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Isotherm and Kinetic Study of Dyes Solution

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Abstract— *One of the biggest global concerns is industrial wastewater, particularly in light of newly discovered materials like synthetic dyes like methyl orange (MO), methylene blue (MB), and rhodamin B (Rh-B), which are continuously released into the environment and have the potential to cause catastrophic environmental issues. Adsorption is one of the outstanding processes for dyes wastewater. It's an effective, efficient and economical treatment method for the removal of dyes. The isotherm and adsorption kinetics are the important characteristics that can describe the adsorption mechanism. The objective of this research is to study the isotherms and kinetic model of the Rh-B, MB and MO dye adsorption process using adsorbents made from low rank coal from East Kalimantan. 60 mg of adsorbent was placed in contact with the dye's solution (50, 100, 150, 200, and 250 mg/L) in the required time (5, 10, 20, 30, 40, 50, and 60 min) with shaker agitation maintained at 150 rpm, 30^{0}C. The dyes concentration was monitored at predetermined time intervals. At the end of the process, the shaker was turned off, and the remained concentration of dyes was measured using UV-Vis spectrophotometer. The pseudo second order kinetic model and the Langmuir adsorption isotherm fit the dye solution's adsorption mechanisms (Rh-B, MB, and MO).*

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

I. INTRODUCTION

One of the liquid wastes produced by the textile industry is dyes which cannot be completely absorbed, this will cause environmental pollution if not processed properly [1]. Rhodamin B (Rh-B), methylene blue (MB) and methyl orange (MO) dye are some of the synthetic dyes most often used in the textile industry [2,3]. Excessive entry of dyes into the environment will change the pH of the waters so that microorganisms and animals in the aquatic environment will be disturbed [4]. In the human body, the accumulation of this dye will cause serious impacts such as poisoning, liver cancer, respiratory tract irritation, skin irritation, and digestive tract irritation [5].

The adsorption method is a relatively simple, effective, and efficient method for dealing with water pollution by dyes [6]. The adsorption process is a process in which molecules from the gas or liquid phase are entangled on the surface of a solid or liquid. The molecules that are bound to the surface are called adsorbates while the substances that bind are called adsorbents. A type of adsorbent that is safe and environmentally friendly is needed so that biological materials are used that do not pollute the environment which are usually called natural adsorbents or commonly called biosorbents [1].

One of the important characteristics that can describe the adsorption mechanism and rate of adsorption of a fluid by an

adsorbent over a period is the isotherm and adsorption kinetics which depend on the physical and chemical properties of the adsorbent as well as the conditions during operation. The adsorption isotherm was evaluated using the Langmuir, Freundlich, Temkin, Dubinin Raduskevich isotherm, meanwhile the pseudo first order, pseudo second order, elovich and intraparticle diffusional kinetic models usually applied to determine the adsorption isotherm and kinetic model for adsorption process [7]. Analysis of isotherms and adsorption kinetics is important to develop equations that can be used for design purposes.

This research aims to study the isotherms and kinetic model of the Rh-B, MB and MO dye adsorption process using adsorbents made from low rank coal from East Kalimantan.

II. METHODOLOGY

2.1 Material

The raw material used in this research was the adsorbent derived from low rank coal of East Kalimantan which came from the Batuah District, Kutai Kartanegara Regency, East Kalimantan.

2.2 *Adsorption of dyes solution*

Batch adsorption experiments were performed in Erlenmeyer flasks with agitation maintained at 150 rpm, 30^{o}C. For the purpose of preparing 50, 100, 150, 200, and 250 mg/L of dye at the ideal pH, about 100 ml of dye solution was utilized. The dyes solution was exposed to 60 mg of adsorbent for the necessary amount of time (5, 10, 20, 30, 40, 50, and 60 min), and the dyes concentration was checked at prearranged intervals. At the end of the process, the shaker was turned off, and the remained concentration of dyes was measured using UV-Vis spectrophotometer.

III. RESULT AND DISCUSSION

3.1 Isotherm Adsorption

In this research, two isotherm models were used, namely the Langmuir and Freundlich isotherm models, for linear regression analysis to describe the equilibrium of dyes adsorbed on the adsorbent. These two models are the most widely used models to analyze dye adsorption from the liquid phase of simulated textile wastewater. The Langmuir model assumes that monomolecular layers are formed during adsorption without any interaction between the adsorbed molecules. This model assumes uniform adsorption energy onto the adsorbent surface and no transmigration of dye molecules on the surface. In contrast, the Freundlich model assumes that heterogeneous adsorption occurs on the surface and the adsorbent has active sites with different energies. Linear plots of Langmuir and Freundlich isotherms, for Rh-B, MB and MO dye adsorption are shown in Fig. 1, and Fig. 2 respectively. The equilibrium constants obtained from the two isotherms are presented in Table 1.

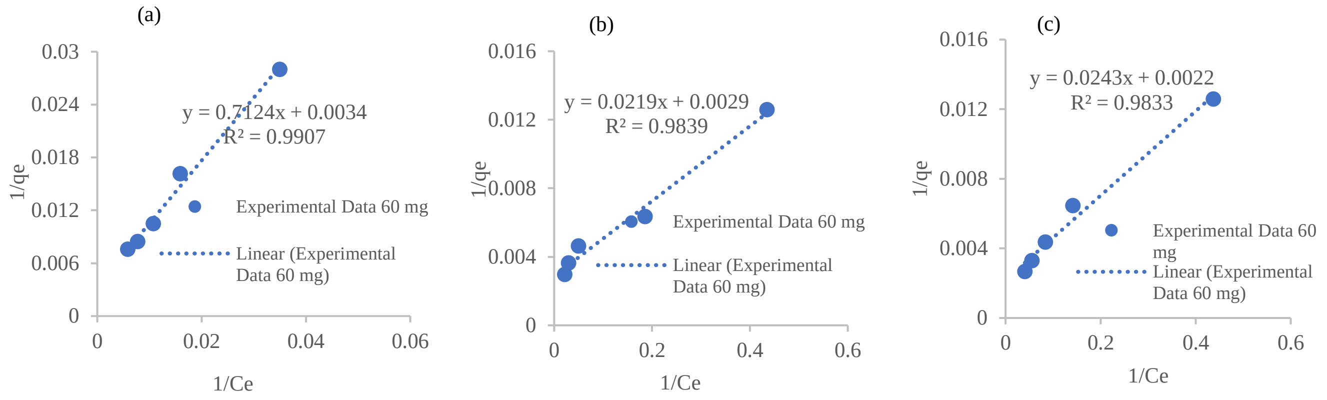

Fig.1. Langmuir isotherm plot for (a). Rh-B, (b). MB, (c). MO dye adsorption.

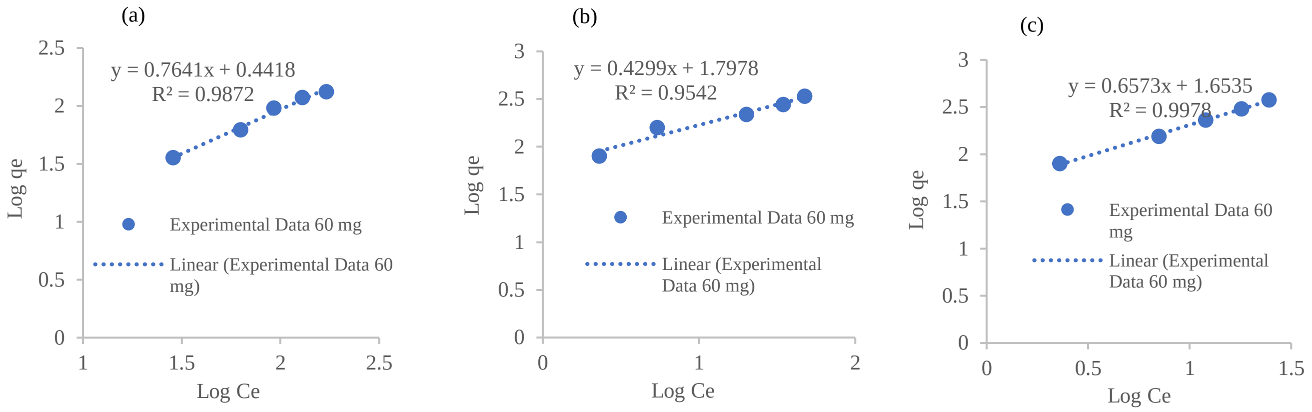

Fig.2. Freundlich isotherm plot for (a). Rh-B, (b). MB, (c). MO dye adsorption.

TABLE I. Isotherm model parameters for dyes adsorption.

Isotherm Models	**Isotherm Parameters**	**Dyes Solution**		
		Rh-B	**MB**	**MO**
Langmuir	q_m (mg/g)	294.1176	344.8276	454.5455
	K_L (L/mg)	0.0048	0.1324	0.0905
	R_L	0.6769	0.0702	0.0995
	R^2	0.9907	0.9839	0.9833
Freundlich	n_f	1.3087	2.3261	1.5214
	K_f	2.7657	62.7769	45.0298
	R^2	0.9872	0.9542	0.9978

The adsorption isotherm was observable and showed that dyes adsorptive behaviour satisfied to Langmuir and Freundlich assumptions. The dimensionless constant separation factor, also known as the equilibrium parameter (R_L), indicated the Langmuir isotherm types, either the irreversible (R_L=0), favourable (0<R_L<1), linear (R_L=1) or unfavourable (R_L>1) types. In this study, the R_L<1 showed that the adsorption of Rh-B, MB and MO dyes are favourable. A higher value of correlation coefficients (R^2) suggested that the experimental data fitted well with the Langmuir and Freundlich isotherm models. However, for the Langmuir isotherm model, the $R^2 \cong 1$, the removal of Rh-B and MB dye solution using low rank coal as adsorbent obeyed the Langmuir isotherm model, meanwhile the removal of MO dye solution obeyed the Freundlich isotherm model.

3.2 Kinetic Adsorption

The kinetic analysis is necessary for determining the best operating parameters for large-scale batch processes. In the present study, the pseudo-first order and pseudo-second order kinetic models were carried out to fit the present adsorption data. For all the investigated dyes concentrations that have been absorbed at 60 mg adsorbent dosage, constant temperature, and pH but with various initial dye concentrations, the pseudo-first and second-order kinetics were plotted.

Figures 3 and 4 show the kinetic model data fit for the Rh-B, MB, and MO dye adsorption process, meanwhile the parameters of pseudo-first order and pseudo-second order kinetics models shown at Table 2.

Fig. 3 shows that the Lagergren pseudo-first-order kinetic plot for Rh-B, MB and MO removal did not fit well with the adsorption kinetics. Meanwhile, the pseudo-second order was shown in Fig. 4 to be the best fit for the Rh-B, MB, and MO dyes removal experimental data. Table 2 represent the parameters of pseudo-first order and pseudo-second order kinetics models, together with the correlation coefficients values obtained at different initial dyes concentrations (50 mg/L to 250 mg/L). The model that best fits the elimination of the Rh-B, MB, and MO dyes was the pseudo-second order, as indicated by the correlation coefficients (R^2) from both models, which show that the pseudo-second order was extremely near to $R^2 \cong 1$.

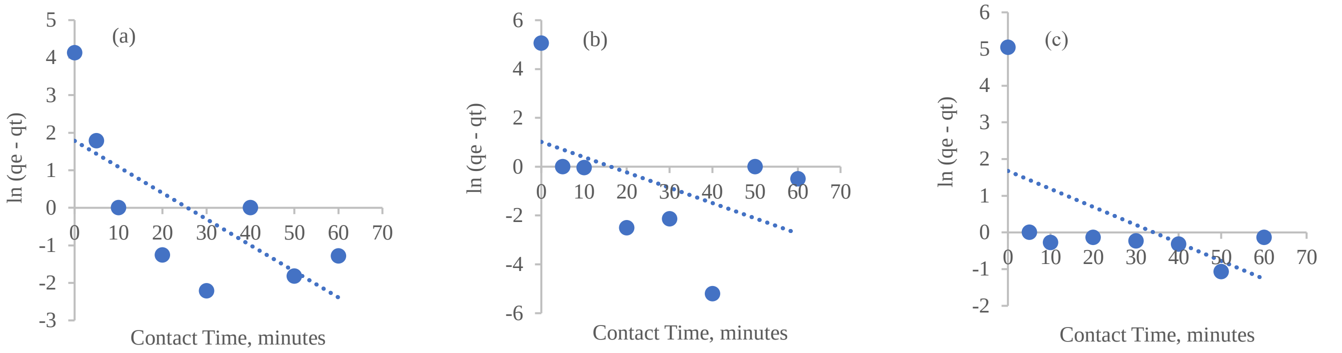

Fig.3. Pseudo-first order kinetic plot for (a). Rh-B, (b). MB, (c). MO dye adsorption.

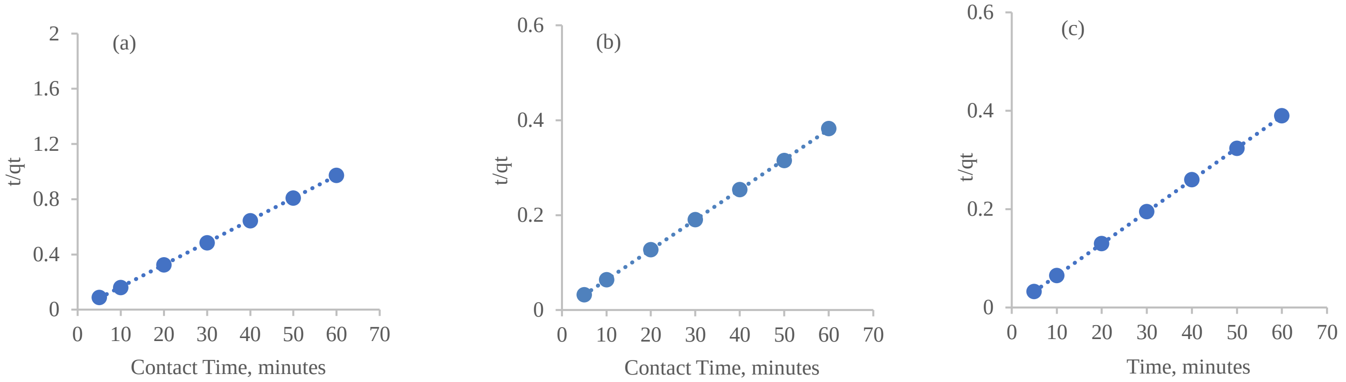

Fig.4. Pseudo-second order kinetic plot for (a). Rh-B, (b). MB, (c). MO dye adsorption.

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

Initial Con., mg/L	Rh-B						MB						MO					
	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	5	0.06	0.542	35.71	0.118	0.999	2.346	0.071	0.376	79.37	0.529	0.999	1.833	0.036	0.149	79.37	0.794	1.000
100	5.957	0.067	0.512	62.11	0.079	0.999	2.766	0.063	0.218	158.7	0.567	0.999	5.348	0.049	0.312	153.9	2.112	1.000
150	6.673	0.069	0.314	96.15	0.024	0.999	7.723	0.071	0.467	217.4	0.106	1.000	5.634	0.055	0.307	227.3	0.194	1.000
200	11.49	0.056	0.455	119.1	0.025	0.999	4.581	0.049	0.217	277.8	1.851	1.000	31.82	0.080	0.429	303.0	0.055	1.000
250	9.246	0.074	0.429	133.3	0.038	0.999	11.49	0.062	0.392	333.3	0.09	1.000	20.57	0.078	0.404	370.4	0.146	1.000

IV. CONCLUSION

Based on the adsorption isotherm and kinetic models for the solutions of Rh-B, MB, and MO dyes, the Langmuir and pseudo-second-order models explained the adsorption behavior.

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