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Short communication

Microwave-assisted preparation of oil palm fiber activated carbon for methylene blue adsorption

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ABSTRACT

The present study explores the viability of microwave irradiation for the preparation of activated carbon (OPAC) from oil palm fiber, abundantly available from the oil palm processing industries. The activation process was performed at the microwave power of 360 W and irradiation time of 5 min. The BET surface area, pore volume and average pore size of OPAC were 707.79 m^2/g, 0.3805 m^3/g and 22.11 Å, respectively. The monolayer adsorption capacity of OPAC for methylene blue was 312.5 mg/g. The finding provides a strong evidence to support the potential use of microwave heating as an alternative activation technique.

1. Introduction

Water scarcity and air pollution rank equal to climate change as the most intricate environmental turmoil for the 21st century. To date, the percolation of textile effluents into the groundwater tables and aquifer systems remains a highly contested agenda from a global point. In particular, activated carbon adsorption process, an adsorbent with its large porous surface area, controllable pore structure, thermo-stability and low acid/base reactivity, is recognized as the most promising fundamental approach in wastewater treatment [1]. For preparation of activated carbons, conventional heating method is usually adopted, in which the energy is produced by convective or conductive heating systems, such as a tubular furnace [2]. Generally, these thermal treatments are carried out at relatively high temperatures (900–1000 °C) while flowing an inert or reducing gas over a suitable carbon precursor [3]. Nevertheless, in some cases, the thermal process may take several hours, even up to a week to reach to the desired level of activation [4]. Another problem lies in the furnace such that the surface heating from the hearth wall does not ensure a uniform temperature for different shapes and sizes of samples. This generates a thermal gradient from the hot surface of sample particle to its interior and impedes the effective removal of gaseous products to its surroundings, thereby resulting in a detrimental effect on the quality of the prepared activated carbons [5]. With the aforementioned, this research was conducted to prepare the oil palm waste based activated carbon (OPAC) using microwave technology. Structural, functional and elemental characterization of the prepared adsorbent was performed. Moreover, the sorption equilibrium of methylene blue (MB) and nitrogen isotherm was outlined and discussed.

2. Materials and methods

2.1. Adsorbate

Methylene blue (MB), an analytical grade cationic dye purchased from Merck (M) Sdn. Bhd, Malaysia was chosen as the targeted adsorbate in this study, without further purification prior to use. Deionized water supplied by USF ELGA water treatment system was used to prepare all the reagents and solutions.

2.2. Preparation of activated carbon

2.2.1. Carbonization

Oil palm fiber used in the present study was obtained from United Palm Oil Mill, Nibong Tebal, Malaysia. The precursor was firstly washed to remove dirt particles from its surface and dried in an oven at 70 °C. The dried sample was then grounded and sieved to discrete sizes (1–2 mm), and carbonized at 700 °C under purified nitrogen (99.995%) flow in a stainless steel vertical tubular reactor placed in a tube furnace.

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2.2.2. Activation

The char produced was soaked in potassium hydroxide (KOH) solution with an impregnation (char:KOH) ratio of 1:0.5 (wt%). The activation step was carried out in a tubular glass reactor placed in a modified microwave oven with a frequency of 2.45 GHz. The microwave power was set as 360 W and 5 min of irradiation time was selected as the heating period based on some preliminary runs. Nitrogen flow (300 cm^3/min) was kept for some time before microwave treatment to outgas air, which was maintained during the activation and cooling stages. The activated product was then washed with 0.1 M hydrochloric acid and deionized water until the pH of the washing solution reached 6–7.

2.3. Characterization of char and OPAC

Surface physical properties of char and OPAC were characterized with Micromeritics ASAP 2020, using N_2 as the adsorbate at 77 K. Scanning electron microscope (SEM) analysis was performed to study the textural structure of the char and OPAC before and after the activation process, while elemental analysis and surface functional groups were detected by elemental analyzer (EA-2400 Series II, PerkinElmer) and Fourier transform infrared (FTIR) spectroscope (FTIR-2000, PerkinElmer) from the scanning range of 4000–400 cm^{-1}.

2.4. Equilibrium studies

Equilibrium studies were conducted in a set of 250 mL Erlenmeyer flasks containing 0.20 g adsorbent and 200 mL MB solutions with various initial concentrations (50, 100, 200, 300, 400, and 500 mg/L) without adjusting pH. The flasks were capped and agitated in an isothermal water bath shaker at 120 rpm and 30 °C for 24 h until the equilibrium was reached. The amount of adsorption at time t, q_t (mg/g), was calculated by Eq. (1):

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (1)$$

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

3. Results and discussion

3.1. Characterization of char and OPAC

Fig. 1 illustrates SEM images of the oil palm fiber derived char and activated carbon. It can be clearly found that the pores formed during the carbonization stage were narrowed, constricted and blocked by deposited tarry substances. However, the microwave irradiated sample exhibits an even, homogeneous, highly porous and well pronounced array of honey-combed structures, indicating good possibility for the dyes to be trapped and adsorbed. The obtained FTIR spectrum of char (Fig. 2) revealed the peaks at 3800–3200, 2378, 1529, 1425, 1036 and 568 cm^{-1}, identical to the presence of –OH (hydroxyl), C≡C (alkyne), $–NO_2$, $–CH_2$ (alkyl), C–O–C (ester, ether and phenol) and C–H functionalities. Meanwhile, surface chemistry of OPAC illustrated some shifts of peaks, at 3800–3200, 2361, 1429, 1053 and 568 cm^{-1}, which correspond to the presence of –OH (hydroxyl), C≡C (alkyne), $–CH_2$ (alkyl), C–O–C (ester, ether and phenol) and C–H derivatives.

Table 1 shows elemental analysis of the oil palm fiber derived char and activated carbon. As suggested by the result, the carbon content increased after 5 min irradiation, and the oxygen content indicated the opposite change trend. Whereas, C/O ratio rose from 3.45 to 6.35, due to the elimination of oxygen containing groups;

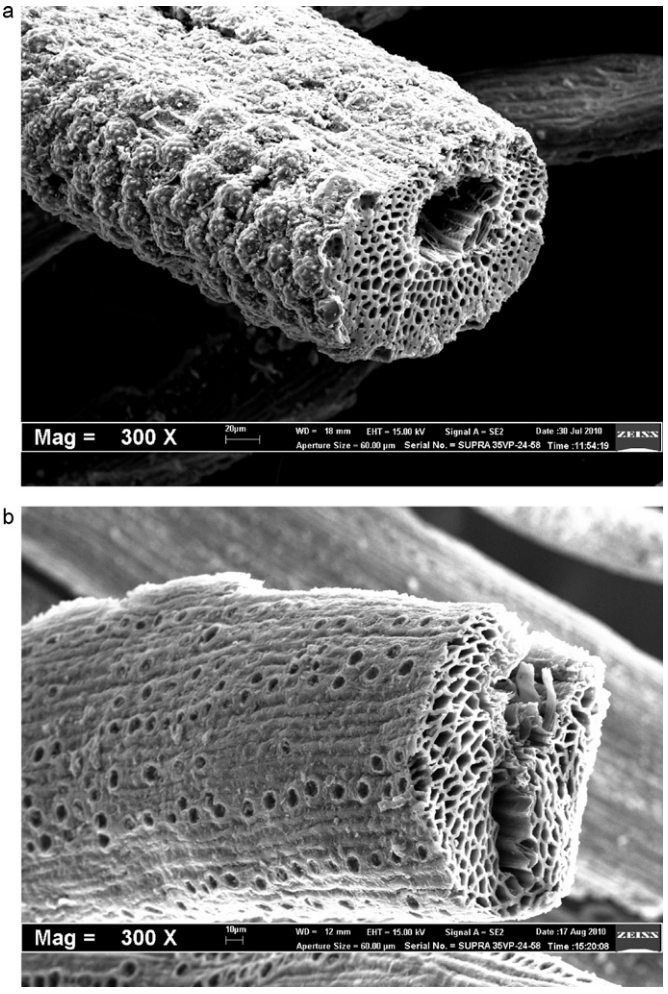

Fig. 1. SEM micrograph of (a) char (300×) and (b) OPAC (300×).

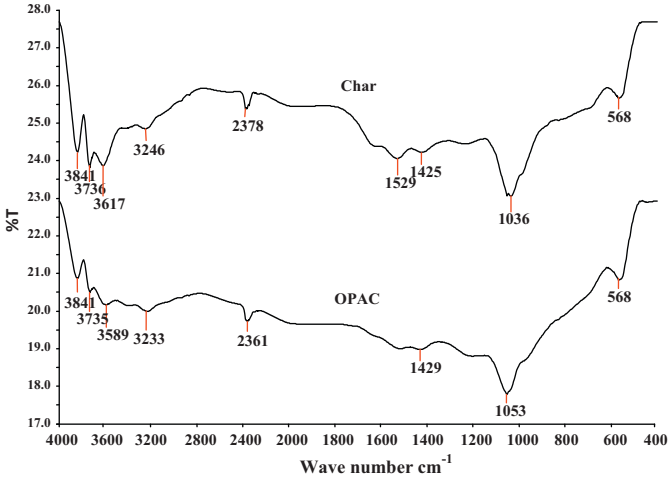

Fig. 2. FTIR of char and OPAC.

Table 1
Elemental analysis of char and OPAC.

Element	Char (wt%)	OPAC (wt%)
Carbon	76.02	85.20
Oxygen	22.02	13.42
Hydrogen	0.81	0.42
Nitrogen	0.91	0.74
Sulphur	0.24	0.22

Table 2
Comparison of adsorption capacities of various adsorbents for MB.

Precursor	Activation method	Activation time (min)	Adsorption capacity (mg/g)	Reference
Oil palm fiber	Microwave heating	5	312.50	Present study
Bamboo	Microwave heating	10	286.10	[8]
Cotton stalk	Microwave heating	10	294.12	[9]
Pine wood powder	Microwave heating	10	200.00	[10]
Coffee grounds	Microwave heating	12	99.43	[11]
Hevea brasiliensis seed coat	Conventional heating	120	227.27	[12]
Oil palm fiber	Conventional heating	120	277.78	[13]
Durian shell	Conventional heating	60	289.26	[14]
Wood chips	Conventional heating	240	263.00	[15]
Piassava fibers	Conventional heating	180	276.40	[16]
Norit SA3 (Commercial grade powdered activated carbon)	–	–	91.00	[17]
Nuchar WWH (Commercial grade granular activated carbon)	–	–	21.50	[17]

however, the content of nitrogen and hydrogen exhibited some fluctuations and the content of sulphur was relatively stable.

3.2. Nitrogen isotherm and adsorption equilibrium study

Nitrogen adsorption is a standard procedure for the determination of porosity of carbonaceous adsorbents. From nitrogen adsorption isotherm analysis (Fig. 3), it can be ascertained that the isotherms of OPAC pertain to intermediate between type I and II of the referred IUPAC classification, which is associated with a combination of microporous and mesoporous structures. Moreover, microwave activation produces a positive effect on the amount of nitrogen adsorbed, indicating development of additional pores in the activated carbon, with the BET surface area, Langmuir surface area, and total pore volume, of 707.79 m^2/g, 1030.25 m^2/g and 0.3805 m^3/g, respectively (compared to 205.21 m^2/g, 306.13 m^2/g and 0.1176 m^3/g for char). Fig. 4 exhibits pore size distributions of char and OPAC. The obtained result detected the sharpest peak at pore diameter between 2 and 5 nm for char, with an average pore size of 23.92 Å. However, OPAC illustrated the rather consistent pore widths ranging from 2 to 3.5 nm, with the average pore size of 22.11 Å.

Generally, adsorption capacity and dye removal efficiency increased with prolonging the contact time. Initially, the amount of dye adsorbed onto the carbon surface increased rapidly, and at some point of time, the process slowed down and reached a plateau. In the present study, the adsorption equilibrium, q_e increased from 50.61 to 310.84 mg/g with an increase in initial concentration from 50 to 500 mg/L. Equilibrium data was then fitted to Langmuir isotherm model (figure not shown). The value of R_L and R^2 in the present investigation has found to be 0.14 and 0.9999, respectively at 30 °C, showing favorable for adsorption of MB and applicability of the isotherm model.

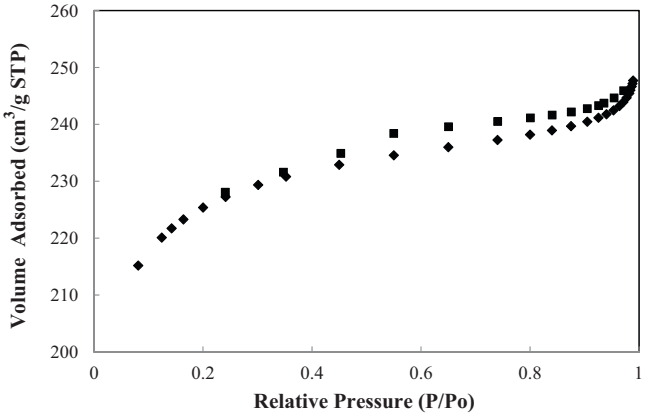

Fig. 3. Nitrogen isotherm of OPAC.

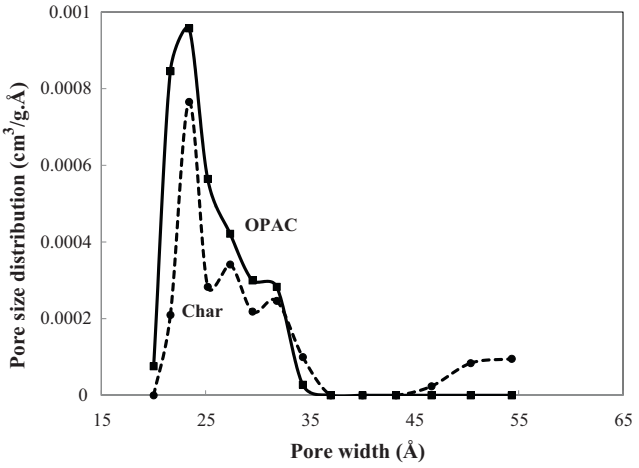

Fig. 4. Pore size distribution of char and OPAC, obtained by Density Functional Theory (DFT) method.

Table 2 exhibits a comparison of maximum monolayer adsorption capacity of MB onto various adsorbents. The adsorbent prepared in this work showed relatively high MB adsorption capacity of 312.50 mg/g, as compared to some previous works reported in the literature. Thus, it is noteworthy that considerable changes in the pore structures were achieved within a short time, which should be attributed to the distinct mechanism of microwave heating.

In conventional heating, the heat source is located outside the carbon bed, and the bed is heated by conduction and/or convection. A temperature gradient is established in the material until conditions of steady state are reached [6]. However, in microwave device, the microwaves supply energy directly to the carbon bed. Energy transfer is readily transformed into heat by dipole rotation and ionic conduction [7]. When high frequency voltages are applied, the response of the molecules with a permanent dipole moment or induced dipole is to change their orientation in the direction opposite to the applied field. The synchronized agitation of molecules then generates heat [5]. As a result, the interior part of activated carbon is heated more favorably under microwave radiation, which facilitates the modification process.

4. Conclusion

The result exhibited the versatility of microwave irradiation in activating the NaOH impregnated oil palm fiber char. The monolayer adsorption capacity of OPAC for MB was 312.50 mg/g, while the BET surface area and total pore volume were 707.79 m^2/g and 0.3805 m^3/g, respectively. The activation time took only 5 min at the microwave power of 360 W, but illustrated a dramatic

improvement, verified by the morphological and equilibrium studies.

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