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# Adsorption Mechanisms of Methylene Blue (MB) Dye on Lignite Coal as Adsorbent

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***Abstract***— *Textile industries are responsible for one of the major environmental pollution problems in the world, because they release undesirable dye effluents which contains dyes mixed with various contaminants. Adsorption is simple and suitable method for the removal of a wide variety of pollutants. The isotherm and adsorption kinetics are the important characteristics that can describe the adsorption mechanism. The objective of this research is to study the adsorption mechanism (isotherms and kinetic model) of MB dye on the adsorption process using the adsorbents made from lignite coal. Different amount of adsorbent (60 mg, 80 mg and 100 mg) was placed in contact with the dye's solution in the required time (5, 10, 20, 30, 40, 50, and 60 min). After the adsorption process was finished, the shaker was turned off and the remained MB dyes concentration was measured using UV-Vis spectrophotometer. The adsorption mechanisme of MB dyes solution fit to Langmuir adsorption isotherm and pseudo second order kinetic model.*

***Keywords***— *Adsorption, isotherm, kinetic,langmuir, pseudo second order.*

## I. INTRODUCTION

Among many pollutants of aquatic ecosystems, dyes are a large and important group of industrial chemicals with over 700,000 tons of waste generated annually [1]. Dyes can be classified into two main categories, namely natural and synthetic dyes. Synthetic dyes are used extensively for textile dyeing and it is estimated that 10–15% of the dye is lost in the effluent during the dyeing process [2]. Methylene Blue (MB) dye is one of the synthetic dyes most often used in the textile industry. All of synthetics dyes can cause eye and skin irritation, respiratory tract irritation and also create permanent injury to the cornea and conjunctiva in human and rabbit eyes [3]. Therefore, environmental legislation commonly obligates textile industries to treat these effluents before discharge into environment.

There are several treatment technologies have been developed and patented to decolorize dyeing wastewater: biological, physical and chemical decolorization such as adsorption, precipitation, oxidation, coagulation, reduction, electrolysis, membrane extraction and integrated treatment processes [4]

Adsorption is one of the outstanding processes for the textile wastewater treatment and has several advantages over another treatment methods. Adsorption is simple and suitable method for the removal of a wide variety of pollutants. It's a non-destructive method and the pollutants are transferred from one phase to another. The adsorption process usually used in tertiary treatment process of textile wastewater after primary treatment process (to remove the suspended solids, excessive quantities of oil, grease, and gritty materials) and secondary treatment process (to provide BOD, COD, TSS removal and stabilize the organic matter) are carried out. The performance of the adsorption process depends on the type of the adsorbent material and high quality adsorbents may be quite expensive [5]. Therefore, there is growing interest in production and application of low cost adsorbents [6]. Natural materials such as coal is one of the widely-known carbonaceous raw materials that could be act as a potentially low-cost adsorbent material for toxic water contaminants [7].

Isotherms and kinetics analysis is of utmost significance to formulate an equation that can be effectively utilized for the goal of design. Most of the research in several countries regarding the isotherm and kinetics of the MB dye adsorption process uses different types of adsorbents such as bituminous coal originating from Maghara, Egypt [8], coal from Rawdown Collary Moira UK [9] and lignite coal originating from Askali, Turkey [7], etc.

The objective of this research is to study the adsorption mechanism (isotherms and kinetic model) of MB dye on the adsorption process using the adsorbents made from lignite coal.

## II. METHODOLOGY

### *2.1 Material*

The adsorbent utilized in this research was made from lignit coal which came from the Tribin Company, East Kalimantan.

### *2.2 Adsorption of MB dye*

Batch adsorption experiments were performed in Erlenmeyer flasks with agitation maintained at 150 rpm, 30oC. About 100 ml of dyes solution was used to prepare 50, 100, 150, 200, and 250 mg/L under an optimum pH of dyes. Different amount of adsorbent (60 mg, 80 mg and 100 mg) was placed in contact with the dye's solution in the required time (5, 10, 20, 30, 40, 50, and 60 min). After the adsorption process was finished, the shaker was turned off and the remained MB dyes concentration was measured using UV-Vis spectrophotometer.

## III. RESULT AND DISCUSSION

### *3.1 Isotherm Adsorption*

In this research, four parameters of isotherm models; the Langmuir, Freundlich, Temkin and Dubinin-R isotherms models, were used for the linear regression analysis to describe the MB dye equilibrium adsorbed onto the adsorbent. The Langmuir model is based on the assumptions that the monomolecular layer is formed during adsorption without any interaction between the adsorbed molecules. The model assumes uniform energies of adsorption into the adsorbent surface and no transmigration of dye molecules in the plane of surface. In contrast, the Freundlich model is based on the assumptions that heterogeneous adsorption occurs on the surface level and adsorbent has active sites with different energies. The Temkin isotherm model assumes that the heat of adsorption of all molecules in the layer would decrease linearly rather than logarithmic with coverage. The uniform distribution of the binding energies up to some maximum binding energy was carried out. Meanwhile, the Dubinin-R model is generally applied to express the adsorption mechanism with a Gaussian energy distribution onto a heterogeneous surface. The linear plots of the Langmuir, Freundlich, Temkin and Dubinin-R isotherms for the MB dye adsorption at different adsorbent dosage are as shown in Figure 1, Figure 2, Figure 3, and Figure 4 respectively, meanwhile the equilibrium constants derived from the four isotherms models are presented in Table 1.

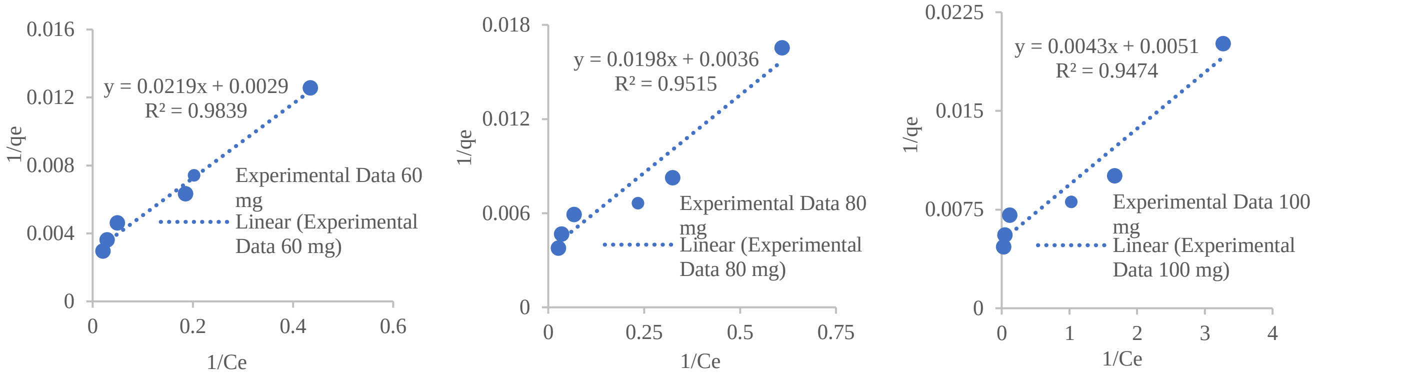



Fig.1. Langmuir isotherm plot for MB dye adsorption.

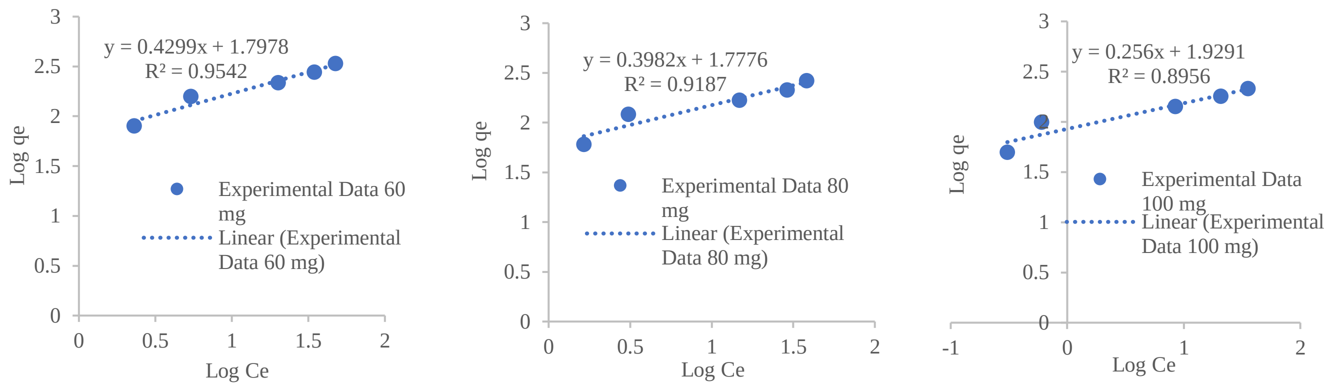



Fig.2. Freundlich isotherm plot for for MB dye adsorption.

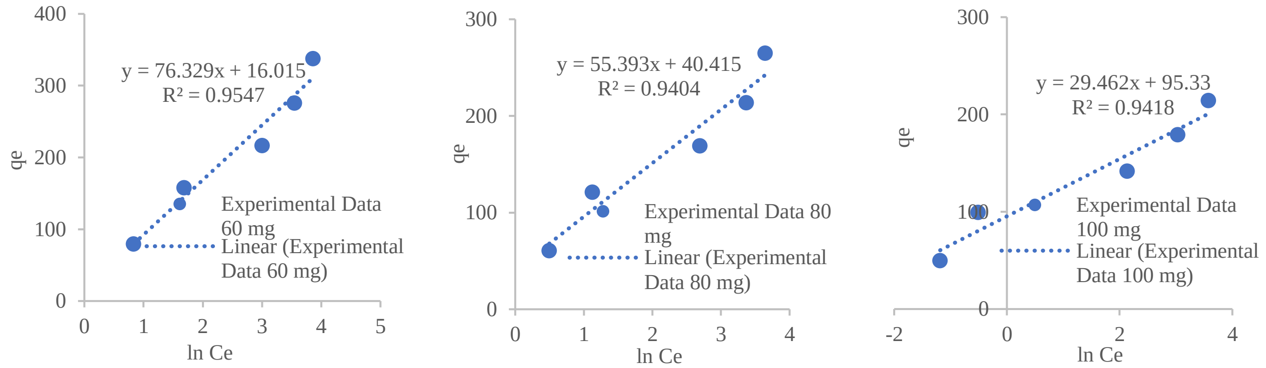



Fig.3. Temkin isotherm plot for for MB dye adsorption.

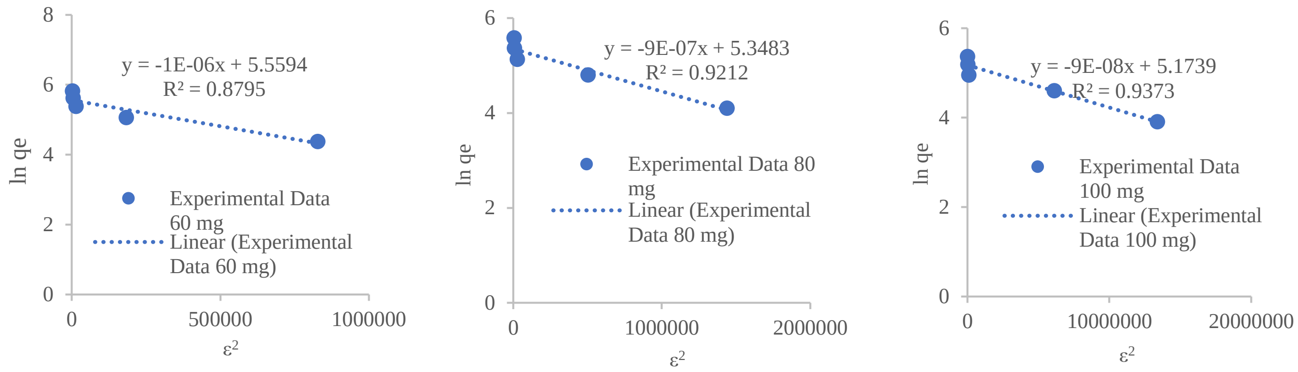



Fig.4. Dubinin-Radushkevich isotherm plot for for MB dye adsorption.

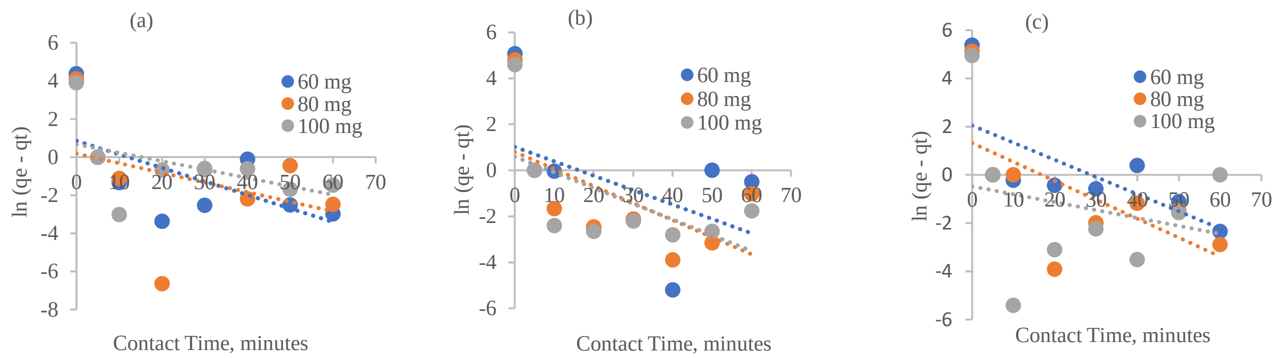
TABLE I. Isotherm model parameters for MB dye adsorption.

| Isotherm Model | Model Parameters | Adsorbent Dosages | | |
|---|---|---|---|---|
| | | 60 | 80 | 100 |
| Langmuir | $q_m$ (mg/g) | 344.8276 | 277.7778 | 196.0784 |
| | $K_L$ (L/mg) | 0.1324 | 0.1818 | 1.186 |
| | $R^2$ | 0.9839 | 0.9515 | 0.9474 |
| | $R_L$ | 0.0702 | 0.0521 | 0.0084 |
| Freundlich | $K_f$ | 62.7769 | 59.9239 | 84.9376 |
| | $n_f$ | 2.3261 | 2.5113 | 3.9063 |
| | $R^2$ | 0.9542 | 0.9187 | 0.8956 |
| Temkin | B (J/mol) | 76.329 | 55.393 | 29.4620 |
| | $A_T$ (L/g) | 1.2334 | 2.0743 | 25.424 |
| | $R^2$ | 0.9547 | 0.9404 | 0.9418 |
| Dubinin-R | $q_m$ (mg/g) | 259.667 | 210.2506 | 176.6022 |
| | $K_{ad}$ (mol$^2$/ k$^2$.J$^2$) | 1.00E-06 | 9E-07 | 9E-08 |
| | E (KJ/mol) | 700.1068 | 745.3560 | 2357.0226 |
| | $R^2$ | 0.8795 | 0.9212 | 0.9373 |

The adsorption isotherm that was observed indicated that the adsorption characteristics of the MB dye at different dosages of the adsorbent were in accordance with the theoretical models offered by Langmuir, Freundlich, Temkin, and Dubinin-R. The equilibrium parameter (RL), which is commonly referred to as the dimensionless constant separation factor, distinguishes between four different types of Langmuir isotherms: irreversible (RL=0), favorable (0<RL<1), linear (RL=1), or unfavorable (RL>1) types. The findings of this investigation indicate that the RL value, which is less than 1, suggests that the adsorption of the MB dye solution is favorable. Correlation coefficients (R2) exhibiting higher values imply a strong fit between the experimental data and the Langmuir and Freundlich isotherm models. Nevertheless, the coefficient of determination (R2) for the Langmuir isotherm model exhibited a strong proximity to R2 ≈ 1. The removal of MB dye from wastewater was conducted utilizing lignite coal as an adsorbent, following the Langmuir isotherm model.

### 3.2 *Kinetic Adsorption*

Since that it fundamentally traces the rate-determining step of the transport mechanism of the dye adsorption process, the kinetic analysis is necessary for determining the best operating parameters for large-scale batch processes. The pseudo-first order and pseudo- second-order kinetic models were carried out to fit the present adsorption data. Using the Lagergren's equation, also known as the pseudo-first order, the '$k_1$' was calculated from the linear plot slope between ln($q_e$-$q_t$) versus '$t$' for different adsorption parameters. Meanwhile, the pseudo-second-order model, was used to characterize the adsorption rate if the depletion of the adsorbate due to adsorption was not negligible. The values for "$q_e$" and "$k_2$" were obtained from the plot of "$t/qt$" versus "$t$," which provided a linear relationship. For all the investigated MB dye concentrations that have been absorbed using lignit coal at constant temperature, constant pH and various initial MB dye concentrations and adsorbent dosage, the pseudo-first and pseudo second-order kinetics were plotted.



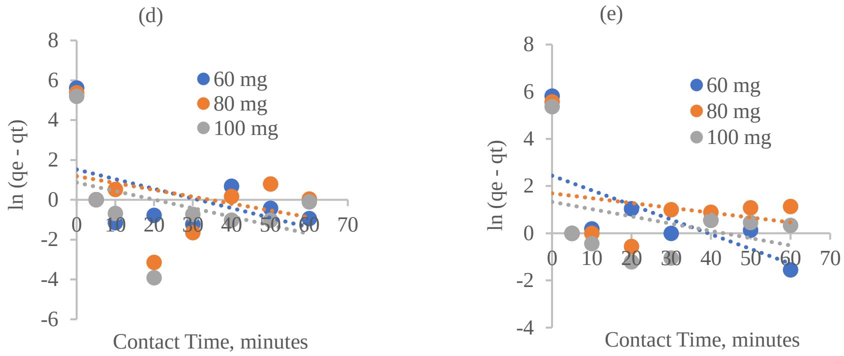



Fig.5. Pseudo-first order kinetic plot for MB dye adsorption (a). 50 mg/L, (b). 100 mg/L, (c). 150 mg/L, (d). 200 mg/L, (e). 250 mg/L.

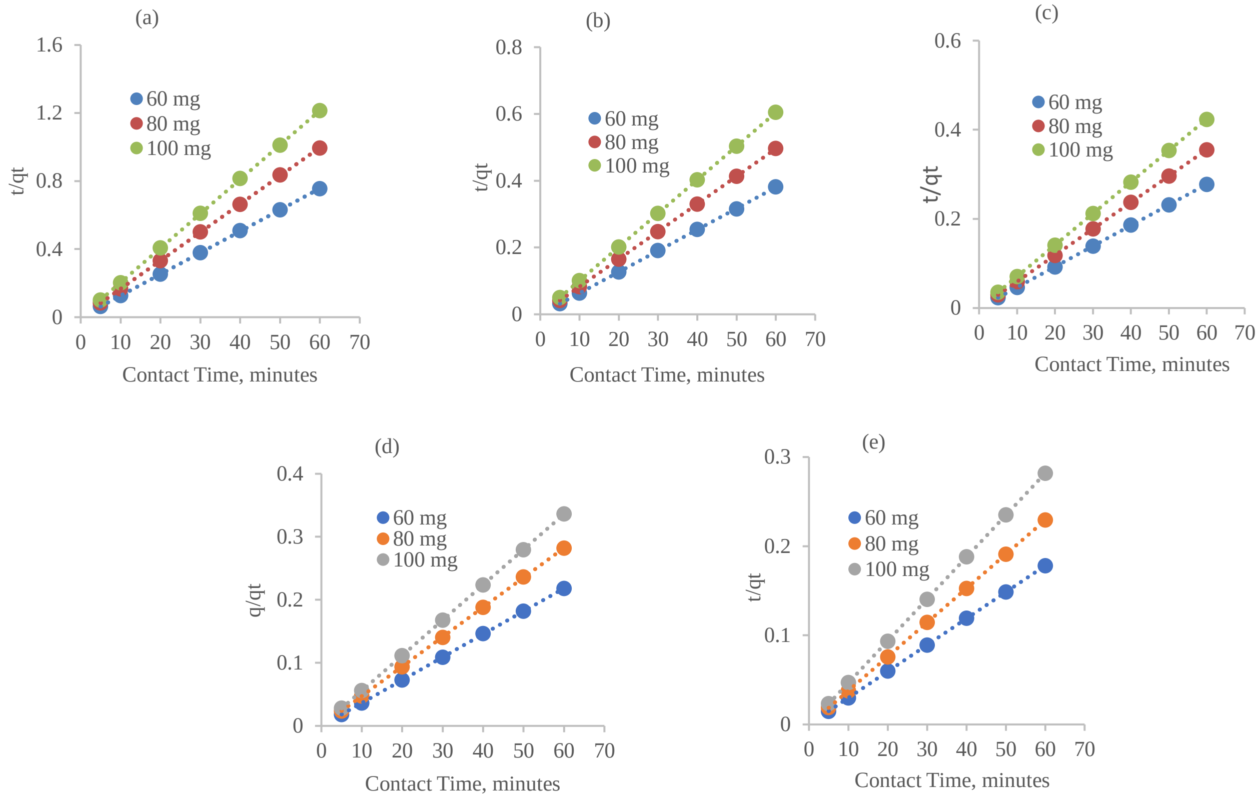



Fig.6. Pseudo-second order kinetic plot for MB dye adsorption (a). 50 mg/L, (b). 100 mg/L, (c). 150 mg/L, (d). 200 mg/L, (e). 250 mg/L.

TABLE 2. Pseudo-first order and pseudo-second order kinetics model parameters for dyes adsorption.

| **Initial Con., mg/L** | **60 mg** | | | | | | **80 mg** | | | | | | **100 mg** | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **Pseudo-first order** | | | **Pseudo-second order** | | | **Pseudo-first order** | | | **Pseudo-second order** | | | **Pseudo-first order** | | | **Pseudo-second order** | | |
| | $q_{e,cal}$ | $k_1$ | $R^2$ | qe,cal | $k_2$ | $R^2$ | $q_{e,cal}$ | $k_1$ | $R^2$ | $q_{e,cal}$ | $k_2$ | $R^2$ | $q_{e,cal}$ | $k_1$ | $R^2$ | $q_{e,cal}$ | $k_2$ | $R^2$ |
| 50 | 2.346 | 0.071 | 0.376 | 79.37 | 0.529 | 0.999 | 1.203 | 0.051 | 0.137 | 60.24 | 0.511 | 0.999 | 1.946 | 0.044 | 0.229 | 49.51 | 0.408 | 1.000 |
| 100 | 2.766 | 0.063 | 0.218 | 158.7 | 0.567 | 0.999 | 2.235 | 0.074 | 0.361 | 120.5 | 0.345 | 0.999 | 1.816 | 0.068 | 0.349 | 99.01 | 1.020 | 1.000 |
| 150 | 7.723 | 0.071 | 0.467 | 217.4 | 0.106 | 1.000 | 3.735 | 0.078 | 0.391 | 169.5 | 0.696 | 1.000 | 0.621 | 0.033 | 0.053 | 140.8 | 0.504 | 1.000 |
| 200 | 4.581 | 0.049 | 0.217 | 277.8 | 1.185 | 1.000 | 3.268 | 0.034 | 0.095 | 212.8 | 0.074 | 1.000 | 2.378 | 0.043 | 0.138 | 178.6 | 0.105 | 1.000 |
| 250 | 11.5 | 0.062 | 0.392 | 333.3 | 0.09 | 1.000 | 5.426 | 0.021 | 0.056 | 263.2 | 0.029 | 1.000 | 3.786 | 0.031 | 0.105 | 212.8 | 0.055 | 1.000 |

The kinetic model data fit for MB dye adsorption process can be seen at Figure 5 and Figure 6 below. Meanwhile the parameters of pseudo-first order and pseudo-second order kinetics models shown at Table 2.

The data presented in Figure 5 indicates that the Lagergren pseudo-first-order kinetic plot, employed to analyze the removal of MB through the utilization of lignite coal as an adsorbent, exhibited a poor fit with the observed adsorption kinetics. In Figure 6, it was observed that the pseudo-second-order model provided the most accurate match for the experimental results of MB dye removal. This conclusion is supported by the high correlation coefficients (R2) obtained from both models, indicating a strong similarity between the pseudo-second-order model and the experimental data ($R2 \approx 1$). Table 2 presents the characteristics associated with the pseudo-first order and pseudo-second order kinetics models, together with the corresponding correlation coefficient values. These parameters were determined for five distinct beginning concentrations of MB dye (ranging from 50 mg/L to 250 mg/L) and various adsorbent dosages (ranging from 60 mg to 100 mg). The pseudo-second order model demonstrated the most accurate fit for the experimental data on the removal of MB dye.

## IV. Conclusion

The adsorption mechanism of MB dye on the adsorption process using lignite coal as adsorbent fits to Langmuir and pseudo-second-order models described the adsorption performance for the MB dye employing the kinetic models and adsorption isotherm.

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