

# Biosorption of Methylene Blue from Aqueous Solution Using *Xanthoceras sorbifolia* Seed Coat Pretreated by Steam Explosion

Zeng-Yu Yao\* and Jian-Hua Qi

Key Laboratory for Forest Resources Conservation and Use in the Southwest Mountains of China, Ministry of Education, Southwest Forestry University, Kunming 650224, China

## Abstract

*Xanthoceras sorbifolia* seed coat (XSSC) is a processing residue of the bioenergy crop. This work aimed to evaluate the applicability of using the steam explosion to modify the residue for dye biosorption from aqueous solutions by using methylene blue as a model cationic dye. Equilibrium, kinetic and thermodynamic parameters for the biosorption of methylene blue on the steam-exploded XSSC (SE-XSSC) were evaluated. The kinetic data followed the pseudo-second-order model, and the rate-limiting step was the chemical adsorption. Intraparticle diffusion was one of the rate-controlling factors. The equilibrium data agreed well with the Langmuir isotherm, and the biosorption was favorable. The steam-explosion pretreatment strongly affected the biosorption in some respects. It reduced the adsorption rate constant and the initial sorption rate of the pseudo-second-order model. It enhanced the adsorption capacity of methylene blue at higher temperatures while reduced the capacity at lower ones. It changed the biosorption from an exothermic process driven by both the enthalpy and the entropy to an endothermic one driven by entropy only. It increased the surface area and decreased the pH point of zero charge of the biomass. Compared with the native XSSC, SE-XSSC is preferable to MB biosorption from warmer dye effluents.

**Key Words:** biosorption, dye, steam explosion, testa, yellow horn

## Introduction

Dyes are extensively used in many industries such as textile, rubber, paper, leather, plastic, cosmetic, and printing, to give us a desirably colorful world. However, discharging dye effluents from these industries into the environment diminishes aesthetic values of ecosystems and disturbs aquatic life (Campos et al. 2001). Therefore, the dyes should be removed from such effluents prior to their discharge into the environment. Among some existing technologies, ad-

sorption holds promise for dye-loaded wastewater treatment. Activated carbon is effective in removing dyes from aqueous solutions. However, its high running cost with the need for regeneration after adsorption is a barrier to the application for the wastewater treatment, at least in developing countries. Therefore, many researchers are exploring cheap and eco-friendly substitutes such as agri-forestry residues, e.g., sugarcane bagasse (Gusmão et al. 2013), rice husk (Han et al. 2007) and sawdust (Ahmad et al. 2009). However, some such residues are poor in adsorption ca-

Received: January 7, 2016. Revised: March 4, 2016. Accepted: March 24, 2016.

**Corresponding author: Zeng-Yu Yao**

Key Laboratory for Forest Resources Conservation and Use in the Southwest Mountains of China, Ministry of Education, Southwest Forestry University, 300 Bailongsi, Kunming 650224, China  
Tel: 86-87163862042, Fax: 86-87163863145, E-mail: z-yao@hotmail.com

capacities and therefore were modified for the improvement. Numerous chemicals have been used for the modifications, including mineral and organic acids, bases, oxidants, and organic compounds (Gong et al. 2008; Janoš et al. 2009; Nasuha and Hameed 2011; Rafatullah et al. 2010). Physical methods are generally very simple and inexpensive. Steaming, thermal drying, lyophilization, and milling have been used for biosorbent modification (Aksu and Isoglu 2007; Robinson et al. 2002). The steam explosion, which was originally used in the pulping process, is a cost-effective technology for pretreating lignocellulosic biomass. It is reported that the steam explosion affected the specific surface area of corn stalk and its structure, making it better for the ethanol holding (Fei and Hongzhang 2009). However, there has been no evidence on whether steam-explosion pretreatment can improve the biosorption performance of lignocellulosic biomass towards pollutants, including dyes.

*Xanthoceras sorbifolia* Bunge, commonly named as yellow horn, is considered as a bioenergy crop because of the high oil content in its kernels. It has been planting in large scale in China and the total area may be over  $5 \times 10^5$  hectares by 2020 (Yao et al. 2013). After separation of the kernels from the seeds for biodiesel production, the seed coats (XSSC), which account for 49% of the dry seeds, remain as a by-product. We have developed this residue as a cheap adsorbent for dye removal, and it showed a good performance of removing methylene blue (MB), a model cationic dye, from aqueous solutions (Yao et al. 2009). In this work, we reported modifying XSSC by the steam explosion for the MB biosorption as the first example to examine the applicability of this technique to improve sorption performance of agri-forestry residues.

## Materials and Methods

### Preparation of adsorbent and MB solution

*X. sorbifolia* seed was collected from Wudan Forest Farm of *X. sorbifolia*, Chifeng, Inner Mongolia, China. The seed coats were peeled manually and steam-exploded at 1.3 MPa for 5 min with a QBS-200B-type steam blasting machine (Bio Energy Co., Ltd., Hebi, China), washed thoroughly with pure water, and dried in an air-blast oven at 348 K for 24 hr. Then they were crushed, sieved through 0.250  $\mu\text{m}$  meshes, and stored in a plastic bottle. An MB

stock solution was prepared ( $1,000 \text{ mg L}^{-1}$ ) by dissolving the desired quantity of the dye in the pure water. The test solutions were prepared by diluting the stock solution to the desired concentrations.

### Determination of $\text{pH}_{\text{pzc}}$ and specific surface area

The pH points of zero charge ( $\text{pH}_{\text{pzc}}$ ) of XSSC and the steam-exploded XSSC (SE-XSSC) were determined as the same as described in our previous work (Yao et al. 2009). Fifty milliliters of  $0.01 \text{ mol L}^{-1}$  NaCl solutions were placed in different closed conical flasks. The pH of each solution in each flask was adjusted to a value between 2 and 12 by adding HCl or NaOH solution. Then, the sample (0.25 g) was added and the final pH measured after 48 hr under agitation at a room temperature. The  $\text{pH}_{\text{pzc}}$  is the point where the curve of final pH versus initial pH crosses the line at final pH = initial pH.

The specific surface area of the sample was determined from  $\text{N}_2$  adsorption isotherms at 77 K by the Brunauer-Emmett-Teller (BET) method with a NOVA 2000E gas adsorption apparatus (Quantachrome, USA).

### Adsorption experiments

All adsorption experiments were conducted by a batch process on a thermostat shaker at 120 rpm. In the pH studies, 0.05 g SE-XSSC and 50 mL MB solution ( $100 \text{ mg L}^{-1}$ ) with a range of pH values from 2 to 13 were transferred into a conical flask and shaken at 298 K for three days. The pH of the solutions was adjusted with HCl or NaOH solutions and measured on a pH meter. In kinetic experiments and those for studying the effects of contact time and initial dye concentration on the MB biosorption, 0.15 g SE-XSSC was added to 150 mL of the dye solutions with various concentrations and shaken at 298 K. Samples of 2.5 mL were taken at predetermined time intervals to analyze the residual dye concentrations of the solutions. For determination of equilibrium adsorption isotherms, 0.05 g adsorbent and 50 mL of MB solutions with different concentrations ( $25\text{--}200 \text{ mg L}^{-1}$ ) were shaken for three days at different temperatures (298–318 K).

After adsorption, the mixtures were filtered through a microporous membrane with a pore size about 1.2  $\mu\text{m}$ , and the MB concentrations in the filtrates were determined using a U-2800 spectrophotometer (Hitachi, Japan) by mon-

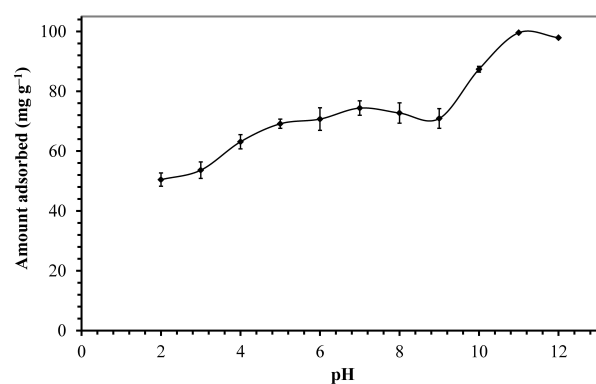
itoring the absorbance at 664 nm.

All the batch experiments were conducted in triplicate, and the mean and standard error values of the three data sets are presented. Fitting the equilibrium and kinetic data to models were solved by linear regression using Microsoft<sup>®</sup> Excel.

## Results and Discussion

### Biomass characterization

The pretreated and native XSSCs were characterized to illustrate the effect of the steam explosion pretreatment on properties of the biomass. The  $pH_{pzc}$  is an important factor of adsorbent which affects the cationic dye adsorption performance of the adsorbent. The steam explosion slightly decreased the  $pH_{pzc}$  from 3.5 for the native biomass to 3.3 for the modified biosorbent. This may be due to the increased acidity of the biomass (Han et al. 2010). Generally, an enlarged surface area provides sorbents with higher sorption capacity. Steam explosion treatment has been shown to expand the specific surface area of some lignocellulosic materials (Fei and Hongzhang 2009). In this study, the pretreatment increased the surface area from  $0.452 \text{ m}^2 \text{ g}^{-1}$  for XSSC to  $0.879 \text{ m}^2 \text{ g}^{-1}$  for SE-XSSC. We also characterized the biomass by Fourier transform infrared spectroscopy and scanning electron microscopy. Unfortunately, no significant difference can be found between two samples with these technologies.



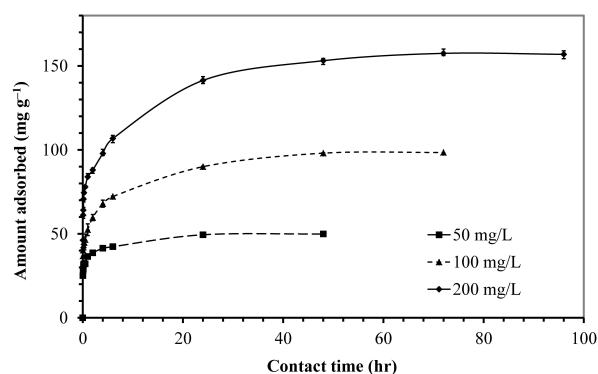
**Fig. 1.** Effect of the solution pH on MB sorption on SE-XSSC (dye concentration:  $100 \text{ mg L}^{-1}$ , adsorbent dosage:  $1.0 \text{ g L}^{-1}$ , temperature:  $298 \text{ K}$ , contact time: 3 days).

### Effect of pH

The pH of the adsorbate solution is an important factor controlling adsorption processes of cationic dyes onto adsorbents. Fig. 1 shows the effect of the initial solution pH on the MB biosorption on SE-XSSC. The amount of MB adsorbed slowly increased from  $50.46$  to  $74.37 \text{ mg g}^{-1}$  with the increase in the pH values from 2 to 7 and abruptly increased to the summit with the increase in the pH values from 9 to 11. The optimum pH was in the range of 5-10 for MB biosorption onto XSSC (Yao et al. 2009), whereas it was 11 for the biosorption onto SE-XSSC in this study. The pH values of the solutions after the biosorption were found to be lower than the initial pH values in almost all the sets of the experiments except those at pH 2, where the system was well buffered with the acid, indicating that the adsorption mechanism should be controlled by ion exchange releasing hydriions from the adsorbent into the solution.

### Effect of initial dye concentration and contact time

Equilibration time is an important parameter for economical wastewater treatment. The effects of contact time and initial dye concentration on the removal are shown in Fig. 2. The adsorption equilibrium was established within 24, 48, and 72 hr for 50, 100, and  $200 \text{ mg L}^{-1}$  MB, respectively, clearly showing that the contact time required for the maximum dye uptake by SE-XSSC strongly depended on the initial MB concentration. Therefore, the agitation time was fixed at 72 hr (three days) for the rest of the batch experiments to make sure that full equilibrium was reached.



**Fig. 2.** Effect of initial concentration and contact time on MB sorption on SE-XSSC (adsorbent dosage:  $1.0 \text{ g L}^{-1}$ , temperature:  $298 \text{ K}$ ).

It also shows in Fig. 2 that the amount of MB adsorbed increased with the increase in the initial dye concentration.

**Sorption kinetics**

Kinetic models were used to elucidate the biosorption mechanism of MB onto SE-XSSC. The pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were used to test the experimental data.

The pseudo-first-order kinetic equation has been widely used for analyzing the adsorption in liquid/solid systems. Its linear form is generally written as the following (Lagergren 1898):

$$\log (q_e - q_t) = \log q_e - k_1 t / 2.303 \dots\dots\dots (1)$$

where  $q_e$  (mg g<sup>-1</sup>) and  $q_t$  (mg g<sup>-1</sup>) are the amounts of MB adsorbed at equilibrium and at any time  $t$  (min), respectively, and  $k_1$  (min) is the rate constant in the pseudo-first-order sorption process. The constants were obtained by plotting  $\log (q_e - q_t)$  vs.  $t$  and are given in Table 1. The plots of the linearized form of the pseudo-first-order equation are shown in Fig. 3A. As seen in Table 1, the determination coefficient,  $R^2$ , for this model were all over 0.95, showing a good fitting. However, the theoretical values of the amounts of MB adsorbed on the biomass derived from this model ( $q_{e,cal}$ ) were far lower than those from the experimental data ( $q_{e,exp}$ ). These findings showed that the kinetic data did not agree with the pseudo-first-order kinetic model.

The pseudo-second-order model proposed by Ho and McKay (2003) generally expressed in the linear form as follows:

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \dots\dots\dots (2)$$

where  $k_2$  (g mg<sup>-1</sup> min<sup>-1</sup>) is the rate constant of adsorption. By plotting a curve of  $t/q_t$  against  $t$ ,  $q_e$  and  $k_2$  can be evaluated.

The initial sorption rate,  $h_0$  (mg g<sup>-1</sup> min<sup>-1</sup>) is defined as (Ho 2003):

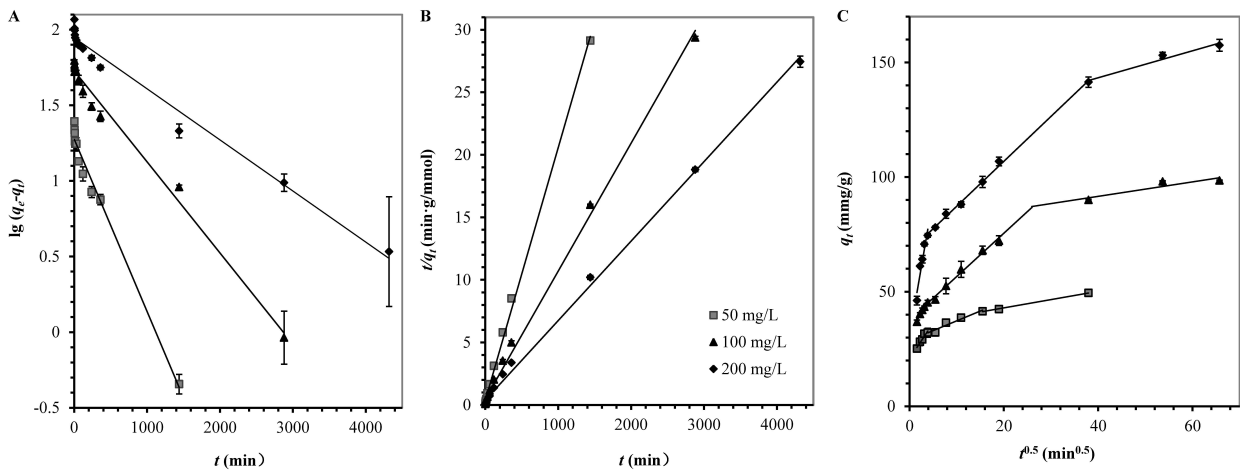
$$h_0 = k_2 q_e^2 \dots\dots\dots (3)$$

The values of  $q_e$ ,  $k_2$ ,  $h_0$  and  $R^2$  are tabulated in Table 1.

**Table 1.** Kinetic parameters of the pseudo-first-, pseudo-second-order and intraparticle diffusion models for MB sorption onto SE-XSSC

$C_0$ (mg L <sup>-1</sup> )	Pseudo-first-order			Pseudo-second-order			Intraparticle diffusion <sup>a</sup>		
	$q_{e,exp}$ (mg g <sup>-1</sup> )	$q_{e,cal}$ (mg g <sup>-1</sup> )	$R^2$	$K_2$ (g 10 <sup>-3</sup> mg <sup>-1</sup> min <sup>-1</sup> )	$h_0$ (mg g <sup>-1</sup> min <sup>-1</sup> )	$R^2$	$K_d$ (mg g <sup>-1</sup> min <sup>-0.5</sup> )	$I$ (mg g <sup>-1</sup> )	$R^2$
50	49.87	18.89	0.9822	1.063	2.606	0.9977	0.8538	28.72	0.9495
100	99.45	50.39	0.9697	0.215	2.071	0.9968	1.889	37.67	0.9892
200	162.32	88.64	0.9802	0.106	2.579	0.9978	1.962	67.61	0.9977

<sup>a</sup>Estimated from the second linear region.



**Fig. 3.** (A) The pseudo-first-order, (B) the pseudo-second-order, and (C) the intra-particle diffusion kinetic plots for MB sorption on SE-XSSC (adsorbent dosage: 1.0 g L<sup>-1</sup>, temperature: 298 K).

The dependence of  $t/q_t$  vs.  $t$  gave excellent straight lines for all the tested concentrations (Fig. 3B), which were confirmed by the extremely high  $R^2$  values in Table 1. The theoretical values calculated from this model ( $q_{e,cal}$ ) were close to the experimental ones ( $q_{e,exp}$ ). This suggests that the MB biosorption onto SE-XSSC abides by the pseudo-second-order kinetic model, which are the same as MB sorption onto the raw XSSC (Yao et al. 2009). Based on the assumption of the pseudo-second-order mechanism (Ho 2003), the rate-limiting step may be chemical adsorption or chemisorption involving valency forces through sharing or exchange of electrons between SE-XSSC and MB. Table 1 also depicts that the rate constant of adsorption ( $k_2$ ) decreased with the increase in the initial dye concentration. Similar findings were reported for the biosorption of MB onto XSSC (Yao et al. 2009) and dyes onto peat (Ho and McKay 1998). By comparing with the parameters for the MB biosorption onto the raw XSSC, we found the steam explosion pretreatment led to reductions of the sorption rate constant ( $k_2$ ) and the initial sorption rate ( $h_0$ ), which is unfavorable to a sorption process.

To examine the biosorption mechanism further, the kinetic data were applied with the intraparticle diffusion model (Weber and Morris 1963):

$$q_t = k_d t^{0.5} + I \dots\dots\dots (4)$$

where  $k_d$  (mg g<sup>-1</sup> min<sup>-0.5</sup>) is the intraparticle diffusion rate

constant, and  $I$  (mg g<sup>-1</sup>) is a constant that gives an idea about the thickness of the boundary layer. If the plot of  $q_t$  versus  $t^{0.5}$  presents a straight line, the adsorption process is controlled by intraparticle diffusion, whereas, if the plot is multi-linear, more than one step influences the adsorption process. In the present study, the plots exhibit a multi-linearity (Fig. 3C), indicating three steps took place. The first is a sharper portion, which may be considered as the diffusion of the adsorbate from the solution through the boundary film toward the interface space; so-called external diffusion. The second describes the gradual adsorption step, attributed to the diffusion of the adsorbate molecules into the pore of the adsorbent, where the intraparticle diffusion is the rate limitation. The last describes the final equilibrium stage, where the intraparticle diffusion starts to slow down because of the extremely low adsorbate concentrations left in the solution (Lorenc-Grabowska and Gryglewicz 2005). The parameters ( $k_d$  and  $I$ ) together with the determination coefficients for the second linear portion are also listed in Table 1. The intraparticle diffusion rate constant,  $k_d$ , increased with the increase in the MB concentrations, which resulted from the elevation of the driving force from the higher MB concentrations for intraparticle diffusion. A similar observation was also found with the MB biosorption onto the raw XSSC (Yao et al. 2009). The findings from this kinetic model show the rate-limiting step at the intermediate stage, indicating that the intraparticle diffusion was not the sole rate controlling step for the MB

biosorption onto SE-XSSC.

**Adsorption isotherms**

Adsorption isotherms can give some pieces of information on the adsorption mechanisms and be used to optimize the design of adsorption systems. Therefore, it is very necessary to establish the most appropriate correlations for the batch equilibrium data using empirical or theoretical equations. To investigate the biosorption isotherms of MB on SE-XSSC, the experimental data were analyzed with respect to two well-known isotherms, *i.e.*, the Langmuir and the Freundlich.

The Langmuir model was obtained by assuming that all the adsorption sites were energetically identical (monolayer adsorption), and the adsorption occurred on a structurally homogeneous adsorbent. For solid/liquid systems, a linear form of the Langmuir isotherm can be given as Eq. (1) (Langmuir 1918):

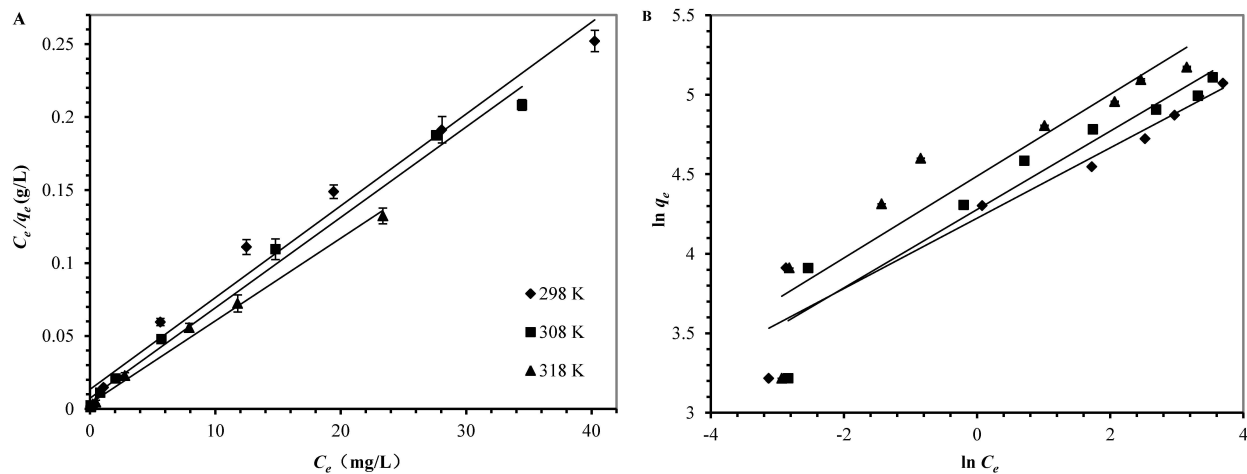
$$C_e/q_e = 1/(q_m K_L) + C_e/q_m \dots\dots\dots (5)$$

where  $C_e$  ( $\text{mg L}^{-1}$ ) and  $q_e$  ( $\text{mg g}^{-1}$ ) are the residual MB concentration and the amount of dye adsorbed per gram of the adsorbent at equilibrium, respectively,  $q_m$  ( $\text{mg g}^{-1}$ ) is the monolayer adsorption saturation capacity, and  $K_L$  ( $\text{L mg}^{-1}$ ) is a Langmuir constant relating to adsorption energy. The values of  $q_m$  and  $K_L$  were determined from the plots of  $C_e/q_e$  vs.  $C_e$  and are listed in Table 2. As can be seen from Fig. 4A, the Langmuir equation gave a good fitting over the entire range of the concentrations for the equilibrium data, and the  $R^2$  values (Table 2) are closer to unity for this model, indicating that the MB biosorption on SE-XSSC followed the Langmuir model and confirmed the homogeneous nature of the biosorbent surface. Further analysis for revealing favorable adsorption of MB on SE-XSSC was carried out using a separation factor ( $R_L$ ) of the Langmuir isotherm, which is defined as (Hall et al. 1966):

$$R_L = 1/(1 + K_L C_0) \dots\dots\dots (6)$$

**Table 2.** Isotherm parameters for MB biosorption on to SE-XSSC at different temperatures

Temperature (K)	Langmuir			Freundlich		
	$q_m$ ( $\text{mg g}^{-1}$ )	$K_L$ ( $\text{L mg}^{-1}$ )	$R^2$	$K_F$ ( $\text{mg}^{1-1/n} \text{g}^{-1} \text{L}^{1/n}$ )	$1/n$	$R^2$
298	159.0	0.4700	0.9807	68.31	0.2214	0.9225
308	161.4	0.8427	0.9911	72.09	0.2465	0.9170
318	176.8	1.4883	0.9938	88.93	0.2576	0.8541



**Fig. 4.** Comparison of different isotherm models for MB biosorption onto SE-XSSC. (A) Langmuir isotherm; (B) Freundlich isotherm (adsorbent dosage: 1.0  $\text{g L}^{-1}$ , contact time: 3 days).

where  $C_0$  (mg/L) is the initial MB concentration. The  $R_L$  value indicates the type of the isotherm to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ) (Hall et al. 1966). The calculated  $R_L$  values at different initial MB concentrations and temperatures are plotted in Fig. 5. The  $R_L$  values dropped within the range of 0-1 in all experimental systems, suggesting the favorable uptake of MB by SE-XSSC. Lower  $R_L$  values at higher initial MB concentrations and temperatures elucidated that the biosorption was more favorable at higher concentrations from warmer solutions. The constants,  $q_m$  and  $K_L$ , went up with the increase in the temperature (Table 2), indicating that the adsorption density was higher and the adsorption energy lower at higher temperatures. In our previous work on MB biosorption with raw XSSC (Yao et al. 2009), with the increasing temperature,  $q_m$  and  $K_L$  decreased while  $R_L$  increased. By comparison of MB biosorption on SE-XSSC with that on XSSC, we found that  $q_m$  and  $K_L$  are lower for SE-XSSC than XSSC at 298 and 308 K, whereas they are higher at 318 K. Therefore, SE-XSSC is preferable for the MB biosorption from warmer dye effluents, while XSSC is more effective for the biosorption from colder ones.

The Freundlich isotherm is based on multilayer adsorption (heterogeneous surface). The logarithmic linear form of this model can be expressed as follows (Freundlich 1906):

$$\ln q_e = \ln K_F + 1/n \ln C_e \dots\dots\dots (7)$$

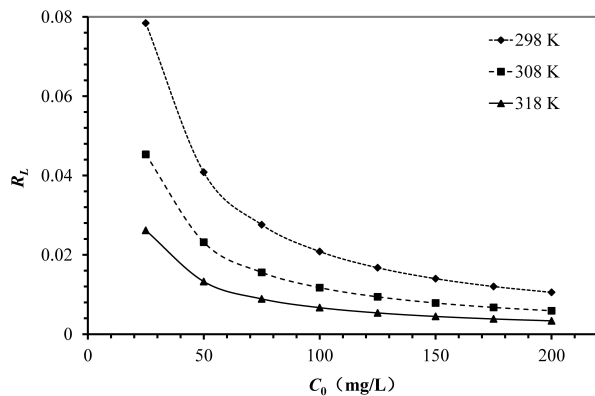


Fig. 5. Plots of separation factor versus initial MB concentration (adsorbent dosage: 1.0 g L<sup>-1</sup>, contact time: 3 days).

where  $K_F$  (mg<sup>1-1/n</sup> g<sup>-1</sup> L<sup>1/n</sup>) is a Freundlich constant related to the sorption capacity and  $1/n$  is another Freundlich constant denoting the sorption intensity. These two constants were calculated by linear regression analysis of  $\ln q_e$  vs.  $\ln C_e$ , and the results are given in Table 2. The Freundlich isotherms are shown graphically in Fig. 4B. It can be seen clearly from Fig. 4B, as well as from the  $R^2$  values in Table 2, that the theoretical values derived from this model farther deviated from the experimental data, implying that the Freundlich isotherm is less effective to characterize MB biosorption on SE-XSSC.

Adsorption thermodynamics

To elucidate the thermodynamic mechanisms of the biosorption process, standard Gibbs energy change ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) were calculated by using the following equations:

$$\Delta G^\circ = -RT \ln K_c^\circ \dots\dots\dots (8)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \dots\dots\dots (9)$$

where  $R$  is the gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>),  $T$  is the absolute temperature (K), and  $K_c^\circ$  (L g<sup>-1</sup>) is an equilibrium constant gotten by multiplying the Langmuir constants  $q_m$  and  $K_L$  (Aksu and İsoğlu 2005).  $\Delta H^\circ$  (J mol<sup>-1</sup>) and  $\Delta S^\circ$  (J mol<sup>-1</sup> K<sup>-1</sup>) can be obtained from the plot of  $\Delta G^\circ$  (J mol<sup>-1</sup>) vs.  $T$  (Fig. 6).

The thermodynamic parameters for the MB biosorption on SE-XSSC are provided in Table 3. The negative values of  $\Delta G^\circ$  indicate the feasibility of the process and the sponta-

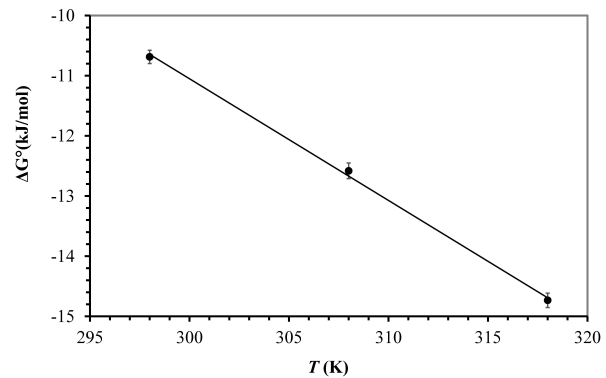


Fig. 6. Thermodynamic plot for MB biosorption by steam-exploded chestnut shell (adsorbent dosage: 1.0 g L<sup>-1</sup>, contact time: 3 days).

**Table 3.** Thermodynamic parameters for MB sorption on SE-XSSC

$T$ (K)	$\Delta G^\circ$ (KJ mol <sup>-1</sup> )	$\Delta H^\circ$ (KJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$R^2$
298	-10.69			
308	-12.58	49.63	202.3	0.9986
318	-14.73			

neous nature of the biosorption. The  $\Delta G^\circ$  value is more negative with increasing temperature, suggesting that higher temperatures make the biosorption easier. The positive value of  $\Delta H^\circ$  reflects that the biosorption is an endothermic process. The positive value of  $\Delta S^\circ$  implies the increase of randomness at the solid/liquid interface and some structural changes in MB and XSSC in the adsorption process, as well as the affinity of the SE-XSSC for MB (Ho et al. 2005). The negative  $\Delta G^\circ$  accompanied with positive  $\Delta H^\circ$  and  $\Delta S^\circ$  suggests that the biosorption process was driven by the entropy. The thermodynamic natures were deeply changed by the steam-explosion treatment of the biomass because we found that the MB biosorption on the raw XSSC was an exothermic process driven by both the enthalpy and the entropy (Yao et al. 2009).

## Conclusions

The optimal pH of the dye solution was 11 for the MB biosorption onto SE-XSSC. The kinetic data followed the pseudo-second-order model, and the rate-limiting step was the chemical adsorption. Intraparticle diffusion was involved in the biosorption process but is not the sole rate-controlling factor. The equilibrium data agreed well with the Langmuir isotherm, and the biosorption was favorable. The steam-explosion pretreatment strongly affected the biosorption in some respects. It reduced the sorption rate constant and the initial sorption rate of the pseudo-second-order model. It enhanced the MB adsorption capacity at higher temperatures while reduced the capacity at lower ones. It changed the biosorption from an exothermic process driven by both the enthalpy and the entropy to an endothermic one driven by entropy only. It also increased the surface area and decreased the  $\text{pH}_{\text{pzc}}$  of the biomass. Compared with the native XSSC, SE-XSSC is preferable to the MB biosorption from warmer dye effluents. In industrial practice, to treat dye-loaded wastewater from

factories with temperature over 318 K, SE-XSSC is recommended, otherwise, XSSC done.

## Acknowledgements

This research was supported by the National Natural Science Foundation of China (Nr 21167016). The scanning electron microscope and the FT-IR spectrometer were supplied by the Valuable Equipment Sharing Platform of Southwest Forestry University.

## References

- Ahmad A, Rafatullah M, Sulaiman O, Ibrahim MH, Hashim R. 2009. Scavenging behaviour of meranti sawdust in the removal of methylene blue from aqueous solution. *J Hazard Mater* 170: 357-365.
- Aksu Z, İşoğlu İA. 2005. Removal of copper (II) ions from aqueous solution by biosorption onto agricultural waste sugar beet pulp. *Process Biochem* 40: 3031-3044.
- Aksu Z, Isoglu IA. 2007. Use of dried sugar beet pulp for binary biosorption of Gemazol Turquoise Blue-G reactive dye and copper (II) ions: equilibrium modeling. *Chem Eng J* 127: 177-188.
- Campos R, Kandelbauer A, Robra KH, Cavaco-Paulo A, Gübitz GM. 2001. Indigo degradation with purified laccases from *Trametes hirsuta* and *Sclerotium rolfsii*. *J Biotechnol* 89: 131-139.
- Fei C, Hongzhang C. 2009. Absorption of ethanol by steam-exploded corn stalk. *Bioresour Technol* 100: 1315-1318.
- Freundlich H. 1906. Concerning Adsorption in Solutions. *J Phys Chem* 57: 385-470.
- Gong R, Zhong K, Hu Y, Chen J, Zhu G. 2008. Thermochemical esterifying citric acid onto lignocellulose for enhancing methylene blue sorption capacity of rice straw. *J Environ Manage* 88: 875-880.
- Gusmão KAG, Gurgel LVA, Melo TMS, Gil LF. 2013. Adsorption studies of methylene blue and gentian violet on sugarcane bagasse modified with EDTA dianhydride (EDTAD) in aqueous solutions: kinetic and equilibrium aspects. *J Environ Manage* 118: 135-143.
- Hall KR, Eagleton LC, Acrivos A, Vermeulen T. 1966. Pore- and Solid-Diffusion Kinetics in Fixed-Bed Adsorption under



- Constant-Pattern Conditions. *Ind Eng Chem Fundamen* 5: 212-223.
- Han G, Deng J, Zhang S, Bicho P, Wu Q. 2010. Effect of steam explosion treatment on characteristics of wheat straw. *Ind Crop Prod* 31: 28-33.
- Han R, Wang Y, Yu W, Zou W, Shi J, Liu H. 2007. Biosorption of methylene blue from aqueous solution by rice husk in a fixed-bed column. *J Hazard Mater* 141: 713-718.
- Ho YS, Chiang TH, Hsueh YM. 2005. Removal of basic dye from aqueous solution using tree fern as a biosorbent. *Process Biochem* 40: 119-124.
- Ho YS, McKay G. 1998. Sorption of dye from aqueous solution by peat. *Chem Eng J* 70: 115-124.
- Ho YS. 2003. Removal of copper ions from aqueous solution by tree fern. *Water Res* 37: 2323-2330.
- Janoš P, Coskun S, Pilařová V, Rejnek J. 2009. Removal of basic (Methylene Blue) and acid (Egacid Orange) dyes from waters by sorption on chemically treated wood shavings. *Bioresour Technol* 100: 1450-1453.
- Lagergren S. 1898. About the Theory of So-Called Adsorption of Soluble Substances. *Kungl Sven Vetenskapsakad Handl* 24: 1-39.
- Langmuir I. 1918. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *J Am Chem Soc* 40: 1361-1403.
- Lorenc-Grabowska E, Gryglewicz G. 2005. Adsorption of lignite-derived humic acids on coal-based mesoporous activated carbons. *J Colloid Interf Sci* 284: 416-423.
- Nasuha N, Hameed BH. 2011. Adsorption of methylene blue from aqueous solution onto NaOH-modified rejected tea. *Chem Eng J* 166: 783-786.
- Rafatullah M, Sulaiman O, Hashim R, Ahmad A. 2010. Adsorption of methylene blue on low-cost adsorbents: a review. *J Hazard Mater* 177: 70-80.
- Robinson T, Chandran B, Nigam P. 2002. Effect of pretreatments of three waste residues, wheat straw, corncobs and barley husks on dye adsorption. *Bioresour Technol* 85: 119-124.
- Weber WJ, Morris JC. 1963. Kinetics of Adsorption on Carbon from Solution. *J Sanit Eng Div* 89: 31-60.
- Yao Z, Wang L, Qi J. 2009. Biosorption of Methylene Blue from Aqueous Solution Using a Bioenergy Forest Waste: *Xanthoceras sorbifolia* Seed Coat. *CLEAN - Soil, Air, Water* 37: 642-648.
- Yao Z-Y, Qi J-H, Yin L-M. 2013. Biodiesel production from *Xanthoceras sorbifolia* in China: opportunities and challenges. *Renew Sustain Energ Rev* 24: 57-65.