



Mesoporous-activated carbon prepared from chitosan flakes via single-step sodium hydroxide activation for the adsorption of methylene blue



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ABSTRACT

In this work, mesoporous-activated carbon (CSAC) was prepared from chitosan flakes (CS) via single-step sodium hydroxide activation for the adsorption of methylene blue (MB). CSAC was prepared using different impregnation ratios of NaOH:CS (1:1, 2:1, 3:1, and 4:1) at 800 °C for 90 min. The adsorption performance of CSAC was evaluated for MB at different adsorption variables, such as MB initial concentrations (25–400 mg/L), solution pH (3–11), and temperature (30–50 °C). The adsorption isotherm data of CSAC-MB were well fitted to Langmuir model with a maximum adsorption capacity 143.53 mg/g at 50 °C. Best representation of kinetic data was obtained by the pseudo-second order model. CSAC exhibited excellent adsorption uptake for MB and can potentially be used for other cationic dyes.

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1. Introduction

Increasing industrialization and consequent technology advancement influence economic progress and threaten our planet. The effluents generated by industries adversely affect the environment. Wastewater containing toxic and hazardous materials, such as dyes, is generated in manufacturing textile, rubber, paper, plastic, explosives, pharmaceuticals, and cosmetics [1]. Approximately 2% of 700,000 tons dyes are discharged as effluents into the environment [2].

Synthetic dyes exhibit stability and flexibility unlike natural dyes. These dyes are categorized as cationic, anionic, and non-ionic dyes according to their charge and nature [3]. Various treatments were developed to reduce or totally remove the concentration of these undesirable compounds in wastewater before being released to an ecosystem. Adsorption that utilizes activated carbon is a popular, preferred, and effective technique to remove dyes from wastewater [4,5].

Powder or granular activated carbons (ACs) exhibit excellent adsorption capacities for organic pollutants because of their well-

developed porous structure and the presence of functional groups [6]. AC demand is increasing; and approximately 4.28 million metric tons of ACs was consumed in 2012. The global demand for ACs is projected increase by 10% over the next five years [7]. Coal is traditionally used as a carbon source to produce commercial ACs. However, coal is expensive and non-renewable. Moreover, the process of synthesizing ACs from coal involves high-temperature regeneration is highly energy intensive.

The use of lignocellulosic materials as a precursor is considered to reduce AC production cost. Lignocellulosic materials may contain cellulose, hemicellulose, and lignin depending on their compositions [8]. These cellulosic materials have a relatively high carbon content that determines the high yield and heterogeneous porosity of the produced ACs to some extent. A large number of materials, such as walnut shell [9], palm dates [10], coconut shell [11], rice husks [4], etc, were successfully converted into low-cost ACs.

Chitin, which is the most common natural biopolymer and its derivative, e.g., chitosan (CS), has been used as a biosorbent to remove metal metals [12,13], dyes [14,15], and proteins [16]. CS has many prominent biological properties, such as hydrophilicity, biodegradability, biocompatibility and non-toxicity [17]. The presence of amino (–NH₂) groups in the CS structure makes this cationic polymer more efficient in attracting anionic dyes than common

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adsorbents [18]. The dye category for which CS has a low affinity is cationic dyes because of electrostatic repulsion [19]. Poor thermo–mechanical properties and low surface area of CS also limit its applications [20]. Many chemical modifications, such as crosslinking, grafting, and carboxymethylation are developed to improve the properties and adsorption capacity of CS towards basic dyes [21,22]. However, these modifications may affect the functional group ($-\text{NH}_2$) of CS and subsequently reduce its adsorption performance [23].

The aim was to prepare mesoporous activated carbon by single-step NaOH activation of CS flakes and its application for methylene blue (MB) removal. The MB initial concentration, solution pH, and temperature effects were also studied. Batch experiments were performed to obtain adsorption isotherm and kinetic data.

2. Materials and methods

2.1. Material

CS flakes (medium molecular weight, 500 CP, 1 wt% in 1% acetic acid, 25 °C) were supplied by Qingdao Yuda Century, China. The activating reagent, sodium hydroxide (NaOH), was acquired from Sigma–Aldrich chemicals Malaysia. The cationic dye, MB, (chemical formula = $\text{C}_{16}\text{H}_{14}\text{N}_3\text{S}\text{Cl}\cdot 3\text{H}_2\text{O}$, molecular weight = 373.90 g/mol, $\lambda_{\text{max}} = 665 \text{ nm}$), was supplied by Merck Chemicals Company Malaysia. Stock solution of 500 mg/L was prepared which was diluted to more dye concentrations by adding distilled water.

2.2. Preparation and characterization of NaOH-activated carbon from chitosan flakes

CS flakes were impregnated with sodium hydroxide to prepare an activated carbon. Chitosan-activated carbons (CSAC) were prepared using different impregnation ratios (IR) NaOH:CS (1:1, 2:1, 3:1 and 4:1). Each experiment was performed as follows. After the impregnation process, the sample was dried at 105 °C overnight. The impregnated samples were activated in a vertical reactor under a nitrogen flow of 100 mL/min at 800 °C, heating rate of 10 °C/min, and 90 min. After activation, the samples were cooled and washed with HCl (1 M) and hot distilled water until the filtrate was neutral. The samples were dried at 105 °C overnight and kept in sealed containers for further use.

The materials were characterized by adopting different techniques. Scanning electron microscope (SEM) (Zeiss Supra 35VP) was applied to scan the surfaces of CS and CSAC. Pore size analyzer (Micromeritics ASAP 2020) was employed to investigate the pore and surface characteristics of CSAC. Surface area was determined by the BET surface area analysis and pore size distribution was calculated by Barrett–Joyner–Halenda (BJH) equation. Fourier Transform Infrared (FTIR) Spectroscopy (2000 FTIR, Model USA) was used to qualitatively determine the available effective groups.

2.3. Adsorption experiments

2.3.1. Effect of initial concentration

The change of MB concentrations with contact time was reported by adding 0.20 g of CSAC to 200 mL of MB solutions ($C_0 = 25\text{--}400 \text{ mg/L}$). The solutions were shaken for 7 h at 125 rpm, natural pH, and temperatures of 30, 40, and 50 °C. The dye concentration after adsorption was determined spectrophotometrically at 665 nm (UV 1700 Shimadzu, Japan). The equilibrium dye amount in the solid phase (q_e , mg/g) was evaluated as follows:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

Table 1
Physical surface characteristics of CSAC adsorbent.

Physical Property	Value
BET surface area (m^2/g)	318.40
Langmuir surface area (m^2/g)	432.60
Total pore volume (cm^3/g)	0.255
Micropore volume (cm^3/g)	0.098
Average pore width (\AA)	32.04

where C_0 and C_e (mg/L) are the MB concentrations in the liquid phase before and after adsorption, respectively, V (L) is the volume of MB, and W (g) is the amount of CSAC.

2.3.2. Effect of solution pH

Solution pH effect on the adsorption of MB onto CSAC was studied using 100 mL solution of MB with an initial concentration of 100 mg/L and adsorbent amount of 0.10 g. The solution was shook for 24 h at 125 rpm and 30 °C. The initial pH (3–11) of the solutions was adjusted using diluted NaOH or HCl solutions and measured using a pH meter (EUTECH Instrument).

2.3.3. Adsorption kinetics

Kinetics was conducted by using the procedure of batch equilibrium studies described above. Different MB samples were withdrawn at predetermined times (0–7 h). The adsorption uptake, q_t (mg/g), at different contact time periods t (min) was determined, as follows:

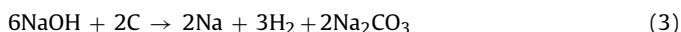
$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

3. Results and discussion

3.1. Selection of adsorbent: effect of NaOH impregnation ratio on yield and MB removal

The effect of the impregnation ratio (IR = 1:1–4:1) on CSAC yield and MB removal was investigated. The yield of CSAC decreased from 16.58% to 5.51% and the MB removal improved from 89.34% to 99.45% when the impregnation ratio was increased from 1:1–4:1. A ratio of two was selected as the best impregnation ratio with a MB removal of 97.57% and an AC yield of 7.46%.

When the amount of NaOH increased, more reactions occurred with CS, and this condition causes a porous surface to develop. When the impregnation ratio increased, excessive NaOH molecules may promote the reduction of Na^+ cation and OH^- anion, as represented below [24],



Additional activation can occur under N_2 flow and high temperature (800 °C) can occur by degrading of Na_2CO_3 into Na, CO, and CO_2 , which results in the development of a porous structure.

3.2. Pore structure characterization

The SEM images of CS and CACS structures are shown in Fig. 1 where chitosan exhibits a compact, dense, and rough surface. The pore structure of CSAC was developed by NaOH chemical activation with the distribution of many irregular cavities on CSAC surface.

The characteristics of CSAC are evaluated and presented in Table 1, which shows the total pore volume and BET surface area 0.255 cm^3/g and 318.40 m^2/g , respectively. The average pore width of 32.04 \AA is within the mesoporosity range (20–500 \AA) of the IUPAC classification. The mesoporous structure of CSAC can also be observed from the nitrogen adsorption and desorption isotherms (Fig. 2), which are categorized as type IV isotherm.

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