Mesoporous activated carbon from date stones (*Phoenix dactylifera* L.) by one-step microwave assisted K₂CO₃ pyrolysis

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ABSTRACT

Preparation of activated carbon (KAC) from date stones (DS) by microwave K₂CO₃ activation has been studied. Methylene blue (MB) dye was sufficiently adsorbed on KAC compared to raw DS. The effects of radiation time (4–12 min), radiation power (540–700 W) and impregnation ratio (0.5–2.5 g/g) on the yield and MB uptake of KAC were studied. MB uptake of 460.12 mg/g and 19.99% yield were reported at 8 min radiation time, 660 W radiation power and 1.5 g/g impregnation ratio. The characteristics of KAC were examined by pore structure analysis, scanning electron microscopy (SEM) and Fourier transforms infrared spectroscopy (FTIR). The BET surface area and total pore volume were 1144.25 m²/g and 0.656 m³/g, respectively. The equilibrium data were well correlated by Langmuir isotherm compared to Freundlich and Temkin isotherms with maximum Langmuir capacities of 256.15 and 485.44 mg/g on DS and KAC, respectively. Pseudo- second order model showed well representation for adsorption kinetics data.

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1. Introduction

Activated carbon (AC) is a carbonaceous material possessing a higher porosity due to which it is commonly used in various applications, concerned mainly with the removal of chemicals by adsorption form the liquid or gas phase [1]. However, heating technique besides type of precursor increases cost of AC which limits its large-scale application. A potential method to reduce the cost is utilization of inexpensive precursors such as agricultural wastes which have attracted an increasing interest in recent years [2]. In addition, microwave heating has been applied due to the advantages of rapid temperature rise, uniform temperature distribution, low activation time, and more saving of energy compared to conventional thermal method [3].

Pyrolysis and activation are the two main steps in preparation of AC where the latter step can be carried out by the physical, chemical, and physiochemical techniques [4]. The preparation using chemical activation offers several advantages which involve single step treatment, higher yields and better porous structure [5].

H_3PO_4, $ZnCl_2$, KOH, NaOH and K_2CO_3 are usually the most common and efficient chemical activators being used in preparation of ACs with large surface areas [6]. Generally, alkali activator is preferred over $ZnCl_2$ and H_3PO_4, because of its low energy requirements and least impact on the environment [7].

Date pits are inexpensive and abundant agricultural wastes in tropical countries which have been successfully converted into well-developed ACs [8]. Activation agent plays a decisive role in affecting the yield and adsorption performance of the carbon adsorbent [9]. Conventional heating techniques have been widely used for preparation of ACs from date pits by chemical [10–13], physical [14,15], and physiochemical activations [16,17]. However, microwave technique has been utilized for AC preparation from date pits by two stages KOH chemical activation [18]. K_2CO_3 is found to act as better activating agent than KOH to produce ACs with high values of yield, surface area and mesopores volume which are preferred for attraction of large molecules such as methylene blue [19]. Besides, K_2CO_3 is not a hazardous chemical and not deleterious as it is frequently used for food additives [20].

Therefore, microwave induced K_2CO_3 activation has been adopted in this study for preparation of AC from date pits with a single stage treatment which has the advantages of shorter time and low energy consumption. The obtained carbon has been applied as adsorbent for attraction of a hazardous cationic dye such as

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methylene blue. The effects of variables on yield and adsorption performance have also been investigated.

2. Materials and methods

2.1. Materials

Date stones (DS) were used as the precursors for the preparation of AC. The collected stones were first washed with water, dried at 110 °C for 24 h, crushed using disk mill, and sieved. Fraction with particle size of (300–600) mm was selected for the preparation. The bulk density, surface area, ash and moisture contents of DS were 0.5997 g/ml, 355.11 m^2/g, 2.2 and 4.7%, respectively. Potassium carbonates K_2CO_3 (purchased from Didactic Company, Espuma) of purity 99.9% was used as a chemical activator. Methylene blue (MB) dye (supplied by Fischer Scientific International Company) of purity 99.9% was used as an adsorbate. MB has a chemical formula of $C_{16}H_{18}N_3SCI$, with molecular weight of 319.86 g/mol, which corresponds to MB hydrochloride with three groups of water. All other chemical were of analytical grades.

2.2. Preparation and characterization

Dried DS (2 g) were impregnated with 10 ml of K_2CO_3 solution at various IR (0.5–2.5 g/g) for 24 h at room temperature. The treated samples were dehydrated by using an oven (Model IH-100, England) at 110 °C and stored for later treatment. The dried samples were activated with the aid of a modified microwave oven (MM717CPJ, China). A quartz glass reactor, described elsewhere [21], was placed inside the modified microwave oven which operated at radiation powers (540–700 W) for radiation times (4–12 min). After activation experiment, the product was allowed to cool in order to be leached with 0.1 M HCl solution. The leaching was conducted at room temperature for overnight, and then the sample was filtered and repeatedly washed with distilled water to remove residual organic matters and alkalis, until the pH of filtrate reached (6.5–7). After that, the sample was dried at 110 °C for 24 h and, subsequently was weighed to determine the yield of the final carbon KAC. The activation performance was evaluated in terms of the yield and MB uptake at equilibrium, q_e (mg/g), which were calculated as follow:

$$\text{Yield } (\%) = \frac{W_f}{W_o} \times 100 \tag{1}$$

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{2}$$

where, W_f and W_o (g) are the weights of KAC and dried DS, respectively, C_0 and C_e (mg/l) are MB concentration at initial and equilibrium, respectively, V (l) is the volume of MB solution, and W (g) is the weight of KAC. The MB uptake was determined as follows: 0.005 g of each prepared KAC, with partial size less than 250 mm was added to 100 ml Erlenmeyer flask containing 10 ml of MB solution with initial concentration of 250 mg/l. These flasks were shaking at 200 rpm for 24 h and room temperature to reach equilibrium. The pH of the solution was 7.64 without any adjustment. After filtration, the concentration of MB in the filtrate was determined using UV–visible Spectrophotometer (Shimadzu UV–160 A) at its maximum wave length of 664 nm.

The surface area, total pores volume and average pore diameter of DS, KAC, and commercial activated carbon CAC were evaluated. Surface area was determined by the application of BET equation to the adsorption–desorption isotherm of N_2 at 77 K. Total pore volume was evaluated by converting the adsorption volume of nitrogen at relative pressure of 0.95 to equivalent liquid volume of adsorbate. KAC and DS structures were also examined by scanning

electron microscopy SEM (VEGA3 TESCAN) and Fourier transforms infrared spectroscopy FTIR (ABB MB3000).

2.3. Adsorption isotherms

The adsorbed amount of MB on DS, KAC, and CAC as a function of equilibrium concentration was determined as follows: 0.005 g of adsorbent was added to Erlenmeyer flasks containing 10 ml of MB solution with various initial concentrations of 50, 150, 250, 350, and 450 mg/l for 24 h. Other parameter such as particle size, solution temperature and agitation speed were similar as the adsorption studies carried out for the determination of MB uptake. Each experiment was duplicated under identical conditions. The uptake at equilibrium, q_e (mg/g), was calculated using Eq. (2). To determine the maximum MB capacity of each adsorbent, the equilibrium isotherm data were correlated by the Langmuir, Freundlich, and Temkin isotherms [22–24]. These equations can be written as follows:

$$\text{Langmuir isotherm} \quad \frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \tag{3}$$

$$\text{Freundlich isotherm} \quad \ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

$$\text{Temkin isotherm} \quad q_e = B \ln K_T + B \ln C_e \tag{5}$$

where q_L (mg/g) is the Langmuir maximum uptake of MB per unit mass of adsorbent, K_L (l/mg) is the Langmuir constant related to adsorption rate, K_F ((mg/g) × (l/mg)$^{1/n}$) and n are Freundlich constants, B and K_T (l/mg) are the Temkin parameters. Statistical analysis was used to analyze experimental data and accuracy of fitting has been given in terms of correlation coefficient R^2.

2.4. Adsorption kinetics

The adsorption kinetics of MB on prepared KAC was investigated by carrying out set of experiments with a procedure similar to that of equilibrium tests at various MB initial concentrations of 50, 250, and 450 mg/l. The samples were separated at predetermined time intervals and MB uptake at time t, q_t (mg/g), was calculated as follows:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{6}$$

where C_t (mg/l) is MB concentration at time t (min). Three kinetic models: pseudo-first order model, pseudo-second order model, and intraparticle diffusion model [25–27] were used to analyze the kinetic data of MB adsorption on KAC. These models can be written as follows:

$$\text{Pseudo-first order model} \quad \ln(q_t - q_e) = \ln(q_e)K_1 t \tag{7}$$

$$\text{Pseudo-second order model} \quad \frac{t}{q_t} = \frac{1}{K_2 q_e{}^2} + \frac{t}{q_e} \tag{8}$$

$$\text{Intraparticle diffusion model} \quad q_t = K_3 t^{1/2} + C \tag{9}$$

where q_e and q_t (mg/g) are the amounts of MB adsorbed at equilibrium and at time t, respectively, K_1 (1/min) is the adsorption rate constant, K_2 (g/mg min) is the rate constant of second-order equation, and K_3 (mg/g min$^{1/2}$) is the intraparticle diffusion rate constant and C (mg/g) is a constant that gives an idea about the thickness of the boundary layer.

3. Results and discussion

3.1. Activated carbon preparation

The effect of radiation time, radiation power, and impregnation ratio IR on yield and MB uptake of KAC is presented in Fig. 1. The