Mesoporous activated carbon from wood sawdust by K$_2$CO$_3$ activation using microwave heating

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ABSTRACT

Wood sawdust was converted into a high-quality activated carbon (WSAC) via microwave-induced K$_2$CO$_3$ activation. The operational variables including chemical impregnation ratio, microwave power and irradiation time on the carbon yield and adsorption capability were identified. The surface physical characteristics of WSAC were examined by pore structural analysis, scanning electron microscopy and nitrogen adsorption isotherms. The adsorptive behavior of WSAC was quantified using methylene blue as model dye compound. The best conditions resulted in activated carbon with a monolayer adsorption capacity of 423.17 mg/g and carbon yield of 80.75%. The BET surface area, Langmuir surface area and total pore volume were corresponded to 1496.05 m^2/g, 2245.53 m^2/g and 0.864 cm^3/g, respectively. The findings support the potential to prepare high surface area and mesoporous activated carbon from wood sawdust by microwave assisted chemical activation.

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1. Introduction

Neobalanocarpus heimii, locally known as Chengal, is a unique tree species belonging to the order Malvales and family of Dipterocarpaceae. The tree is typically 60–65 m tall and has a diameter of 5.33 m (Ashton, 1969). Chengal trees are dominant in mixed dipterocarp tropical rainforests. The wood is heavy, pale-yellow and moderately lustrous, with an air-dry density of 915–980 kg/m^3. Chengal is an important natural resource primarily used for the production of particleboards, fiberboards, furniture and packing materials. It plays a key role in the manufacture of household commodities, and is suitable for all forms of architectural moldings and heavy constructions, particularly boat-buildings, bridges, railway sleepers, power line posts and rubber coagulating tanks, where great strength and durability are required (Iwata et al., 2000).

Processing of the wood generates lignocellulosic biomass, in the form of wood sawdust, off-cuts and chips, which can amount to 20% of the total input mass (Gan et al., 2004). These residues are disposed of by on-site combustion deposition in landfills. In an effort to upgrade this abundantly available biomass, microwave irradiation for preparation of activated carbon from Chengal sawdust via K$_2$CO$_3$ activation was explored. The significant influences of microwave power, radiation time and chemical impregnation ratio on the carbon yield and adsorption capacity were investigated systematically. Textural, functional and surface characteriza-

tion of the prepared adsorbent was performed and adsorption equilibrium, isotherms and kinetics were outlined.

2. Methods

2.1. Adsorbate

Methylene blue (MB), a monovalent cationic dye with the molecular structure C$_{16}$H$_{18}$N$_3$SCl, was selected as the model adsorbate in the present study. A stock solution of 1000 mg/L was prepared by dissolving an appropriate quantity of MB in double distilled water and then diluted to the desired concentrations.

2.2. Preparation of activated carbon

Locally obtained Chengal wood sawdust (WS) was thoroughly washed, air-dried and sieved to obtain particles of 1–2 mm in diameter. The carbonization process was carried out by loading 500 g of dried wood particles into a tubular furnace and heating to a carbonization temperature of 700 °C under purified N$_2$ flow (150 cm^3/min) (Foo and Hameed, 2012a). The char produced was mixed with K$_2$CO$_3$ pellets with different impregnation ratio (IR), defined as:

$$IR = \frac{w_{K_2CO_3}}{w_{char}} \tag{1}$$

where $w_{K_2CO_3}$ and w_{char} is the dry weight of K$_2$CO$_3$ pellets (g) and char (g).

Microwave heating was conducted in a 2.45 GHz commercial microwave oven. The oven has a power controller to select different power levels and a timer for various exposure times at a set microwave power level. Activation was performed in a reactor fixed in the chamber of the microwave oven. Nitrogen gas at a pre-set flow rate of 300 cm^3/min was used to purge air in the reactor before the start of microwave heating and it continued to flow during the activation stage. The resultant activated carbon was washed with 0.1 M hydrochloric acid and rinsed repeatedly with hot and cold distilled water until the filtrate reached neutral pH. The yield was defined as the weight of activated carbon per weight of char utilized for activation (Foo and Hameed, 2012a).

2.3. Adsorption equilibrium studies

Batch adsorption experiments were undertaken in a set of 250-mL Erlenmeyer flasks containing 0.20 g of adsorbent and 200 mL of solutions containing 50–500 mg/L of the dye. The mixture was agitated in a thermostatic orbital shaker at 30 °C with an agitation speed of 120 rpm. The dye concentration in the supernatant was determined using a double beam UV–Vis spectrophotometer (UV-1601 Shimadzu, Japan) at 668 nm. Each experiment was carried out in triplicates under identical conditions and an average value was determined. MB uptake at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{2}$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V (L) is the volume of the solution, and W (g) is the mass of adsorbent used.

The effect of pH on dye removal was examined by varying the pH from 2 to 12, with initial dye concentration of 500 mg/L, carbon (WSAC) dosage of 0.20 g/200 mL and adsorption temperature of 30 °C. The initial pH of the dye solution was adjusted by addition of 0.10 M HCl or NaOH. The pH was measured using a pH meter (Ecoscan, EUTECH Instruments, Singapore).

2.4. Adsorption isotherm

2.4.1. Freundlich isotherm

Freundlich isotherm (Freundlich, 1906) is a model describing non-ideal, reversible and multilayer adsorption, with non-uniform distribution of adsorption heat and affinity over the heterogeneous surface. The Freundlich isotherm was derived as:

$$q_e = K_F C_e^{1/2} \tag{3}$$

where K_F (mg/g)(L/mg)$^{1/n}$ and $1/n$ are the Freundlich adsorption constant and a measure of adsorption intensity, respectively.

2.4.2. Langmuir isotherm

Langmuir isotherm (Langmuir, 1916) assumes monolayer adsorption can only occur at a finite number of localized sites that are identical and equivalent. The mathematical expression of Langmuir isotherm is defined as:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \tag{4}$$

where Q_0 (mg/g) and K_L (L/g) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively.

2.4.3. Temkin isotherm

The Temkin isotherm (Tempkin and Pyzhev, 1940) assumes the heat of adsorption (function of temperature) of all molecules in the layer decreases linearly rather than logarithmically with coverage.

Its derivation is characterized by a uniform distribution of binding energy. The Temkin isotherm has been used in the form of:

$$q_e = B \ln(A C_e) \tag{5}$$

where $B = RT/b$, with b (J/mol), A (L/g), R (8.314 J/mol K) and T (K) are the Temkin constant related to heat of sorption, equilibrium binding constant, gas constant and absolute temperature, respectively.

2.4.4. Redlich–Peterson isotherm

The Redlich–Peterson isotherm (Redlich and Peterson, 1959) is a hybrid isotherm featuring both Langmuir and Freundlich isotherms, which incorporates three parameters into an empirical equation given by:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^g} \tag{6}$$

where K_R (L/g) and a_R (1/mg) are Redlich–Peterson isotherm constants, and g is the isotherm exponent. The model can be applied either in homogeneous or heterogeneous systems. It approaches the Freundlich isotherm model at high concentration and in accordance with the low concentration limit of the ideal Langmuir condition.

2.4.5. Hill isotherm

The Hill equation (Hill, 1910) was postulated to describe the binding of different species onto homogeneous substrates defined as:

$$q_e = \frac{q_{s_H} C_e^{n_H}}{K_D + C_e^{n_H}} \tag{7}$$

where K_D, n_H, and q_{s_H} (mg/L) are Hill isotherm constant, Hill cooperativity coefficient of the binding interaction and Hill isotherm saturation uptake. The model assumes that adsorption is a cooperative phenomenon by which ligand binding at one site of the macromolecule may influence different binding sites on the same macromolecule.

2.4.6. Toth isotherm

The Toth isotherm model (Toth, 1971) is another empirical equation developed to improve Langmuir isotherm fittings. It is useful in describing heterogeneous adsorption systems, and satisfies both low and high-end boundary of concentrations:

$$q_e = \frac{K_T C_e}{(a_T + C_e)^{1/2}} \tag{8}$$

where K_T (mg/g), a_T (L/mg) and t are the Toth isotherm constants. Its correlation presupposes an asymmetrical quasi-Gaussian energy distribution where most binding sites have an adsorption energy lower than the peak value.

The validity of the models was verified by root-mean-square deviation (RMSD), the commonly used statistical tool measuring the predictive power of a model derived as:

$$\text{RMSD} = \frac{\sqrt{\sum_{i=1}^{n}(q_{exp} - q_P)^2}}{n-1} \tag{9}$$

where q_{exp} (mg/g) and q_p (mg/g) are the experimental and theoretical adsorption capacity, respectively.

2.5. Adsorption kinetics

For interpretation of kinetic experimental data, the aqueous samples were withdrawn at different time intervals and the