seed shell	500	60	1530	Present study

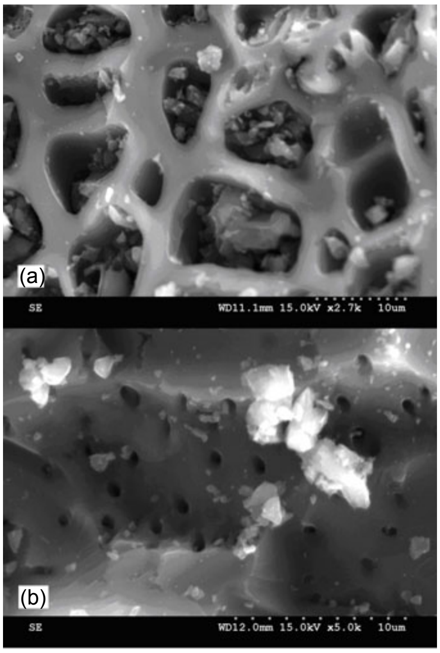

Fig. 3 SEM images of TAC under different magnifications: (a) 2700×; (b) 5000×

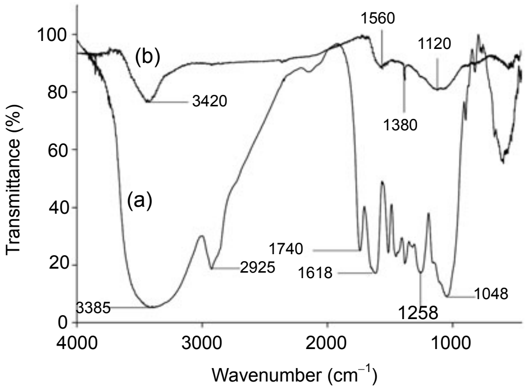

Fig. 4 FTIR spectra for the tea seed shell (a) and TAC (b)

1 618 cm^{-1} is ascribed to the olefinic (C=C) vibrations. The band at 1 258 cm^{-1} may be attributed to esters, ethers or phenol groups and the band at 1 048 cm^{-1} corresponded to the alcohol groups (R–OH) (Baccar *et al.*, 2009). For the spectrum of the precursor, the band around 1 560 cm^{-1} arose from C=C stretching in an aromatic ring. The band at 1 380 cm^{-1} could be assigned to the C=C stretching of aromatic rings polarized by oxygen atoms bound near one of the C atoms (Njoku and Hameed, 2011). The peak occurring at 1 120 cm^{-1} was ascribed to the presence of C–O. So, it can be concluded that the surface functional groups were significantly different between samples treated with $ZnCl_2$ and those not treated. The changes in the FT-IR spectrum of TAC were evidence of the formation of structures containing multiple carbon-carbon bonds as well as the elimination of originally present oxygen and hydrogen atoms (Chen *et al.*, 2011). As can be seen from Table 1, the pH_{pzc} value was 6.30 indicating the acidic nature of the TAC.

3.3 Adsorption kinetics

Kinetic study is important to the adsorption process because it depicts the uptake rate of adsorbate and controls the residual time of the whole adsorption process (Demirbas *et al.*, 2009). To explore the controlling mechanism of the adsorption process, the experimental data were fitted to the pseudo-first-order, pseudo-second-order, and intraparticle diffusion models.

The linear forms of the pseudo-first-order and the pseudo-second-order are represented by

$$\ln(q_{\mathrm{e}}-q_t)=\ln q_{\mathrm{e}}-K_1t, \tag{4}$$

$$\frac{t}{q_t}=\frac{1}{K_2q_{\mathrm{e}}^2}+\frac{t}{q_{\mathrm{e}}}, \tag{5}$$

where K_1 (min^{-1}) and K_2 (g·mg^{-1}·min^{-1}) are the rate constants of the pseudo-first-order and pseudo-second-order, respectively.

The parameters of kinetic models parameters and the correlation coefficient (R^2) values for different initial concentrations are listed in Table 3. As can be seen, the R^2 values obtained from the pseudo-second-order were consistently higher than those from the pseudo-first-order. In addition, the q_{e} values coincided with the expected q_{e} values ($q_{\mathrm{e,exp}}$). That indicates that the adsorption perfectly obeys the pseudo-second-order model meaning the controlling rate step is chemisorption. Meanwhile, the result showed that the rate of adsorption depended on the availability of adsorption sites on the surface of adsorbent rather than MB concentration in bulk solution (Liu, 2008).

To evaluate the contribution of intraparticle diffusion to the sorption mechanism, an intraparticle diffusion model is introduced in this paper. The equation is expressed as

$$q_t=K_{\mathrm{p}}t^{0.5}+C, \tag{6}$$

Table 3 Kinetic model parameters and correlation coefficients for adsorption of MB at different initial concentrations onto TAC (25 °C, pH=7.5)

C_o (mg/L)	$q_{e,exp}$ (mg/g)	Pseudo-first-order			Pseudo-second-order		
		K_1 (min^{-1})	q_e (mg/g)	R^2	K_2 (g·mg^{-1}·min^{-1})	q_e (mg/g)	R^2
150	149.9	0.01423	3.600	0.8678	0.012700	150.2	1.000
200	199.7	0.01700	15.01	0.9160	0.004040	200.4	1.000
250	248.8	0.01330	46.11	0.8220	0.001090	250.0	1.000

where K_p represents the rate constant (mg·g^{-1}·min$^{-0.5}$), and C (mg/g) is a constant reflecting the significance of the boundary layer or mass transfer effect.

As can be seen from Fig. 5, the plot of q_t vs. $t^{0.5}$ can be divided into two straight portions for different initial concentrations. In the first portion, it is attributed to the instantaneous utilization of the adsorbing sites on the adsorbent surface and the second portion is ascribed to a very slow diffusion of the MB from the surface film into the micropores, which are the least accessible sites of adsorption (Ma *et al.*, 2011). This suggested that the intraparticle diffusion was not the only rate-controlling step. Meanwhile, this also indicated that external mass transfer of MB molecules onto sorbent particles is also significant in the sorption process, especially at the initial reaction period (Hameed *et al.*, 2009).

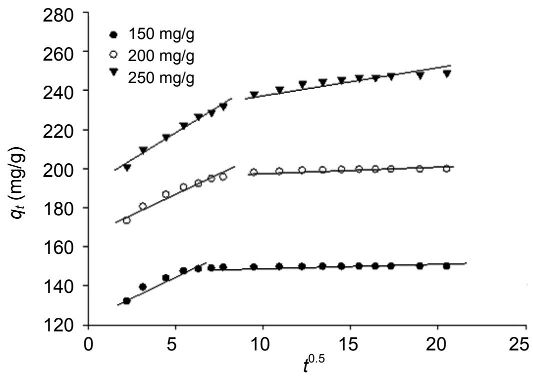

Fig. 5 Intraparticle diffusion plots for adsorption of MB at different initial concentrations

3.4 Adsorption isotherms

Adsorption isotherms describe qualitative information of the nature of the solute-surface interaction as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature (Li and Wang, 2009). The equilibrium data were analyzed by fitting them to two isotherm models, namely the Langmuir and Freundlich isotherm models.

3.4.1 Langmuir isotherm model

The Langmuir model assumes monolayer adsorption onto a surface containing a finite number of adsorption sites of uniform energies of adsorption with no transmigration of adsorbate in the surface plane (Baccar *et al.*, 2010).

The model is represented by

$$\frac{C_e}{q_e}=\frac{1}{q_m K_L}+\frac{C_e}{q_m}, \tag{7}$$

where q_m (mg/g) and K_L (L/mg) are related to the maximum adsorption capacity and Langmuir constant, respectively. The Langmuir dimensionless constant separation factor or equilibrium parameter R_L is calculated by (Hall *et al.*, 1966)

$$R_L = 1/(1+K_L C_o), \tag{8}$$

where R_L indicates the shape of the isotherm to be either unfavorable (R_L>1), linear (R_L=1), favorable (0<R_L<1), or irreversible (R_L=0).

It can be observed from Fig. 6 that all values of R_L are between 0 and 1 indicating the adsorption process was favorable. The values of R_L at low temperatures are smaller than those at high temperatures, from which it can be deduced that the adsorption behavior is more effective at low temperature.

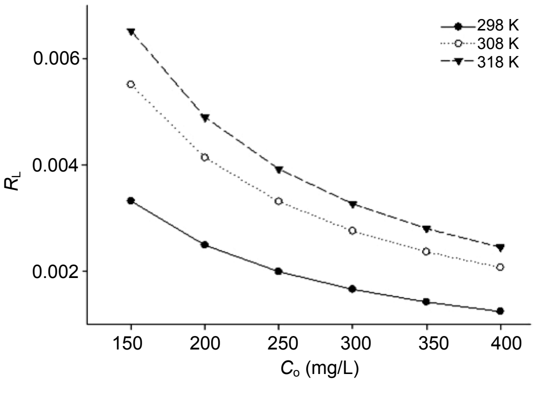

Fig. 6 R_L values under different initial concentrations of MB at different temperatures

3.4.2 Freundlich isotherm model

The empirical Freundlich model, which is known to be satisfactory for low concentrations and based on sorption on a heterogeneous surface (Baccar, *et al.*, 2010), is expressed by

$$\lg q_e = \lg K_f + \frac{1}{n}\lg C_e, \qquad (9)$$

where n and K_f ((mg/g)(L/mg)$^{1/n}$) are Freundlich constants related to the favorability of adsorption process and the adsorption capacity of the adsorbate, respectively. If $1/n<1$, it indicates a favorable adsorption. Table 4 lists the values of $1/n$ at different temperatures, it can be seen that all the values of $1/n$ are smaller than 1. The favorability of the adsorption process was further confirmed by the result.

The parameters of the isotherm models calculated from the experimental data and the values of correlation coefficient (R^2) are presented in Table 4. According to the results, the R^2 values for the Langmuir are higher than those in Freundlich isotherm model. It is clear that the equilibrium adsorption data comply with Langmuir isotherm model, which suggests that the adsorption is a process which occurs in a homogeneous surface. Additionally, these results also demonstrated no interaction and transmigration of dyes in the plane of the neighboring surface (Foo and Hameed, 2011c). As can be seen from Table 4, the value of K_L decreased with temperature increase, which implied that low temperature favored the adsorption process. For the sake of comparison, Table 5 lists the maximum monolayer adsorption of MB onto activated carbons derived from different precursors. Based on the data in Table 5, it was found that TAC displayed a relatively high adsorption capacity of MB.

3.5 Adsorption thermodynamics

The thermodynamic parameters such as free energy (ΔG^0), enthalpy (ΔH^0), and entropy (ΔS^0) give a description of adsorption behavior related to temperature. Parameters can be calculated from

$$\Delta G^0 = -RT\ln K_L, \qquad (10)$$

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT}, \qquad (11)$$

where K_L (L/mol) is from Langmuir equation, R is the gas constant (8.314 J/(mol·K), and T (K) is the temperature in Kelvin.

As can be seen from Table 6, the values of ΔG^0 were consistently negative at all temperatures measured, which revealed the adsorption process was feasible and spontaneous in nature. Furthermore, the absolute values of ΔG^0 decrease with the increase of the temperature indicating that the sorption process is more favorable at low temperature. The negative

Table 4 Isotherm model parameters and correlation coefficients for adsorption of MB onto TAC at different temperatures

Temperature (K)	Langmuir isotherm model			Freundlich isotherm model		
	q_m (mg/g)	K_L (L/mg)	R^2	K_f ((mg/g)·(L/mg)$^{1/n}$)	$1/n$	R^2
298	324.7	2.000	0.9997	221.8	0.1010	0.9481
308	319.5	1.204	0.9992	206.1	0.1102	0.9342
318	313.5	1.016	0.9991	205.1	0.09785	0.9530

Table 5 Comparison of maximum monolayer adsorption of MB onto activated carbons from different precursors

Precursor	Agent	Adsorption capacity (mg/g)	Reference
Posidonia oceanica dead leaves	$ZnCl_2$	285.7	Dural *et al.* (2011)
Cotton stalk	$ZnCl_2$	193.5	Deng *et al.* (2009)
Date stones	KOH	316.1	Foo and Hameed (2011b)
Oil palm empty fruit bunch	KOH	344.8	Foo and Hameed (2011d)
Cashew nut shell	KOH	68.7	Kumar *et al.* (2011)
Vetiver roots	H_3PO_4	423.0	Altenor *et al.* (2009)
Durian shell	K_2CO_3	289.3	Chandra *et al.* (2007)
Tea seed shells	$ZnCl_2$	342.7	This work

Table 6 Thermodynamic parameters for adsorption of MB onto TAC

ΔH^0 (kJ/mol)	ΔS^0 (J/(mol·K))	ΔG^0 (kJ/mol)		
		298 K	308 K	318 K
−26.80	−84.64	−1.720	−0.467	−0.0420

value of ΔH^0 was indicative of the exothermic nature of the adsorption process. The negative value of ΔS^0 suggested the decreased randomness at the solid-solute adsorption systems, which indicated that gain of entropy caused by the water molecules displaced is less than that lost by the MB molecules.

4 Conclusions

In the present study, tea seed shells were modified by using $ZnCl_2$ in a one-step method at relatively low energy consumption. The kinetic adsorption complied well with the pseudo-second-order model. The results of the intraparticle diffusion model suggest that intraparticle diffusion was not the sole rate determining step. It was found that the Langmuir isotherm model yielded the best for equilibrium data with the maximum monolayer adsorption of 324.7 mg/g for methylene blue. Thermodynamics studies indicated the spontaneous and exothermic nature of the sorption process.

Compliance with ethics guidelines

Jun-jie GAO, Ye-bo QIN, Tao ZHOU, Dong-dong CAO, Ping XU, Danielle HOCHSTETTER, and Yue-fei WANG declare that they have no conflict of interest.

This article does not contain any studies with human or animal subjects performed by any of the authors.

References

Aksu, Z., 2005. Application of biosorption for the removal of organic pollutants: a review. *Process Biochem.*, **40**(3-4): 997-1026. [doi:10.1016/j.procbio.2004.04.008]

Altenor, S., Carene, B., Emmanuel, E., Lambert, J., Ehrhardt, J.J., Gaspard, S., 2009. Adsorption studies of methylene blue and phenol onto vetiver roots activated carbon prepared by chemical activation. *J. Hazard. Mat.*, **165**(1-3): 1029-1039. [doi:10.1016/j.jhazmat.2008.10.133]

Attia, A.A., Girgis, B.S., Fathy, N.A., 2008. Removal of methylene blue by carbons derived from peach stones by H_3PO_4 activation: batch and column studies. *Dyes Pigments*, **76**(1):282-289. [doi:10.1016/j.dyepig.2006.08.039]

Avelar, F.F., Bianchi, M.L., Gonçalves, M., da Mota, E.G., 2010. The use of piassava fibers (*Attalea funifera*) in the preparation of activated carbon. *Bioresource Technol.*, **101**(12):4639-4645. [doi:10.1016/j.biortech.2010.01.103]

Azevedo, D., Araujo, J., Bastos-Neto, M., Torres, A.E.B., Jaguaribe, E.F., Cavalcante, C.L., 2007. Microporous activated carbon prepared from coconut shells using chemical activation with zinc chloride. *Microp. Mesop. Mat.*, **100**(1-3):361-364. [doi:10.1016/j.micromeso.2006.11.024]

Baccar, R., Bouzid, J., Feki, M., Montiel, A., 2009. Preparation of activated carbon from Tunisian olive-waste cakes and its application for adsorption of heavy metal ions. *J. Hazard. Mat.*, **162**(2-3):1522-1529. [doi:10.1016/j.jhazmat.2008.06.041]

Baccar, R., Blánquez, P., Bouzid, J., Feki, M., Sarrà, M., 2010. Equilibrium, thermodynamic and kinetic studies on adsorption of commercial dye by activated carbon derived from olive-waste cakes. *Chem. Eng. J.*, **165**(2):457-464. [doi:10.1016/j.cej.2010.09.033]

Boudrahem, F., Soualah, A., Aissani-Benissad, F., 2011. Pb(II) and Cd(II) removal from aqueous solutions using activated carbon developed from coffee residue activated with phosphoric acid and zinc chloride. *J. Chem. Eng. Data*, **56**(5):1946-1955. [doi:10.1021/je1009569]

Chandra, T.C., Mirna, M., Sudaryanto, Y., Ismadji, S., 2007. Adsorption of basic dye onto activated carbon prepared from durian shell: studies of adsorption equilibrium and kinetics. *Chem. Eng. J.*, **127**(1-3):121-129. [doi:10.1016/j.cej.2006.09.011]

Chen, Y., Zhu, Y., Wang, Z., Li, Y., Wang, L., Ding, L., Gao, X., Ma, Y., Guo, Y., 2011. Application studies of activated carbon derived from rice husks produced by chemical-thermal process—a review. *Adv. Colloid Interf. Sci.*, **163**(1):39-52. [doi:10.1016/j.cis.2011.01.006]

Demiral, H., Gündüzoğlu, G., 2010. Removal of nitrate from aqueous solutions by activated carbon prepared from sugar beet bagasse. *Bioresource Technol.*, **101**(6): 1675-1680. [doi:10.1016/j.biortech.2009.09.087]

Demirbas, A., 2009. Oil from tea seed by supercritical fluid extraction. *Energy Sources, Part A*, **31**(3):217-222. [doi:10.1080/15567030701524340]

Demirbas, E., Kobya, M., Sulak, M., 2008. Adsorption kinetics of a basic dye from aqueous solutions onto apricot stone activated carbon. *Bioresource Technol.*, **99**(13): 5368-5373. [doi:10.1016/j.biortech.2007.11.019]

Demirbas, E., Dizge, N., Sulak, M., Kobya, M., 2009. Adsorption kinetics and equilibrium of copper from aqueous solutions using hazelnut shell activated carbon. *Chem. Eng. J.*, **148**(2-3):480-487. [doi:10.1016/j.cej.2008.09.027]

Deng, H., Yang, L., Tao, G., Dai, J., 2009. Preparation and characterization of activated carbon from cotton stalk by microwave assisted chemical activation—application in methylene blue adsorption from aqueous solution. *J. Hazard. Mat.*, **166**(2):1514-1521. [doi:10.1016/j.jhazmat.2008.12.080]

Dural, M.U., Cavas, L., Papageorgiou, S.K., Katsaros, F.K., 2011. Methylene blue adsorption on activated carbon prepared from *Posidonia oceanica* (L.) dead leaves: kinetics and equilibrium studies. *Chem. Eng. J.*, **168**(1): 77-85. [doi:10.1016/j.cej.2010.12.038]

Foo, K., Hameed, B., 2011a. Microwave-assisted preparation and adsorption performance of activated carbon from biodiesel industry solid reside: influence of operational parameters. *Bioresource Technol.*, **103**(1):398-404. [doi:10.1016/j.biortech.2011.09.116]

Foo, K., Hameed, B., 2011b. Preparation of activated carbon from date stones by microwave induced chemical activation: application for methylene blue adsorption. *Chem. Eng. J.*, **170**(1):338-341. [doi:10.1016/j.cej.2011.02.068]

Foo, K., Hameed, B., 2011c. Preparation and characterization of activated carbon from sunflower seed oil residue via microwave assisted K_2CO_3 activation. *Bioresource Technol.*, **102**(20):9794-9799. [doi:10.1016/j.biortech.2011.08.007]

Foo, K., Hameed, B., 2011d. Preparation of oil palm (*Elaeis*) empty fruit bunch activated carbon by microwave-assisted KOH activation for the adsorption of methylene blue. *Desalination*, **275**(1-3):302-305. [doi:10.1016/j.desal.2011.03.024]

Gupta, V., 2009. Application of low-cost adsorbents for dye removal: a review. *J. Environm. Manag.*, **90**(8): 2313-2342. [doi:10.1016/j.jenvman.2008.11.017]

Hall, K., Eagleton, L., Acrivos, A., Vermeulen, T., 1966. Pore-and solid-diffusion kinetics in fixed-bed adsorption under constant-pattern conditions. *Ind. Eng. Chem. Fundam.*, **5**(2):212-223. [doi:10.1021/i160018a011]

Hameed, B., Salman, J., Ahmad, A., 2009. Adsorption isotherm and kinetic modeling of 2,4-D pesticide on activated carbon derived from date stones. *J. Hazard. Mat.*, **163**(1):121-126. [doi:10.1016/j.jhazmat.2008.06.069]

Han, R., Ding, D., Xu, Y., Zou, W., Wang, Y., Li, Y., Zou, L., 2008. Use of rice husk for the adsorption of Congo red from aqueous solution in column mode. *Bioresource Technol.*, **99**(8):2938-2946. [doi:10.1016/j.biortech.2007.06.027]

Kalderis, D., Bethanis, S., Paraskeva, P., Diamadopoulos, E., 2008. Production of activated carbon from bagasse and rice husk by a single-stage chemical activation method at low retention times. *Bioresource Technol.*, **99**(15): 6809-6816. [doi:10.1016/j.biortech.2008.01.041]

Kula, I., Uğurlu, M., Karaoğlu, H., Çelikc, A., 2008. Adsorption of Cd(II) ions from aqueous solutions using activated carbon prepared from olive stone by $ZnCl_2$ activation. *Bioresource Technol.*, **99**(3):492-501. [doi:10.1016/j.biortech.2007.01.015]

Kumar, P.S., Ramalingam, S., Sathishkumar, K., 2011. Removal of methylene blue dye from aqueous solution by activated carbon prepared from cashew nut shell as a new low-cost adsorbent. *Korean J. Chem. Eng.*, **28**(1): 149-155. [doi:10.1007/s11814-010-0342-0]

Kyzas, G.Z., Lazaridis, N.K., Mitropoulos, A.C., 2012. Removal of dyes from aqueous solutions with untreated coffee residues as potential low-cost adsorbents: equilibrium, reuse and thermodynamic approach. *Chem. Eng. J.*, **189-190**:148-159. [doi:10.1016/j.cej.2012.02.045]

Li, K., Wang, X., 2009. Adsorptive removal of Pb(II) by activated carbon prepared from *Spartina alterniflora*: equilibrium, kinetics and thermodynamics. *Bioresource Technol.*, **100**(11):2810-2815. [doi:10.1016/j.biortech.2008.12.032]

Li, Y., Du, Q., Wang, X., Zhang, P., Wang, D., Wang, Z., Xia, Y., 2010. Removal of lead from aqueous solution by activated carbon prepared from *Enteromorpha prolifera* by zinc chloride activation. *J. Hazard. Mat.*, **183**(1-3): 583-589. [doi:10.1016/j.jhazmat.2010.07.063]

Liu, Y., 2008. New insights into pseudo-second-order kinetic equation for adsorption. *Colloids Surf. A: Physicochem. Eng. Aspects*, **320**(1-3):275-278. [doi:10.1016/j.colsurfa.2008.01.032]

Lorenc-Grabowska, E., Gryglewicz, G., 2007. Adsorption characteristics of Congo red on coal-based mesoporous activated carbon. *Dyes Pigments*, **74**(1):34-40. [doi:10.1016/j.dyepig.2006.01.027]

Ma, J., Jia, Y., Jing, Y., Yao, Y., Sun, J., 2011. Kinetics and thermodynamics of methylene blue adsorption by cobalt-hectorite composite. *Dyes Pigments*, **93**(1-3):1441-1446. [doi:10.1016/j.dyepig.2011.08.010]

Mohanty, K., Jha, M., Meikap, B., Biswas, M., 2005. Preparation and characterization of activated carbons from *Terminalia arjuna* nut with zinc chloride activation for the removal of phenol from wastewater. *Ind. Eng. Chem. Res.*, **44**(11):4128-4138. [doi:10.1021/ie050162+]

Nal, Y., 2006. Kinetics of adsorption of dyes from aqueous solution using activated carbon prepared from waste apricot. *J. Hazard. Mat.*, **137**(3):1719-1728. [doi:10.1016/j.jhazmat.2006.05.036]

Njoku, V., Hameed, B., 2011. Preparation and characterization of activated carbon from corncob by chemical activation with H_3PO_4 for 2,4-dichlorophenoxyacetic acid adsorption. *Chem. Eng. J.*, **173**(2):391-399. [doi:10.1016/j.cej.2011.07.075]

Ren, L., Zhang, J., Li, Y., Zhang, C., 2011. Preparation and evaluation of cattail fiber-based activated carbon for 2,4-dichlorophenol and 2,4,6-trichlorophenol removal. *Chem. Eng. J.*, **168**(2):553-561. [doi:10.1016/j.cej.2011.01.021]

Sahari, M.A., Ataii, D., Hamedi, M., 2004. Characteristics of tea seed oil in comparison with sunflower and olive oils and its effect as a natural antioxidant. *J. Am. Oil Chem. Soc.*, **81**(6):585-588. [doi:10.1007/s11746-006-0945-0]

Sun, K., Jiang, J.C., 2010. Preparation and characterization of activated carbon from rubber-seed shell by physical activation with steam. *Biomass Bioenergy*, **34**(4):539-544. [doi:10.1016/j.biombioe.2009.12.020]

Uçar, S., Erdem, M., Tay, T., Karagöz, S., 2009. Preparation and characterization of activated carbon produced from pomegranate seeds by $ZnCl_2$ activation. *Appl. Surf. Sci.*, **255**(21):8890-8896. [doi:10.1016/j.apsusc.2009.06.080]

Wang, S., Boyjoo, Y., Choueib, A., Zhu, Z., 2005. Removal of dyes from aqueous solution using fly ash and red mud. *Water Res.*, **39**(1):129-138. [doi:10.1016/j.watres.2004.09.011]

Xiao, H., Peng, H., Deng, S., Yang, X., Zhang, Y., Li, Y., 2012. Preparation of activated carbon from edible fungi residue by microwave assisted K_2CO_3 activation—application in reactive black 5 adsorption from aqueous solution. *Bioresource Technol.*, **111**:127-133. [doi:10.1016/j.biortech.2012.02.054]