Characterization of Banana peels waste adsorbent for preliminary study of methylene blue removal from aqueous solution

M Z A Zamri¹, N Y Yahya¹*, R S Ramli¹, N Ngadi² and M Widia³
¹Faculty of Civil Engineering Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang Darul Makmur, Malaysia
²School of Chemical and Energy Engineering, Faculty of Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor Darul Takzim, Malaysia
³Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang, Lebuhraya Tun Razak, 26300 Gambang, Kuantan, Pahang Darul Makmur, Malaysia
*E-mail: yahida@ump.edu.my

Abstract. This paper presents the removal of methylene blue (MB) from aqueous solution using adsorbent produced from Banana peels waste (BPW). Banana peels waste adsorbent (BPWA) was prepared via carbonization in laboratory muffle furnace for 1 h. A preliminary study was performed on the adsorption reaction by varying the initial concentration of MB, adsorbent dosage, contact time, pH and temperature of the aqueous solution. Under the best conditions obtained, the maximum percentage removal of MB is approximately 99 %. The potential of BPWA as dyeing wastewater adsorbent was proven by Scanning Electron Microscopy (SEM) analysis, N₂ adsorption-desorption analysis and Fourier Transform Infrared Spectroscopy (FTIR). From the results, the synthesized adsorbent shown a good percentage removal of MB. In addition, the optimum conditions for the adsorption study are 1 g of adsorbent in the 1 g L⁻¹ of MB initial concentration, for 1 h at pH 8 in 65 ℃. This study reveals potential of BPW in removal of MB dyes from aqueous solution however, further studies are required to establish the applicability of the synthesized adsorbent for the treatment of wastewater from textile industry.

1. Introduction
Wastewater containing dyes is produced by various industries such as textile, food, paper, plastic and cosmetic [1,2]. Effluent discharge containing dyeing wastewater led to negative effects to the environment and human [1,3]. Thus, it is crucial to develop an eco-friendly and effective wastewater treatment and management for this type of water pollution [4]. Numerous approaches are currently being used for treatment of industrial and municipal wastewater, including adsorption, membrane filtration, electroflotation, flocculation and coagulation as well as biological treatment [5,6]. Nevertheless, as various contaminants commonly present in such wastewaters, combination of more than a few approaches in wastewater treatment process is necessary. In treatment of dyeing wastewater, adsorption is more practical than the other processes, as this method involves low cost material and facile operation [7]. Development of new adsorbents that are hydrophobic, porous, cost-effective and possess high adsorption capacity is necessary to ameliorate the negative impacts of dyeing wastewater on the environment and human [8,9]. Banana peels waste (BPW) is one of the potential materials for dyeing wastewater treatment. Banana or is scientific name Musa is one of local fruit in Malaysia. Banana has benefits such as provide nutrient, helps the digestive system and improve insulin sensitivity. It was used to produce a product such as jams, chips, and juice. Banana
peels could be prepared as an adsorbent for dye removal due to its chemical composition which contained a high amount of hemicellulose, pectin, cellulose, lignin and contained various polar functional groups such as phenolic acid groups, carboxylic and hydroxyl [10,11]. 40% of total weight of banana comes from the peel. However, the peels are generated as a waste product and dumped as solid waste [12]. Production of adsorbent from BPW reduces the amount of agricultural waste that ends up in landfills as well as this value-added biomass is not harmful to the flora and fauna. In this study, BPW was synthesized through carbonization process. The adsorbent preparation method is cost effective which can replace the high cost of conventional adsorbent preparation. The problem faced by conventional adsorbent was, it required complicated pre-treatment that use high amount of chemical and required high usage of energy. By utilizing this resource and preparation method, it will be able to reduce the amount of chemical the usage of energy. The preliminary study of adsorption reaction was carried out to study several adsorption parameters such as initial concentration of MB, adsorbent dosage, contact time, pH and temperature of the aqueous solution toward the percentage of MB removal. The result of this preliminary study is important to evaluate the significant of the material used and the preparation method to be improved in the future.

2. Materials and method

2.1. Materials and chemicals
Banana peels waste (BPW) was collected from local area near campus. Methylene blue (MB) was obtained from Sigma-Aldrich.

2.2. Synthesis of Banana peels waste adsorbent (BPWA)
Banana peels waste (BPW) was collected and subsequently washed with distilled water until the dirty completely removed. Next, the BPW was cut into small pieces and dried in a hot air oven at 105 °C for 24 h. Then, the dried BPW was crushed into granules and sieved to 200 µm particle size. Finally, the powder was carbonized in muffle furnace at 550 °C for 2 h to developed porosity and high adsorption efficiency of the synthesized adsorbent.

2.3. Preparation of methylene blue (MB) dye solution
Aqueous methylene blue (MB) stock solution with concentrations of 100 mg·L⁻¹ was prepared by mixing 100 mg of MB powder with 1 L of distilled water. To prevent decolourization by direct sunlight, the stock solution was stored in a dark place before being used.

2.4. Characterization of banana peels waste adsorbent (BPWA)
The functional groups of banana peels waste adsorbent (BPWA) was characterized using Fourier Transform Infrared (FTIR) Spectroscopy (IRTracer-100 Spectrophotometer, Shimadzu Cooperation, Japan). The spectra were recorded from 400 to 4000 cm⁻¹. The surface morphology of BPW adsorbent was observed using Scanning Electron Microscopy (SEM) (Hitachi SU8020). The surface area and pore size of were measured by a N₂ Adsorption-Desorption Isotherm Analyzer (NAD) model Micromeritics 3 Flex Surface Characterization Analyser. Sample was degassed at -196.15 °C under nitrogen gas flow for 4 h prior to analysis.

2.5. Batch mode adsorption study
The prepared banana peels waste (BPW) adsorbent was evaluated for removal of methylene (MB) from aqueous solution through batch equilibrium adsorption studies. The effects of various process parameters, such as initial dye concentration (0.1-1 g L⁻¹), adsorbent dosage (0.1-1 g), pH of the solution (3-10), contact time (10-60 min) and temperature (25-70 °C) on the adsorption capacity of MB were evaluated. Batch experiments were performed using 50 mL glass vials with 50 mL dye solution and 250 rpm stirring on a shaking incubator. At the end of each experiment, solid and liquid phases were separated from each other by filtration process. The remaining concentration of MB in
solution after adsorption on BPW adsorbent was determined using UV-Vis spectroscopy (Shimadzu 1800) at 630 nm. The percentage removal of MB dye, %R was calculated by Eq. (1) as follow:

\[
\text{Percentage removal of MB dye, } \%R = \frac{C_o - C_e}{C_o} \tag{1}
\]

where \(C_o\) and \(C_e\) denote the initial and equilibrium concentration (mg·L\(^{-1}\)) of MB dye.

3. Results and discussion

3.1. Adsorption study

Figure 1 shows the parametric effects on the percentage removal of MB after the adsorption study. For the effect of initial dye concentration on percentage removal of MB (Figure 1(a)), the graph shown that the capacity of the adsorption of the BPWA increase with the increase in the initial concentration of MB which can be explained by the increase of the adsorbate (MB ions) on the free active sites (pores in the adsorbent surface). This is because, at high initial concentration, the driving force to overcome all resistances between ions of aqueous and solid phases is also high, yet increasing the uptake. Also, increasing the initial ions concentration of MB increases the number of collisions between the dye ions and the adsorbent, hence enhancing the adsorption process [13]. On the other hands, Figure 1(b) demonstrates the effect of the adsorbent dosage on the percentage removal of MB. It is obvious that, the percentage removal of MB increases significantly with the increase in the amount of adsorbent from 0.1 g to 0.3 g. This can be due to greater availability of surface area for adsorption reaction to occur which leads to the introduction of more binding sites during the reaction [14]. An increase in the percentage removal was also observed when the dosage was further increased from 0.3 g to 0.5 g. Any further addition of adsorbent beyond this amount did not cause significant change in adsorption performance. This may be due to the overlapping of adsorption sites as a result of overcrowding of adsorbent particles [15]. For all adsorbents dosage ranging from 0.5 g to 1 g, maximum removal of all studied MB removals was obtained at the adsorbent dosage of 1 g with up to approximately 99 % of MB removal. Moving on to Figure 1(c), the effect of pH on the adsorption of methylene blue was not significant due to the low dosage of adsorbent which 0.1 g. This can be explained by the fact that at low values of the initial pH, the surface of the adsorbent would be surrounded by the ions H\(^+\) inducing repulsive forces and hence decreasing the interaction of the ions of the MB with the sites of the adsorbent. Thus insignificant in the adsorption rate at low pH value can be due to the high concentration and the mobility of the ions H\(^+\). Conversely, at high pH, the concentration of H\(^+\) decreases and the total surface of the adsorbent become negatively charged, enhancing the sorption of the ions dye, by means of electrostatic interactions. As a result, the highest percentage removal of MB was at pH 8 with approximately 25 %. This findings is similar to that reported by [16]. It also can be seen from Figure 1(d) that by increasing the contact time from 10 min to 30 min the percentage removal increases. After that, the percentage removal was decrease from 30 min to 50 min. This can be attributed to the availability of sites for the sorbate. In addition, a very high adsorption driving force at the beginning resulted in a higher adsorption rate. After the initial period, slower adsorption may be attributed to the slower diffusion of molecules into the interior pores of the adsorbent, and the molecules subsequently occupy the positions within the adsorbent framework. For effect of temperature on percentage removal of MB, BPW adsorbent shows higher percentage removal of MB as the temperature increase. When the temperature increase, it will decrease the solubility of MB and increase the adsorption of MB.
Figure 1. Effect of parameters on percentage removal of MB. a) Initial dye concentration b) Adsorbent dosage c) pH d) Time e) Temperature

3.2. Characterization of banana peels waste adsorbent (BPWA)

3.2.1. Morphology analysis

Scanning electron microscopy (SEM) is one of the important tool for characterizing the surface morphology of adsorbent surface. The SEM of BPWA was recorded and showed in Figure 2. The analysis of BPWA showed an uneven surface with many small pores sized 2 μm to 3 μm. The existence of the pores sizes can be due to the carbonization processes [17]. Generally, the percentage removal of MB highly related with the pores size of the adsorbent. The appropriate pores size can make MB particles entrance into the internal parts of the adsorbent easier and helpful in the sorption process [18].
3.2.2. N\textsubscript{2} adsorption-desorption analysis

The N\textsubscript{2} adsorption-desorption curve (Figure 3), provides qualitative information on the BPWA. From the Figure 3, it can be summaries that BPWA adsorbed large amount of N\textsubscript{2} molecules at relatively high pressure. From the figure, the best-fit for N\textsubscript{2} adsorption-desorption curve for the adsorbent is type II isotherm, which refers to unrestricted mono-multilayer adsorption and adsorbent is macro pores. The surface physical parameters obtained from the N\textsubscript{2} adsorption-desorption isotherms are summarized in Table 1. From the data, it is marked that the BET surface area of BPWA was 9.6363 m\textsuperscript{2}.g\textsuperscript{-1}. Therefore, it can be the reason for the higher percentage removal of MB during the adsorption reaction.

| Parameter                        | Method       | Characteristic |
|----------------------------------|--------------|----------------|
| Total surface area, S\textsubscript{BET}/m\textsuperscript{2}.g\textsuperscript{-1} | BET          | 9.6363         |
| Micropore surface area/m\textsuperscript{2}.g\textsuperscript{-1} | t-plot       | NA             |
| Microporous volume/cm\textsuperscript{3}.g\textsuperscript{-1} | t-plot       | NA             |
| Mesoporous volume/cm\textsuperscript{3}.g\textsuperscript{-1} | BJH adsorption | 0.014834       |

In this study, the BJH method has been used to determine the pore distribution of the adsorbent (Figure 3). From the plotted curves, the pore size distribution curves showed the highest peaks at pore widths of 1884.7 nm. According to the classification of IUPAC-pore dimensions, the pores of adsorbents were grouped into micropore (d < 2 nm), mesopore (d = 2-50 nm) and macropore (d >50 nm). Thus, the adsorbent was identified as a macro pores material. From the table above, it shows that the surface area of the adsorbent is considers as large.
3.2.3. Spectroscopic study

The purpose of spectroscopic study is to examine the functional groups presence in the BPWA surface. In BPWA, it is observed that various peaks present which indicates the of multiple functional groups in the adsorbent. A wide peak at 3447.05 cm\(^{-1}\) for BPWA is due to the free hydroxyl group of polymeric compounds \[19,20\]. This is likely caused by inter/intra-hydrogen bonding (O-H) stretching which is associated to hydroxyl groups that can be found in alcohols, phenols and carboxylic structures. The O-H group has the ability to adsorb MB. The adsorbent also showed stretching adsorption bands at 1636.79 cm\(^{-1}\). This can be correlate to carboxyl group C=O present in acetyl derivatives, ketone groups, aldehydes and esters. Weak bands observed at around 600 cm\(^{-1}\) to 700 cm\(^{-1}\) for the adsorbent were ascribed as amines groups. It can be found that BPWA has hydroxyl and carbonyl groups. These groups have negative charge where can be good sites for adsorption of MB.

Figure 3. \(\text{N}_2\) adsorption-desorption isotherms for BPWA, as well as pore size distribution of BPWA.
4. Conclusions
As the conclusion, the BPW adsorbent show good percentage removal of MB. From the BET test, it can be confirmed that total surface area and mesoporous volume of BPW adsorbent was higher. Presences of hydroxyl, carbonyl and amines in BPW adsorbent were confirmed through FTIR test. These groups have negative charge where can be good sites for adsorption of MB. The optimum condition for adsorption study by using BPW adsorbent are 1 g L⁻¹ MB, 1 g of adsorbent for 1 hr at pH 8 in 65 °C.

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