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Application of ANOVA to study the effect of factors on basic dye adsorption

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ABSTRACT
ANOVA one way used at this study to validate the experimental data of the effect of particle size, pH and temperature on the adsorption of methylene blue dye (MB) onto treated kenaf fibre char (H-KFC). The experimental data of the adsorption onto char of particle size of 500-1000 μm, the pH effect (at 100 ppm of initial dye concentration) and the temperature effect (30, 40 and 50 °C) was obtained from our previous study made by Mahmoud et al., (2012). At present work, further adsorption experiments were made on the adsorption onto H-KFC of different particle size (45 and 125-250 μm) and the pH effect (at different initial dye concentration). Based on the ANOVA statistical table, the value of F is lower than FCritical and the probability (P-value) is higher than 0.05, which indicate that the null hypothesis is accepted. Only one value was different at 50 ppm of the particle size effect, where the null hypothesis is rejected. That means there is no significant effect of particle size, pH and temperature at all initial dye concentrations; except the value at initial dye concentration of 50 ppm of the particle size effect.

Keywords: Adsorption, Basic dye, Effective factors, ANOVA

1. Introduction

Dye wastewater is one of the most difficult to treat. Adsorption has been observed to be an effective process for color removal from dye wastewater (Srinivasan and Viraraghavan, 2010). The adsorption capacity of an adsorbent depends strongly on various factors. Particle size of an adsorbent played a very important role in the adsorption capacity of dye (Aljeboree et al., 2014), where it is related to the increase or decreases of the surface area. The pH factor also is an important in the adsorption process especially for dye adsorption. The pH of a medium will control the magnitude of electrostatic charges which are imparted by the ionized dye molecules (Önal et al., 2006). Temperature is an indicator for the adsorption nature whether it is an exothermic or endothermic process (Mohd Salleh et al., 2011).

Although the estimation of maximum amount adsorbed is useful to study the effect of factors on adsorption process, but still not enough to identify the best condition for each effective factor at all initial dye concentrations. Since Analysis of Variance ANOVA is probably the most useful technique in the field of statistical inference (Wikipedia, 2010), therefore ANOVA can be used for deep understand of adsorption process.

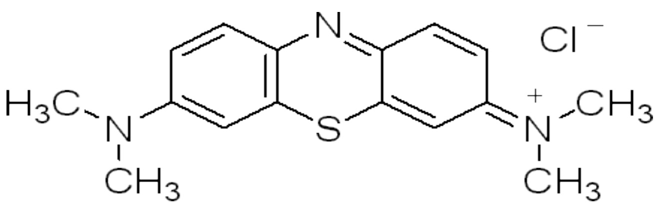
ANOVA one way used at this study to validate the experimental data of the effect of particle size, pH and temperature on the adsorption of methylene blue dye (MB) onto treated kenaf fibre char (H-KFC). The experimental data of the adsorption onto H-KFC of particle size of 500-1000 μm, the pH effect (at 100 ppm of initial dye concentration) and the temperature effect (30, 40 and 50 °C) was obtained from our previous study made by Mahmoud et al., (2012). At present work, further adsorption experiments were made on the adsorption onto H-KFC of different particle size (45 and 125-250 μm) and the pH effect (at different initial dye concentration).

2. Materials and methods

2.1. Adsorbate

Methylene blue dye (MB) was supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia. The properties of MB dye are presented in Table 1. MB dye was made up in stock solution of concentration 1000 mg/L and was diluted to the required concentrations (50-200 mg/L).

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. Adsorbent

The preparation procedure of H-KFC was referred to our previous work (Mahmoud et al., 2012).

2.3. Batch equilibrium studies

Batch adsorption experiment was carried out by adding 0.5 g of H-KFC into a number of 250 mL Erlenmeyer flasks containing 100 mL of different initial MB dye concentration and then placed in a shaking incubator (VS-8480 SRN, Korea) at 150 rpm and 30 °C for 24 h.
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 amount of sorption at time t, q_t (mg/g), was calculated by:

$$q_t = \frac{(C_o - C_t)V}{M} \qquad (1)$$

Where C_t (mg/L) is the liquid-phase concentration of dye at any time.

The amount of adsorption at equilibrium, q_e (mg/g), was calculated by:

$$q_e = \frac{(C_o - C_e)V}{M} \qquad (2)$$

Where C_o and C_e (mg/L) are the liquid-phase concentrations of dye at the initial and at equilibrium, respectively. V (L) is the volume of the solution and M (g) is the mass of dry sorbent used.

2.4. Effect of particle size

The experiment of the effect of particle size on adsorption process was carried out by adding (0.5 g) of different particle sizes of H-KFC (45 and 125-250 μm) into 250 ml Erlenmeyer flasks containing 100 ml of different initial MB dye concentrations (50–200 mg/L). The conical flasks then were placed in a shaking incubator (VS-8480 SRN, Korea) at 150 rpm for 24 h at 30 °C. The result of adsorption MB onto H-KFC of 500-1000 μm was obtained from our previous study (Mahmoud et al., 2012).

2.5. Effect of pH

Test on the effect of pH solution on the adsorption process was conducted by adding 0.5 g of H-KFC into a number of 250 mL Erlenmeyer flasks containing 100 mL of different initial MB dye concentration and then placed in a shaking incubator (VS-8480 SRN, Korea) at 150 rpm for 24 h at 30 °C. The pH was adjusted by adding NaOH (1 M) or HCl (1 M) solutions. The pH measurement was conducted using a pH meter (Jenway-3305, UK).

2.6. The Langmuir isotherm model

The Langmuir isotherm model (Langmuir, 1918) assumes that the adsorption occurs at homogeneous sites at adsorbent surface, and saturation takes place when the dye molecules fill the sites where no more adsorption can occur at that site. The linear form of the Langmuir isotherm can be represented by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (3)$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g), q_{max} is the maximum monolayer adsorption capacity of the adsorbent (mg/g), C_e is the equilibrium concentration of adsorbate (mg/L) and K_L is the Langmuir adsorption constant related to the free energy adsorption (L/mg). The constant (K_L and q_{max}) values can be evaluated from the intercept and the slope of the linear plot of experimental data of (C_e/q_e) versus C_e.

3. Results and discussion

3.1. Characterization of adsorbent

Table 2 BET surface area of different particle sizes of H-KFC

Particle size of H-KFC (µm)	45	125-250	500-1000 (Mahmoud et al., 2012)
BET surface area (m^2/g)	150.142	306.056	346.570

3.2. Effect of particle size

The maximum amount of adsorbed dye for different particle sizes of H-KFC (45, 125-250 and 500-1000 µm) were calculated from Langmuir relation (Figs.1, 2 and 3).

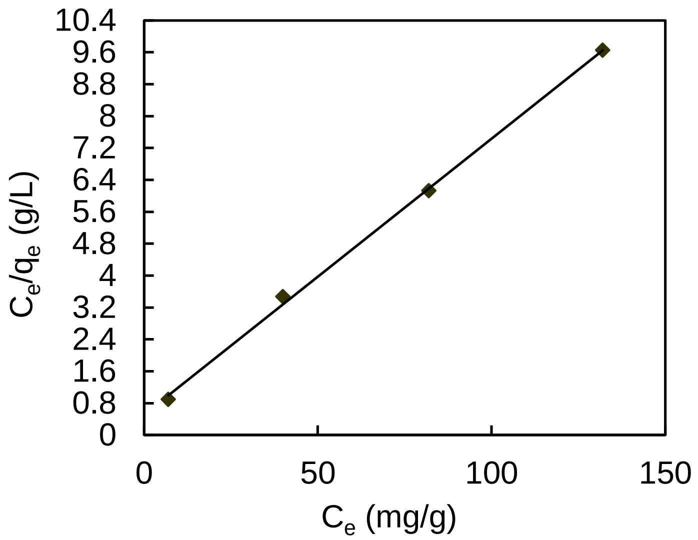


Fig.1. Langmuir isotherm for the sorption of MB onto H-KFC of 45 µm particle size

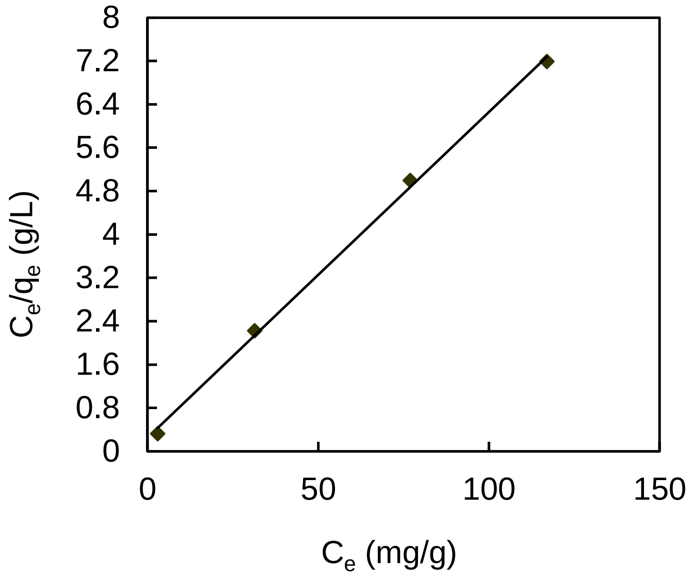


Fig.2. Langmuir isotherm for the sorption of MB onto H-KFC of 150-250 μm particle size

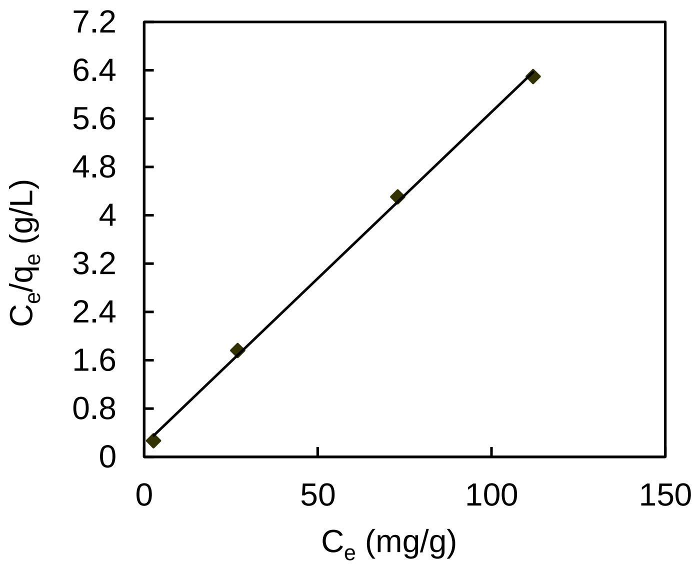


Fig.3. Langmuir isotherm for the sorption of MB onto H-KFC of 500-1000 μm particle size (Mahmoud et al., 2012).

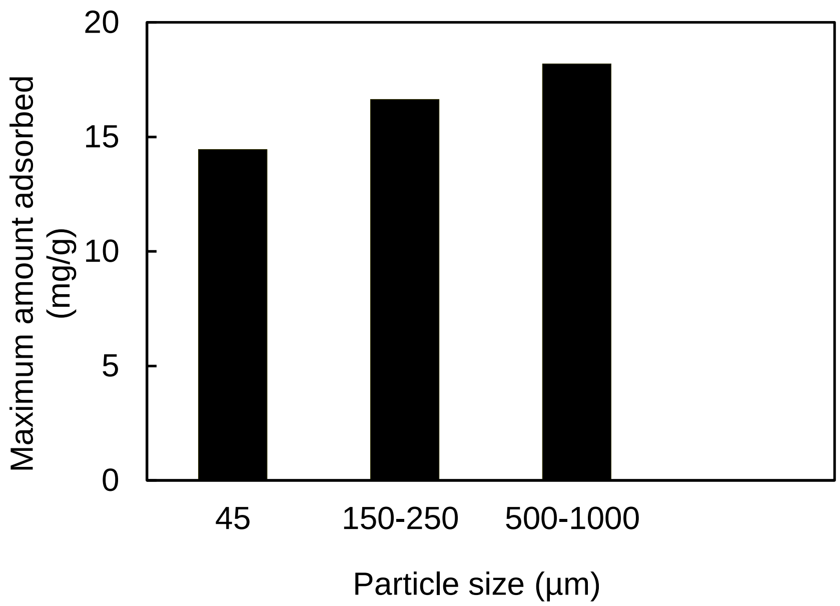


Fig.4. Effect of particle size on maximum adsorption capacity of H-KFC.

According to Fig.4, it was found that the maximum adsorption capacity of H-KFC was increased with particle size increasing. This may be due to increase in the surface area of the adsorbent and accessibility of the adsorbent pores towards the dye (Mittal et al., 2009).

3.3. Effect of pH and temperature

At our previous study (Mahmoud et al., 2012), the effect of pH (at 100 ppm of initial dye concentration) and the effect of temperature (30, 40 and 50 °C) on adsorption of H-KFC were studied. We concluded that the adsorption capacity increase with pH increasing up to 8.5, then decreased for a pH higher than 8.5. Also the maximum adsorption capacity of H-KFC was increased with the increase of temperature.

Further experiment made at this work to study the effect of pH at different initial dye concentrations. The maximum adsorption capacity of H-KFC was found to be increase with pH increasing up to 8.5.

3.4. Analysis of variance (ANOVA)

ANOVA one way used at this study to validate the experimental data of the effect of particle size, pH and temperature on the adsorption process. ANOVA test was done by applying the change in amount of dye adsorbed (mg/g) at each concentration (mg/L). The null hypothesis will be that all population means are equal. If the observed value of $F \geq F_{Critical}$ and the probability (P-value) <0.05 then the null hypothesis is rejected. That mean the data has significant difference between the means of groups. Table 3 list the ANOVA of different particle sizes at different initial dye concentration.

Table 3 ANOVA of different particle size at different initial dye concentration.

Initial dye concentration (ppm)	Particle size (μm)	Average	P-value	F	F critical
50	45	4.444	0.030	3.870	3.259
	125-250	5.324			
	500-1000	7.593			
100	45	7.182	0.131	2.149	3.259
	125-250	8.726			
	500-1000	10.705			
150	45	8.703	0.290	1.282	3.259
	125-250	10.159			
	500-1000	11.785			
200	45	9.153	0.246	1.459	3.259
	125-250	10.820			
	500-1000	12.527			

Table 3 shows that the average value of data of amount of dye adsorbed increase with increasing particle size meaning that the higher the particle size, the higher change in adsorption capacity, which agrees with conclusion of experimental result.

From ANOVA comparison between different particle sizes, it can be noticed that, at 50 ppm the value of F is higher than $F_{Critical}$ and the probability (P-value) is less than 0.05, which indicate that the null hypothesis is rejected. That means there is significant difference between the data at different particle sizes at this concentration. While for other initial dye concentrations (100, 150 and 200 ppm), the value of F is lower than $F_{Critical}$ and the probability (P-value) is higher than 0.05, which indicate that the null hypothesis is accepted. That means there is no significant difference between the data at different particle sizes at 100, 150 and 200 ppm. In other words, the effect of particle size seems obviously at initial dye concentration of 50 ppm.

Table 4 ANOVA of different pH at different initial dye concentration.

Initial dye concentration (ppm)	pH	Average	P-value	F	F critical
50	2.5	5.933	0.653	0.547	2.798
	4.5	6.372			
	6.5	7.593			
	8.5	6.522			
100	2.5	9.488	0.907	0.184	2.798
	4.5	10.100			
	6.5	10.705			
	8.5	10.711			
150	2.5	10.709	0.917	0.169	2.798
	4.5	11.088			
	6.5	11.785			
	8.5	11.948			
200	2.5	11.461	0.906	0.185	2.798
	4.5	12.199			
	6.5	12.527			
	8.5	12.981			

Table 4 list the ANOVA of different pH values at different initial dye concentration. it can be noticed that the average value of data of amount of dye adsorbed seem to be increase with increasing pH except the value at pH of 8.5 and 50 ppm (6.522). That means the higher the pH value, the higher change in adsorption capacity, which agrees with conclusion of experimental result. Although of this conclusion, ANOVA shows that at all initial dye concentrations, the value of F is less than $F_{Critical}$ and the probability (P-value) is higher than 0.05, which indicate that the null hypothesis is accepted. That means there is no significant difference between the data at different pH values.

Table 5 ANOVA of different temperatures at different initial dye concentration.

Initial dye concentration (ppm)	Temperature °C	Average	P-value	F	F critical
50	30	7.593	0.846	0.167	3.259
	40	6.938			
	50	7.606			
100	30	10.705	0.809	0.213	3.259
	40	11.806			
	50	11.850			
150	30	11.785	0.592	0.531	3.259
	40	13.624			
	50	13.893			
200	30	12.527	0.317	1.185	3.259
	40	15.503			
	50	15.945			

From Table 5, it can be observed that the average value of data of amount of dye adsorbed seem to be increase with increasing temperature except the value at 40 °C and 50 ppm (6.938). That means the higher the temperature, the higher change in adsorption capacity, which agrees with conclusion of experimental result. Although of this conclusion, ANOVA comparison between different temperatures showed that at all initial dye concentrations the value of F is less than $F_{Critical}$ and the probability (P-value) is higher than 0.05, which indicate that the null hypothesis is accepted. That means there is no significant difference between the data at different temperatures.

4. Conclusions

Analysis of Variance ANOVA one way used at this study to validate the experimental data of the effect of particle size, pH and temperature on the adsorption of methylene blue dye (MB) onto treated kenaf fibre char (H-KFC). ANOVA analysis showed that the value of F is lower than $F_{Critical}$ and the probability (P-value) is higher than 0.05, which indicate that the null hypothesis is accepted. That means there is no significant difference between the data at different effective factors (particle size, pH and temperature). Only one value was different at 50 ppm of the particle size effect, where the null hypothesis was rejected meaning there is significant difference between the data at different particle sizes at this concentration. In other words, there is no significant effect of particle size, pH and temperature at all initial dye concentrations; except the value at initial dye concentration of 50 ppm of the particle size effect. This may be due to the small difference between the values of amount of dye adsorbed at different values of particle size, pH or temperature.

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