Preparation of sawdust functionalized with aspartic acid and its sorption capacity, kinetics and thermodynamics for basic dyes

Renmin Gong*, Na Li*, Shoujun Ni*, Pingzhen Guo*, and Fenghong Huang**,†

*College of Life Science, Anhui Normal University, Wuhu 241000, P. R. China
**Oil Crops Research Institute Chinese Academy of Agricultural Science, Wuhan 430062, P. R. China

Abstract−An ion exchanger with carboxyl groups as active sites was prepared by activating sawdust with epichloro-hydrin, followed by coupling the epoxy-activated sawdust with aspartic acid. The optimal sorption condition, sorption capacity, kinetics and thermodynamics of basic dyes on sawdust ion exchanger (SIE) from aqueous solution were investigated in a batch system. Two basic dyes, methylene blue (MB) and crystal violet (CV), were selected as sorbates. The optimal pH value of MB and CV solutions for favorable sorption was pH 4 and above. The removal ratios of MB and CV on SIE increased with increasing sorbent dose but decreased with increasing dye concentration. The isothermal data of MB and CV sorbed on SIE correlated basically with the Langmuir model. The maximum sorption capacity (Q_m) of SIE for MB and CV was 222.22 and 232.56 mg/g, respectively. The sorption equilibriums of MB and CV on SIE were reached at about 9 h, and the sorption processes could be described by the pseudo-second-order kinetic model. The thermodynamic study indicated that the sorptions of MB and CV on SIE were spontaneous and endothermic at the predetermined temperatures. High temperatures were favorable for the sorption processes.

Key words: Sawdust Ion Exchanger, Basic Dye, Sorption, Kinetics, Thermodynamics

INTRODUCTION

Dyes are extensively used in the textile, paper, rubber, plastic, leather, cosmetic, food, and drug industries. Over 100,000 commercially available dyes exist and more than 7×10^5 metric tons of dyes are produced worldwide annually [1,2]. Dye wastewater discharged by various industries causes certain hazards and environmental problems. From the environmental viewpoint, the removal of dyes from wastewater is a great mission, since some dyes or their metabolites may be toxic as well as carcinogenic, mutagenic and teratogenic [3,4].

It is difficult to remove the color from wastewater since dyes are not only stable to light and heat but also resistant to oxidation and biodegradation. Since biological aerobic/anaerobic treatment is ineffective for removing dyes from wastewater, so other forms of treatment need to be explored. Activated carbon is an effective sorbent in wastewater treatment [5], but there is a growing interest in using other low cost sorbents as its substitute. Some lignocellulosic materials, including kudzu [6], rice husk [7], peanut hull [8], wheat shell [9], wheat bran [10], lemon peel [11], sunflower seed shell [12], broad bean peel [13], pomelo peel [14], and yellow passion fruit waste [15], have been employed as low-cost sorbents for removal of dyes from waters. Some chemical modification has been used for improving dye sorption capacity of lignocellulosic materials [16-19].

Dişbudak et al. [20] employed cysteine supported on polymer for heavy metal sorption and determination. Gupta et al. [21] obtained cation exchanger from cellulose through consecutive chemical reactions with epichlorohydrin and iminodiacetic acid. Oshita

et al. [22] functionalized serine onto chitosan resin for uranium concentration. Lei et al. [23] prepared anion exchanger from cellulose after reaction with epichlorohydrin and diethylamine. In this paper, a new ion exchanger with carboxyl groups as active sites is synthesized by activating sawdust with epichlorohydrin, followed by coupling the epoxy-activated sawdust with aspartic acid. The optimal sorption condition, sorption capacity, kinetics and thermodynamics of basic dyes on sawdust ion exchanger (SIE) from aqueous solution were investigated in a batch system. To the best of our knowledge, it is first time that an ion exchanger was prepared from lignocellulosic material functionalized with aspartic acid.

MATERIALS AND METHODS

1. Synthesis of SIE

Sawdust (*Castanopsis sclerophylla (Lindl.) Schott.*), supplied by a local wood processing factory, was washed with tap water to remove impurity, and then dried overnight at 50 °C. Dried sawdust was sieved to retain the 420-850 μm fractions for further chemical synthesis.

20 g of sawdust was suspended in 240 mL of dioxane. While stirring the suspension on a thermostatic stirrer, 24 mL of 20% NaOH was added followed by 40 mL of epichlorohydrin and the reaction suspension was stirred for 5 h at 60 °C. After keeping it overnight at ambient temperature, the reaction suspension was collected by suction filtration in a sintered glass funnel and washed thoroughly with dioxane followed by 0.1 mol/L Na$_2$CO$_3$-NaHCO$_3$ buffer (pH 9.5). For the coupling of the functional ligand, the epoxy-activated sawdust was immediately resuspended in 240 mL of dioxane containing 8 g of aspartic acid, and a drop of phenolphthalein was added followed by dropwise addition of 20% NaOH with stirring until the aspartic acid dissolved and pink color appeared. The reaction
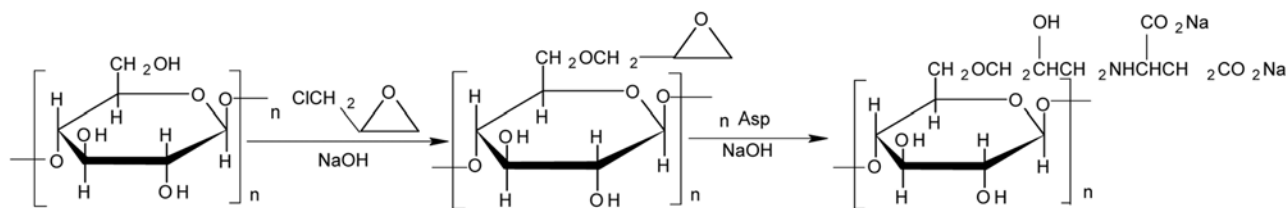
Fig. 1. The chemical mechanism of activation-coupling process of sawdust.

mixture was stirred for 4 h at 50 °C and then left overnight at ambient temperature. The final reaction product was recovered by suction filtration and washed extensively with Milli-Q water. Subsequently, it was dried at 50 °C for 24 h in a forced air oven and preserved in a desiccator for further use as ion exchanger. Its surface area calculated by the BET method was 180 m^2/g. The activation-coupling process of sawdust is presented in Fig. 1.

2. Preparation of Dye Solutions

Methylene blue (MB) and crystal violet (CV) were selected as sorbates. MB and CV are basic dye of phenothiazine type (C.I. No 52,015, FW=319.86, λ_{max}=670 nm) and basic dye of triphenylmethane type (C.I. No 42,555, FW=407.99, λ_{max}=584 nm), respectively. Their chemical structures are shown in Fig. 2. Two basic dyes, in commercial purity, were used without further purification. The dye stock solutions were prepared by dissolving accurately weighted dyes in Milli-Q water to the concentration of 700 mg/L. The experimental solutions were obtained by diluting the dye stock solutions in accurate proportions to different initial concentrations.

3. Sorption Experiments and Measurements

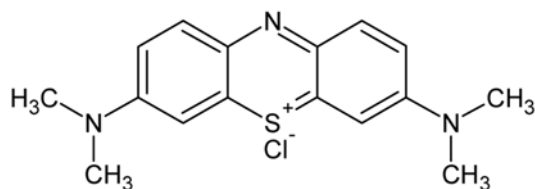Except for the study on the effect of initial dye concentration and

sorption kinetics, other sorption experiments were carried out in a rotary shaker at 150 rpm and ambient temperature (20±2 °C) using 250 mL shaking flasks containing 100 mL of 250 mg/L dye solution in different initial pH values. The initial pH values of the dye solutions were previously adjusted with dilute HNO$_3$ or NaOH using a pH meter. Different doses of SIE were added to each flask, one flask with dye solution but no SIE was used as control, and then the flasks were sealed up to prevent change of volume of the solutions during the experiments. After the flasks were shaken for predetermined time intervals at selected temperatures, the samples were withdrawn from the flasks and the dye solutions were separated from the sorbent by filtration/centrifugation. Dye concentrations in the solutions were determined by spectrophotometry and computed from the calibration curve. The amount of dyes sorbed on SIE was calculated by the mass balance equation. Each run of the experiments was replicated at least three times.
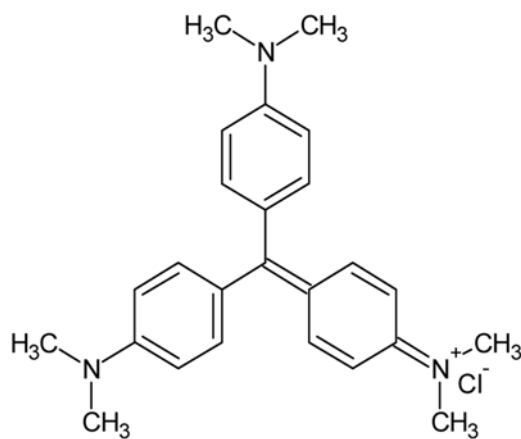
RESULTS AND DISCUSSION

1. IR Spectra and SEM Photographs of SIE

The IR spectra of crude sawdust and SIE are shown in Fig. 3. Compared with the IR spectrum of crude sawdust, it can been seen that there was an obvious characteristic stretching vibration absorption band of carboxyl group at 1,735 cm^{-1} in IR spectrum of SIE. This result confirmed that the aspartic acid had been incorporated into sawdust.

The SEM photographs of SIE before and after dye sorption are shown in Fig. 4. The SEM photograph before dye sorption revealed the rough surface texture and heterogeneous porosity of SIE. After

Fig. 2. The chemical structures of two basic dyes used in this study.
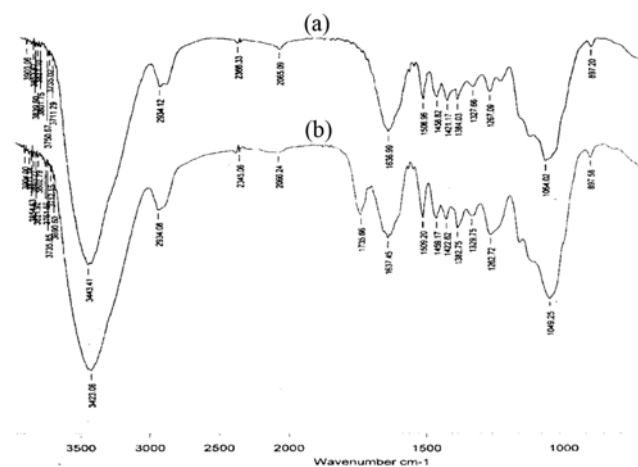

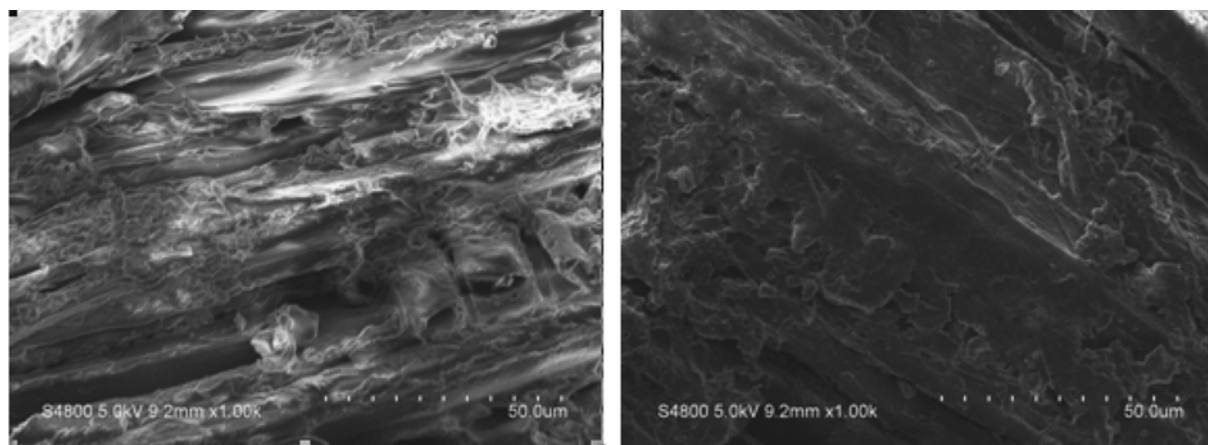**Fig. 3. IR spectra of sawdust ((a) crude sawdust; (b) SIE).**

Fig. 4. SEM photographs of SIE (left: before dye sorption; right: after dye sorption).

dye sorption, SIE presented a smooth surface texture because the dye molecules were trapped into these pores and homogeneously sorbed on its surface.

2. Influence of Initial pH and SIE Dosage

The experimental results indicated that the sorption percents of dyes increased along with increase of initial pH from pH 2 to 4. The increase of initial pH led to negative charges of carboxyl groups on SIE increased, so the sorption amounts of dyes increased. Beyond pH 4, the maximum sorption ratios of dyes were reached and the sorption amounts of dyes kept almost unchangeable. For this reason, the natural pH values of dye solutions (pH>4) were selected as the optimum pH value for the other experiments.

When the SIE dosage was increased from 0.25 to 2.0 g/l, the sorption percents of dyes increased from 55.49 to 95.96% and from 57.91 to 96.21% in MB and CV, respectively. Above 2.0 g/l of SIE dose, the sorption equilibriums of dyes were reached and the removal ratios of dyes kept basically constant. So, the SIE dosage of 2.0 g/L

was chosen for the further experiments.

3. Sorption Isotherm

The relationships between the initial dye concentrations and sorption amounts of dyes are shown in Fig. 5. When the dye concentrations were increased from 50 to 700 mg/L, the amounts of sorbed MB and CV increased from 24.80 to 224.46 mg/g and from 24.82 to 231.74 mg/g, respectively. But the removal ratios of MB and CV on SIE decreased with increasing dye concentration.

With the data in Fig. 5, the Langmuir equation was used to study the sorption isotherm of MB and CV:

$$q_e = aQ_mC_e/(1+aC_e) \tag{1}$$

The above equation can be linearized in the following reciprocal form:

$$C_e/q_e = 1/(aQ_m) + C_e/Q_m \tag{2}$$

where C_e (mg/L) is the concentration of the dye solution at equilibrium, q_e (mg/g) is the amount of sorbed dye at equilibrium, Q_m is the maximum sorption capacity and represents a practical limiting sorption capacity when the sorbent surface is fully covered with monolayer sorbate molecules and a is the Langmuir constant. The Q_m and a values were obtained from the slopes ($1/Q_m$) and intercepts ($1/aQ_m$) of linear plots of C_e/q_e versus C_e.

Table 1 gives the Langmuir equations, values of parameters and correlation coefficients of the experimental data. The result indicated that the sorption isotherms of MB and CV on SIE basically followed the Langmuir model. The sorption capacity (Q_m) of SIE for MB and CV was 222.22 and 232.56 mg/g, respectively. The sorption capacities (Q_m) of some sorbents for MB and CV are compared in Table 2. It was found that SIE showed great sorption capability for MB and CV.

4. Sorption Kinetics

The sorption kinetics of dyes was examined under four different
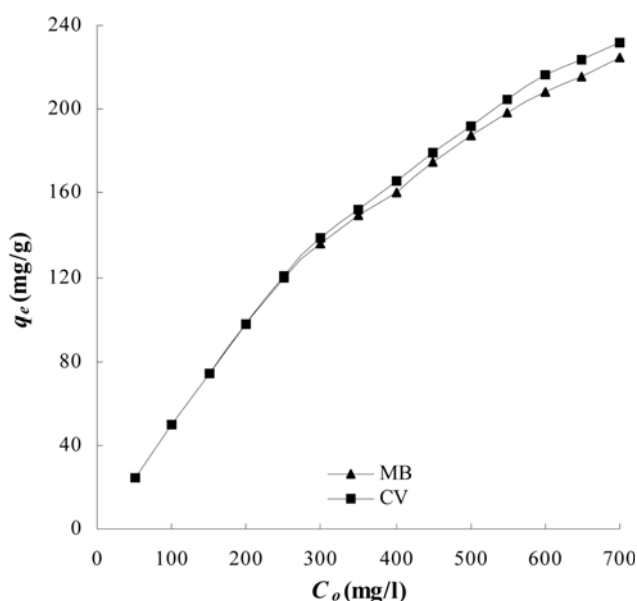

Fig. 5. Influence of dye concentration on sorption of MB and CV by SIE.

Table 1. The Langmuir equations, the values of parameters and correlation coefficients

Dye	Equation	Q_m (mg/g)	a	R^2
MB	$C_e/q_e = 0.0045C_e + 0.0592$	222.22	0.076	0.9857
CV	$C_e/q_e = 0.0043C_e + 0.0539$	232.56	0.080	0.9867

Table 2. The sorption capacities (Q_m) of various sorbents for MB and CV

Dye	Sorbent	Q_m (mg/g)	Reference
MB	SIE	222.22	Present study
	Broad bean peel	192.7	[13]
	Peanut hull	68.03	[8]
	Rice husk	40.6	[7]
	Wheat shell	16.6	[9]
CV	Charred sawdust	341.3	[24]
	SIE	232.56	Present study
	Humic acid immobilized pillared clay	197.77	[25]
	Jute fiber carbon	27.99	[26]

initial dye concentrations. The removal rates of dyes were very rapid at the initial stages of sorption. This was caused by the fast diffusion and sorption of dye molecules onto the external surface of SIE. After a very rapid sorption, dye uptake rates slowly declined with lapse of time and reached equilibrium values at about 9 h for the two dyes. This process was controlled by the pore diffusion velocities of dyes into the intraparticle matrix of SIE.

The experimental kinetic data were treated with the following Ho's pseudo-second-order rate equation:

$$t/q_t = 1/k_{ad}q_e^2 + t/q_e \tag{3}$$

where q_e and q_t (mg/g) refer to the amount of dye sorbed at equilibrium and time t (min), respectively, and k_{ad} (g/mg·min) is the rate constant. The q_e and k_{ad} values could were calculated from the slopes ($1/q_e$) and intercepts ($1/k_{ad}q_e^2$) of the linear plots of t/q_t versus t. The pseudo-second-order rate equations, values of parameters and correlation coefficients of the experimental data under different initial dye concentrations are shown in Table 3. The excellent linear correlation coefficients showed that sorption processes MB and CV on SIE could be described by the pseudo-second-order rate kinetic model.

5. Sorption Thermodynamics

The thermodynamic experiments were carried out at 293.15, 303.15, 313.15, and 323.15 K. The thermodynamic parameters, ΔH^o and ΔS^o, were obtained from the following van't Hoff equation:

$$\ln(q_e/C_e) = \Delta S^o/R - \Delta H^o/RT \tag{4}$$

where q_e/C_e (mL/g) is the equilibrium constant, ΔS^o (J/mol·K) is standard entropy, ΔH^o (J/mol) is standard enthalpy, T (K) is the absolute temperature, and R (8.314 J/mol·K) is the gas constant. The ΔH^o and ΔS^o values could be evaluated from the slope ($-\Delta H^o/R$) and intercept ($\Delta S^o/R$) of the linear plot of $\ln(q_e/C_e)$ versus 1/T. Based on the experimental data under different temperature, the van't Hoff equations of MB and CV sorbed on SIE were given as follows:

$$\ln(q_e/C_e) = 9.782 - 742.56/T, \ R^2 = 0.9903 \tag{5}$$

$$\ln(q_e/C_e) = 12.969 - 1694.6/T; \ R^2 = 0.9958 \tag{6}$$

The thermodynamic parameter, ΔG^o, was calculated from the following Gibbs-Helmholtz equation:

$$\Delta G^o = \Delta H^o - T\Delta S^o \tag{7}$$

where ΔG^o (kJ/mol) is the standard free energy. The ΔG^o values under different temperatures as well as ΔH^o and ΔS^o values, which were evaluated from Eqs. (5), (6) and (7), are presented in Table 4. The negative values of ΔG^o and the positive values of ΔH^o indicated that the sorptions of dyes were spontaneous and endothermic. High temperatures were favorable for the sorption processes.

CONCLUSIONS

This study confirmed that SIE is an excellent sorbent for removal of basic dyes from aqueous solution. The optimal pH value of MB and CV solutions for favorable sorption was pH 4 and above. The removal ratios of MB and CV on SIE increased with increasing sorbent dose but decreased with increasing dye concentration. The optimal SIE dosage was 2 g/L for 250 mg/L of MB and CV solu-

Table 3. The pseudo-second-order rate equations, the values of parameters and correlation coefficients

Dye	Concentration (mg/l)	Equation	q_e (mg/g)	k_{ad} (g/mg·min)	R^2
MB	250	t/qt=0.009t+0.0326	111.11	2.48×10^{-3}	0.9983
	200	t/qt=0.0113t+0.0357	88.50	3.58×10^{-3}	0.9982
	150	t/qt=0.015t+0.049	66.67	4.59×10^{-3}	0.998
	100	t/qt=0.0223t+0.0724	44.84	6.87×10^{-3}	0.998
CV	250	t/qt=0.009t+0.0285	111.11	2.84×10^{-3}	0.9989
	200	t/qt=0.0112t+0.0313	89.29	4.01×10^{-3}	0.9988
	150	t/qt=0.0149t+0.0426	67.11	5.21×10^{-3}	0.9987
	100	t/qt=0.0221t+0.0628	45.25	7.78×10^{-3}	0.998

Table 4. The values of thermodynamic parameters for sorption of MB and CV by SIE

Dye	ΔH^o (kJ/mol)	ΔS^o (J/mol·K)	ΔG^o (kJ/mol)			
			293.15 K	303.15 K	313.15 K	323.15 K
MB	6.17	81.33	−17.67	−18.49	−19.30	−20.11
CV	14.09	107.82	−17.52	−18.60	−19.67	−20.75

tions. The isothermal data of MB and CV sorbed on SIE basically followed the Langmuir model. The maximum sorption capacity (Q_m) of SIE for MB and CV was 222.22 and 232.56 mg/g, respectively. The sorption processes of MB and CV could be described by the pseudo-second-order kinetic model. The thermodynamic study indicated that the sorptions of MB and CV were spontaneous and endothermic.

ACKNOWLEDGEMENTS

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