Microwave-assisted preparation and adsorption performance of activated carbon from biodiesel industry solid reside: Influence of operational parameters

K.Y. Foo, B.H. Hameed *

School of Chemical Engineering, Engineering Campus, Universit Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia

ABSTRACT

Preparation of activated carbon has been attempted using KOH as activating agent by microwave heating from biodiesel industry solid residue, oil palm empty fruit bunch (EFBAC). The significance of chemical impregnation ratio (IR), microwave power and activation time on the properties of activated carbon were investigated. The optimum condition has been identified at the IR of 1.0, microwave power of 600 W and activation time of 7 min. EFBAC was characterized by scanning electron microscopy, Fourier transform infrared spectroscopy and nitrogen adsorption isotherm. The surface chemistry was examined by zeta potential measurement, determination of surface acidity/basicity, while the adsorptive property was quantified using methylene blue as dye model compound. The optimum conditions resulted in activated carbon with a monolayer adsorption capacity of 395.30 mg/g and carbon yield of 73.78%, while the BET surface area and total pore volume were corresponding to 1372 m^2/g and 0.76 cm^3/g, respectively.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

The dwindling reserves of fossil fuel and surging prices for the petroleum-based fuels has triggered the pressing needs for renewable energy as their sustainable fuel substitute (Singh et al., 2011). According to the statistical data reported by the International Energy Agency, a 53% increase in the global energy consumption is foreseen by 2030. This energy consumption is mainly based on fossil fuels which account for 88.1%. At the current production rates, the global proven reserves for crude oil and natural gas are forecasted to last for the next 41.8 and 60.3 years (Ong et al., 2011). A number of renewable energy sources, namely solar, wind, hydrothermal, geothermal and biofuels have been carried out extensively (Cheng and Hu, 2010; Gnansounou and Dauriat, 2010; Yin et al., 2010).

Biodiesel, produced by transesterification of renewable oils, fats and fatty acids is recognized as a new emerging sector in the oil palm industry, due to the similarity with conventional diesel in terms of its chemical structure and energy content. Another attraction of biodiesel as diesel fuel is its liquid nature – portability, higher combustion efficiency, lower sulfur and aromatic content, higher cetane number and biodegradability. Simultaneously, no modification in diesel engine is required as biodiesel is compatible with the existing transportation engine models (Yung and Gon, 2010; Zhang et al., 2010).

Today, biodiesel market is booming in Europe countries and the United States. In Malaysia for particular, 12 biodiesel plants are fully operational with capability of producing one million tons of biodiesel per year. By the end of 2011, the nationwide palm oil consumption is estimated at 5,00,000 tones, underlying the implementation of blended biodiesel program as its key drivers (Mekhilef et al., 2011). The refining process however, is accompanied by the co-production of lignocellulosic biomass, in the form of empty fruit bunch (EFB), oil palm fiber and oil palm shell. For each ton of crude palm oil refined, approximately 1.1 ton of EFB can be obtained. In the formal practice, some quantity of these residues are used as boiler fuel, for the preparation of fertilizers or mulching material, where major portion is discarded by open burning or left in mill premises itself (Evald, 2006).

This urged research towards upgrading and utilization of the available biomass from the oil palm refineries and biodiesel manufacturing plants. In the previous work, the viability of microwave irradiation for preparation of activated carbon (AC) from EFB has been presented (Foo and Hameed, 2011). The present work is aimed at evaluating the operational conditions for further improve the porosity development and adsorption capacity of the prepared EFBAC. The influences of radiation power, radiation time and chemical impregnation ratio on the yield and adsorption capacities of EFBAC were investigated systematically. Structural, functional and surface chemistry of the prepared adsorbent was performed. Moreover, the adsorption equilibrium, isotherms, kinetics and thermodynamics were elucidated.

* Corresponding author. Tel.: +60 45996422; fax: +60 45941013.
E-mail address: chbassim@eng.usm.my (B.H. Hameed).

2. Methods

2.1. Adsorbate

Methylene blue (MB), a basic dye with the molecular structure $C_{16}H_{18}N_3SCl$ (molecular weight 319.85), supplied by Merck (M) Sdn. Bhd, Malaysia was chosen as the adsorbate in this study. The dye stock solution was prepared by dissolving accurately weighed dye in distilled water to a concentration of 1000 mg/L. The experimental solution was obtained by diluting the dye stock solution in accurate proportions to different initial concentrations.

2.2. Preparation of activated carbon

2.2.1. Carbonization of EFB
Empty fruit bunches used as raw materials in this study were obtained from United Palm Oil Mill, Nibong Tebal, Malaysia. The raw precursors were manually chosen, cleaned with deionized water, dried at 110 °C for 48 h and ground with a roller mill to obtain the particle size of 1–2 mm. The carbonization process is carried out by loading 500 g of dried precursor into a muffle furnace, under N_2 gas flow (150 cm^3/min) and heated up to a carbonization temperature of 700 °C, at heating rate of 10 °C/min. The yield of char was found to be around 43.17%.

2.2.2. Activation of EFB char
Microwave heating was conducted in a 2.45 GHz commercial microwave oven with suitable modifications. The char produced was mixed with KOH solution of varying impregnation (KOH: char) ratio. The oven has a power controller to select different power levels (90, 180, 360, 600 and 800 W) and a timer for various exposure times at a set microwave power level. The reaction was performed in a glass reactor fixed in the chamber of microwave oven. Nitrogen gas at a pre-set flow rate (300 cm^3/min) was used to purge air in the reactor before the start of microwave heating and it continued to flow through the reactor during the activation stage. The resultant EFBAC was washed repeatedly with hydrochloric acid of 0.1 M and deionized water until pH 6–7 was reached in the residual liquid. The yield is defined as the weight of activated carbon per weight of char utilized for activation.

2.3. Characterization of activated carbon

Scanning electron microscopy (SEM) analysis was carried out to study the textural morphologies of EFBAC (Zeiss Supra 35VP). Fourier transform infrared spectroscopy (FTIR) was used to qualitatively identify the chemical functionality of EFBAC (FTIR-100, Shimadzu). FTIR spectra were recorded between 4000 and 400 cm^{-1}. The surface physical properties of EFBAC were characterized with Micromeritics ASAP 2020, using N_2 as the adsorbate at 77 K.

2.4. Surface acidity and basicity

The surface acidity was estimated by mixing 0.20 g of EFBAC with 25 cm^3 of 0.05 M NaOH solution in a closed flask, and agitated for 48 h at room temperature. The suspension was then decanted, and the remaining NaOH was determined by titration with 0.05 M HCl solution. The surface basicity was obtained by a similar procedure, where 0.05 M HCl solution was contacted with 0.20 g of EFBAC and the titration solution was 0.05 M NaOH.

2.5. Zeta potential measurement (pH_{pzc})

Fifty cubiccentimeter of 0.01 M NaCl solution was placed in a closed Erlenmeyer flask and the pH of the solution was adjusted to a value from 2 to 12. Then, 0.15 g EFBAC was added and solution pH after 48 h of agitation was measured. The pH_{pzc} is the point where $pH_{final} - pH_{inital} = 0$.

2.6. Equilibrium adsorption studies

The batch adsorption experiments were conducted in a set of 250-mL Erlenmeyer flasks containing 0.20 g adsorbent and 200 mL dye solutions with various initial concentrations (50, 100, 200, 300, 400, and 500 mg/L). The flasks were agitated in a thermostatic orbital shaker at 120 rpm and 30 °C until the equilibrium was reached. Dye concentrations in the supernatant solutions were measured using a UV–Vis spectrophotometer. MB uptake at equilibrium, q_e (mg/g), was determined by:

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

where C_0 and C_e (mg/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. V (L) is the volume of the solution, and W (g) is the mass of adsorbent used. The effect of pH on dye removal was examined by varying the pH from 2 to 12, with initial dye concentration of 300 mg/L, EFBAC dosage of 0.20 g / 200 mL and adsorption temperature of 30 °C. The initial pH of the dye solution was adjusted by addition of 0.10 M solution of HCl or NaOH.

3. Results and discussion

3.1. Preparation of activated carbons

3.1.1. Effect of chemical impregnation ratio
The effect of chemical impregnation ratio, microwave power, and irradiation time on the carbon yield and adsorption capacity, together with the error bars representing the deviation errors for the replicates data was shown in Fig. 1. Effect of chemical impregnation ratio (IR) on the carbon yield and adsorption equilibrium of MB, evaluated at the microwave input power of 360 W and irradiation time of 8 min was depicted in Fig. 1a. It can be observed that increasing IR from 0.25 to 1.00, showed an enhancement of carbon yield from 65.99% to 73.78%. Beyond the value, further increase in IR illustrated a gradually decrease of carbon yield. Similarly, augmenting IR from 0.25 to 1.00 indicated an increase of adsorption capacity from 132.74 to 253.44 mg/g, and then decreased. The development of porosity was associated with gasification according to the reaction (Basta et al., 2009):

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3 \tag{2}$$
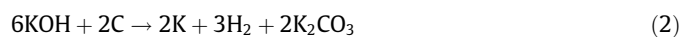
It was assumed that metallic potassium formed during the gasification process would diffuse into the internal structure of char matrix widening the existing pores and created new porosities. Therefore, by increasing the ratio of KOH/char, the activation process would be strengthened. Correspondingly, the adsorption capacity was further enhanced. When IR reached its optimum value, the active sites on the carbons had reacted completely and the adsorption capacity has reached its maximum amount. Beyond the optimum value, the pores would be widened and burnt off lowering the adsorption capacity and yield. Therefore, the KOH/char impregnation ratio was proposed at 1.00 for effective activation at minimum consumption of activating agent.