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Original Research Paper

Preparation and characterization of distillers' grain based activated carbon as low cost methylene blue adsorbent: Mass transfer and equilibrium modeling

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A B S T R A C T

In this study, an orthogonal array design method was employed to optimize carbon preparation from distillers' grain (DGAC). The physical and chemical properties of the produced DGAC were characterized using scanning electron microscopy (SEM), N_2 adsorption–desorption technique (Brunauer-Emmett-Teller, BET), and fourier transform infrared spectroscopy (FTIR). The BET surface area of DGAC was found to be 1430 m^2/g, with average pore diameter of 2.19 nm. Batch experiments were carried out to study the adsorption of methylene blue (MB) onto DGAC. External mass transfer model, internal diffusion model, Boyd model and pseudo-second-order model were used to fit the adsorption kinetic process of MB adsorption onto DGAC. The results shows the external mass transfer model could only describe the adsorption for the initial 5 min, and later the internal diffusion in the pores of the carbon particles became a main resistance, chemisorption was also involved in the adsorption process. The adsorption equilibrium was described best by Langmuir isotherm with maximum adsorption capacity of 934.6 mg/g of MB at 55°C, thermodynamic studies confirmed that the adsorption of MB onto DGAC was spontaneous and thermodynamically favourable. These findings support the potential of using distillers' grain as raw material to prepare well-developed porous texture adsorbent with huge MB removal capacity.

1. Introduction

Considerable amount of textile wastewater was continuously generated by industries such as textile, leather, paper, printing, etc. Textile wastewaters are biodegradable resistance due to the presence of complex chemical structure. The presence of even very small amounts of dyes in water – less than 1 ppm for some dyes – is highly visible and undesirable [1], for they can impede light transmission and upset the biological metabolism processes. Besides, dyes are toxic to human for they may cause allergy, dermatitis, skin irritation, cancer, and mutations in humans [2]. Therefore, treatment of dye containing effluent is of significant concern. Physic-chemical processes are generally applied to treat dye-containing wastewater, such as adsorption, flocculation, coagulation, membrane filtration, photocatalytic degradation, electrochemical destruction, and ozonation [3–9]. Among these technologies, adsorption is favorable in dye water pollution control because of it is cost effective, easy operation, insensitive to toxic substances as compared to the conventional treatment methods [9].

Activated carbon is one of the most common used adsorbents in the adsorption process, for activated carbon has large surface area, high porosity and structural stability However, its widespread use is restricted due to its relatively high cost, thus there is growing interest to develop low-cost activated carbon with well-developed porosity and high adsorptive capacity towards dyes [2]. During the past decades, low-cost activated carbons have been successfully produced from organic-based materials such as sawdust, corncob, walnut shell and seeds [10]. Distillers' grain (DG) is s a waste from ethanol industry, it contains moderate protein and lipid, as well as trace minerals [11], it has the potential to be converted into carbonaceous adsorbent, however, little information is available regarding how to convert DG into an adsorbent with high adsorption capacity towards dyes.

The adsorptive removal of dye can generally be characterized by four consecutive steps [12,13]: (1) Transport of dye molecules from bulk solution to the exterior surface of the adsorbent; (2) mass transfer across the boundary layer (film diffusion); (3) Intraparticle diffusion of dye molecules within the pores of adsorbent

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Nomenclature

SEM	Scanning electron microscopy
BET	Brunauer-Emmett-Teller
FTIR	Fourier transform infrared spectroscopy
MB	Methylene blue
DG	Distillers' grain
DGAC	Distillers' grain based activated carbon
S_{BET}	specific surface area
V_{N2}	total pore volume
pH_{pzc}	pH point of zero charge
C_0	initial concentration of MB in the aqueous solution (mg/L)
C_e	equilibrium concentration of MB in the aqueous solution (mg/L)
V	volume of the solution (L)
M	mass of carbon used (g)
RSD	the maximum relative standard deviation
C_s	solute concentrations (mol/m^3) on the surface of adsorbent
k_f	mass transfer coefficient between bulk solution and solid surface (m/s)
a_m	specific area of the particle (m^2/m^3)
m	concentration of the particles in water (kg/m^3)
d_p	average particle diameter (m)
ρ_p	particle density (kg/m^3)
ρ_b	particle bulk density (kg/m^3)
ε_p	particle porosity
k_{id}	constant of internal diffusion rate (mg/(g $h^{1/2}$))
B_t	a function of F
T	time in minutes
K_2	equilibrium rate constant of pseudo-second-order adsorption (g/mg min)
Q_m	theoretical maximum adsorption capacity when DGAC is completely covered with monolayer (mg/g)
q_e	amount of MB adsorbed at equilibrium (mg/g)
K_L	binding constants for Langmuir models (L/mg)
K_F	binding constants for Freundlich models ((mg/g) (L/mg) 1/n)
n	freundlich exponent related to adsorption intensity
R	gas constant, 8.314 J/(mol K)
T (K)	the absolute temperature
K_d	thermodynamic equilibrium constant of the adsorption process
ΔS^0	entropy change (J/(mol K)
ΔH^0	enthalpy change (kJ/mol)
ΔG^0	Gibbs free energy change (kJ/ mol)
DFT	density functional theory
λ_{max}	wavelength of maximum adsorption
SSE	sum of squared errors
$q_{t,exp}$	experimental MB uptake amount (mg/g)
$q_{t,pred}$	the predicted MB uptake amount (mg/g)
N	number of data points
rpm	rounds per min

(pore diffusion); (4) adsorption of dye molecules on the surface of the adsorbent through molecular interactions (reaction). The concentration of the dye and agitation speed may affect step 1, thus in well mixed batch adsorption, step 1 is very fast, and the resistance for the adsorbent transport from the bulk solution to the external surface can be neglected. In most cases, step 2 and 3 may control the adsorption phenomena, that is, external and internal diffusion are usually considered as the rate determining process, which certainly would affect the adsorption of dyes onto the adsorbent. For adsorption is often a time-dependent process, identification of actual rate controlling steps would enable efficient design of adsorption system.

In this paper, distillers' grain based activated carbon (DGAC) was prepared and optimized by orthogonal array experiment using KOH as activation agent. The ability of DGAC to adsorb MB is studied by batch experiments. Different kinetic models, i.e., the external mass transfer model, internal diffusion model, Boyd model, and pseudo-second-order reaction model were employed to simulate the adsorption of dye onto DGAC under different agitation speeds, the rate constants were evaluated and rate controlling step was identified. Besides, the adsorption isotherms and thermodynamic studies were also discussed to prove the feasibility of using distillers' grain as raw material to prepare porosity adsorbent with high MB removal efficiency.

2. Material and methods

2.1. Material and carbon preparation

Distillers' grain (DG) was collected from a sorghum production company in Chengdu, China. Prior to use, DG was washed with distilled water for several times to remove dust and other inorganic impurities, after that, DG was dried at 105 °C for 12 h to reduce the moisture content, and then crushed and ground to pass through a 60-mesh sieve before activation. All the chemicals including KOH, NaOH and HCl were of analytical grade and obtained from Kelong Chemical Co. (China), they were used as received. Solutions were prepared with Milli-Q water.

To manufacture the activated carbon, 10 g of the dried DG was mixed with KOH solution with impregnation ratio of 1:3 (w/v), after mixing in an ultrasound (frequency = 40 kHz, power = 200 W, and temperature = 25 °C) for 0.5 h, the mixing slurry was dried in an oven at 105 °C overnight. The dried samples were later placed in a crucible, heated in chamber furnace (QSX2-8-10PF, Chengdu, China) at a constant heating rate of 10 °C/min to desired temperatures of 700–900 °C in N_2 atmosphere (99.99%, 200 mL/min) and held at the temperature for 60–120 min, after that, the carbonization samples were cooled down to room temperature in the furnace under N_2 flow. The final product was washed repeatedly with hot distilled water until the effluent pH was close to neutral and then dried in a vacuum oven at 105 °C overnight, after cooled in a desiccator, the produced carbons were crushed and sieved to pass through a 200-mesh sieve for further tests. Orthogonal array testing with 3 levels and 3 factors, L9 (3^3), was designed in this study to determine the optimum conditions for the preparation of distillers' grain based activated carbon. The control parameters were activating agent concentration (KOH of 1 mol/L, 2 mol/L and 3 mol/L), activation time (60 min, 90 min and 120 min) and activation temperature (700 °C, 800 °C and 900 °C).

2.2. Characterization of activated carbon

Textural characterization of the prepared activated carbon was carried out by N_2 adsorption at 77 K using a surface area analyzer (ASAP 2046, Micromeritics, USA), The specific surface area (S_{BET}), total pore volume (V_{N2}) and pore size distribution of the produced carbons were calculated from the N_2 adsorption–desorption

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