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Mesoporous and adsorptive properties of palm date seed activated carbon prepared via sequential hydrothermal carbonization and sodium hydroxide activation

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HIGHLIGHTS

- Mesoporous activated carbon (AC) was prepared from sodium hydroxide activation of hydrochar of palm date seed.
- The BET of AC prepared using 1:3 NaOH impregnation ratio was 1282.49 m^2/g and 20.73 Å average pore width.
- The maximum MB adsorption capacities of 612.1, 464.3, and 410.0 mg/g were obtained at 30, 40, and 50 °C, respectively.

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ABSTRACT

Mesoporous activated carbon (AC) was prepared via sodium hydroxide (NaOH) activation of hydrochar from the hydrothermal carbonization (HTC) of palm date seed (PDS). The textural, morphological, and chemical properties of the produced hydrochar AC were investigated. NaOH activation enhanced the porosity and surface functionality of the hydrochar. Batch equilibration methods were performed to explore the process parameters that affected the adsorption of the prepared AC on methylene blue (MB), including initial concentration, contact time, solution pH and temperature. The Freundlich isotherm model better depicted the equilibrium data compared with the Langmuir isotherm model. Temperature was found to negatively affect the adsorption capacity of the prepared AC, which exhibited 612.1, 464.3 and 410.0 mg/g maximum MB adsorption capacities at 30, 40 and 50 °C, respectively. The pseudo-second order kinetic model best described the kinetic data. HTC and NaOH activation was proven to be an effective method in preparing highly porous AC from PDS, with good potential for cationic dye removal from liquid phase.

1. Introduction

Activated carbon (AC) is conventionally synthesized using char from the pyrolysis of organic material, which then undergoes a physical or chemical activation process at a high temperature. A potential alternative method of converting biomass into char in a more energy-efficient process is via hydrothermal carbonization (HTC). HTC is a thermochemical synthesis method used to produce functional carbon materials from pure carbohydrates or lignocellulosic biomass with tunable chemical structures [1]. HTC is a thermal conversion process at a comparatively low temperature and has been proven to be environmentally favorable for the conversion of various precursors into value-added products [2–5]. Three products are formed from HTC, namely, a solid hydrochar, an aqueous soluble liquid, and a gas that mainly consists of carbon dioxide. HTC is more energy-efficient than pyrolysis mainly because milder thermal conditions are used in HTC. In addition, HTC is exothermic; thus, wet materials can be used directly without any drying process [6,7].

A number of studies have been reported recently on HTC of various biomass materials. However, most research has been mainly focused on the production of bio-oil, with only few studies investigating the applications of hydrothermal carbon or hydrochar. Falco et al. [1] investigated the influences of biomass precursor (i.e., D-glucose, cellulose, rye straw) and HTC temperature on porosity

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formation in the AC manufactured by KOH activation. Highly microporous ACs were generated with high performance in gas storage applications regardless of the precursor used. Physical activation of HTC-sewage sludge by using hot steam was conducted by Saetea and Tippayawong [6] to prepare AC. The sewage sludge-based hydrochar AC was found to have good potential for adsorption or soil conditioning. Pari et al. [8] obtained spherical AC from cassava and tapioca flour via HTC and KOH activations. The prepared AC was predominantly spherical and exhibited excellent textural and morphological properties. Similarly, improved surface area and micropores were observed in the AC prepared from hydrothermally carbonized beer waste via H_3PO_4 activation [9]. Zhu et al. [10] investigated the characteristics and tetracycline adsorption behavior of a novel porous carbon prepared from hydrochar. High activation temperatures ranging from 500 to 700 °C were found to work well for hydrochar carbonization, which resulted in high surface areas (>270 m^2/g). Functional nanoporous carbons prepared from hydrothermally treated hazelnut shells were characterized for their textural properties and tested for methylene blue (MB) adsorption by Unur [11]. Regmi et al. [12] produced hydrochar from switch grass and AC via KOH activation of the hydrochar and investigated their adsorption performances on copper and cadmium aqueous solutions. However, the hydrochar modified with NaOH has not been reported in literature for the production of AC.

Therefore, the innovative aspects of this work were the pretreatment of palm date seed (PDS) by HTC under mild conditions and subsequently chemical activation by sodium hydroxide (NaOH) to produce mesoporous AC. The prepared AC was subjected to textural and morphological studies. MB was used as the model dye to evaluate the adsorption performance of the PDS hydrochar AC in aqueous solutions. Adsorption equilibrium, isotherms, kinetics, mechanism, and thermodynamics were considered for the adsorption studies.

2. Materials and methods

2.1. Adsorbate

A 1000 mg/L stock solution was prepared by dissolving an exact amount of MB dye (Sigma–Aldrich) in distilled water. The different concentrations of MB for the entire study were prepared from this stock solution. MB has a molecular weight of 373.9 g/mol, molecular formula is $C_{16}H_{18}N_3SCl$ and its solubility in water is 40 g/L. All other chemicals, such as NaOH and HCl, were laboratory grade and were purchased from different renowned suppliers.

2.2. Preparation of NaOH-activated hydrochar

PDS, which is used as the precursor for hydrochar and AC productions in this study, was obtained locally in Malaysia. The entire raw PDS material was washed several times with normal water and then with distilled water to remove dirt and flesh. The samples were then dried at room temperature (28 ± 2 °C) and were crushed in a grinder to obtain 1–2 mm particle sizes. An automated stainless-steel hydrothermal reactor with 200 mL water capacity was used for HTC. Exactly 5 g of the PDS sample (1–2 mm size) was transferred to the hydrothermal reactor and added with 100 mL of distilled water to ensure that the sample was completely submerged. The reactor was sealed and heated to 200 °C for 5 h at 5 °C/min heating rate. After which, the reactor was immediately removed from the furnace and cooled at room temperature. The brownish hydrochar, which was obtained as a solid residue from the reactor, was labeled as PDS–HTC. The recovered PDS–HTC was washed several times with distilled water and then heated in an oven at 105 °C for 24 h. After which, the PDS–HTC hydrochar was impregnated with NaOH at ratios of 1:1, 1:2, and 1:3 PDS–HTC:NaOH (w/w), stored overnight, then oven-dried at 105 °C for 24 h. An automatic electric vertical furnace was used to activate the NaOH-pretreated hydrochar at 600 °C under a continuous nitrogen (N_2, 99.995%) flow at 150 cm^3/min. A 10 °C/min heating rate was set for 1 h. After cooling the furnace to room temperature, the produced AC was collected and repetitively rinsed with hot distilled water to decrease the pH of the washing solution from 6 to 7. Finally, the wet ACs were dried in an oven at 105 °C for 24 h and stored in a tightly closed container for further use. The ACs were designated as HTC–PDS1, HTC–PDS2, and HTC–PDS3 based on different NaOH impregnation ratios of 1:1, 1:2, and 1:3, respectively.

2.3. HTC–PDSAC characterization

The surface area and the micropore volume of HTC–PDS ACs were quantified under N_2 gas at 77 K by using a physisorption analyzer (Micromeritics, Model ASAP 2020, USA) determined by Brunauer–Emmett–Teller (BET) method and *t*-plot method. On the other hand, the pore size distribution was obtained by the Barrett–Joyner–Halenda (BJH) method. The scanning electron microscope (SEM) micrographs of the hydrochar and hydrochar ACs were obtained using Zeiss (Model Supra 35 VP, Germany). A Perkin Elmer Fourier-transform infrared (FTIR) spectrometer (Model 2000 FTIR, USA) was used to verify the organic structure of the HTC–PDS AC surface before and after adsorption. Solid addition method [13] was used to calculate the point of zero charge on the ACs.

2.4. Adsorption equilibrium and kinetic studies

Adsorption equilibrium and kinetic experiments were conducted in a temperature-controlled water-bath shaker. About 200 mL of the MB solutions at different concentrations (50, 100, 200, 300, 400, and 500 mg/L) was poured in 250 mL Erlenmeyer flasks. Equal HTC–PDS ACs adsorbent dosages (0.20 g) were placed in each flask and were shaken isothermally with 120 rpm agitation speed at 30 °C. The initial pH of the MB solutions was kept constant at pH 7 by using 0.1 M HCl and 0.1 M NaOH. The solution pH was measured using a pH meter (EUTECH Instruments, Model Ecoscan, Singapore). The concentrations of the MB solutions were analyzed at predetermined time intervals. The supernatants were collected using disposable syringes, and the MB concentrations in the solutions were determined at 668 nm by using a UV–visible spectrophotometer (Shimadzu, Model UV 1700, Japan). For thermodynamic studies, similar procedures were conducted at 40 °C and 50 °C, with the other factors remaining constant. A 3–11 pH range was selected by using a constant initial MB concentration (100 mg/L) and adsorbent dosage (0.20 g/200 mL solution) to evaluate the effect of pH on the MB dye removal of HTC–PDS ACs.

The adsorption at equilibrium, q_e (mg/g), adsorption at time *t*, q_t (mg/g), and removal percentage (*R*%) were evaluated using Eqs. (1)–(3), respectively:

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

$$q_t = \frac{(C_{i-}C_t)V}{W} \quad (2)$$

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100 \quad (3)$$

where C_i, C_e, and C_t (mg/L) are the liquid phase concentrations at initial, equilibrium, and time *t* (min), respectively, *V* is the solution volume (mL) and *W* is the adsorbent mass used (g).