Agriculture waste from banana peel as low cost adsorbent in treating methylene blue from batik textile waste water effluents

A A Abu Bakar*, W N R Wan Mazlan, N A Akbar, S Badrealam and K A Muhammad Ali
Faculty of Civil Engineering, Universiti Teknologi MARA, Cawangan Pulau Pinang

*amalina.amirah@uitm.edu.my

Abstract. Batik industrial textile waste water effluent if improperly disposed to the catchment can cause the water pollution that will endanger human health and the environment. The contaminants discharge in the dye processing causes the water pollution. Banana peel is a potential agriculture waste that can be used to reduce the concentration of color from synthetic dye effluents. This study is aim to determine the potential of banana peel as agricultural waste adsorbent for Methylene Blue (MB) removal at different contact time (15 minutes, 30 minutes, 45 minutes, 90 minutes, 120 minutes, 150 minutes, and 180 minutes) and different adsorbent dosage (0.05, 0.1, 0.15, 0.2, 0.25, 0.3, and 0.4 gram) and to develop kinetic model for Methylene Blue (MB) removal. The experiments were conducted at room temperature using batch study. As the banana peel dosage is added from 0.05 g to 0.4 g in 100 ml of Methylene Blue solution, the percentage of MB solution removal also increase from 34.69 % to 86.88 %, indeed due to the increase in phenolic compounds adsorption rates. The adsorption process reached the optimum contact time at 150 minutes with MB solution removal of 86.22 %. The kinetic data obtained specified that the data follow closely the pseudo-second-order. It is concluded that banana peel can act effectively as natural adsorbent in treating Methylene Blue (MB) from batik textile wastewater effluents.

1. Introduction

In Kelantan, batik textile industry develops rapidly according to increase demand all over Malaysia. This industry used a lot of water and consequently discharge high rate of contaminant wastewater. When the effluents from this industry improperly dispose, it endangers human health and also contributes to a negative impact to the environment. The occurrence of contaminant such as hazardous compound organic dyes structure in the water body could potentially cause toward cancer and tumours in human [1]. In the other hand, the effluents from batik textile industries that discharge during the dye process are considered among the most polluting contributor compare to other industrial sectors since the effluent contribute extremely to surface water deterioration. Therefore, there is a need to develop environmental protection before the effluent is discharging to the river to minimise pollution in the water body.

There are several processes in treating textile wastewater by reducing polluted compounds that include physical, chemical, biological, and combined treatment process [2]. Polluted compound that present in the textile industry like sulphide compounds that are environmental concerns due to their
harmful nature, therefore, a combination of biological and chemical methods is being reviewed for sulphur treatment [3]. Physical and chemical treatment processes are suitable for dye treatment in wastewater. Chemical method such as electrochemical method can be use to decolourize the dye wastewater. However, those techniques happen to be considerably expensive and lead to problems on operations [4].

Physical method commonly used in textile waste water such as adsorption. Adsorption is considerable the best method among the treatment processes since this method is more economical and effective. There are several studies using batch adsorption to treat waste water. Many types of adsorbent could be used to treat waste water such as agriculture waste [5], industrial waste [6], and activated carbon [7]. Each adsorbent use to remove pollutants in waste water has its own advantage and disadvantage. The most efficient adsorbent in treating waste water is from activated carbon as it is the most efficient classical way since its removal rate can be more than 99%. However, the cost of activated carbon is high, unsustainable and can’t be recycled. In this study the potential of agriculture waste adsorbent namely banana peel is explored to treat waste water discharge from batik textile industry. This adsorbent is known as low cost material since the peel is usually wasted and unused for commercialise purposes. Moreover, banana peel is an environmentally friendly material since it is biodegradable and safe to the environment.

Banana is an ordinary fruit that growth widely all over the world. The fruit waste that can act as an adsorbent is effective to treat polluted waste water [8]. The fruit peel is about 30 - 40 % where the part is the highest waste compare to the whole usage of the fruits. Previous research shows that daily household or marketplaces garbage contain banana peels wastage contributed to disposal problems and affected to an environmental nuisance like producing leachate. Carboxyl, hydroxyl and amide groups are different types from a group of chemicals exist on the surfaces of banana peel to perform as an important function under the adsorption method [8].

Therefore, the aim of this study is to determine the potential of banana peel as an adsorbent to remove Methylene Blue (MB) at various contact time and dosage and to develop the kinetic model for MB removal in batik textile waste water. In order to study the effect of different controlling parameters such as dosage of banana peel and contact time on MB adsorption capacity of banana peel, batch study adsorption experiment was carried out. A varied amount of adsorbent was added into 250ml closed conical flask containing 100 ml of synthetic waste water and then shaking in a rotary shaker at fixed rpm, for various contact time at a room temperature. The behaviour of adsorption mechanism was then analyzed based on mathematical modelling using pseudo-first order and pseudo-second order kinetic models.

This study used banana peels without chemically treated in a form of small cut pieces (0.5-1.0cm) range between 0.05-0.4g that is differ from previous study which use banana peel in a form of powder [9,10]. In this study, raw banana peal as abandoned agro waste is introduced as an adsorbent in treating textile waste water and has a potential to be used at lower dosage where the treated water is saved to be released into the water body.

2. Methodology
2.1 Adsorbent preparation
Banana peel which is abundantly wasted at local fried banana stalls was collected. The adsorbent was washed many times by distilled water to get rid of dirt like dust and soil. Then, the adsorbent was cut into small pieces at a range of 0.5 to 1 cm and dried 24 hours in convection (Model: BINDER ED 720) with temperature ±10°C until the adsorbent weight is constant.

The waste water sample was stored in sealed containers collected directly after the textile dyeing process ceased in the pond located at the batik textile industry in Pasir Mas, Kelantan. The containers were once rinsed with the effluent to avoid dilution and rinsed to make sure the sample is clean from additional contamination. Then, the samples are stored in the refrigerator with temperature 4 °C before the initial colour values is determined. The synthetic batik textile waste water was simulated close to the
effluent from batik industry located in Kelantan to ensure the consistency of initial colour values for each sample in this study.

The synthetic waste water was prepared by adding 21.0 mg of Methylene Blue (C_{16}H_{18}ClN_{3}S) powder with 1000 ml of deionized water to obtain initial Methylene Blue water sample in the range of 320 to 341 PtCo which is matching with the initial colour value of batik textile waste water. Equation (1) is used to measure the concentration of Methylene Blue powder for the preparation of MB stock:

\[ M_1 V_1 = M_2 V_2 \]  

(1)

Where \( M_1 \) is the concentration in molarity (moles/ Liters) of the concentrated solution, \( V_1 \) is the volume of the concentrated solution (L), \( M_2 \) is the concentration in molarity of the dilute solution (moles/ Liters), and \( V_2 \) is the volume of the dilute solution (L).

2.2 Adsorption equilibrium study

Adsorption capacity of banana peel to remove MB from the waste water sample was carried out using batch adsorption study. The effect of dosage is ranging from 0.05 to 0.4 g, contact time is ranging from 0 to 180 min at speed of 150 rpm was investigated in this method.

2.2.1 Varied dosage

Different amounts of adsorbent (i.e.: 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, and 0.4 gram) were mixed with 100 ml of Methylene Blue solution in 250 ml closed conical flasks. The conical flasks were placed in orbital shaker and agitated for 90 minutes at speed of 150 rpm in a room temperature. The water sample then is allowed to rest for 60 minutes before the final colour concentration value is determined by using HACH DR2800 spectrophotometer. Graph of % removal of MB versus varied dosage is plot and value of optimum dosage is determined.

2.2.2 Varied contact time

After the optimum dosage is determined from previous method stated in section 2.2.1, 8 numbers of conical flask is placed in the orbital shaker and agitated for different contact time (i.e.: 15 minutes, 30 minutes, 45 minutes, 90 minutes, 120 minutes, 150 minutes, and 180 minutes) at speed of 150 rpm in a room temperature. After shaking process ceased, the water sample then is allowed to rest for 60 minutes before the final colour concentration value is determined by using HACH DR2800 spectrophotometer. The removal efficiency of the adsorbent can be expressed in Equation (2).

\[ \text{%removal} = \left( \frac{C_i - C_t}{C_i} \right) \times 100 \]  

(2)

The adsorption capacity of adsorbent can be expressed in Equation (3).

\[ q_e = \frac{(C_i - C_t)V}{m} \]  

(3)

Where \( C_i \) and \( C_t \) is the initial and final concentration of MB solution (mg/L), \( V \) is the volume of sample (L) and \( m \) is the mass of adsorbent (g).
2.2.3 Kinetic study
From the adsorption equilibrium study, the behaviour of adsorption mechanism then is analysed using pseudo-first order and pseudo-second order kinetic model.

Kinetic study is a mathematical model to describe the adsorption behaviour and the mechanism of adsorbent onto adsorbate. The adsorption mechanism of banana peel in removing Methylene Blue (MB) in the synthetic wastewater was analysed using pseudo-first order kinetic and pseudo-second order kinetic models. The equation for both kinetic models are presented in Equation (4) and (5).

\[
\log (q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{4}
\]

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \tag{5}
\]

The pseudo-first order kinetic equation is expressed in Equation (4) where \(q_e\) and \(q_t\) represent the MB uptake (mg/g) at equilibrium and at time \(t\) (min), while, \(k_1\) (min\(^{-1}\)) is the pseudo-first order constant rate of adsorption. \(q_e\) and \(k_1\) can be obtained from the gradient of plotting \(\log (q_e - q_t)\) versus time \(t\), while, \(q_t\) is the measured of MB at time \(t\).

Pseudo-second order kinetic equation is expressed in Equation (5). In this linear equation, \(k_2\) represent the pseudo-second order constant rate and it can be determined by the interception of plotting \(t/q_t\) versus time \(t\).

3. Result and Discussion
3.1 Effect of varied dosage on adsorption
Figure 1 indicates the effect of dosage adsorption of MB in the synthetic wastewater. In general, the increment of the media dosage used in the batch study leads to increase the removal percentage of Methylene Blue (MB). At dosage 0.3 g and 0.4 g, the percentage removal of Methylene Blue begin to constant and slowly decrease where the adsorbent become saturated and become less efficient.

The optimum percentage removal of Methylene Blue from the synthetic wastewater is 86.88% at 0.3 g of banana peel dosage. The increment of dosage also affects the adsorption capacity as shown in Figure 2. The adsorption capacity is reduce from 222.00 mg/l to 53.20 mg/l as the dosage is increase.

![Figure 1. Percentage of colour removal versus dosage](image)

At high concentration of adsorbent where the adsorbent efficiently removes MB, availability of greater surface area occurred. Adsorption is a surface phenomenon where adsorbate molecules occupy
this area. Adsorbate molecules will engage in specific sites where these sites are commonly known as active site [11]. The concentration of these active site on the surface is further related to the pore size and pore volume availability. This explains why increasing the dosage of adsorbent results in increased of adsorption rate. Even though the results discovered that initially the percentage removal increasing rapidly, however, after sometimes the rate of colour removal will becomes slowly lessen. The reduction of adsorption capacity is caused by the decrease of effective adsorbent surface area. In the other word, all the available active sites on the adsorbent have been occupied and there are no further sites and hence no further adsorption is possible.

![Figure 2. Adsorption capacities versus dosage](image)

3.2 Effect of varied contact time on adsorption
Figure 3 shows the effect of varied contact time in removing MB from the synthetic wastewater. Generally, there is a significant effect on the removal of MB efficiency during the agitation process that involved a mixture between adsorbents and Methylene Blue solution due to difference contact time. As the contact time becomes longer from 15 minutes to 150 minutes, the result shows a subsequent increment percentage of Methylene Blue removal. This could be a sign to the increment rate of mass transfer and molecular diffusion from the bulk solution to the adsorbent [12]. The fast kinetics process observed at the initial stage can be attributed to the abundant availability of an active binding site on the adsorbent. At contact time of 150 minutes, the percentage removal of Methylene Blue is 86.22 % which reach the optimum state. However, percentage removal of Methylene Blue is lessening after 150 minutes of agitation process. It is documented that the percentage of MB removal at 180 minutes drops to 83.87% from the optimum state before.

As the contact time gets longer from 15 minutes to 120 minutes, the adsorption capacity begins to increase. This can be shown in Figure 4. The adsorption achieves the optimum capacity of 29.40mg/l at 150 minutes. After 150 minutes the adsorption capacity lessen due to the decreasing available binding site and reduce in total adsorbent surface area which is later occupied as the process proceeds.
3.3 Kinetic study
The behaviour of adsorption mechanism was analysed using pseudo-first order and pseudo-second order kinetic model. From Figure 5, it can be seen that the adsorption data were well represented by a pseudo-first model with $r^2 = 0.9783$ for all contact time mentioned previously while Figure 6 shows that the pseudo-second-order model fits the kinetic study very well with $r^2 \geq 0.99$.

Based on Table 1, the removal of MB from synthetic wastewater followed pseudo-second order kinetic model since the value of regression coefficient, $r^2$ in this model is 0.9934. The $r^2$ value for this model is higher compared to first order kinetic model. In the first order kinetic model, the value of $r^2$ is low which is only 0.9783. Thus, the model did not follow the first order kinetic model. Therefore, the adsorption of MB in synthetic wastewater using banana peel adsorbent followed the second order kinetic model due to higher value of $r^2$. Likewise, previous studies have found that adsorption of dies in wastewater were fitted with pseudo-second order kinetic [10, 13].
4. Conclusion
It is concluded that this study shows that the removal percentage of Methylene Blue increase with the increment amount of adsorbent dosage. As the adsorption increase, the adsorption mechanism will become saturated and less efficient. In this study, the optimum percentage removal of Methylene Blue is 86.88% for varied in dosage where optimum dosage is 0.3g and 86.22% for varied in contact time where optimum contact time is 150 minutes. The adsorption kinetic model is best fitted by pseudo-second-order model with correlation, $r^2 = 0.9934$. The use of banana peel as waste-agro adsorbent proved to be a better adsorbent due to high percentage removal in wastewater treatment compare to others waste-agro adsorbent. Banana peel is environmentally friendly, cost effective and locally available has a potential to be used as agriculture waste adsorbent to remove Methylene Blue in batik textile waste water.
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