Removal of Methylene Blue from Aqueous Solution using Porous Biochar Obtained by KOH Activation of Peanut Shell Biochar

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Biochar from peanut shell was used as the precursor for the preparation of porous biochar by KOH activation. The pore structures of porous biochar also were characterized by scanning electron microscopy (SEM) and N_2 adsorption/desorption. The adsorption performance for the removal of methylene blue (MB) was deeply investigated. The effects of impregnation ratio (KOH/biochar: w/w), activation temperature, and activation time on the removal of methylene blue by porous biochar were evaluated. In addition, the effects of initial MB concentration and pH value on the adsorption process were also studied. The optimum conditions for preparing porous biochar were obtained with 1.5:1 of impregnation ratio, 800 °C of activation temperature, and 90 min of the holding time in activation. Results indicated that the adsorption capacity was high even at higher initial MB concentrations. The adsorption process followed pseudo-second-order kinetics. The experimental adsorption isotherm was found to be best fitted with the Langmuir model, which implying that the adsorption of MB by porous biochar proceeded as a monolayer adsorption, and the maximum monolayer adsorption capacity of MB was 208 $mg \cdot g^{-1}$.

Keywords: KOH activation; Adsorption kinetics; Adsorption isotherms; Thermodynamic modeling

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INTRODUCTION

With the development of the dye industry, the associated wastewater pollution has drawn increasing attention. Due to the structural stability and complexity of dye molecules, they represent a real threat to the environment and human health (Njoku *et al.* 2014). The traditional methods for the removal of dyes from the wastewater include air flotation (Liang *et al.* 2014), sorbents adsorption (Tichonovas *et al.* 2013), membrane separation (Türgay *et al.* 2011), extraction (Bakheet *et al.* 2013), chemical oxidation (Kumar *et al.* 2013), electrochemistry (del Río *et al.* 2011), froth floatation, and biological methods (Liu *et al.* 2006). However, owing to the fact that adsorption is simple and can be carried out in a small area, approaches based on adsorption have been increasingly considered to remove dye from wastewater (Kaouah *et al.* 2013).

Methylene blue (MB) a cationic dye has been studied as dye pollution not only because of its toxicity but its color as well (Bestani *et al.* 2008). MB has very wide applications which make it one of the common pollutants or constituent of color effluents. Several attempts have been made by previous researchers to address MB health effect as a

pollutant in wastewater through the development and application of different adsorbents for its uptake (Rafatullah *et al*. 2010; Auta and Hameed 2014).

Activated carbon has become a popular adsorbent due to its high surface area, rich porous structure, good thermal stability, and so on. But the cost of the preparation of activated carbon is relatively higher than biochar, and it cannot be easily regenerated. This situation has led many researchers to seek an economical and effective resource to replace it (Emami and Azizian 2014). The removal abilities of the sorbents mainly have depended on the preparation conditions as well as the characteristics of the precursor (Omri *et al.* 2013). Recently some studies focusing on the preparation of activated biochar from agricultural byproducts have been reported, such as wool wastes (Gao *et al.* 2013), chestnut shell (Hu *et al*. 2012), sugarcane leaves (Liu *et al*. 2012), rice husk (Liao *et al*. 2011; Liu *et al*. 2012), fruit shell (Tongpoothorn *et al.* 2011), peanut hull (Zhong *et al.* 2012), and bamboo (González *et al.* 2014), which have been identified as economic sources for the preparation of activated biochars with the advantage of mitigating environmental pollution. Physical activation usually requires a high activated temperature and a long activation time. However, chemical activation was under short activation time, which makes it possible to achieve a high surface area and rich porous structure, so it is widely used in preparation of activated biochar. KOH (Gao *et al*. 2011; Foo e*t al*. 2011), H_3PO_4 (Ould-idriss *et al*. 2011; Sun *et al*. 2014), and $ZnCl_2$ (Kula *et al*. 2008; Karagoz *et al*. 2008) are three common activating agents in chemical activation. The precursors are first impregnated with an activating agent, then heated under inert atmosphere, and then washed with acid and hot deionized water repeatedly (Shi *et al.* 2010).

In this study, biochar from peanut shell was used as the precursor to prepare porous biochar via KOH activation at high temperature. The biomaterial was selected due to its abundance, rapid regeneration, and low cost. Though there have been many published reports on agricultural byproducts to prepare biochar, little information is available on the effects of impregnation ratio, activation temperature, and activation time on the physic-chemical properties of obtained porous biochar by KOH activation. Moreover, to our knowledge, its application in adsorption removal of dye molecules has seldom been mentioned. The aim of this work was to find the optimum activation conditions for preparing of porous biochar, and to study the effect of pH, initial methylene blue concentration, and temperature on the adsorption of methylene blue by porous biochar. In addition, the adsorption kinetics and thermodynamics were explored to describe the adsorption behavior of the porous biochar.

EXPERIMENTAL

Materials

Pyrolysis of peanut hull was carried out at 450 °C using a vertical kiln made of refractory bricks under oxygen-deficient environment at the Sanli New Energy Company, Henan Province (China), producing a black powder that was used as material in this experiments. KOH, which was obtained from Kermel Company of Tianjin with a purity of more than 85%, was used as the activating agent. Methylene blue was get from Yongda Chemical Reagents Development Center of Tianjin. Hydrochloric acid was obtained from Sinopharm Chemical Reagent. High-purity nitrogen was used to provide the inert atmosphere. The water used in this study was distilled water.

Preparation of Porous Biochar

Biochar was washed with distilled water repeatedly in order to remove the impurities and then dried at 105 °C (24 h) and sieved to a uniform size of 0.75 mm. The biochar was impregnated with a certain quantity of KOH for 24 h in a beaker. The mixtures were dried at 105 °C for 24 h. Then the mixtures were heated in a tubular furnace at 800 °C for 2 h with a linear rise of 10 °C·min^{-1} under nitrogen protection. After cooling to room temperature, the mixtures were firstly washed with hydrochloric acid and then hot distilled water until the pH was neutral. Then they were dried at 105 °C overnight and stored in a dryer for subsequent use (Yu *et al*. 2013).

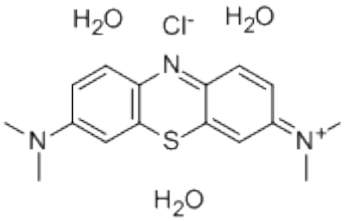
Characterization of Porous Biochar

The BET surface area, pore volume, and pore size distribution of porous biochar were characterized with an automated gas sorption apparatus (Model ASAP 2020, USA) using nitrogen adsorption/desorption isotherm at 77 K. The surface area was calculated according to the BET equation; the total pore volume was calculated with the liquid volume of N_2 at a relative pressure of 0.98; the pore size distribution was calculated with BJH model. The morphology character of Porous biochar was characterized with Scanning Electron Microscopy (SEM) (Hitachi, S-520, Japan).

All data were expressed as means plus or minus one standard deviation. Differences between the treatments were examined using a two-way analysis of variance (ANOVA, confidence level $p<5\%$). All statistical analyses were carried out using SPSS, version 20.0 (SPSS Institute, USA).

Adsorption Experiments

In this study, methylene blue was used as the adsorbate to study the removal properties of the porous biochar. The chemical structure of methylene blue is given in Scheme1.



Scheme 1. Chemical structure of methylene blue

The adsorption experiments were carried out in 250 mL Erlenmeyer flasks, containing 0.1 g of porous biochar and 100 mL of methylene blue solution. The ranges of experimental parameters were selected as follows: initial concentrations of methylene blue (80 to 500 mg·L^{-1}), pH (2 to 10), and temperature (20 to 40 °C). The pH was adjusted with 5% HCl and 5% NaOH. The Erlenmeyer flasks were placed in a shaker and then shaken at a certain temperature with a speed of 150 rpm for 24 h. After that, the mixtures were placed into a centrifuge with a speed of 3000 rpm for 10 min to separate the solid and liquid. The mixtures were filtrated, and the supernatants were detected by UV-vis spectrophotometer (TU-1901, China) at 665 nm. The per unit mass adsorption capacity of methylene blue by porous biochar was calculated by mass balance equation (Bayram *et al.* 2009),

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

where C_0 is the initial concentration of methylene blue, Ce is the equilibrium concentration of methylene blue (mg·L^{-1}), W is the mass of the biochar (g), and V is the volume of the methylene blue solution (mL). The removal percentage of methylene blue is calculated from the equation,

$$R = \frac{C_0 - C_t}{C_0} \times 100\% \quad (2)$$

where C_0 and C_t are the initial and t-time concentration of methylene blue (mg·L^{-1}) and R is the removal percentage (%).

Adsorption Kinetics Model

In adsorption kinetics, the pseudo-first-order and the pseudo-second-order models are commonly employed to fit the data. The linear form of pseudo-first-order model is given by Eq. 3:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

The linear form of pseudo-second-order is given by Eq. 4 (Ho and McKay 1998).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (4)$$

In these equations q_e and q_t are the adsorption capacities corresponding to the equilibrium and time t (mg·g^{-1}), k_1 is the pseudo-first-order constant (h^{-1}), k_2 is the pseudo-second-order constant (g·mg^{-1}·h^{-1}), and t is the contact time (min).

Adsorption Isotherms Model

In a liquid-solid system, adsorption isotherm is important in describing the interaction of adsorbates and adsorbents. Langmuir models and Freundlich models are the two most commonly used isotherm models. The Langmuir model is based on an assumption of equivalent, non-interacting adsorption sites. The Freundlich model provides a means of fitting data related to adsorption on heterogeneous surfaces. Langmuir model is given by Eq. 5 (Langmuir 1918):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (5)$$

The Freundlich model is given by Eq. 6:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

In Eqs. 5 and 6, C_e is the equilibrium concentration of methylene blue (mg·L^{-1}), q_e is the equilibrium adsorption capacity (mg·g^{-1}), q_m is the maximum adsorption capacity (mg·g^{-1}), K_L is the Langmuir constant related to the free energy of adsorption (L·mg^{-1}), K_F is Freundlich parameters related to adsorption capacity, and n is the adsorption intensity.

RESULTS AND DISCUSSION

Effect of Activation Conditions on Preparation of Porous Biochar

In KOH activation, activation conditions have an important effect on the specific surface area and porous structure of porous biochar. The effect of activation conditions, such as impregnation rate, activation temperature, and activation time, on the adsorption capacity q_e and removal percentage of methylene blue by obtained porous biochar were thoroughly studied.

As shown in Fig.1a, the adsorption capacity q_e was increased from 72.28 mg·g^{-1} to 149.65 mg·g^{-1}, and the removal percentage increased from 48.19% to 99.97% with the increasing of impregnation ratio (KOH/biochar, w/w) from 0.5 to 1.5. However, when the impregnation ratio increased from 1.5 to 3, q_e was found to be decreased from 149.95 mg·g^{-1} to 81.41 mg·g^{-1}, and the removal percentage were decreased from 99.97% to 54.27%. These results made it clear that impregnation ratio played an important role in the preparation of porous biochar. Two different mechanisms dominated the whole chemical activation process. In the first stage, the mesoporous structure in porous biochar was formed, which resulted in an increase of the surface area and the adsorption capacity of porous biochar, as can be seen in the impregnation ratio ranging from 0.5 to 1.5. In the second stage, the C-KOH reaction enhanced the widening of pores, which resulted in a reduction of surface area and the adsorption capacity of porous biochar; this is seen in the impregnation ratio range from 1.5 to 3.0.

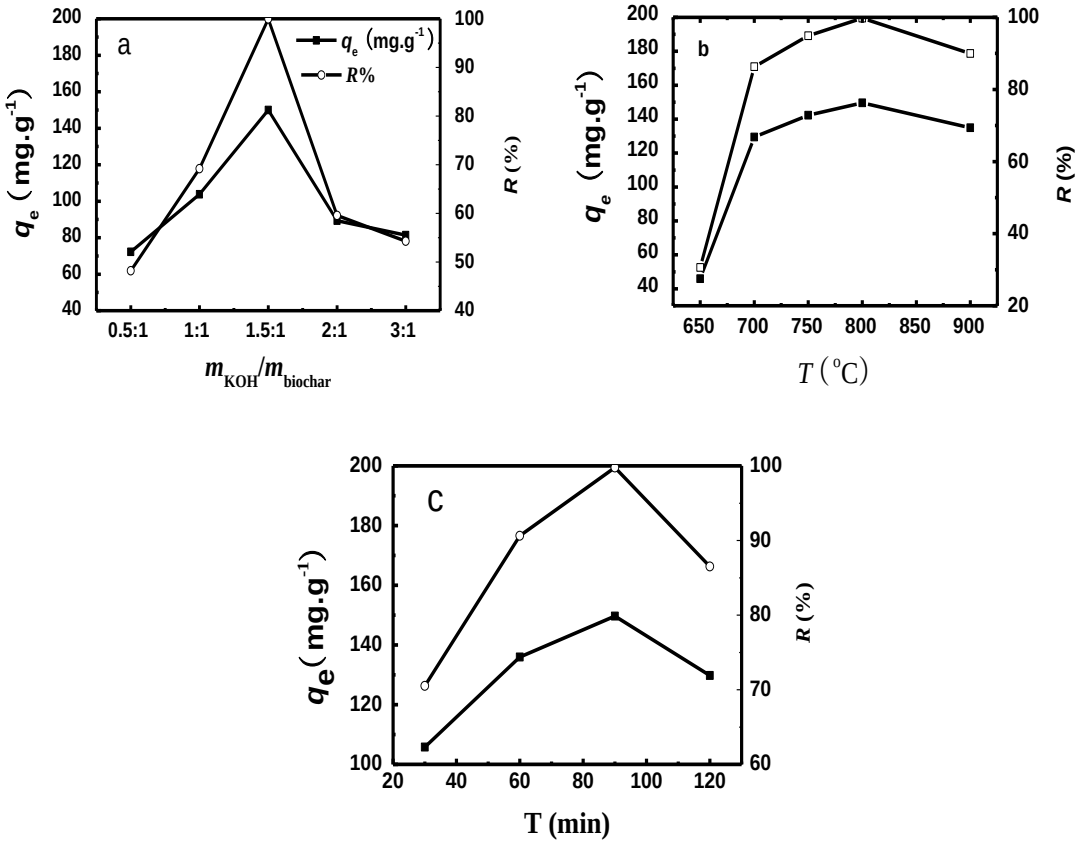


Fig. 1. Effect of activation conditions on MB adsorption. Impregnation rate (a), activation temperature (b), and activation time (c)

When the impregnation ratio was set as 1.5:1 and the activation time was 90 min, with the increasing of the activation temperature from 650 °C to 800 °C, q_e increased from 45.95 mg·g^{-1} to 149.65 mg·g^{-1}, and the removal percentage increased from 30.63% to 99.77%. However, when the activation temperature increased from 800 °C to 900 °C, the q_e decreased from 149.65 mg·g^{-1} to 134.96 mg·g^{-1}, and the removal percentage decreased from 99.97% to 89.97% (Fig. 1b). As stated in the literature (Guo *et al.* 2002), KOH and biochar matrix may react as $6KOH+2C=2K+K_2CO_3+3H_2$ at higher temperature with enough energy, which results in the formation and widening of mesoporous structure. As for the activation time, 90 min was exactly suitable for the biochar activation and the formation of mesoporous structure (Fig. 1c). However, with an activation time longer than 90 min, the adsorption capacity q_e and removal rate of methylene blue decreased due to the widening of aforementioned mesoporous structure. So when the impregnation ratio was 1.50, the activation temperature was 800 °C and the activation time was 90 min, the activation conditions were judged to be the best.

Characterization of Porous Biochar and Biochar from Peanut Shell

The main properties of porous biochar and biochar from peanut shell are summarized in Table 1. Prior to activation, the surface area of biochar was 12.28 m^2·g^{-1}, the total pore volume was 0.017 cm^3·g^{-1}, and the average pore diameter was 14.49 nm. After KOH activation, the surface area of porous biochar reached 640.57 m^2·g^{-1}, the total pore volume was 0.76 cm^3·g^{-1}, and the average diameter was 3.39 nm. These changes are attributed to the intrusion of KOH into the internal structure of biochar, where it reacted with the carbon, enabling the formation of pores.

Table 1. Textural Properties of Porous Biochar and Biochar from Peanut Shell

Sample	Porous Biochar	Biochar
S_{BET} (m^2·g^{-1})	640.57	12.28
$S_{Langmuir}$ (m^2·g^{-1})	798.31	16.45
S_{Ext}(m^2·g^{-1})	219.47	3.82
S_{mi} (m^2·g^{-1})	491.34	2.36
V_t (cm^3·g^{-1})	0.76	0.017
V_{mi} (cm^3·g^{-1})	0.22	0.004
V_{mecro} (cm^3·g^{-1})	0.61	0.012
W_{BJH} (nm)	3.39	14.49

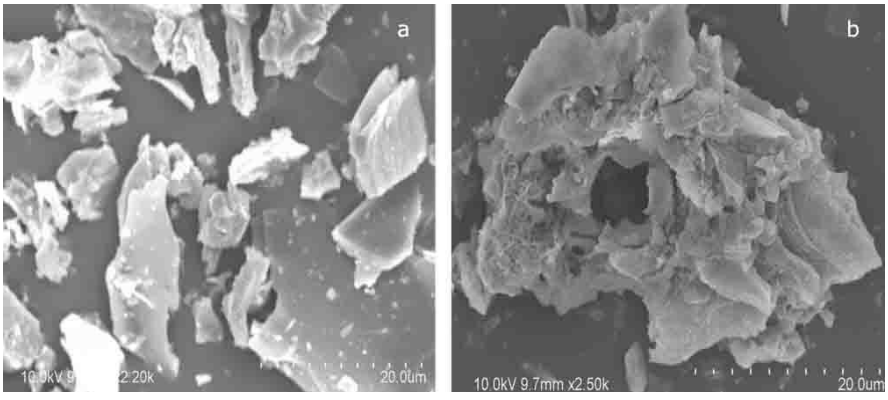


Fig. 2. SEM of biochar (a) and porous biochar (b) from peanut shell

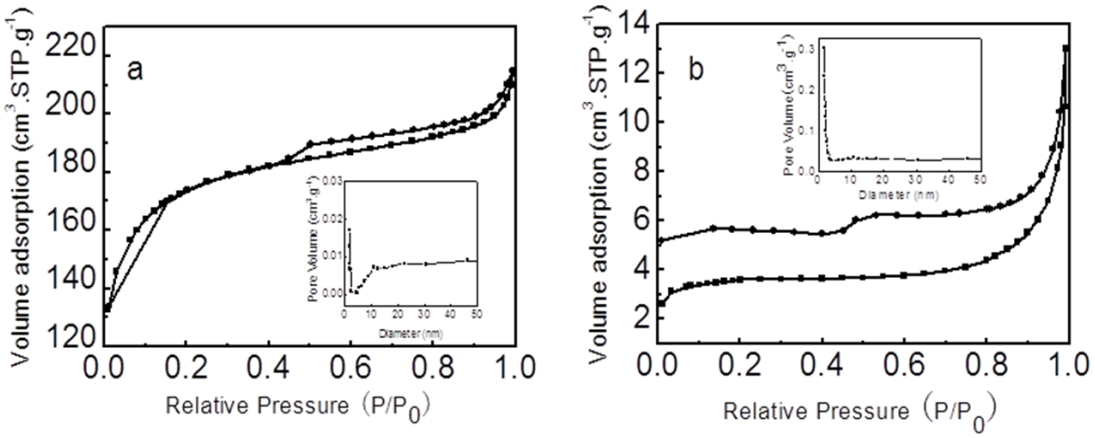


Fig. 3. N_2 adsorption -desportion isothems and mecrospore distribution of biochar (a) and porous biochar (b) from peanut shell

Figure 2 shows SEM images of porous biochar and biochar. The surface of biochar (Fig. 2a) was smooth, and there were a lot of impurities on it, so the pores were filled by those impurities. By contrast, after KOH activation, the pore structure was uniform, and there were many mesopores and microspores on the surface of porous biochar, such that the surface area was increased (Fig. 2b).

Figure 3 shows the N_2 adsorption-desortion isotherm and the mesopores of porous biochar and biochar. According to the International Union of Pure and Applied Chemistry (IUPAC), the structures of activated carbons were classified into three groups: microporous (diameter < 2 nm), mesoporous (2 to 50 nm), and macroporous (>50 nm) (Foo and Hameed 2012). The type of N_2 adsorption of porous biochar and biochar belong to type I. The mecrospore size distribution of porous biochar exhibited one peak around 3 nm (Fig. 3b), which indicated that the pore structure of porous biochar was mainly a mesoporous structure.

Adsorption Removal of MB

Effects of activation

The adsorption of methylene blue from solution by biochar before and after activation was investigated. The initial concentration of methylene blue was 150 $mg \cdot L^{-1}$, and the results are shown in Fig. 4. Results showed that after KOH had been activated, the adsorption capacity of methylene was better. This was mainly because, after KOH activation, the surface area and the pore structure of porous biochar were higher.

Effects of initial MB concentration

The initial concentration of methylene blue (varied with 100, 200, 300, and 500 $mg \cdot L^{-1}$) on the adsorption removal of methylene blue from solution by porous biochar at 30 °C was investigated, and results are shown in Fig. 5. Results showed that the adsorption capacity increased rapidly in the first 15 min, and then increased slowly until reaching equilibrium. The calculated adsorption capacity q_e of methylene blue by porous biochar increased from 99.88 $mg \cdot g^{-1}$ to 311.25 $mg \cdot g^{-1}$ as the initial methylene blue concentration increased from 100 $mg \cdot L^{-1}$ to 500 $mg \cdot L^{-1}$.

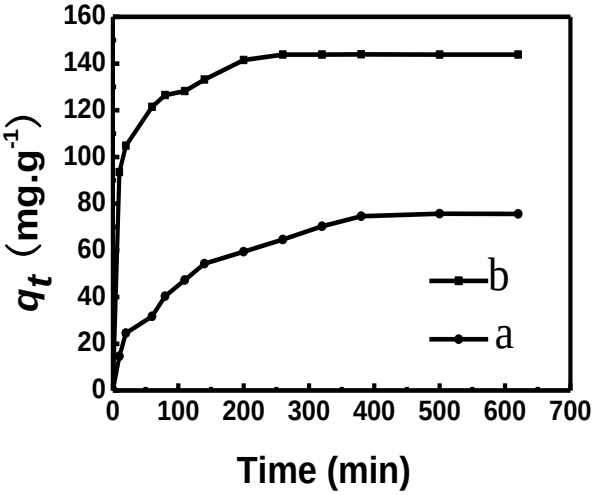


Fig. 4. Adsorption of methylene blue from solution by biochar (a) and porous biochar (b)

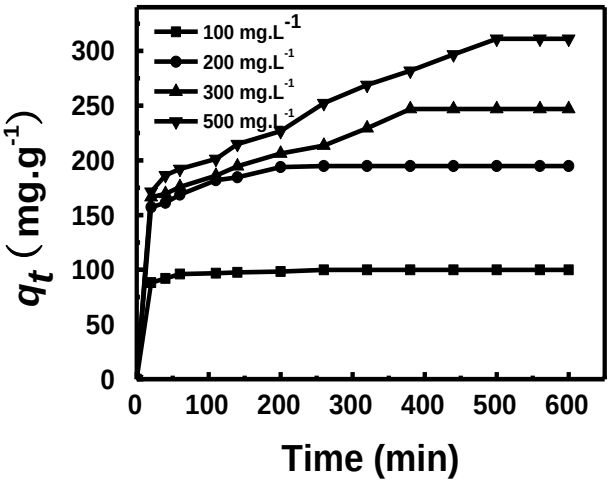


Fig. 5. Effect of initial concentration on the adsorption of methylene blue from solution

Effects of solution pH

The effect of pH on the adsorption removal of methylene blue by porous biochar was studied with the pH ranging from 2.0 to 10.0 at 30 °C (Fig. 6). It was obeserved that the adsorption capacity q_e increased rapidly with the increasing pH value from 2.0 to 6.0. By contrast, when the pH was changed from 6.0 to 10.0, the adsorption capacity q_e remained unchanged. It was obvious that the adsorption removal of methylene blue by porous biochar was better in neutral or alkaline conditions than in acidic condition.

In the lower pH range, the low adsorption of methylene blue also exhibits the possibility of development of a neutral or weakened charge at the porous biochar surface, which decreases the electrostatic motivation for the adsorption of methylene blue onto it. However, in the basic medium the formation of electric double layer changes its polarity and consequently the methylene blue uptake increases (Guo *et al*. 2002; Hameed and El-khaiary 2008).

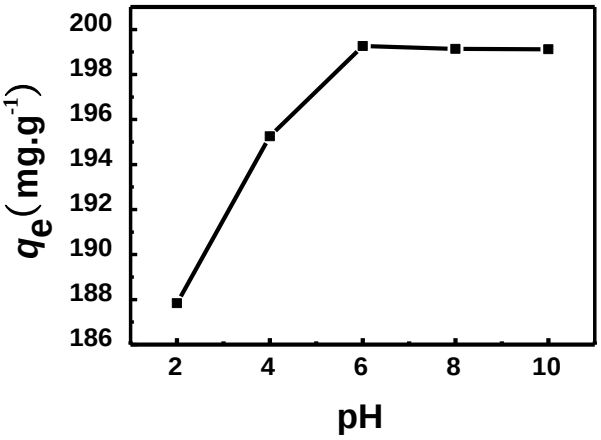


Fig. 6. Effect of pH value on the adsorption of methylene blue by porous biochar

Adsorption kinetics

The adsorption mechanism depended on the mass transport as well as the physical or chemical characteristics of the adsorbent. Figure 7 shows the linear regression curves of $\ln(q_e\text{-}q_t)$ against t and t/q_t against t, respectively. The kinetic parameters were obtained from the slopes and intercepts (Table 2). Results showed that the pseudo-second-order kinetic model fitted better with the adsorption experiment data of the methylene blue adsorption by porous biochar (R^2 >0.999) than the pseudo-first-order kinetic model (R^2 <0.970).

The pseudo-first order equation assumes the adsorption of one MB molecule onto one active site on the porous biochar surface, while in pseudo-second order model one MB molecule is adsorbed onto two active site (Khan *et al*. 2015). It was clear that the adsorption process for porous biochar was rapid at the beginning, and then increased slowly until the plateau of adsorption equilibrium was achieved. The fast adsorption rate at the incipient stage could be attributed to the increase of driving force provided by the concentration gradient of MB in aqueous solutions and the existence of the great number of available active sites on the surface of porous biochar (Olgun *et al*. 2013). These results suggested that both physical and chemical adsorption might be involved in the adsorption process (Liu and Zhang 2015).

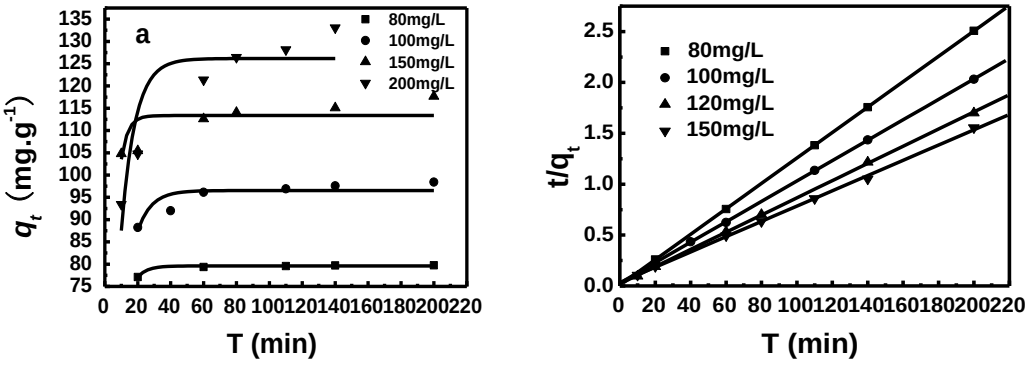


Fig. 7. Linear regression curves of pseudo-first-order (a) and pseudo-second-order (b) for adsorption removal of methylene blue by porous biochar

Table 2. Estimated Constants for Adsorption of Methylene Blue by Porous Biochar

C_{MB}/mg·L^{-1}	Pseudo-first-order				Pseudo-second-order		
	$q_{e,exp}$ /mg·g^{-1}	K_1/h^{-1}	$q_{e,cal}$/mg·g^{-1}	R^2	K_2/g·(mg·h)$^{-1}$	$q_{e,cal}$/mg·g^{-1}	R^2
80	79.97	0.132	2.14	0.9636	0.020	80	0.9999
100	99.88	0.011	10.86	0.9526	0.004	100	0.9999
120	119.88	0.010	15.45	0.9007	0.405	119.65	0.9998
150	143.81	0.011	49.58	0.8182	0.162	149.95	0.9991

Adsorption isotherms

The linear regression curves of two isotherm models for the adsorption of methylene blue by porous biochar at three temperatures are shown in Fig. 8, and the values of q_m, K_L, K_F, 1/n, and R^2 are also given in Table 3. Results showed that the adsorption isotherm agreed well with the Langmuir model (R^2 >0.9995) and less well with the Freundlich model, which indicated that the adsorption of methylene blue by porous biochar may be a monolayer adsorption, and the surface sites were relatively homogeneous.

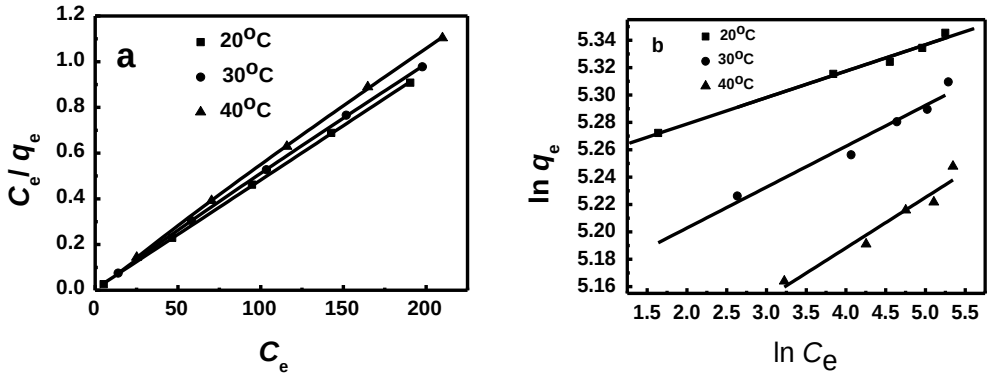


Fig. 8. Langmuir (a) and Freundlich (b) isotherm plots for the adsorption of methylene blue by porous biochar

Table 3. Isothermal Parameters for Adsorption of Methylene Blue by Porous Biochar

Langmuir model					Freundlich model			
T/K	Equation	q_m/mg·g^{-1}	K_L/L·mg^{-1}	R^2	Equation	K_F	1/n	R^2
298	C_e/q_e=0.048C_e+0.0048	208.33	0.81	0.9999	lnq_e=0.193q_e+5.2401	186.69	0.02	0.9895
308	C_e/q_e=0.049C_e+0.0133	204.08	0.37	0.9996	lnq_e=0.299q_e+5.1430	171.23	0.03	0.9578
318	C_e/q_e=0.052C_e+0.0207	192.31	0.25	0.9995	lnq_e=0.369q_e+5.0407	154.58	0.04	0.9476

Thermodynamic modeling

The adsorption thermodynamic parameters determined the reaction process of methylene blue by porous biochar. The changes of standard free energy (ΔG_0, KJ·mol^{-1}), standard sorption entropy (ΔS_0, KJ·mol^{-1}), and standard sorption enthalpy (ΔH_0, KJ·mol^{-1}) were calculated from Eqs. 7, 8, and 9,

$$\Delta G_0 = \Delta H_0 - T\Delta S_0 \quad (7)$$

$$K = \frac{C_A}{C_e} \quad (8)$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (9)$$

where R is the thermodynamic parameter 8.314J·mol^{-1}, Ce is the equilibrium concentration of methylene blue, C_A is the concentration of MB in solid-solution phase, and ΔH_0 and ΔS_0 were determined from the slope and intercept of the Eq (9) of ln$K$ versus 1/T, respectively.

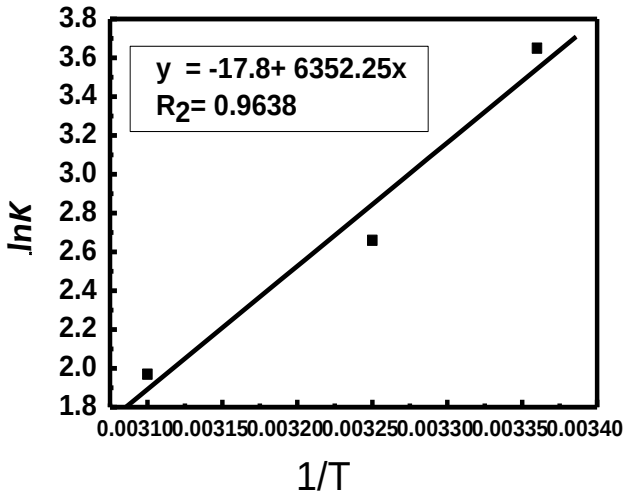


Fig. 9. Van't Hoff plot for adsorption of methylene blue by porous biochar

Table 4. Thermodynamic Parameters for Adsorption of Methylene Blue by Porous Biochar

T (K)	ΔG_0(KJ·mol^{-1})	ΔH_0(KJ·mol^{-1})	ΔS_0(J·mol^{-1}·K^{-1})
298	-9.04	-27.15	-67.11
308	-6.81		
318	-5.21		

As shown in Table 4, ΔG_0 was negative, which indicates that the adsorption of methylene blue by porous biochar was a spontaneous process (We *et al*. 2012). The smaller the ΔG_0 value, the higher the adsorption capacity q_e was. When the temperature was 298 K, ΔG_0 was the least, and the adsorption capacity q_e of methylene blue by porous biochar was the highest. ΔH_0 was negative, indicating that the adsorption removal of methylene blue by porous biochar was an exothermic process. The ΔS_0 value was negative, which indicated the adsorption occurred leading to a smaller disorder degree in the whole system.

CONCLUSIONS

1. Biochar from peanut shell was found to be a good precursors for preparing of porous biochar through KOH activation. The adsorption removal percentage for methylene blue dye was affected by impregnation ratio, time, and temperature. The best activation

conditions were found as follows: impregnation ratio 1.5:1, activation temperature 800 °C, and holding time 90 min. The BET surface area of obtained porous biochar under optimum conditions was calculated as 640.57 $m^2 \cdot g^{-1}$ with 0.76 $cm^3 \cdot g^{-1}$ of total pore volume.

2. The pH value and the initial methylene blue concentration influenced the adsorption of methylene blue from solution. The adsorption data of methylene blue by porous biochar was fitted well with a pseudo-second-order kinetic model.
3. The Langmuir model could well describe the adsorption mechanism of methylene blue by obtained porous biochar from solution. Thermodynamic parameters indicated that the adsorption of methylene blue by porous biochar was a spontaneous, exothermic, and decreased the disorder degree of the process.

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