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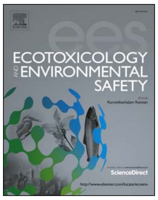

Mesoporous activated carbon prepared from NaOH activation of rattan (*Lacosperma secundiflorum*) hydrochar for methylene blue removal

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ABSTRACT

Hydrothermal carbonization of biomass wastes presents a promising step in the production of cost-effective activated carbon. In the present work, mesoporous activated carbon (HAC) was prepared by the hydrothermal carbonization of rattan furniture wastes followed by NaOH activation. The textural and morphological characteristics, along with adsorption performance of prepared HAC toward methylene blue (MB) dye, were evaluated. The effects of common adsorption variables on performance resulted in a removal efficiency of 96% for the MB sample at initial concentration of 25 mg/L, solution pH of 7, 30 °C, and 8 h. The Langmuir equation showed the best isotherm data correlation, with a maximum uptake of 359 mg/g. The adsorbed amount versus time data was well fitted by a pseudo-second order kinetic model. The prepared HAC with a high surface area of 1135 m^2/g and an average pore size distribution of 35.5 Å could be an efficient adsorbent for treatment of synthetic dyes in wastewaters.

1. Introduction

Carbonization and activation are the basic steps in preparing activated carbon. These steps mainly affect their performance and cost in addition to the type of raw precursor, activating agent, and regeneration technique. Recently, hydrothermal carbonization (HTC) has been considered as a novel and cost-effective technique for converting wet biomass to a solid product known as hydrochar (Danso-Boateng et al., 2015). HTC is carried out under mild conditions (180–250 °C) and pressure conditions in a closed aqueous system, in which the pressure source is mostly related to steam. The reaction mechanism involves sequential steps, which include dehydration, decarboxylation, polymerization, and aromatization (Reza et al., 2015). Hydrothermal treatment presents several advantages, such as high conversion yield, avoidance of an energy-intensive drying process, and relatively low-temperature operation in comparison with thermal carbonization (Zhang et al., 2015; Pala et al., 2014).

Hydrochars have been applied as sorbents in the removal of metals (Alatalo et al., 2013), dyes (Parshetti et al., 2014), and pesticides (Flora et al., 2013) from aqueous solutions. However, low surface area, poor porosity, and low adsorption capacity limit their applications in environmental protection (Falco et al., 2013). Hence, a modified hydrochar is needed to enhance adsorption performance in pollutant removal. The high carbon content, coal-like composition, low ash content, low extent of aromatization, and high content of oxygenated functional groups of hydrochars promote their use as precursors for highly porous activated carbons (Basso et al., 2015). The oxygenated functional groups of hydrochar can increase porosity by their ability to enhance the reactivity with activator, thereby improving the utilization of hydrochar as a precursor for effective sorbents in the treatment of gaseous and liquid pollutants (Sun et al., 2014; Zhu et al., 2014a).

Abundance, renewability, favorable characteristics, and high lignocellulosic composition render biomass as sufficient precursors for carbonaceous adsorbents (Sayğılı and Güzel, 2016; Shi et al., 2016; Anoop Krishnan et al., 2016; Li et al., 2013; Sudha et al., 2015). HTC technique has been adopted by numerous researchers to produce hydrochar from various biomass wastes as a precursor for activated carbon (AC). Fernandez et al. (2015) utilized HTC to obtain orange peel hydrochar as a precursor for AC by H_3PO_4 activation for treating pharmaceutical pollutants (diclofenac sodium, salicylic acid, and flurbiprofen). Jain et al. (2015) tested the ability of using coconut shell hydrochar prepared by HTC method as a precursor for mesoporous AC by $ZnCl_2$ activation to remove phenol pollutants. Regmi et al. (2012) produced hydrochar from switch grass by HTC reaction and modified

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the hydrochar to AC by KOH activation for adsorption of metals. Zhu et al. (2014b) synthesized ACs from *Salix psammophila* hydrochar by K_2CO_3 activation with high potential for attracting malachite green dye molecules.

Rattan (*Lacosperma secundiflorum*) is a non-timber forest plant that grows into a long slender stem (15–30 m). A uniform diameter is maintained throughout its length. Rattan palm is commonly native to numerous parts of the tropics such as Malaysia and Indonesia. In Malaysia, major attention has been given to rattan management and utilization in furniture manufacturing, in which rattan poles and other species are converted into furniture (Adewole and Onilude, 2011). The high wastage of raw rattan, especially poles, which often become a burden to the environment through open burning and illegal dumping, is a major problem associated with the furniture industry (Olorunnisola and Adefisan, 2008). Over 30% of rattan stems harvested at any particular time for furniture industry is wasted (Olorunnisola, 2005). A promising approach to manage these wastes that is yet to be explored is their utilization in the production of high value-added products. Therefore, the present work focuses on HTC of rattan furniture wastes to hydrochar, followed by alkali activation to carbon. NaOH was used as an activator because of its ability to produce carbons with well-developed pore structure, as well as significant recovery, less corrosive ability, and cost (Dobele et al., 2012). The aim of this work is to utilize rattan waste for the production of high surface area activated carbon by carbonization fallowed by NaOH activation to be employed as a better low-cost adsorbent for the methylene blue (MB) dye removal. In addition, the surface characteristics of prepared activated hydrochar (HAC) and adsorption behavior of MB onto HAC in terms of isotherms, kinetics, and thermodynamics is illustrated.

2. Materials and methods

2.1. Materials

Rattan stalks were collected locally (Nibong Tebal, Penang, Malaysia) and utilized as raw materials for HAC preparation. The stalks were dried at room temperature and crushed in an electrical grinder to obtain 1–2 mm particle size. MB (Sigma–Aldrich), with a molecular weight of 374 g/mol, chemical formula of $C_{16}H_{18}N_3SCl$, and solubility in water of 40 g/L, was used as adsorbate. All other regents were commercially available and of analytical grade.

2.2. Hydrothermal carbonization

Exactly 5 g of rattan precursor and 100 ml of distilled water were hydrothermally treated in a 200 ml stainless steel autoclave. The batch reactor was heated to 200 °C for 5 h at a rate of 5 °C/min and then allowed to cool to ambient temperature. The reaction temperature (200 °C) and time (5 h) were fixed based on high yield according to our preliminary experiments. The solid product, which was named rattan hydrochar, was separated by filtration. The obtained rattan hydrochar was repeatedly washed with distilled water and then placed in an oven at 105 °C for 24 h for dehydration.

2.3. Chemical activation of rattan hydrochar

Dried hydrochar samples were impregnated with NaOH solutions at a ratio of 3:1 (w/w) over night and placed in an oven at 105 °C for drying. The modified hydrochar was activated in an electric tubular furnace at a temperature of 600 °C (according to our preliminary experiment) and a rate of 10 °C/min under N_2 (99.9% purity) flow of 150 cm^3/min for 1 h. The activated char was allowed to cool to ambient temperature and continually washed with hot distilled water until the pH of the filtrate was reduced to 6–7. The final activated hydrochar (HAC) was placed in an oven at 105 °C for 24 h for drying and then kept in a desiccator for dye treatment.

2.4. Adsorption performance and characterization

The adsorption performance of HAC toward MB was determined in terms of removal percentage and uptake. The dependence of the performance on the most important adsorption variables, which are represented by contact time, initial concentration, and solution pH, was investigated by performing a set of batch experiments. Dye solution (200 ml) with the required concentration and pH was added into 250 ml conical flasks. The flasks were subsequently placed on a shaker at an agitation speed of 120 rpm for the required time and at 30 °C. The influences of initial concentration and contact time were tested at 30 °C, natural pH, and different dye concentrations (25–350 mg/L). The effect of initial pH was demonstrated at a dye concentration of 100 mg/L over a pH range of 3–11 and with modification by 0.1 M HCl or NaOH solution. The final concentration of the MB solution was measured by a UV–Vis absorption spectrophotometer (UV-1700, Shimadzu, Japan) at a wavelength of $\lambda_{max} = 668$ nm. The uptake, q_e (mg/g), and removal (%) were determined as follows:

$$qe = \frac{(C_o - C\ )\,V}{W} \tag{1}$$

$$Removal\ (\%) = \frac{Co - C}{Co}\, x\ 100 \tag{2}$$

where C_o and C (mg/L) are MB concentrations at initial and final steps, respectively, V (L) is the volume of dye solution, and W (g) is the mass of HAC. The surface characteristics of HAC were tested by N_2 adsorption and desorption isotherms at a temperature of 77 K within various relative pressure values. Surface area was evaluated by using Brunauer–Emmett–Teller (BET) method, and the volumes of micropores and mesopores were computed by t-plot procedure. HAC structure was also identified by scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR). For the point of zero charge (pHpzc) determination the initial pH (pH_i) of aqueous solutions (100 ml) were adjusted to a pH range of 2–12 using 0.1 M HCl or NaOH. Then, 0.1g of HAC was added to each adjusted solution. The dispersions were shaken for 48 h at 30 °C, and the final pH of the solutions (pH_f) was determined. The point of zero charge (pHpzc) is the point where the curve pH_f vs. pH_i intersects the line $pH_f = pH_i$.

2.5. Adsorption isotherms and kinetics

Equilibrium isotherm and kinetic studies were conducted in a set of batch mode experiments. Adsorption isotherms for MB-HAC system were performed by adding about 200 ml of the MB solutions at different concentrations (25 mg/L to 350 mg/L) to 250 ml Erlenmeyer flasks. Equal HAC dosages (0.20g) were placed in each flask at 30 °C with shaking at 120 rpm for 30 h. The MB solutions were kept under neutral medium of pH 7 using 0.1 M HCl or NaOH solution. The pH reading was recorded by using a portable meter (Ecoscan, EUTECH Instruments, Singapore) and the quantity of MB in the solution was tested after 30 h. For kinetics studies, a similar procedure was adopted to analyze various samples collected within preset time intervals and the adsorbed amount at each time was determined.

3. Results and discussion

3.1. Pore structure characterization

The surface area and pore characteristics of prepared HAC have been evaluated. The N_2 adsorption-desorption isotherm and pore size distribution curve of HAC is shown in Fig. 1. Results showed that the surface area and micropore and mesopore volumes are 1135 m^2/g and 0.17 and 0.44 cm^3/g, respectively. In addition, the average pore diameter of 35.5 Å revealed the mesoporous structure of prepared HAC according to the IUPAC classification. The tendency of NaOH