Utilization of Leucaena leucocephala wood char as bioenergy by-product for methylene blue adsorption: Production, characterization and application

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ABSTRACT

Leucaena leucocephala wood char (LC) was produced by a pyrolysis process at 1000 °C. The characteristics of char were identified using scanning electron microscopy (SEM), fourier transform infrared (FTIR) spectroscope, ultimate analysis and BET surface area. Adsorption of methylene blue (MB) dye onto produced LC was tested. The maximum MB dye removals were 65.77, 78.48, 86.14, 90.02 and 90.21 % at 0.5, 0.7, 1, 1.2 and 1.4 g of LC dose respectively.

Keywords:. Pyrolysis, Leucaena leucocephala wood,Char, Adsorption, Methylene blue

1. Introduction

Coloured effluents from textile industries represent one of the major problems concerning textile wastewaters (Hameed et al., 2007). Wastewater generated from the textile processing industries contains suspended solids, high amounts of dissolved solids, un-reacted dyestuffs (colour) and other auxiliary chemicals (Rajkumar et al., 2007). Most of dyes are difficult to decolourise due to their complex structure and synthetic origin. The discharge of dye wastewater in the environment is aesthetically undesirable and can cause serious environmental impact (Demirbas et al., 2008). Adsorption is known to be a promising technique, which has great importance due to the ease of operation and comparable low cost of application in the decolouration process (Eren and Afsin, 2007). Activated carbon's extensive use should be avoided due to it is costly and therefore frequent approaches have been seeking for cheaper and effective adsorbents (Asgher and Bhatti, 2012).

In Malaysia, Leucaena leucocephala that locally known as petai belalang, is widespread throughout the tropics and is abundant in villages in the northern part. It is widely used as livestock forage, fuel-wood, reforestation material and green manure (Normaniza et al., 2008; Wan-Mohd-Nazri et al., 2011).

Leucaena leucocephala is a small, fast-growing mimosoid tree. It has a very fast growth rate; young trees reach a height of more than 6 meters in two to three years. White lead tree, jumbay, and white popinac are the common names of Leucaena leucocephala (Wikipedia, 2013). Fig. 1 shows the Leucaena leucocephala tree and its parts.

Leucaena leucocephala Leaves and flowers

Leucaena leucocephala wood and bark

Fig. 1. Leucaena leucocephala tree and its parts

Malaysia will be one of the first to explore Leucaena for biofuels on a large scale. Since the shrub Leucaena leucocephala or petai belalang holds great promise in the production of biofuels, thus the idea is that it will run on Leucaena, with wood chips from the tree used both as an energy source to produce steam and electricity to run the factories, and as a raw material for processing (Heng, 2013).

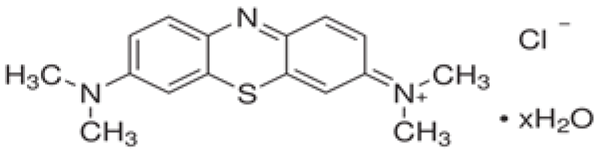
The utilization of industrial by-product char for adsorption purposes is an advantage and an important step in the pursuit of "green" technology. Due to its molecular structure, biochar is chemically and biologically more stable than the original carbon form (Shafie et al., 2012). Therefore in this study Leucaena leucocephala wood char will be produced from a pyrolysis process at 1000 °C and then used to investigate the ability of Leucaena leucocephala wood char to remove methylene blue dye (MB) from aqueous solutions.

2. Materials and methods

2.1. Adsorbate

The methylene blue dye (MB) was supplied by Sigma-Aldrich (M) Sdn. Bhd., Malaysia. The properties of the MB dye are presented in Table 1. The MB dye was made up as a stock solution of concentration of 1000 mg/L and was diluted to the required concentrations.

Table 1 Properties of MB dye

Properties	
Dye name	Methylene blue
Molecular formula	$C_{16}H_{18}ClN_3S \cdot xH_2O$
Molecular weight, g/mol	319.85
λ max. (nm)	661
Chemical structure	

2.2. Production of Leucaena leucocephala wood char

Leucaena leucocephala wood was supplied by the Universiti Teknologi MARA (UITM), Pahang, Malaysia. The Leucaena leucocephala wood pieces were washed with distilled water, dried and cut into small pieces (2, 2.5, 0.5 cm^3). The pieces were loaded on a cylindrical stainless steel reactor with 500 mm length and outer and inner diameters of 28 and 25 mm, respectively. The reactor was located inside an electric furnace with 10 °C/min heating rate. The wood pieces were then pyrolysed under a nitrogen flow of 100 ml/min to the final pyrolysis temperature of 1000 °C, with a heating rate of 10 °C/min. The sample was held at the pyrolysis temperature for 5min. The produced char was washed with hot deionised water, filtered, dried in an oven at 100 °C overnight and stored in a closed container ready for further use and labeled as LC.

2.3 Characterization of Leucaena leucocephala wood char

The LC was characterized using Scanning electron microscopy (SEM) (HITACHI, S-3400N, Japan) to study its surface texture before and after MB adsorption. The surface functional groups of the LC were detected by Fourier transform infrared (FTIR) spectroscope (Perkin-Elmer 100 series, USA). The spectra were recorded from 500–4000 cm^{-1}.
The analysis of the elemental constituents in LC was determined using a CHNS/O Analyzer (model LECO TruSpec CHNS932, USA) following the ASTM D-5291 method. The BET surface area was estimated from the adsorption isotherms using BET equations within the range of P/Po, from 10^{-6} to 1. The mesopore distribution was calculated by the Barrett–Joyner–Hanlenda (BJH) method.

2.4 Char evaluation for adsorption study

The adsorption process was carried out in a batch process. Batch adsorption experiment was carried out by adding different amounts (0.5, 0.7, 1, 1.2 and 1.4 g) of LC into a number of 250 ml Erlenmeyer flasks each containing 100 ml of fixed initial MB dye concentration (100 mg/L) and then placed in a shaking incubator (Heidolph Incubator 1000) at 150 rpm for 24 h at 30°C. The initial and equilibrium dye concentrations were determined by absorbance measurement using a double beam UV–Vis spectrophotometer (Spectronic Helios Alpha, Thermo Electron Corporation, UK) at 661 nm. It was then computed into dye concentration using a standard calibration curve. The dye removal percentage can be calculated as follows:

$$\%C = \frac{(C_{Ao} - C_e)}{C_{Ao}} \times 100 \quad (1)$$

where C_{Ao} and C_e (mg/L) are the liquid-phase concentrations of dye at the initial and equilibrium, respectively.

3. Results and discussion

3.1. Characterization of the adsorbent

The SEM image for LC before adsorption as shown in Fig. 2 (a) reveals that the available pores on the char surface are highly heterogeneous, well pronounced and arranged in an array of honey-comb structures. The SEM image after dye adsorption in Fig. 2 (b) reveals that the adsorbent surface is covered with a thick layer of MB dye molecules.

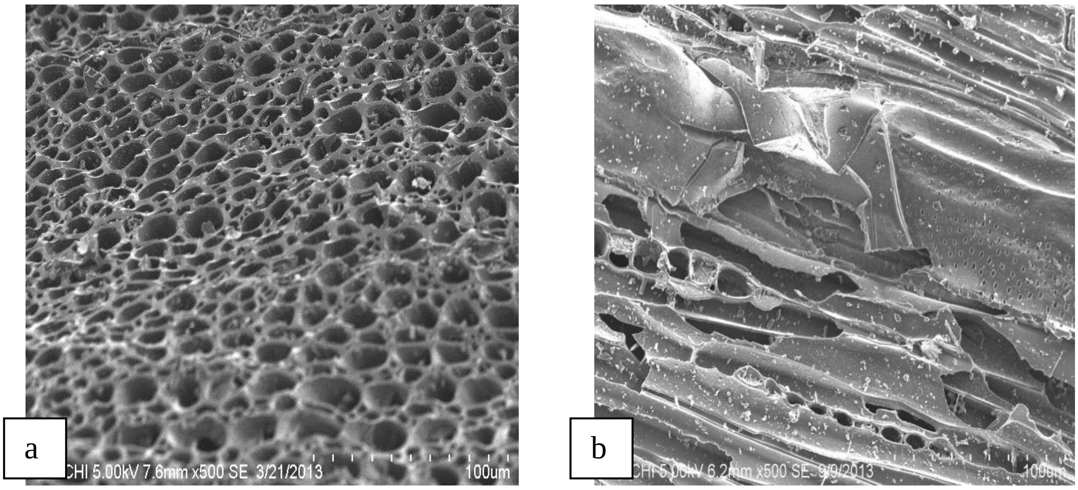


Fig.2. SEM micrograph (magnification: 500 SE) of: (a) LC before adsorption and (b) LC after adsorption.

The FTIR spectrum of the LC is shown in Fig. 3, where it can be seen that the presence of C-H stretches for alkanes, alkenes or aromatic ring groups are detected in the LC. Also the LC confirmed the vibration of the O-H bond for alcohols and phenols groups. Furthermore the LC confirmed the vibration of the O-H bond for carboxylic acids. The vibration of C=C in the aromatic rings and C-O stretches for alcohols, ethers, carboxylic acids and esters were detected in the LC. The C=O stretches for aldehydes, ketones, carboxylic acids and esters also appeared in the LC.

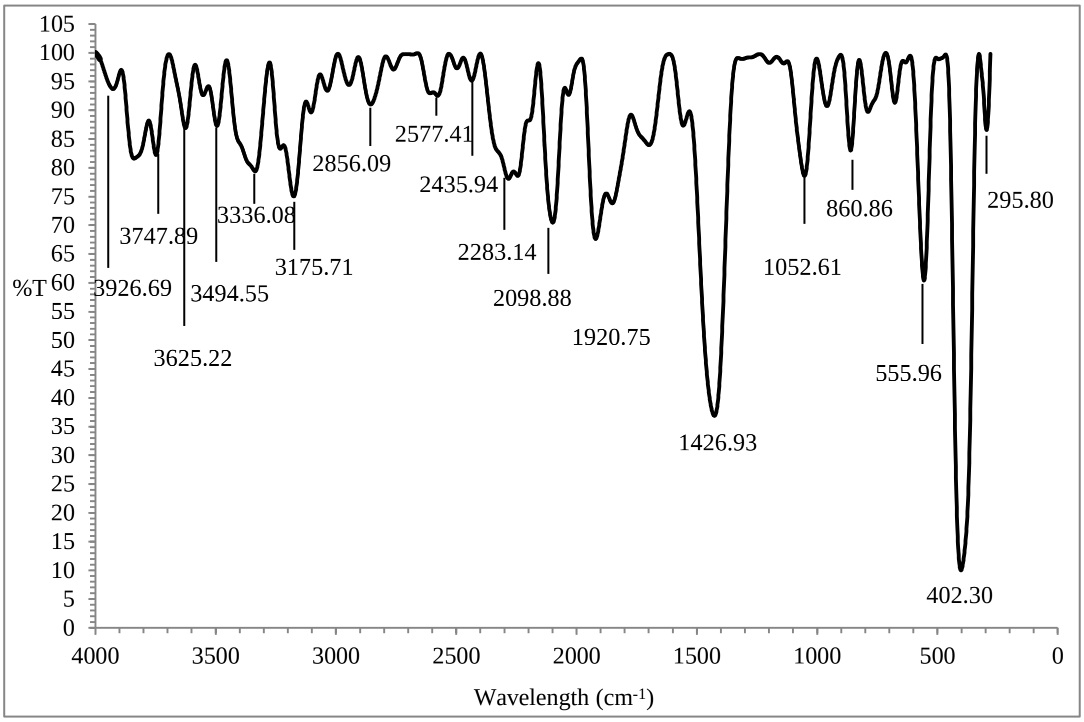


Fig. 3. Fourier Transforms Infrared Spectroscopy (FTIR) of LC

The acidic groups, specifically carboxylic acids, are known to be the binding sites for basic dyes such as methylene blue. Acidic groups such as carboxylic groups favour MB adsorption due to electrostatic interactions between the MB molecules and the carboxylic groups. Hence the presence of this group can improve the adsorption capacity of carbon (Kurniawan and Ismadji, 2011; Altenor et al., 2009). Table 2 listed the LC properties including the ultimate analysis, BET surface area, average pore diameter. The BET surface area was 77.017 m^2/g. There is good inference was obtained on the correlation of internal surface area with methylene blue adsorb abilities (Arida et al., 1992). The average pore diameter was 3.4 nm which indicate a mesoporous structure where the presence of mesopores is favoured for MB adsorption (Altenor et al., 2009). Same conclusion obtained by Mahmoud et al., (2012), for the adsorption of MB on acid treated kenaf fibre char.

Table 2 Properties of LC

Ultimate analysis (%)	
Carbon	81.32
Hydrogen	1.13
Nitrogen	0.807
Sulfur	0.06
Oxygen	6.621
BET surface area (m^2/g)	77.017
Average pore diameter (nm)	3.4

The oxygen content was calculated by obtaining the difference (100 − (elemental composition + ash))

3.2 Char evaluation for adsorption study

Fig. 4 shows the percentage removal of MB dye on different doses of LC. According to fig. 4, the maximum MB dye removals were 65.77, 78.48, 86.14, 90.02 and 90.21 % at 0.5, 0.7, 1, 1.2 and 1.4 g of LC dose respectively. The percentage of dye removal increased with increasing adsorbent dosage from 0.5 to 1.2 g because the number of sorption sites on the adsorbent surface will increase (Ofomaja, 2008). The removal remained almost constant over the dose ranges of 1.2–1.4 g.

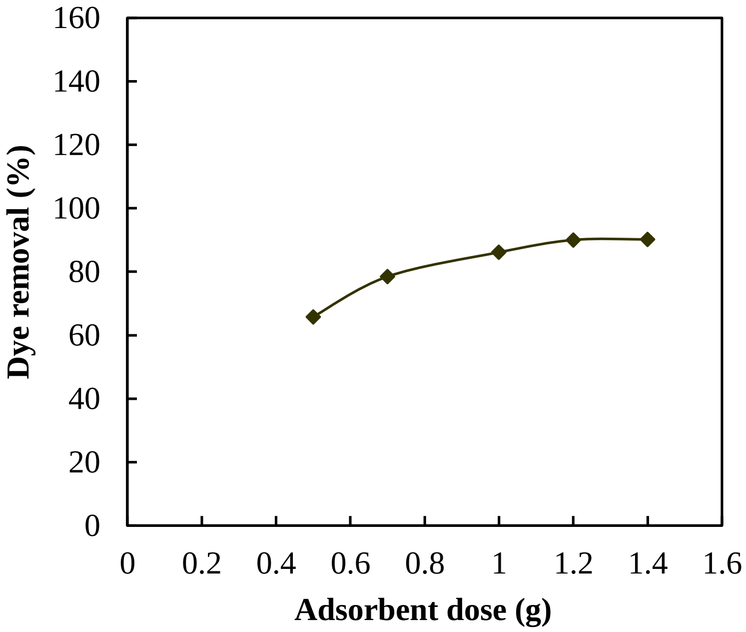


Fig. 4. Percentage removal of MB dye on different doses of LC

4. Conclusions

In this study, Leucaena leucocephala wood char (LC) was produced by a pyrolysis process at 1000 °C. The characterization of char revealed that the pores on the char surface were highly heterogeneous and various groups were detected in the char where, carboxylic acids are important for the basic dye adsorption. The average pore diameter indicates a mesoporous structure which is favoured for MB adsorption. The adsorption of methylene blue dye (MB) on Leucaena leucocephala wood char (LC) was investigated. The application of LC as bioenergy by-product can be good choice as adsorbent for removal of MB from aqueous solution.

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