Equilibrium Isotherm Models for the Adsorption of Methylene Blue from Wastewater

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Abstract. This research evaluates the equilibrium isotherm models for the adsorption of Methylene Blue (MB) from wastewater by using sawdust red wood and beech wood. The sawdust acts as the low-cost adsorbent by using agriculture by product in order to treat the wastewaters. The objectives for this study are two folds. Firstly, to choose the significant factors (parameters) for the adsorption process. The factors applied in this study are mass of the adsorbent, concentration of the MB solution, pH of the MB solution and contact time between adsorbent and adsorbate. Secondly to determine the best isotherm model on the adsorption process of MB by sawdust. The isotherm models used in this research are Langmuir, Freundlich, Dubinin-Radushkevich and Temkin. Results show that concentration of MB solution is the one and only significant factor for the adsorption process to occur using red wood. Mass of adsorbate, concentration of MB solution and pH of MB solution are the significant factors for the adsorption process to occur using beech wood. The result for the second objective shows that Freundlich is the best model that describe the adsorption process of beech wood as for MB by red wood, Temkin is the best model.

1. Introduction
One of the major problem for human being and environment is the adverse effect of synthetic dyes [1]. These dyes existed in the market for a long time. Synthetic dyes are used in manufacturing, textile production, paper production and etc. One of the dyes used in dyeing wood, cotton and silk is Methylene Blue (MB). In order to remove these dyes from water channel, researchers introduce various biological matters as an adsorbent due to its low cost.

There are many biological sources that are used as an adsorbent in adsorption process. Example of alternative adsorbsents are coir pith, orange peels, guava seed, rice hull, almond shells and many more. These alternative adsorbsents are environmentally friendly, cheap and easily available [2] where the most effective adsorbent that can be used for dye removal is activated carbon. It has an ability to treat the waste water and produce high quality of clean water.

The usage of dye has given the serious adverse effect to the water channel. Consequently, it will affect the human lives and other living things. Therefore, treatment on the polluted water are necessary. [3], reported that the sewage water from Riyadh contains a certain amount of heavy metals as most of the effluents from industrial waste are discharged into water drainage channels.

According to [4], there are numerous methods used to treat the waste water such as chemical oxidation and reduction, electrochemical methods, chemical precipitation, reverse osmosis and ion exchange. All these treatments are ineffective and expensive. Furthermore, they sometimes generate secondary wastages.
One of the alternatives to replace traditional treatment is by applying or using biosorption (or adsorption using biological materials) method. This method is effective. The advantages of using biosorption process is it has high efficiency of metal removal, low cost, possibility to recover the metal and environmentally friendly materials.

In this research we apply MB (waste in water) as the adsorbate and sawdust as the adsorbent following the research done by [5]. The tremendous results obtained from the experiment (majority of the results gave the adsorption more than 80 %) motivate researchers to apply the Mathematical and Statistical approaches to solve this problem [6]. The objectives of this research are to identify the significant factors for the adsorption process to occur and to determine the best isotherm model on the adsorption process of MB by sawdust red wood and beech wood.

2. Methodology
The data in this research are secondary data obtained from [5] research paper. The number of observations are 34 with four independent variables and two dependent variables. The two dependent variables are mass, concentration, time and pH. Mass is referred to mass of adsorbent in gram (g). Concentration is referred to concentration of adsorbate in part per million (ppm). Time is referred to Time of contact between adsorbent and adsorbate in minutes (min). pH is referred to the pH of MB solution and have no unit. Dependent variable is percentage (%) of adsorption by red wood and beech wood.

Normality, multicollinearity, significance, skewness and kurtosis test are conducted to ensure the data meet the regression assumptions. There are two software being used in this research. They are SPSS Statistics and Microsoft Excel.

The original data are not normal therefore do not meet the regression assumptions. The data are transformed using fractional rank and inverse distribution function (IDF.Normal) as these data are the input to the four isotherm models. The equations and descriptions of the parameters of the four isotherm models chosen are tabulated in Table 1. Table 2 shows the equations and descriptions of the error analysis.

| Isotherm Models       | Description of the parameters                                                                                                               |
|-----------------------|-----------------------------------------------------------------------------------------------------------------------------------------------|
| Langmuir              | \( \frac{C_e}{q_e} = \frac{1}{q_m K_m} + \frac{1}{q_m} C_e \)  \( C_e \) is the concentration of adsorbate at equilibrium in mg/g  \( q_e \) is the amount of adsorbate adsorbed onto the adsorbent in mg/g  \( q_m \) and \( K_m \) is the Langmuir isotherm constant |
| Freundlich            | \( \log q_e = \log K_f + \frac{2}{n} \log C_e \)  \( C_e \) is the concentration of adsorbate at equilibrium in mg/g  \( q_e \) is the amount of adsorbate adsorbed onto the adsorbent in mg/g  \( K_f \) is the Freundlich constant or estimate adsorption capacity (mg/g) \( 1/n \) is the adsorption intensity |
| Dubinin-Radushkevich | \( \ln q_e = \ln C_m - K_{DR} \varepsilon^2 \)  \( \varepsilon = RT \ln (1 + 1/C_e) \)  \( K_{DR} = 1/(2E) \)  \( C_e \) is the concentration of adsorbate at equilibrium in mg/g  \( q_e \) is the amount of adsorbate adsorbed onto the adsorbent in mg/g  \( \varepsilon \) (kJ/mol) is the Polanyi potential  \( K_{DR} \) is the D-R constant (mmol/J/mol)  \( C_m \) (mg/g) is the maximum adsorption capacity  \( C_{ads} \) (mg/L) is the adsorbed ions of metal onto the adsorbent surface  \( E \) is the mean adsorption energy with the unit of (kJ/mol) |
| Temkin                | \( Q_e = B_T \ln K_T + B_T \ln C_e \)  \( B_T = \frac{R T}{b_T} \)  \( C_e \) is the concentration of adsorbate at equilibrium in mg/g  \( q_e \) is the amount of adsorbate adsorbed onto the adsorbent in mg/g  \( B_T \) and \( b_T \) are Temkin constant  \( K_T \) is Temkin (L/g) adsorption potential. |
## Error Analysis

| Error Analysis | Description of the parameters |
|----------------|-------------------------------|
| Marquardt’s Percent Standard Deviation (MPSD) | \[ MPSD = 100 \left( \frac{1}{n-p} \sum_{i=1}^{n} \left( \frac{q_{e,exp} - q_{e,mod}}{q_{e,exp}} \right)^2 \right) \] |
| Least Absolute Errors (LAE) | \[ LAE = \sum_{i=1}^{n} |q_{e,mod} - q_{e,exp}| \] |
| Sum of Squared Residuals (SSR) | \[ SSR = \sum_{i=1}^{n} (q_{e,mod} - q_{e,exp})^2 \] |
| a) Chi-Square Test (CST) | \[ \chi^2 = \frac{\sum_{i=1}^{n} (q_{e,mod} - q_{e,exp})^2}{q_{e,mod}} \] |
| Average Percent Error (APE) | \[ \text{Error(\%)} = \frac{100}{N} \sum_{i=1}^{n} \left| \frac{q_{e,mod} - q_{e,exp}}{q_{e,exp}} \right| \] |

### 3. Results and Discussion

Table 3 shows the descriptive statistics for dependent and independent variables. The mean values for percentage of adsorption by beech wood and red wood are 78.10 and 78.33 respectively. From the value of skewness it can be said that the data distribution is approximately symmetric. The kurtosis values for all variables are negative showing that data have lighter tails than normal.

| Type of Variables | Variables          | Mean  | Standard Deviation | Skewness | Kurtosis |
|-------------------|--------------------|-------|--------------------|----------|----------|
| Dependent         | %Ads Beech Wood    | 78.1055 | 22.68277          | 0.194    | -0.260   |
|                   | %Ads Red Wood      | 78.3393 | 21.74691          | 0.181    | -0.287   |
| Independent       | Mass               | 0.3047  | 0.2905             | 0.0030   | -2.0560  |
|                   | Concentration      | 3.6000  | 3.3481             | 0.0000   | -2.0560  |
|                   | Time               | 47.5000 | 41.8511            | 0.0000   | -2.0560  |
|                   | pH                 | 2.0000  | 0.9850             | 0.0000   | -2.0560  |

### 3.1. Data Pre-Processing

After the transformation, p-value for red and beech wood are 0.999 and 1.000 respectively and thus, the data become normal. The normal probability plot of residuals from Figure 1 (percentage of adsorption...
with red wood) and Figure 3 (percentage of adsorption with beech wood) show that the points were lying very close to the straight line. It can be concluded that the residuals are normally distributed and thus the normality assumptions are satisfied. Figure 2 and 4 show the box plot for percentage of adsorption for red wood and beech wood respectively. The box plot for both figures showed that the data are almost symmetric. There was no skewedness for both red wood and beech wood. The boxplots also show no outlier exist for both red wood and beech wood.

Skewness and kurtosis of the data can be measured by z-score where the data are considered skewed if z-score is less than -1.96 and more than +1.96 (-1.96 < z-score < +1.96). Z-score can be calculated by dividing the skewness value to its standard error of skewness (skewness/standard error of skewness). Same goes to kurtosis. It considered kurtotic if z-score lies in the range of less than -1.96 and more than +1.96 (-1.96 < z-score < +1.96). Z-score for kurtosis can be calculated by dividing the kurtosis value to its standard error of kurtosis (kurtosis/standard error of kurtosis). The z-score (skewness) for red and beech wood are 0.4491 and 0.4813. All the z-scores are within the range of -1.96 and +1.96. Thus, there was no skewness in the data. The z-score (kurtosis) for red and beech were -0.3642 and -0.3299. All the z-scores were within the range of -1.96 and +1.96. Thus, there are no kurtosis in the data. All the tolerance values is 1 which was greater than 0.1 (Tolerance > 0.1). The value of VIF is equal to 1 (less than 10). Thus, multicollinearity does not exist in the data.

3.2. Data Validation

The overall F-test used to check the significance of linear regression model. The model of this study is significant since the p-value is 0.000 for red and beech wood which is less than 0.05 (p < 0.05). The coefficient of determination, R2 for red wood is 0.730 and beech wood is 0.871. These values are closed to one. Thus, the data is fitted with the model.

3.3. Determination of Significant Factors

Table 4 shows the p-value of the independent variables for both red wood and beech wood. From the table, the significant factor for red wood is only concentration where the p-value is less than 0.05 (p <
Since the p-value for mass, time and pH is more than 0.05, thus, mass, time and pH are not the significant factors for the adsorption process to occur. The significant factors for beech wood are mass, concentration and pH. However, time is not the significant factor for the adsorption process to occur.

### Table 4. Individual T-Test for Independent Variables.

| Model     | Red Wood | Beech Wood |
|-----------|----------|------------|
|           | t        | Sig.       | t        | Sig.       |
| Mass      | 2.040    | 0.051      | 5.257    | 0.000      |
| Concentration | -5.304  | 0.000      | -7.431   | 0.000      |
| Time      | 0.823    | 0.417      | 1.869    | 0.072      |
| pH        | 0.205    | 0.839      | 2.285    | 0.030      |

#### 3.4. Application of the Adsorption Isotherm Model

The values of the amount of MB adsorbed at equilibrium (Qe) are calculated using Equation 1. V is the volume of solution (L) and m is the mass of the sawdust (adsorbent) in gram. Figure 5, 7, 9 and 11 show the Langmuir, Freundlich, D-R and Temkin isotherm models for red wood. Figure 6, 8, 10 and 12 show Langmuir, Freundlich, D-R and Temkin isotherm models for beech wood.

\[
Q_e = \frac{C_0 - C_e \times V}{m} \quad (1)
\]
Table 5 and 6 show the ranking of isotherm models based on the error values and R². Table 5 shows the ranking for beech wood. In this table, it is clearly shown that Freundlich has sit the first ranking due to its highest R². The value of R² for Freundlich is 0.4203. The second sit is Temkin, followed by Dubinin-Radushkevich and lastly is Langmuir. The R² for Temkin, Dubinin-Radushkevich and Langmuir are 0.3086, 0.2388 and 0.0147 respectively.

Table 6 shows the ranking for red wood. In this table, it is clearly shown that Temkin has sit the first ranking due to its highest R². The value of R² for Temkin is 0.4203. The second sit is Freundlich, followed by Dubinin-Radushkevich and lastly is Langmuir. The R² for Freundlich, Dubinin-Radushkevich and Langmuir are 0.0146, 0.0135 and 0.000006 respectively.

**Table 5. Ranking of the Isotherm Models for Beech Wood.**

| Isotherm Model          | R²         | MPSD | LAE   | SSR    | CST    | APE    | Ranking |
|------------------------|------------|------|-------|--------|--------|--------|---------|
| Freundlich             | 0.420300   | 671.98 | 279.70 | 8911.87 | 3562.72 | 6291.37 | 1       |
| Temkin                 | 0.308600   | 20948.55 | 488.48 | 7855.39 | 432.10 | 1061.01 | 2       |
| Dubinin-Radushkevich   | 0.238800   | 27151.24 | 612.33 | 11762.64 | 826.18 | 227483.76 | 3       |
| Langmuir               | 0.014700   | 966.17 | 289.16 | 9805.30 | 10144.84 | 8344.22 | 4       |
Table 6. Ranking of the Isotherm Models for Red Wood.

| Isotherm Model                  | R²    | MPSD | LAE   | SSR   | CST   | APE   | Ranking |
|--------------------------------|-------|------|-------|-------|-------|-------|---------|
| Temkin                         | 0.070000 | 1378.49 | 394.70 | 15916.77 | 35573.58 | 276.99 | 1       |
| Freundlich                     | 0.014600 | 389.89  | 258.33 | 15225.80 | 10670.38 | 3867.60 | 2       |
| Dubinin-Radushkevich           | 0.013500 | 8283.25 | 501.47 | 14172.66 | 862.70   | 73371.39 | 3       |
| Langmuir                       | 0.000006 | 9136.16 | 443.04 | 11566.92 | 1600.91  | 75680.37 | 4       |

4. Conclusion

In choosing the best parameter that contribute to adsorption process. The output from the transformed data’s clearly shown that mass of adsorbate is the factor (parameter) that contribute to adsorption process of sawdust to occur. Concentration of MB solution show the one and only significant factor for the adsorption process to occur using red wood. Mass of adsorbate, concentration of MB solution and pH of MB solution show the significant factors for the adsorption process to occur using beech wood.

The second objective of this research is to choose the best isotherm model that describes the adsorption process of MB by sawdust. The results show that Freundlich is the best model that describe the adsorption process of beech wood. As for the adsorption of MB by red wood, the best model is Temkin. Since every single isotherm has at least one minimum error value, thus, error value cannot be measured to determine the best model. R² values play important role in determining the best model in this experiment.

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5. References

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