Removal of methylene blue from water using sugar palm agro industry waste adsorbent

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Abstract. This research was batch experiment conducted using palm powder waste (SPPW) from the palm agro industry. Variables studied were initial of solution pH and SPPW dose. Langmuir and Freundlich isotherm models were used for equilibrium analysis. For kinetics analysis, this study used Lagergren's pseudo-first-order kinetics model, Ho’s pseudo-second-order kinetics, Ritchie and intraparticle diffusion. The study was found that the increase solution pH would increasing of adsorption capacity from 30.31 mg g⁻¹ at pH 2 to 66.70 mg g⁻¹ at pH 8. The dye removal was increase from 83% to 95% for the adsorbent dose from 0.5 gL⁻¹ to 2 gL⁻¹ while adsorption capacity was reduced from 66.70 to 19.01 mg g⁻¹. The equilibrium studies well interpreted by the Freundlich and maximum adsorption capacity (qm) is 312.5 mg g⁻¹. The kinetic studies found that the adsorption followed the pseudo second order.

1. Introduction

Various types of industry currently use dyes, one of the functions of dyes in the resulting product is to attract buyers. For example, coloring product packaging design even has an appeal compared to the function of the product itself. Previously, natural dyes came from plants. Currently, synthetic dyes have been used, even thousands and are generally used in the plastics, paint, food, photo, textile, printing ceramics, paper, chemical, leather, and pharmaceutical industries [1]-[3]. One of the dyes that are widely used is methylene blue, which is widely used in the textile industry. Methylene blue belongs to the category of cationic dyes, the dye is divided into 3 categories, namely anionic, cationic and non-ionic. [4]. Methylene blue is not a dye that has a high toxic level, but it still causes negative impacts on the environment such as water pollution and health, such as heart rate increasing, nausea and vomiting [5]. Some methods have been used for the dye wastewater treatment process. Research on reducing dye waste has been carried out with membrane filtration technology [6], nanofiber membrane [7], composite film [8], nanosheet [9], applied chemical coagulation / flocculation [10], adsorption [1]-[4]. Of the various wastewater treatment processes, adsorption is an effective and simple process. Dye adsorbents there are form biomass, agricultural waste, agro-industrial waste, and natural materials.

In the last few decades there has been an increase in biomass waste, especially agricultural waste & agro-industrial waste. This waste increases along with the increase in the number of agricultural and agro-industrial to meet increasing food needs as the population increases [11]. This agricultural waste and agro-industrial waste can even have a negative impact on the surrounding environment. This agricultural waste and agro-industrial is very abundant, cheap, and can be used as an adsorbent. In the
utilization of adsorbent, it can be used directly with a simple process and with the addition of a more complicated process.

Various studies of dye adsorption application use adsorbent from agricultural waste and agro-industrial coconut leave [2], rice husk bio-composite [4] Magnoliaceae leaves [12], Arthospira platensis [13], biomass of Bacillus Subtilis [14], Catharanthus roseus dried bark [15], oil palm fronds [16], soursop seeds [17], peanut shell [18], rice husk [19], spent rice biomass [20], and many other studies. Various of agricultural waste and agro-industrial have been used as adsorbent which contains lignocellulose. Agro-industry waste, one of which is of sugar palm starch industry. In the palm starch industry, it produces several biomass including dregs which consists of 2 forms, there are fibers and powder. This study aims to obtain equilibrium the equilibrium and kinetic study of the adsorption of sugar palm dregs in the form of powder / sugar palm powder waste (SPPW) to methylene blue.

2. Methods
2.1. Materials of sugar palm powder waste biomass (SPPW)
The biomass from sugar palm starch industry waste used in this research was taken from small industries centre of sugar palm extraction mills. The collected materials were then separated to 2 forms, fibre and powder. In this research the material used is sugar palm powder waste (SPPW). Distilled water was used to wash the material, then oven at 100°C for 4 hours. The material reduced in size using a grinder, the last sieved by size +60 to −100 mesh (150 µm – 250 µm).

2.2. Effect of initial pH
Analysis of the effect of differences in pH in the initial solution was carried out from pH 2 to 8. To increase pH use 0.1 M NaOH and to decrease pH use 0.1 M HCl solution. Batch experiments were 100 mL at the concentration of 40 mgL⁻¹ of methylene blue solution agitated with of material dosage 0.5 gL⁻¹ use magnetic stirrer at 30°C, speed of agitation is 200 rotations/min, the times is 120 min. The sample was then analyzed using a spectrophotometer at 664 nm, previously for 10 minutes it was centrifuged at 3500 rpm. The amount of biosorption, qₑ (mg g⁻¹), was calculated by:

\[ qₑ = \frac{(C₀ - Cₑ)V}{M} \]  

where \( C₀ \) (mgL⁻¹) initial concentration and \( Cₑ \) (mgL⁻¹) concentration at time \( t \), \( V \) volume (L), and \( M \) is SPPW added (g)

2.3. Effect of biosorbent dosage
The effect of SPPW dosage on the removal of methylene blue were studied by varying the dosage from 0.5 gL⁻¹, 1 gL⁻¹, 1.5 gL⁻¹, and 2 gL⁻¹ at the concentration is 40 mgL⁻¹. Keeping all other parameters constant at 30°C and pH of 8. Batch experiments performed the same on the analysis of the effect of pH.

The percentage of dye removal:

\[ \text{Removal percentage} = \frac{C₀ - Cₜ}{C₀} \times 100\% \]  

where \( Cₜ \) (mg L⁻¹) is concentrations of dye at the end of agitation time (min).

2.4. Equilibrium studies
The equilibrium experiment was carried out using various concentrations of methylene blue solution there are 20, 30, 40, and 50 mgL⁻¹. The amount of solution for each experiment was 100 mL with a dose of 0.5 gL⁻¹ SPPW at 30 °C and pH of 8.
2.5. Kinetic studies
The initial dye concentration is 40 mgL\(^{-1}\), the dosage of SPPW is 0.5 gL\(^{-1}\). Keeping all other parameters constant at 30°C and pH of 8. Then stirred using magnetic stirrer, speed of agitation is 200 rotation/min. Experiments were performed with time intervals of 15 min, a starting time of 15 up to 120 min. The sample was then analyzed using a spectrophotometer at 664 nm, previously for 10 minutes it was centrifuged at 3500 rpm.

3. Results and discussion
3.1. Effect of pH
The initial pH solution is one of the most important factor of adsorption process of dyes [14], [18], [21], [22], particularly in the rate and capacity of adsorption [18]. The dye ionization and charge on the adsorbent surface are influenced by pH [21]. Based on the aspect of charge distribution on the adsorbent and adsorbate, the pH of the solution is an important aspect that determines the level of electrostatic or molecular interactions [22].

![Figure 1. Effect of initial pH (C₀: 40 mgL\(^{-1}\); V:100 mL; M: 0.05 g, temperature 30°C).](image)

From Figure 1, it can be seen dye adsorption was increased from 30.31 mg g\(^{-1}\) at pH 2 to 66.70 mg g\(^{-1}\) at pH 8. This showed and indicated that increasing pH effect of the adsorptions. At the lower pH may be related to the protons competition with methylene blue for the available adsorption sites [5]. The methylene blue, classified as cationic dye category [4] so it is positively charged. The adsorption process will take place optimally if the adsorbent used is negatively charged, so that the binding process between positive and negative charges can occur. At low pH (pH2), SPPW is positively charged, therefore there is a large amount of repulsion and a low rate of dye adsorption. The opposite occurs when the pH of the solution increases, causing the SPPW to be negatively charged. Therefore, it will increase the attractiveness between the cationic dye and the adsorbent, so that the adsorption rate increases with increasing pH [23]. The results of this study are the same as those that have been reported by several previous studies [24], [25].
3.2. Effect of biosorbent concentration

Figure 2 showed the relationship between dye absorbed (qe) and SPPW dose. To investigate the influence of SPPW dose on the value of dye adsorbed and percentage of dye removal, by running various doses of the SPPW to methylene blue solutions. From the graph it can be seen that the removal of the dye increases with the increase in the SPPW dose. This condition is influenced by the increasing number of adsorbent surfaces, so that the amount of dye absorbed increases [22].

![Figure 2](image)

**Figure 2.** Effect of SPPW dosage (C_0: 40 mgL⁻¹; V:100 mL; pH:8; temperature: 30°C).

The dye removal was from 83% to 95% for an increase in the SPPW dose from 0.5 gL⁻¹ to 2 gL⁻¹. From the figure, it can be seen that the value of the dye absorbed is a decrease in qe with an increase in the SPPW dose. The amount of dye absorbed reduced from 66.7 to 19.01 mg g⁻¹ for an increase in the SPPW dose from 0.5 gL⁻¹ to 2 gL⁻¹. Decrease in the amount of dye adsorbed of the SPPW with increase in the SPPW dose is mainly due to in saturation of adsorbent sites while the adsorption [14]. The results of this study are the same as those that have been reported by several previous studies [25]-[27].

3.3. Equilibrium studies

Isotherm analysis used to estimate the amount of adsorbent that is applied to adsorb the adsorbate content in solution. [28]. The equilibrium analysis by Langmuir and Freundlich.

The Langmuir model [29] is given by:

\[
\frac{Ce}{qe} = \frac{1}{qm} + \frac{Ce}{qm} \frac{1}{bCo}
\]

Dimensionless adsorption intensity RL given by [30]:

\[
RL = \frac{1}{1 + bCo}
\]

Where
- \(q_e\) : dye adsorbed (mg g⁻¹)
- \(Ce\) : the equilibrium concentration (mgL⁻¹),
- \(qm\) : the monolayer adsorption capacity (mg g⁻¹)
- \(b\) : the Langmuir constant (Lmg⁻¹)
- \(Co\) : the initial concentration of dye (mg L⁻¹).

The value of RL indicates the type of isotherm to be irreversible (RL = 0), favourable (0 < RL < 1), linear (RL = 1) or unfavourable (RL > 1).
The Freundlich isotherm assumes a heterogeneous absorption surface. Freundlich's model is given by [31]:

$$\ln q_e = \ln K_f + \frac{1}{n_f} \ln C_e$$ (5)

Where $K_f$ : Freundlich constants related to adsorption capacity [mg/g (mg/L)$^{-1/n}$]

$n_f$ : Adsorption intensity of adsorbents

|                | Langmuir          |              |
|----------------|-------------------|--------------|
| $b$ (Lmg$^{-1}$) | $q_m$ (mg g$^{-1}$) | $R^2$       |
| 0.0615         | 312.5             | 0.8987      |

|                | Freundlich        |              |
|----------------|-------------------|--------------|
| $K_f$ (mg g$^{-1}$) (mg L$^{-1}$)$^{-1/n}$ | $n_f$ | $R^2$ |
| 14.4313        | 1.214             | 0.9951      |

The Freundlich model describes multilayer adsorption onto heterogeneous surfaces and there are interactions between adsorbent molecules [32]. The values of the Freundlich constant is 1.214, indicating a favourable sorption of methylene blue. Based on correlation coefficient, adsorption models of methylene blue by the SPPW follows the Freundlich model ($R^2 = 0.9951$). The adsorption process of SPPW on methylene blue solution occurs heterogeneously and there is a interactions between the adsorbent causing a high absorption rate.

### 3.4. Kinetic studies

One of the most important factors in the application of the adsorption system is to estimate the process rate, the benefit is to determine the residence time of the adsorbate and the dimensions of the reactor, this is known by the system kinetics analysis [34]. Kinetics studies can be used to determine the adsorption efficiency and adsorption kinetics are important in evaluating the scale-up feasibility of the adsorption process [35]. This process has been studied in an attempt to find a suitable mechanism and kinetics to obtain the best environmental solution. To explore the adsorption mechanism, many kinetic...
models have been recommended [34]. There are several kinetic study models to show the absorption kinetics.

The pseudo-first order [36]:

\[
\frac{1}{q} = \frac{1}{K_1 q_{et}} + \frac{1}{q_e}
\]

(6)

Where \( q_e \) : Dye adsorbed

\( K_1 \) : the pseudo-first order rate constant of sorption

**Figure 5.** pseudo-first order kinetic model.

The pseudo-second order [37]:

\[
\frac{t}{q} = \frac{1}{K_2 q_{e}^2} + \frac{t}{q_{e}}
\]

(7)

Where \( K_2 \) : The pseudo-second order rate constant

The Ritchie kinetic [38]:

\[
\frac{1}{q} = \frac{1}{K_r q_{et}} + \frac{1}{q_e}
\]

(8)

Where \( K_r \) : is the rate constant

**Figure 6.** pseudo-second order kinetic model.

The intraparticle diffusion model [39]:

\[
q = k_p t^{0.5} + C
\]

(9)

where \( k_p \) : the intraparticle diffusion rate constant

\( C \) : constant which gives information about the thickness of the boundary layer

**Figure 7.** Intraparticle diffusion kinetic models.
Table 2. Kinetic parameters for sorption of methylene blue.

|                      | Pseudo first order                   | Pseudo second order                  | Ritchie               | Intraparticle diffusion |
|----------------------|--------------------------------------|--------------------------------------|-----------------------|-------------------------|
|                      | k1 (min⁻¹)                           | qe (mg g⁻¹)                          | R²                    | kp (mg g⁻¹ min⁻¹/2)     | C (mg g⁻¹)              | R²        |
|                      | 0.00049                              | 68.965                               | 0.8426                | 0.815                   | 59.25                  | 0.4576    |
|                      |                                      |                                      |                       |                         |                       |           |

Table 2 shows that pseudo second-order kinetics is the best kinetics model suitable for methylene blue adsorption on SPPW, this can be seen from the R² (0.9997) value which is the highest R² models. This model relates the rate of reaction to the amount of solute adsorbed on the surface and at the adsorbent equilibrium.

4. Conclusions
In this research showed that the agroindustry waste sugar palm powder waste (SPPW) effective used as an adsorbent for methylene blue removal. The amount methylene blue sorption varies at initial pH solution and adsorbent dose. The equilibrium data well interpreted by the Freundlich isotherm with a qm is 312.5 mg g⁻¹. The adsorption process the best described by the pseudo-second order kinetic model.

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