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Abstract. This study was carried out to examine the effectiveness of sugarcane bagasse, an agricultural waste available in bulky quantity in Malaysia, to remove basic dye (e.g., methylene blue) from aqueous solution by adsorption. Batch mode experiments were carried out to study the effects of shaking speed, contact time, adsorbent dosage, and pH. Furthermore, equilibrium adsorption isotherms and kinetics were investigated. In the optimum operation condition, about 96.9 and 95.5 removal percentage of colour was obtained at 200 rpm shaking speed, 6 hr contact time and 0.2 g AC dosage. The experimental data were analyzed by the Langmuir, and Freundlich models of adsorption. The adsorption isotherm data were fitted well to Langmuir isotherm. The kinetic data has been analyzed using a pseudo-first-order, pseudo-second-order equation and intraparticle diffusion equation. The experimental data fitted very well the pseudo-second-order kinetic model with $R^2 > 0.99$. Consequently, the adsorption of MB onto the AC driven from sugarcane bagasse has a great potential to be used textile waste water treatment.

Keywords: sugarcane bagasse; Methylene blue; Adsorption isotherm; Kinetic models

1. INTRODUCTION

One of the main reasons of environmental pollution is the effluent generated from industries. Dyes are one of the effluent discharges from various industries which cause serious problem to the environment. There are more than 10,000 types of dye which are commonly used in industries such as textile, food, paper, plastic, rubber, leather, cosmetic, and pharmaceutical industries (Mondal, 2008). Different sources of residual dye are introduced into natural water resources or wastewater treatment plant which contains characteristically high level of colour and organic pollutant. Textile industries cause serious pollution problems to environment in worldwide because its wastewater contains dye (Zaharia and Suteu, 2012). Discharging of coloured wastes into water bodies affect nature of the water and make it unable to use by human (Gunasekar and Ponnusami, 2012). Besides, it’s not only affect the nature aesthetic but also affect the penetration of sunlight and hence decreases the photosynthesis activity (Maryam et al., 2013).

Methylene blue (MB) is not considered as acutely toxic, but it can have a variety of dangerous effects. On inhalation, it can give rise to short periods of rapid or difficult breathing, while ingestion through the mouth produces a burning sensation and may cause nausea, vomiting, diarrhea, and gastritis. A large amount creates abdominal and chest pain, severe headache, profuse sweating, mental confusion, painful micturation, and methemoglobinemia-like syndromes (Forgacs et al., 2004). Consequently, due to large-scale production and extensive application, synthetic dyes can cause substantial environmental pollution and health-risk. Thus, removal of dyes from wastewater is very necessary.

Due to their chemical structure, dyes are difficult to be treated once discharge into water bodies. Generally, dyes are hard to treat by conventional and biological process because the dyes are non-biodegradable, very toxic and their metabolites have teratogenic, mutagenic, and carcinogenic which affect aquatic life and human beings (Gunasekar and Ponnusami, 2012). Adsorption has been shown to be very effective for removal of dyes and other pollutants from aqueous solutions (Maryam et al., 2013). Saad et al. (2010) reported that activated carbon (AC) is the most commonly used absorbents due to its high capability to adsorb organic compound. Thus, AC is
widely used for textile wastewater treatment. Unfortunately, Activated carbon is still considered costly adsorbent and the higher the quality the superior the cost. Both chemical and thermal reactivation of spent carbon is costly, impractical on a large-scale and creates additional effluent and results in considerable loss of the adsorbent. This has led numerous researchers to search for the use of low cost and competent alternative materials (Aksu, 2005).

In this study, we attempt to utilize Sugarcane bagasse (SCB), an agricultural waste abundantly existing in Malaysia as a sorbent to eliminate MB from aqueous solution. SCB is one of the biggest agricultural wastes in the world (Loh et al., 2013). The SCB waste accumulates in the agro-industrial yards, has no important industrial and profitable employs, but becomes an issue and contributes to serious environmental problems. Therefore, any effort to reuse this waste will be helpful. The objective of this work was to study the potential of sugarcane bagasse waste as adsorbent in the removal of the basic dye, MB, from aqueous solutions.

2. MATERIALS AND METHODS

2.1. Adsorbate

Methylene blue (MB) purchased from Sigma–Aldrich was used as a basic dye in this study. The MB was chosen due its known strong adsorption onto solids. The maximum absorption wavelength of this dye is 668 nm. The structure of MB is shown via Figure 1.

![Chemical structure of MB](image)

Fig. 1: Chemical structure of MB

2.2. Preparation and characterization of adsorbent

The SCB used was collected from the fruit market of Kampar, Perak. SCB was cut into small pieces, then blended using blender (Model HGB 550, USA). After that, the blended SCB was cooked by using stirrer hot plate (Model HS707V2, Malaysia) as shown until it is boiling. Then, tap water was used to rinse the sugar out from the SCB and the SCB was dried in the oven (Model Memmert Universal Oven, Germany) for overnight with temperature of 105°C. After dried, the SCB was grinded sieved using sieving shaker (Model RX-29, USA) to obtain a particle size range of 0.5-1.7mm. The sieving size is less than 1.7 mm and more than 500 µm. No other chemical or physical treatments were used prior to adsorption experiments. The sieved husk was placed into the vertical circular column in a carbonization unit as at the temperature of 700°C for 2 hours in the presence of 150 cm³/min purified nitrogen gas (N₂) flow to produce char. Then the carbonized char was activated using chemical activation. The char produced was mix with potassium hydroxide solution (KOH) to produce AC with char: KOH impregnation ratio of 1:2.73 with stirring lightly using the stirrer hot plate. After mixing the AC was dried under oven overnight at 105°C. Then, the AC was heated again for 3hr at temperature of 2 hours in the presence of N₂ and CO₂.

2.3. Adsorption studies

The batch sorption experiments were carried out in 250-mL Erlenmeyer flasks where 0.10 g of the adsorbent and 100 L of the MB solutions (100 mg/L) were used. In this study, the influences of treatment process variables (e.g., AC dosage, shaking speed, contact time and pH) were investigated. The amount of adsorption at equilibrium, \( q_e \) (Pt-Co/g), was calculated by

\[
q_e = \frac{(C_0 - C_e) V}{W} \quad (1)
\]

where \( C_0 \) and \( C_e \) (Pt-Co/L) are the liquid-phase concentrations of dye at initial and equilibrium, respectively. \( V \) is the volume of the solution (L) and \( W \) is the mass of dry adsorbent used (g). The concentration of the MB in the solution after equilibrium adsorption was measured as above. Kinetic studies of adsorption were also carried out at various concentrations of the MB wherein the extent of adsorption was investigated as a function of time.
2.4. Analytical Method

Concentration of colour was tested before and after each experiment. All the tests were conducted according to the Standard Methods for the Examination of Water and Wastewater (APHA 2005). Colour concentration was measured as apparent color by a DR 6000 Hach spectrophotometer pH was measured by a portable digital pH/Mv meter.

3. RESULTS AND DISCUSSIONS

3.1. Effect of various factors on dye adsorption

Shaking speed is a significant parameter in the adsorption process affecting the distribution of the solute in the bulk solution and the formation of the external boundary film (Maryam et al., 2013). The graph of colour removal efficiency versus shaking speed was plotted as shown in Figure 2. The effect of shaking speed was studied using 100 mL of dye solution with a concentration of 0.1 mg/L, 2 hours contact time and varied shaking speed from 0 - 300 rpm. Refer to the results obtained, the removal efficiencies of colour increase when the shaking speed increases. By increasing the shaking speed, there is a further raised in the biosorption due to the binding sites are free for further biosorption. With shaking, the external mass transfer coefficient raises causing the faster adsorption of the MB (Maryam et al., 2013). The optimum shaking speed obtained from experiment was 200 rpm with the removal efficiency of 69.16 %. After reached the equilibrium state, if the shaking speed continued to increase, the removal rate tends to remain constant.

Figure 3 shows the effect of contact time on the study parameter. The effect was studied using 100 mL of dye solution with the concentration of 0.1 g/L, 0.1 g of AC, 200 rpm of shaking speed and contact time varied from 0 - 8 hours. The colour WAS removed significantly in the first 10 min. After 10 min, the removal retard gradually until it reached the equilibrium which is 77.07 % for colour. This phenomenon occurs because plenty of empty surface sites are available for adsorption during the early stage and after some time the remaining empty surface sites are hard to be occupied because of the repulsive force between the solute molecules on the solid surface and in bulk phase. From the result obtained, the adsorption of MB onto SCB reached to the equilibrium after shaking for 6 hours.

AC dosage is a significant factor in investigating the quantitative uptake of pollutants. The results of the colour removal by using various dosages of AC from SCB are shown in Figure 4. The contact time, dye concentration, shaking speed and the volume of solution were set to 6 hours, 0.1g/L, 200 rpm and 100 ml, respectively. The AC dosage was varied from 0 - 0.5 g. The colour removal efficiencies increase with the increase of the AC dosage from 0 - 0.2 g. The best result obtained was 0.2 g of AC dosage with 96.96 % removal efficiency.

In this study, pH of dye solutions were adjusted v from 3–11 with the concentration of MB of 0.1 mg/L, 0.04 g of AC, 200 rpm and 6 hours contact time. The removal efficiencies vs. pH are shown in Figure 5. Figure 5 shows that at lower pH, the removal efficiencies for colour are low and when the pH increases, the removal efficiency increases. Salleh et al., (2011) stated that, the positive charge at a high pH solution interface decrease and the adsorbent surface becomes negatively charged. Therefore, the cationic dye adsorption increase and anionic dye adsorption shows a decrease and vice versa.
3.4. Adsorption isotherms

The experimental adsorption data was normally described by equilibrium isotherm equations. Langmuir and Freundlich model are commonly used to describe the surface adsorption of single-solute systems and adsorption characteristics of absorbent (Bashir et al., 2012). The theoretical Langmuir isotherm is valid for adsorption of a solute from a liquid solution as monolayer adsorption on a surface containing a finite number of identical sites. Langmuir isotherm model assumes uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface.
Expression of the Langmuir model is given by Eq. (2)

$$\frac{1}{q_e} = \frac{1}{QbC_e} + \frac{1}{Q}$$

(2)

where, \(C_e\) = equilibrium liquid-phase concentration of pollutants, \(Pt-Co / L\) \(q_e\) = equilibrium uptake capacity, \(Pt-Co/g\), \(Q\), \(Pt-Co/g\) and \(b\), L/mg = Langmuir constants

Expression of the Freundlich model is given by Eq. (3)

$$Q = k_f C_e^{1/n}$$

(3)

where, \(q_e\) = equilibrium uptake capacity, \(Pt-Co / g\), \(C_e\) = equilibrium liquid-phase concentration of pollutants, \(Pt-Co/L\), \(1/n\) = the intensity of the adsorption, \(K\) = indicator of the adsorption capacity in mg/g (L/mg)

The equilibrium data were fitted to the Langmuir isotherm. The constants values together with the \(R^2\) value are listed in Table 1. The capacity for colour adsorption on the AC was 2500 Pt-Co/g. Then the sorption energy for colour and was 0.0104 L/mg and the \(R^2\) was 0.937. The Freundlich adsorption isotherm was also studied. The Freundlich isotherm is an empirical equation that assumes the adsorption process to take place on heterogeneous surfaces. The value of \(K\), \(1/n\) and \(R^2\) are presented in Table 1. The values of \(K\) and \(1/n\) for colour adsorption were 159.772 mg/g (L/mg) 1/n) and 0.381, respectively. The calculated results of the adsorption of colour by the Langmuir and Freundlich isotherm were reasonably explained. Nevertheless, the Langmuir model gave the best fit because the value of \(R^2\) was slightly higher compared with Freundlich.

**Table 1: Isotherm equations parameter for colour adsorption onto SCB**

<table>
<thead>
<tr>
<th></th>
<th>Langmuir Isotherm Coefficient</th>
<th>Freundlich Isotherm Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Q</td>
<td>b</td>
</tr>
<tr>
<td>Pt-Co/g</td>
<td>2.500</td>
<td>0.0104</td>
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<tr>
<td>L/mg</td>
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3.5. Adsorption kinetics

The rate of solute uptake which controls the residence time of adsorbate uptake at the interface of solid-solution is best described by adsorption kinetics (Mohamed et al., 2007). Pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic models were used to analyse adsorption of organic compound:

- **Pseudo-first-order** equation
  $$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303}$$

  (4)

- **Pseudo-second-order** equation
  $$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

  (5)

  where, \(K_1\) = pseudo-first-order adsorption rate constant of, 1/min; \(q_e\) and \(q_t\) = amount of adsorbed dyes, mg/g at time \(t\) and at equilibrium; \(K_2\) = pseudo-second-order adsorption rate constant, g/(mg·min); \(q_e^2\) = initial adsorption rate, mg/(g·min)

  Intra-particle diffusion model
  $$q_t = K_{diff}^{1/2} + C$$

where; \(k_{diff}\) = rate constant of intra-particle diffusion, mg/(g.min)\(^{1/2}\); \(C\) = the intercept; \(q_e\) = the amount of dye adsorbed at time, \(t\)

The kinetics adsorption controlled the experimental efficiency. There were few kinetic models can be used to predict the mechanisms related to the adsorption process (Chabani et al., 2007). The kinetic modelling was usually used to study the controlling mechanism of adsorption process such as mass transfer, diffusion control, and chemical reaction (Hameed 2009). The calculated and analysed values of \(R^2\), \(q_e\), \(K_1\), and \(K_2\), are presented in Table 2. The values of \(R^2\) for the pseudo-first-order, pseudo-second-order and intra-particle diffusion models for colour were 0.935, 0.993, and 0.836, respectively. Hence it can be said that pseudo-second order equation model has the highest \(R^2\) (0.993) for colour adsorption among the models. The high values of \(R^2\) mean that the adsorption kinetics of the parameter is well defined by the model. The maximum adsorption capacities \((q_e)\) determined from the pseudo-second-order equation was closed to the experiment value. From the value obtained, it can be concluded that the pseudo-second-order kinetic model gave a good correlation for the bio-adsorption of MB onto the SCB.
4. CONCLUSION

It can be concluded that AC prepared from SCB can be effectively used as adsorbent for the removal of textile dyes. The optimum operation treatment condition for removal of MB using AC prepared from SCB was 200 rpm of shaking speed, 6 hours of contact time and 0.2 g/100 mL of AC dosage which achieved about 96.96% of colour removal. Adsorption equilibrium data were fitted to the Langmuir isotherms model for both colour removals with $R^2$ of 0.993. The kinetics data was best described by pseudo-second-order kinetics model as the $R^2$ closed to unity which was 0.993. Hence, the adsorption of MB onto the SCB has the great potential to be used in removal of dye colour.

REFERENCES


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