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Adsorption of methylene blue by residue biochar from copyrolysis of dewatered sewage sludge and pine sawdust

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ABSTRACT

The potential of residue biochar derived from copyrolysis of dewatered sewage sludge (80% of moisture content) and pine sawdust for the adsorption of methylene blue (MB) from aqueous solution was studied. The biochar was characterized by scanning electron microscope, X-ray fluorescence, and Brunauer–Emmet–Teller (BET). Adsorption experiments were carried out to investigate effects of various parameters on MB adsorption and evaluate the batch adsorption kinetics and isotherms. The results showed that the biochar had a BET surface area of 168.27 m^2/g and the maximum adsorption capacity of 16.75 mg/g for MB at 35°C. The adsorption process was followed the second-order kinetic equation, suggesting that the adsorption might be a chemisorption process. The experimental adsorption isotherm data were well fitted with both Langmuir model and Freundlich model.

Keywords: Adsorption; Biochar; Dewatered sewage sludge; Methylene blue

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1. Introduction

Sewage sludge is the major by-product generated in the urban wastewater treatment process [1]. The output of sewage sludge would be gradually increased in the coming decades, owing to the development of population, urbanization, and industrialization [2]. In China, the amount of sewage sludge produced in 2010 was estimated to reach 8.0 million tonnes. Conventional methods currently adopted for sludge disposal would be in limit [3]. A high demand to develop alternative processes of sewage sludge for energy purposes can be expected in the near future.

Sludge pyrolysis had attracted much attention as an economically and environmentally acceptable method for the beneficial utilization of sewage sludge in recent years [4]. The organic matter in sewage sludge could be converted via pyrolysis into bioenergy [5] and the waste volume could be reduction by 50% [6]. Pyrolysis of dried sewage sludge as feedstocks for obtaining bio-oil or fuel gas was extensively studied in bench-scale and pilot-scale [7–9]. However, the drying pretreatment of dewatered sewage sludge resulted in raising energy consumption and disposal cost. In order to reduce the drying process, copyrolysis of dewatered sewage sludge (80% of moisture content) and forestry waste with steam *in situ* (generated from the moisture

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content of feedstock) was investigated in the previous study [10]. Synergistic effects in the copyrolosis process of both the two materials were found in the experimental conditions. The obtained results also revealed that the yield and quality of fuel gas were improved with the addition of pine sawdust in an optimum blend proportion.

However, the copyrolysis process still yielded approximately 20% of residue biochar derived from unconverted inorganic and organic matters in feedstock. Biochar was usually considered as a potential adsorbent, since the inherent porous structures and high specific surface area. According to numerous authors [11–13], the biochar produced from many kinds of biomass should be employed for the elimination of contaminants such as heavy metals, dyes, and pesticide. The use of low-cost biochar adsorbent would be an ideal alternative to the current expensive methods.

In this study, biochar derived from copyrolysis of dewatered sewage sludge (80% of moisture content) and pine sawdust for hydrogen-rich gas was used as adsorbents. The feasibility of the biochar-adsorbing Methylene Blue (MB) from aqueous solution was investigated. The kinetics, isotherm, and thermodynamics were employed for evaluating the adsorption process. The objective of this work was to investigate potential application of the residue biochar as a cheap adsorbent for wastewater treatment.

2. Materials and methods

2.1. Preparation of MB solutions

MB ($C_{16}H_{18}N_3SCl{\cdot}3H_2O$) was supplied by Wuhan Chemical Reagents Company. Molecule structure of MB is shown in Fig. 1. It has a maximum visible absorbance at a wavelength of 665 nm. The aromatic moiety of MB contains nitrogen and sulfur atoms. In the aromatic unit, dimethylamino groups attach to it. The aromatic moiety is planar and the molecule is positively charged. The dye was commercial grade and without further purification before used. MB stock solutions were prepared by dissolving accurately weighed dye in deionized water to the concentration of 1,000 mg/L. Experimental solutions of various concentrations were obtained by further dilution. Standard curves were developed via absorbance measurements of MB solutions by UV-vis spectrophotometer (Cary 5,000, Varian USA).

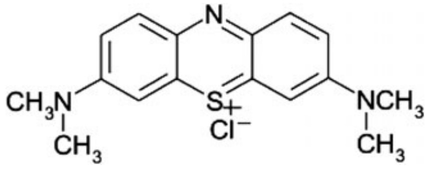

Fig. 1. Molecule structure of MB.

2.2. Preparation of biochar

Dewatered sewage sludge (80% of moisture content) by filter press was obtained from a municipal sewage treatment plant (Wuhan City, China). Pine sawdust was collected from a farm in Wuhan City, China. The raw material was dried under the sun for a period of 7 days to reduce the moisture content and then was shredded into particle size of 0.125–0.25 mm. Biochar was prepared from copyrolysis of dewatered sewage sludge and pine sawdust with the mass ratio of 1:1. The ratio was the optimum value determined by our previous studies [10]. Copyrolysis experiments were carried out at atmospheric pressure in a fixed-bed quartz reactor. The feedstock was pyrolyzed from ambient temperature to 800℃ with 40℃/min of heating rate and then stayed at 800℃ for 15 min. During the pyrolysis process, the volatile matter evolved from the sample was collected as fuel gas. The collected residue biochar was sieved to the particle diameters between 0.125 and 0.15 mm, washed several times with deionized water, dried in a furnace at 105℃ for 24 h, and then stored as adsorbents.

2.3. Analytical methods

Ultimate analysis was obtained with a CHNS/O analyzer (Vario Micro cube, Elementar). Such analysis gives the weight percent of carbon, hydrogen, nitrogen, and sulfur in the sample simultaneously, and the weight percent of oxygen is determined by difference. The thermogravimetric analyzer (Diamond TG/DTA, PerkinElmer Instruments) was used to carry out the proximate analysis which was expressed in terms of moisture, volatile matter, fixed carbon, and ash. Specific surface area was measured by Static Nitrogen Adsorption Instrument (JW-BK122 W, Beijing JWGB Sci. & Tech. Co., Ltd.), and Brunauer–Emmet–Teller (BET) surface area was calculated from the N_2 adsorption–desorption isotherm data. The surface physical morphology of biochar was observed by a scanning electron microscope (SEM, Sirion 200, FEI). The content of metal oxide in biochar was measured by X-ray fluorescence (XRF, EAGLE III, EDAX. Inc.).

2.4. Adsorption experiments

Adsorption experiments were performed in batch mode to evaluate the effects of various parameters on adsorption of MB. In each experiment, 100 mL of dye solution with 1 g/L of adsorbent was added in a 250-mL conical flask at 30 ± 0.1℃. The sample was shaken at 190 rpm for 240 min. The equilibrium adsorption capacity of MB per unit mass, q_e (mg/g), was calculated using the following equations:

$$q_e = \frac{V(C_0 - C_e)}{m} \tag{1}$$

Concentration of MB was determined by standard curves using UV-vis spectrophotometry. All experiments were carried out three times and mean values were taken for calculations.

2.5. Adsorption kinetics

Adsorption kinetic experiments were performed in conical flasks at constant temperature 30 ± 0.1 ℃ with the initial MB concentration of 20 mg/L. The samples were taken at predetermined time intervals, centrifuged, and analyzed for the residual MB concentrations. The kinetic data were analyzed using pseudo-first-order and pseudo-second-order models.

Pseudo-first-order model was generally expressed as [14]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

The kinetic constant k_1 can be determined by plotting $\ln(q_e - q_t)$ against t.

Pseudo-second-order equation was expressed as [14]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

If the pseudo-second-order equation was applicable, the plot of t/q_t against t of the above equation should give a linear relationship. This equation provided an advantage that the adsorption capacity of q_e can be obtained from the slope of the linear plot.

2.6. Adsorption isotherms

Adsorption isotherm experiments were performed in conical flasks containing 100 mL of MB solutions of varying initial dye concentrations from 20 to 50 mg/L. The sealed flasks were then put in a shaker bath at various constant temperatures (±0.1℃) for 240 min, shaken at the 190 rpm. In order to determine the effect of temperature on adsorption, isotherms were established at 25, 30 and 35℃. After equilibrium, samples were centrifuged and analyzed for the residual dye concentrations. The amount of MB adsorbed onto biochar was calculated using Eq. (1). The equilibrium of adsorption was evaluated by using Langmuir and Freundlich isotherm models.

Langmuir isotherm was expressed as [15]:

$$\frac{1}{q_e} = \frac{1}{q_m K_L} \times \frac{1}{C_e} + \frac{1}{q_m} \tag{4}$$

Freundlich isotherm was expressed as [15]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

3. Results and discussion

3.1. Characteristics of biochar

Table 1 shows the ultimate analysis and proximate analysis of the biochar. It is clear that the biochar has the low amount of volatile matter (5.64%) and high amounts of fixed carbon (48.36%) and ash (46.00%). The results were quite different from the composition of char from pyrolysis of sewage sludge alone. The most distinctive feature of sewage sludge chars, if compared to those of lignocellulosic origin, was their high ash content [1]. Sewage sludge-derived carbon materials by one single pyrolysis stage have 67.35% of ash and only 13.64 % of fixed carbon [16]. Ultimate analysis shows that significant amounts of C and O are retained after pyrolysis. H/C atomic ratio was found to be low, which has been attributed to the predominance of aromatic structures in the biochar [17].

The organic content of biochar reduced during pyrolysis, while most of the inorganic content remained in the solid matrix [18]. XRF was performed to confirm the content of inorganic metal oxide of the

Table 1
Ultimate and proximate analyses of biochar sample

	Proximate analysis, %			Ultimate analysis, %				
	Volatile matter	Fixed carbon	Ash	C	H	O[b]	N	S
Biochar[a]	5.64	48.36	46.00	35.87	1.66	13.89	2.06	0.52

[a] Dry basis.

[b] By difference.

Table 2
XRF analysis of biochar sample

Oxide[a]	%	Oxide[a]	%
MgO	2.03	TiO_2	0.56
Al_2O_3	20.47	Cr_2O_3	0.04
SiO_2	50.71	MnO	0.25
P_2O_5	10.38	Fe_2O_3	4.64
SO_3	2.23	CuO	0.05
K_2O	2.19	ZnO	0.09
CaO	6.30	SrO	0.06

[a] Ash basis.

Table 3
Characteristics of porous structure of biochar sample

Sample	S_{BET} ($m^2 g^{-1}$)	Total pore volumes ($cm^3 g^{-1}$)	Average pore size (nm)
Biochar	168.270	0.157	3.730

biochar. The results were listed in Table 2, showing that the biochar mainly contained aluminum oxide, silica, and calcium oxide.

Specific surface area and pore structure characteristics of the biochar are listed in Table 3. The BET surface area of the biochar was 168.27 m^2/g. The total pore volume was found to be 0.16 cm^3/g with the average pore diameter of 3.73 nm. The results of analysis suggested that the biochar contained high surface area and total pore volume compared with other sludge-based activated carbon materials. Li et al. [19] reported that specific surface area of activated carbon prepared from paper mill sewage sludge by carbonization at low temperature was about 130–140 m^2/g. Monsalvo et al. [20] showed that BET surface areas of activated carbons prepared from dried sewage sludge using CO_2, air and KOH as activating agents were below 100 m^2/g. However, the biochar have a lower specific surface area than commercial activated carbons, which typically have specific surface area of about 400–1,500 m^2/g. It demonstrated that further activation processing should be needed for improving the adsorption property of the biochar.

For the characterization of biochar, one of the important parameters is surface morphology. Guerrero et al. [21] suggested that the pyrolysis of biomass materials generally develops porosity in the chars, resulting in a micro- and macroporous structured particles. Ioannidou et al. [22] showed that the morphology of activated carbons from woody material displayed fibrous like structure in nature with long ridges, resembling a series of parallel lines. For sewage sludge, the breakdown of the granules walls and the internal part during the pyrolysis resulted in a regular and highly porous surface [23,24]. SEM micrograph of the biochar at 1,000 × magnification is depicted in Fig. 2. It is observed that the lignocellulosic structure became brittle and collapsed due to devolatilization. The obtained biochar was characteristic of irregular shape and heterogeneous pore structure. The SEM image was anastomosing with the measurement result of the pore structure.

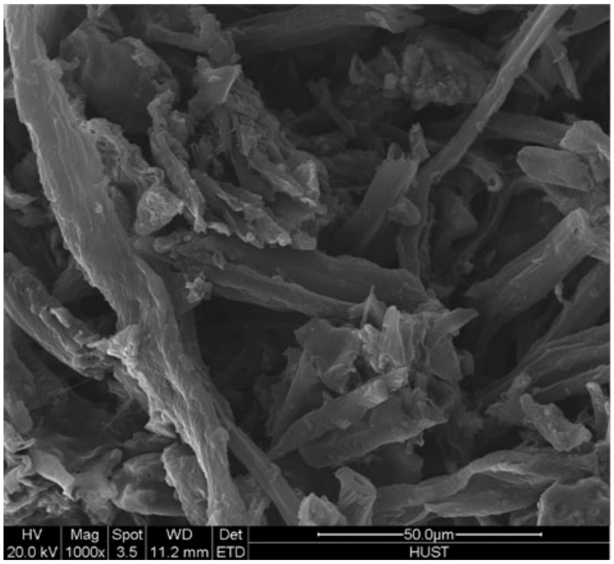

Fig. 2. SEM image of biochar (1,000×).

3.2. Effect of initial dye concentration

The plot of adsorption capacity vs. the contact time at various initial MB concentrations is shown in Fig. 3. It is observed that the adsorption process can be divided into three stages. The first stage was the rapid initial adsorption within 30 min. The following stage was slow adsorption process within the range of 30–180 min. The increase of adsorption capacity became much slower than that of first stage. Finally, the adsorption capacity did not vary significantly after 180 min, which indicated a state of dynamic adsorption equilibrium between MB desorption and adsorption. Fig. 3 also showed that the equilibrium adsorption capacity increased from 13.47 to 15.11 mg/g with the increasing initial MB concentration from 20 to 50 mg/L. When the initial concentrations increased, the mass transfer driving force became larger and the interaction between MB and adsorbent was enhanced, hence resulting in higher adsorption capacity.

3.3. Effect of temperature

Effect of temperature on adsorption capacity for MB onto biochar was investigated at different temperatures of 25, 30 and 35℃. As shown as in Fig. 4, the magnitude of adsorption was proportional to the solution temperature. The adsorption capacity of MB on biochar increases from 14.23 to 16.75 mg/g when temperature of the solution increased from 25 to 35℃. It is seen that higher temperature will result in an increase in MB adsorption on the biochar, suggesting that the dye adsorption is an endothermic process.

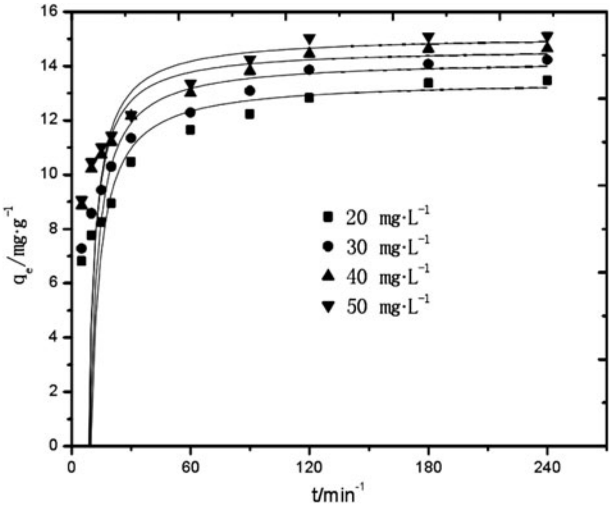

Fig. 3. Effect of initial concentration on MB adsorption.

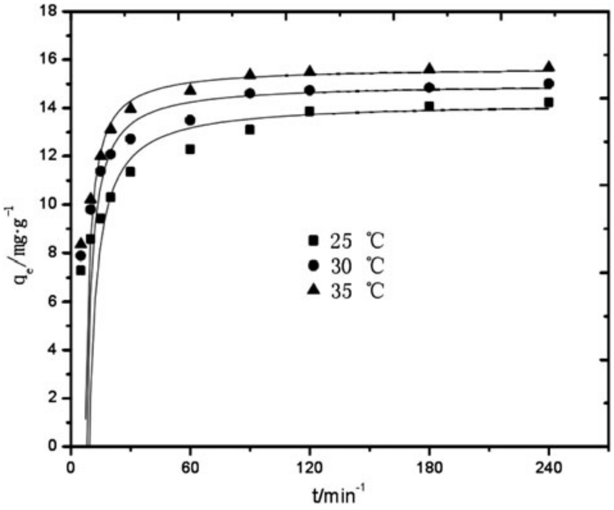

Fig. 4. Effect of temperature on MB adsorption.

3.4. Adsorption kinetics

Kinetic study was helpful in the prediction of the adsorption rate and provided important information for designing and modeling the processes. Pseudo-first-order and pseudo-second-order kinetic models were employed to model the adsorption data over the entire time range.

Table 4 presented the fitting parameters of the pseudo-first-order and pseudo-second-order kinetic models for MB adsorbed onto the biochar. It is can be seen that the correlation coefficients (R^2) obtained from pseudo-second-order model were almost higher than 0.99. The values were also higher than those of the pseudo-first-order model. Furthermore, the calculated values of $q_{e,cal}$ obtained from the pseudo-second-order model perfectly agreed with the experimental values of $q_{e,exp}$ under the experimental conditions. The results suggested that the adsorption of MB onto the biochar followed second-order kinetics. The pseudo-second-order model suggested that the rate-limiting step might be chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between adsorbent and adsorbate [25]. Similar kinetic results had also been reported for the adsorption of MB onto other biomass material, such as activated carbons from sunflower oil cake [26] and activated carbon from date pits [27].

3.5. Equilibrium isotherms

Adsorption isotherms are important for describing the adsorption mechanism for the interaction of dye molecules on the adsorbent surface. In this study, Langmuir and Freundlich isotherm equations were applied to describe the equilibrium process. The calculated adsorption constants of MB onto the

Table 4
Fitting parameters of pseudo-first-order and pseudo-second-order kinetic models

Initial concentrations (mg L^{-1})	$q_{e,exp}$ (mg g^{-1})	Pseudo-first order kinetic			Pseudo-second order kinetic		
		$q_{e,cal}$ (mg g^{-1})	k_1 (min^{-1})	R^2	$q_{e,cal}$ (mg g^{-1})	k_2 g (mg min)$^{-1}$	R^2
20	13.47	8.08	0.0239	0.9783	13.99	0.0075	0.9993
30	14.23	7.65	0.0227	0.9593	14.66	0.0082	0.9994
40	14.56	8.78	0.0343	0.9547	15.04	0.0109	0.9995
50	15.11	8.82	0.0338	0.9568	15.40	0.0122	0.9989

Table 5
Parameters of Langmuir and Freundlich models for MB adsorption

Temperature (℃)	Langmuir model			Freundlich model		
	q_m (mg g^{-1})	K_L (L mg^{-1})	R^2	K_F	$1/n$	R^2
25	12.95	3.31	0.9543	9.44	0.0990	0.9686
30	14.24	4.71	0.9434	10.41	0.1018	0.9786
35	15.86	6.73	0.9650	11.20	0.1026	0.9718

biochar were listed in Table 5. Two isotherm models were seen to be appropriate for the experimental data because all values of R^2 were higher than 0.9. The results indicated that the adsorption process might be a heterogeneous adsorption.

Langmuir isotherm is based on the hypothesis that uptake occurs on a homogeneous surface by monolayer adsorption without interaction between the absorbed materials [28]. Langmuir constant, q_m, represents the monolayer saturation at equilibrium when the surface is fully covered with dye molecules and assists in the explanation of adsorption performance [29]. The values of q_m for MB adsorption onto the biochar increased with the increasing temperature. Freundlich model applies to adsorption on heterogeneous surfaces with the interaction between the adsorbed molecules. The values of $1/n$ implied the type of isotherm and can be classified as irreversible ($1/n=0$), favorable ($0<1/n<1$) and unfavorable ($1/n>1$) [30]. The obtained values of $1/n$ ($0.1<1/n<1$) suggested that the adsorption of MB onto biochar was favorable.

4. Conclusions

Residue biochar from copyrolysis of dewatered sewage sludge and pine sawdust was developed as adsorbents for the adsorption of MB. The biochar was characteristic of heterogeneous pore structure and had 168.27 m^2/g of BET surface area. The maximum adsorption capacity for MB was found to be 16.75 mg/g at 35℃. The kinetic results suggested that the adsorption of MB onto the biochar followed second-order kinetics. Both Langmuir and Freundlichs isotherm models were seen to be appropriate for the experimental data, which indicated a heterogeneous adsorption Furthermore, thermodynamic results indicated that adsorption of MB onto the biochar was spontaneous and endothermic under examined conditions. As a waste, biochar can be used as an effective, low-cost alternative adsorbent for the removal of dyes from aqueous solutions.

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List of symbols

C_e — equilibrium concentration of MB in solution, mg/L
C_0 — the initial MB concentration, mg/L
k_1 — rate constant of pseudo-first-order adsorption, 1/min
k_2 — rate constant of pseudo-second-order sorption, g/(mg min)
K_F — Freundlich isotherm constants
K_L — Langmuir equilibrium constant, L/mg
m — weight of adsorbent, g
q_e — equilibrium adsorption capacity of MB per unit weight of adsorbent, mg/g
q_m — maximum uptake capacity, mg/g
q_t — adsorbed amount per unit weight of adsorbent at time t, mg/g
R — universal gas constant, 8.314 J/(mol K)
T — absolute temperature, K
V — volume of solution, mL

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