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Research Article

Preparation of Ca/Al-Layered Double Hydroxides/Biochar Composite with High Adsorption Capacity and Selectivity toward Cationic Dyes in Aqueous

Risfidian Mohadi[1,3], Neza Rahayu Palapa[2], Aldes Lesbani[2,3,*)]

[1]Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, South Sumatera, Indonesia.
[2]Graduate School, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, South Sumatera, Indonesia.
[3]Research Center of Inorganic Materials and Complexes, Faculty of Mathematics and Natural Sciences, Universitas Sriwijaya, South Sumatera, Indonesia.

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Abstract

Widely reports have evaluated the use of biochar (BC) composites to layered double hydroxide (LDH) to adsorb dyes from wastewater. However, its applicability for adsorbing a mixture of cationic dyes such as Malachite green (MG), Rodhamine-B (Rh-B), and Methylene blue (MB), which causes carcinogenic and mutagenic effects on aquatic life, has not been studied. In this work, we compared the performance of CaAl-LDH/BC adsorbent with or without the addition of BC in the adsorption of cationic dyes. The adsorption study was prepared in a batch system using various temperatures, concentrations, and also contact time. The results of the characterization of Ca/Al-Biochar composite showed the unique diffraction of XRD pattern, and also showed two characteristics of starting materials. Surface area analysis by BET method showed Ca/Al-Biochar composite has a higher surface area than starting material. The results of the adsorption study of MG showed that Ca/Al-Biochar follows the pseudo-second-order kinetic model. The adsorption capacity of MG on Ca/Al-Biochar was up to 71.429 mg/g and shows selectivity toward MG in an aqueous solution.

Keywords: Al-Layered Double Hydroxides; Cationic Dyes; Ca/Al-LDH; Biochar; Composite Materials

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1. Introduction

The dyes are dissolved organic compounds. Dyes have high solubility in water that is difficult to remove by conventional methods [1]. Dyes are used in various industries, such as: textiles, plastics, papers, pharmaceuticals, and cosmetics. Dyes are an essential type of pollutants in industrial wastewater and cause serious environmental problems [2]. The effect of dyes includes a threat to human health owing to mutagenic and carcinogenic [3]. Various methods for dye removal in the aquatic environment were attempted, such as:

* Corresponding Author.
Email: aldeslesbani@pps.unsri.ac.id (A.Lesbani)

adsorption, coagulation / flocculation, photocatalytic decolorization, microbial decomposition, and electrochemical methods [4–7].

Among these methods, adsorption has been reported to be the most effective method, which has a relatively economical, flexible, and simple design, easy in operation, and efficient for the treatment of dyes on wastewater. The effectivity of the adsorption process is related to the quality and properties of the adsorbent. Several adsorbents have been used for the removal of dyes from wastewater [8]. Adsorbents that can be used to adsorb dyes from wastewater include activated carbon, algae, alumina-MOF, sawdust modification, kaolin, bentonite, and layered double hydroxide (LDH) [9–11]. However, LDH is a favored adsorbent due to its low cost, high stability, low toxicity, reusability, and facile synthesis. The LDH is a two-dimensional (2D) nanostructured material also termed anionic clay or hydrotalcite. The chemical composition of LDH is generally represented as:

$[M^{2+}{}_{1-x}M^{3+}{}_{x}\text{-}(OH)_2]^{x+}[(A^{n-}).mH_2O]^{x}$

where M^{2+} and M^{3+} represent bivalent and trivalent cations respectively, while, A^{n-} are interlayer anions. Another aspect favoring the use of LDH as adsorbents for anionic dyes is their simple intercalation and modification techniques, enhancing their removal efficiency [12].

Removal of dyes by LDH has been reported by many researchers. There are two types of dyes, namely anionic (methyl orange) and cationic (crystal violet), which are used to study the ability of Ni/Al LDH in removing dyes in an aqueous solution [13]. The granular structure of LDH can limit the adsorption capacity. Biochar (BC) can assist maximize the work of LDH in removing pollutants. Li *et al.* [14] were reported that the precipitation to composite preparation as adsorbent consisted of core-shell Fe_3O_4-LDHs. The kinetics study results from the adsorption process of congo red dye using composite MgFe showed a significant maximum capacity of around 9127.08 mg/g [15]. Research conducted by Meili *et al.* [16] utilizes a composite of MgAl-LDH with BC to remove cationic dyes in an aqueous solution. This adsorption process obtained a higher maximum capacity at 323 K of 406.47 mg/g and achieved equilibrium up to 20 minutes with an adsorption ability reaching 95% at pH 12. As similarly reported by Palapa *et al.* [11] using a composite of CuAl-BC for the adsorption of Malachite green (MG) reaching equilibrium at 40 minutes with an adsorbed concentration of 108.96 mg/L.

Among all these literature research have been studied, the adsorption of the dyes have been studied widely, but in this research, the preparation of Ca/Al LDH and its composite with BC to form Ca/Al-Biochar is used to remove the mixture cationic dyes in aqueous solution to compare the competitive ones to adsorb more into Ca/Al-Biochar. The competition of adsorbed dyes will be studied in selectivity adsorption. Various conditions of the process of adsorption were studied, such as: dye mixture selectivity, times adsorption, dye concentration, and temperature adsorption. The mixture adsorption selectivity was carried out using cationic dyes, *i.e.* MG, Rhodamine-B (Rh-B), and methylene blue (MB), as shown in Figure 1. The kinetics of adsorption, isotherm, and thermodynamics of the adsorption process of dye using Ca/Al LDH, BC, and Ca/Al-Biochar will be discussed in this article.

2. Materials and Methods

2.1 Chemical and Instrumentations

The chemicals, such as: calcium(II) nitrate, aluminum(II) nitrate, and sodium hydroxide, were analytical grade (p.a) from Merck and Sigma-Aldrich. Water was supplied from the Research Center of Inorganic Materials and Complexes FMIPA Universitas Sriwijaya. The purified water was obtained after cycling proses using Purite® ion water purification system. Characterization of materials was

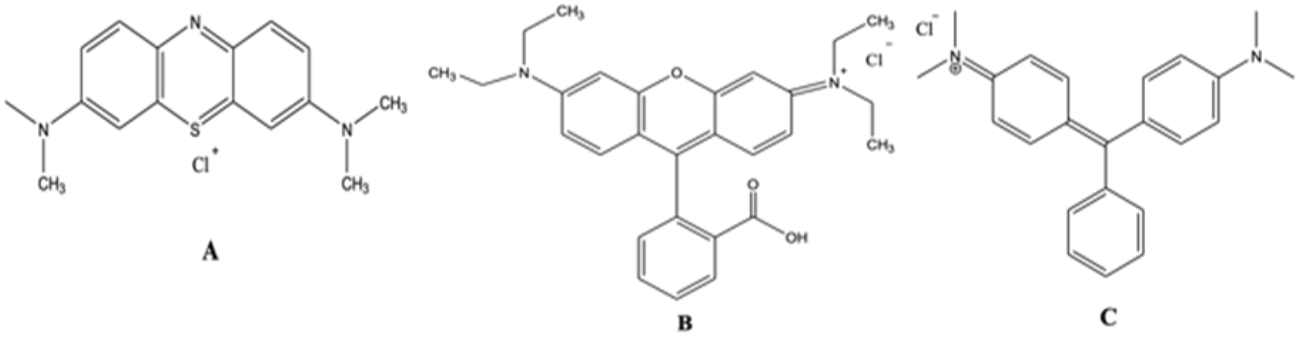

Figure 1. Chemical structure of cationic dyes: MB (A), Rh-B (B), and MG (C).

conducted using XRD Rigaku miniflex-6000. Materials were scanned from 5-80 degrees at a scan speed 1 deg/min. Functional groups were analyzed using FT-IR Shimadzu Prestige-21 at wavenumber 400–4000 cm^{-1} using KBr pellet. Adsorption-desorption of N_2 was conducted using Quantachrome Micrometic ASAP. The concentration of dyes was measured using Spectrophotometer UV-Visible Biobase BK-UV 1800 PC.

2.2 Biochar Preparation

Rice husk-BC was produced through thermal treatment of the rice husk; the thermal treatment was carried out in a furnace at 873 K under nitrogen flow (283 K/min) for two hours. Thereafter, the reactor was cooled down and the prepared BC was characterized. The BC thus prepared was used in the preparation of composites material and the adsorption experiments.

2.3 Preparation of Ca/Al-LDH

Ca/Al LDH was synthesized using the co-precipitation method. A 100 mL of calcium(II) nitrate 0.75 molar was mixed with 100 mL of aluminum(II) nitrate. The mixture was stirred for an hour and pH was adjusted using NaOH 2 M until 10. The reaction was kept at 333 K for 12 hours to form Ca/Al LDH. The solid material was filtered and washed with water then dried at 373 K overnight.

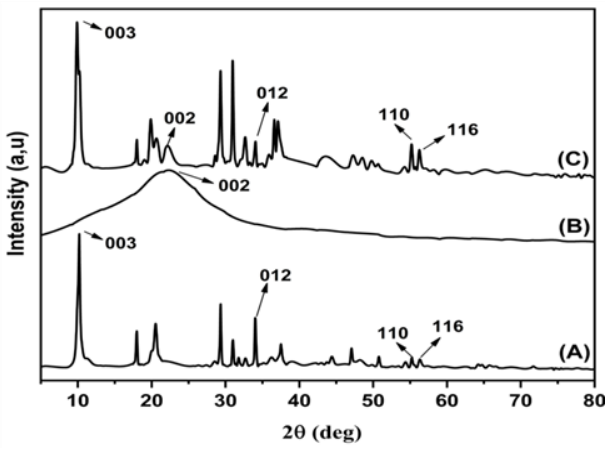

Figure 2. XRD powder patterns of Ca/Al LDH (A), BC (B), and Ca/Al-Biochar (C).

2.4 Preparation of Ca/Al-Biochar

The preparation of Ca/Al-Biochar was carried out by calcium(II) nitrate 10 mL and aluminum(II) nitrate 10 mL with a molar ratio 3:1. In other beakers, a three g of rice husk BC was dissolved by 10 mL water. The metal salt solution was added to BC solution. The pH of the mixture was adjusted to 10 by addition 2 M sodium hydroxide. The reaction was stirred at 333 K for three days. The composite was filtered and dried at room temperature overnight.

2.5 Adsorption Selectivity Study

The selectivity adsorption process of dyes was carried out by 20 mL of mixtures dyes (MG, MB, Rh-B) with 2 mg Ca/Al and Ca/Al-Biochar, respectively. The reaction was stirred for several minutes and concentration of each dye was analyzed by UV-Vis spectrophotometer. The adsorption process was studied by variation of adsorption times, initial concentrations, and adsorption temperatures using maximum adsorption amount of dye in the selectivity study. The variation of adsorption times was conducted at 5–180 minutes. The variation of concentrations was studied at 50, 60, 70, 80, and 90 mg/L of dye. Variation of adsorption temperatures was carried out at 303, 313, 323, and 333 K. Concentration of dye on the solution was analyzed using UV-Vis spectrophotometer.

3. Results and Discussion

XRD powder pattern of adsorbent was presented in Figure 2. The diffraction peak of Ca/Al-Biochar shows the characteristic of Ca/Al LDH according to JCPDS 31-0245 and broad diffraction of BC. The characteristic of Ca/Al LDH was denoted with reflection (003), (006), (012), (110), and (116), which was indicated the interlayer space of LDH at (003). According to Palapa *et al.* [17] the reflections of (003), (006), and (110) were essential characteristics to determine a crystallographic parameter. The interlayer space at (003) indicates the composites of BC took place on the interlayer and surface was increased from 8.42 Å (Ca/Al LDH) to 9.00

Table 1. Surface area properties of materials.

Materials	Surface Area (m^2/g)	Pore Volume$_{BJH}$ (cm^3/g)	Pore Diameter$_{BJH}$ (nm)	Interlayer $d_{(003)}$ (Å)
Ca/Al LDH	29.333	0.0072	13.033	8.42
BC	50.936	0.00475	12.089	–
Ca-Al-LDH/BC	158.291	0.0174	12.474	9.00

Å (Ca/Al-Biochar). The increase of interlayer distance was also related to the increased surface area. The surface area analysis was listed in Table 1.

The surface area and pore analyses were determined using BET and BJH method, respectively. The surface area after formation of Ca/Al-Biochar composites was increasing fifth-fold from 29.333 m^2/g to 158.291 m^2/g. The increased interlayer of Ca/Al LDH was related to the characteristic of starting materials. The BC has high surface area properties, which can reduce the agglomeration of LDH [18]. Besides, the decrease in pore diameter and increase the pore volume occurs due to the composites of BC particles within the LDH layers. This can be attributed to the intercalation of BC within the LDH layers, leading to the formation of larger pores, which can act as active binding sites [19].

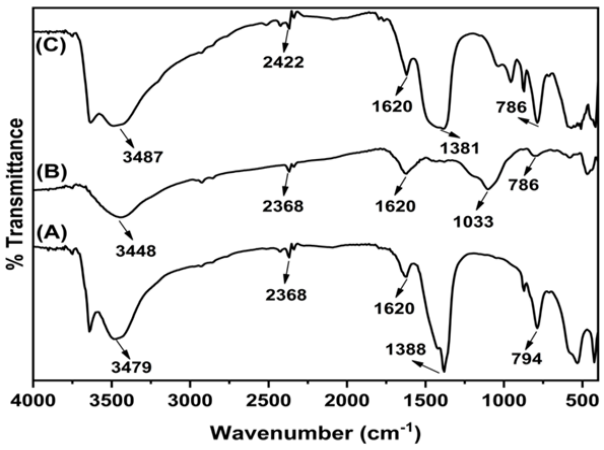

Figure 3. FTIR Spectrum of Ca/Al LDH (A), BC (B), and Ca/Al-Biochar (C).

FT-IR spectra for Ca/Al LDH, BC and Ca/Al-Biochar were shown in Figure 3. The FT-IR spectra of Ca/Al LDH and Ca/Al-Biochar showed a similar spectrum. The characteristic of Ca/Al LDH has intense nitrate bending at 1381 cm^{-1}. The stretching and bending vibrations of OH^- from H_2O were found at wavenumber 3480 cm^{-1} and 1620 cm^{-1}, respectively. Thus, the vibrations of M^{2+} and M^{3+} were indicated at under 800 cm^{-1}. The unique vibration of BC appeared at 1103 cm^{-1}, which was denoted as a silicate-oxide and at 470 cm^{-1} as aluminum-oxide.

The performance of Ca/Al LDH, BC and Ca/Al-Biochar as selective adsorbents was tested to remove dye mixtures. In addition, the selective adsorption from the mixtures was important to determine the adsorption capacity and active sites adsorbent. Therefore, mixing three cationic dyes on aqueous solution, *i.e.* MG, MB, and Rh-B, were studied for the adsorption experiments by Ca/Al LDH, BC and Ca/Al-Biochar, which are presented in Figure 4.

MG was more adsorbed from mixtures solution using Ca/Al LDH after 90 min, while MB and Rh-B showed slightly decreased adsorption after 90 min. Thus, Ca/Al-Biochar exhibited high selectivity for cationic dyes actually for MG. MG was removed entirely at 90 min. This phenom indicated that the larger surface area of Ca/Al-Biochar than pristine LDH affected the adsorption of cationic MG. Also, the moderate adsorption ability for Rh-B and MB than MG is probably caused by the larger size of Rh-B than MG and MB. In another case, as reported by Wan *et al.* [20], the presence of pH can be affected the

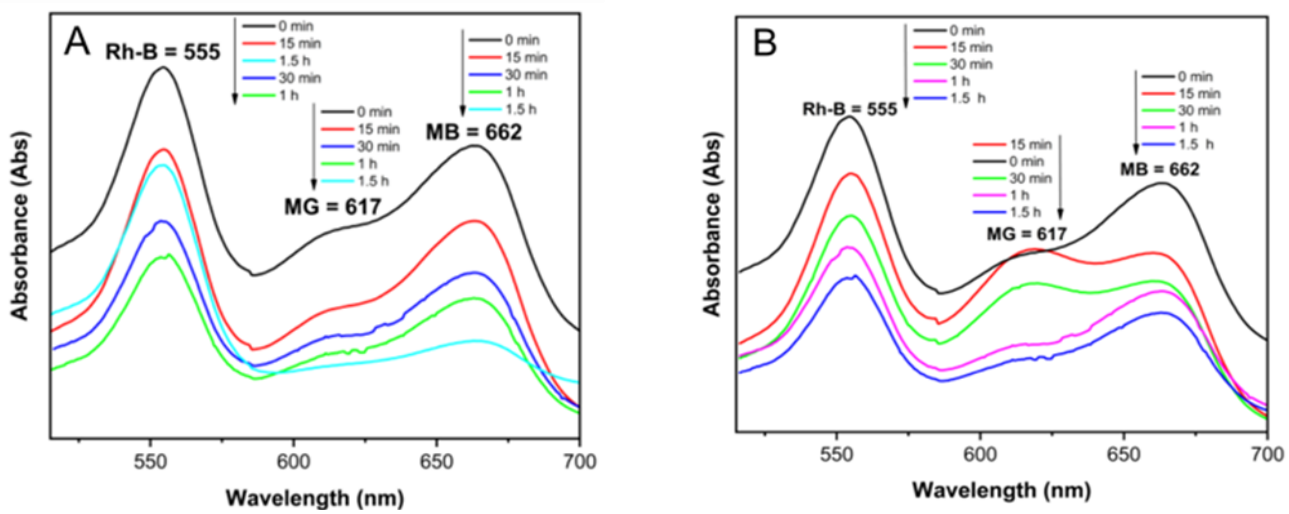

Figure 4. Adsorption selectivity of cationic dyes mixtures adjusted at pH 7 in various adsorption time (A) Ca/Al LDH and (B) Ca/Al-Biochar.

selectivity of adsorption in a mixture between MB and MG due to cationic dyes which have positive charges and LDH has positive charges which did not favor the adsorption of positively charged dye cations due to electrostatic repulsion. Therefore, Ca/Al-Biochar showed good adsorption ability and selectivity toward MG on aqueous solutions.

Furthermore, MG was selected as a representative dye to determine adsorption study in an aqueous solution. Firstly, the adsorption process was tested in several pH conditions, acid until base conditions as presents in Figure 5. The effect of pH condition on Ca/Al LDH showed that acid or base conditions did not affect dye adsorbed. However, on Ca/Al-Biochar, it was increased sharply until pH 6 and decreased remarkably in base condition. The value of MG adsorbed onto Ca/Al-Biochar uptake 180 mg/g at pH 6. According to Das *et al.* [19] the increasing dye adsorbed was due to surface-active charge of materials and electrostatic bonds between surface and dye molecule.

The adsorption process has studied the effect of time adsorption, temperature and initial concentration. The adsorption process was set between pH 6-7 for all materials. The effect of adsorption times was calculated using kinetic parameter models, *i.e.* pseudo first order (PFO) and pseudo second order (PSO). Figure 6 was presented the MG adsorbed capacity *vs.* contact time adsorption, which was calculated using PFO and PSO models. The equations were described as:

$$\log\left(q_e - q_t\right) = \log q_e - \left(\frac{k_1}{2.303}\right)t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (2)$$

where, q_e is dye adsorbed capacity at equilibrium (mg/g); q_t is dye adsorbed capacity at times (mg/g); t is time adsorption (min); k_1 is kinetic adsorption rate at PFO (min^{-1}); k_2 is adsorption kinetic rate at PSO (g/mg.min).

Figure 6 showing the dye uptake increased rapidly for these materials after 90 minutes then reached equilibrium. The higher MG uptake onto Ca/Al-Biochar had an adsorption capacity 75.190 mg/g. The MG adsorption capacity of Ca/Al LDH was 52.598 mg/g, as similarly reported as Wan *et al.* [20]. The increasing dye adsorbed capacity on composite was caused by the higher surface area and interlayer space for the composite material. The kinetic parameter was presented in Figure 6 and Table 2 following Eq. 1 and 2. Table 2

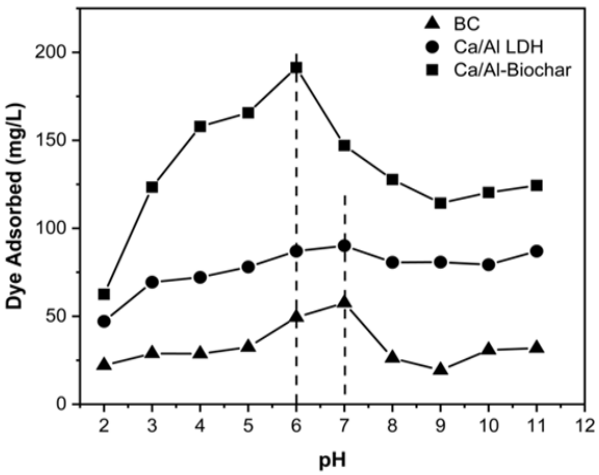

Figure 5. Effect of pH of MG adsorption on Ca/Al LDH, BC, and Ca/Al-Biochar.

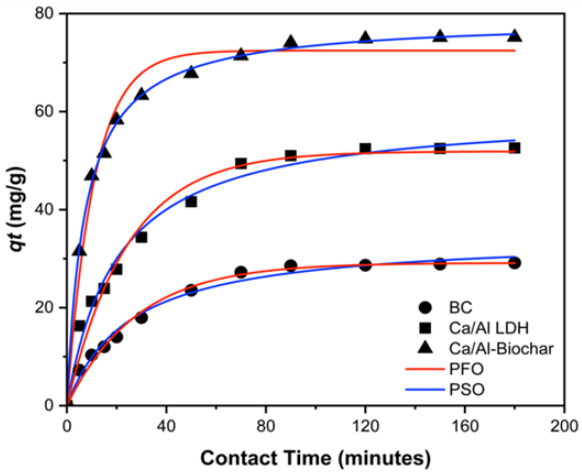

Figure 6. Effect of adsorption time and kinetic adsorption model.

Table 2. Adsorption kinetic parameter.

Adsorbents	Initial Concentration (mg/L)	$Qe_{experiment}$ (mg/g)	PFO			PSO		
			Qe_{Calc} (mg/g)	R^2	k_1	Qe_{Calc} (mg/g)	R^2	k_2
Ca/Al LDH	99.251	52.598	50.711	0.983	0.037	22.941	0.986	0.002
BC	99.251	29.132	26.509	0.998	0.002	33.445	0.995	0.001
Ca/Al-Biochar	99.251	75.190	50.153	0.982	0.041	78.125	0.9988	0.002

indicated the kinetic adsorption process belongs to PSO based on coefficient correlation (R^2). Besides, this process denotes that electrostatic bonds between the dye molecule and adsorbent were occurred and indicated the adsorption process was chemisorption [21]. However, this adsorption process should be supported using other adsorption parameters such as isotherm adsorption model and thermodynamic parameters.

To investigate isotherm adsorption, the adsorption process was carried out using several initial concentrations and temperatures. Furthermore, the Langmuir parameter can be used to predict if the adsorption was favorable or not. The parameter had two models, which were calculated by plotting q_e *vs.* C_e in several adsorbents with the same concentration as presented data in Figure 7. Figure 7 showing the slightly increasing dye adsorbed capacity

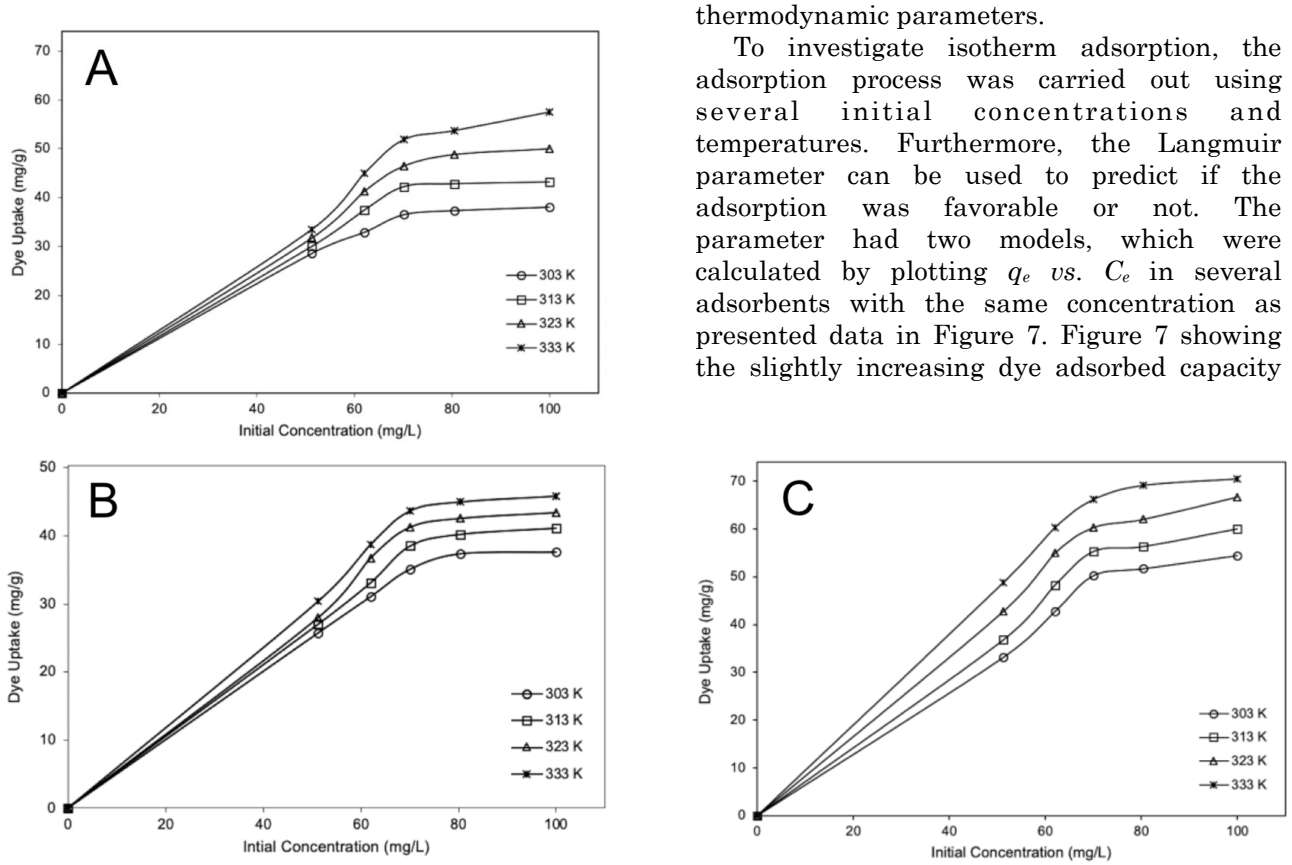

Figure 7. Effect of initial concentration and temperature (A) Ca/Al LDH, (B) BC and (C) Ca/Al-Biochar.

Table 3. Isotherm Freundlich and Langmuir models.

Adsorbents	Adsorption Isotherm	Adsorption Constant	T (K)			
			303	313	323	333
Ca/Al LDH	Langmuir	Q_{max}	43.860	58.480	53.476	70.423
		k_L	0.112	0.050	0.302	0.110
		R^2	0.995	0.999	0.999	0.997
	Freundlich	n	2.456	2.707	10.571	3.717
		k_F	8.145	9.709	34.770	21.380
		R^2	0.979	0.999	0.899	0.934
BC	Langmuir	Q_{max}	45.045	44.444	48.780	51.020
		k_L	0.083	0.219	0.152	0.175
		R^2	0.986	0.999	0.990	0.991
	Freundlich	n	1.012	9.872	13.680	15.361
		k_F	1.046	27.352	32.412	35.392
		R^2	0.999	0.905	0.942	0.945
Ca/Al-Biochar	Langmuir	Q_{max}	67.114	63.694	70.922	71.429
		k_L	0.100	0.394	0.445	3.256
		R^2	0.991	0.998	0.999	0.999
	Freundlich	n	8.928	7.962	7.981	32.154
		k_F	35.522	37.757	43.063	63.709
		R^2	0.999	0.999	0.999	0.967

with increasing temperature indicated that the adsorption process was favored at high temperature. The calculation results of the coefficient correlation, which was identified that the Langmuir model was better fitted than the Freundlich model for composite material as presented in Table 3. These results suggest that the surfaces of adsorbents were homogeneous with the adsorption mechanism of monolayer process. The higher maximum adsorption capacity was obtained by Ca/Al-Biochar (71.429 mg/g) than Ca/Al LDH (70.423 mg/g) and BC (51.020 mg/g). The MG adsorption capacity of Ca/Al-Biochar was relatively higher than pristine materials. Further experiments confirm that the modification of Ca/Al LDH with BC significantly increased the dye removal due to the synergetic effect of BC and Ca/Al in the composite. A presented in Table 4, several adsorbents were tested as MG removal agents. Among these adsorbents, Ca/Al LDH/BC in our research had in the middle results of others researches but the advantages of this study were high surface area properties of composite and simple preparation methods to obtain Ca/Al-Biochar composite.

Effect of temperature on the adsorption process of MG onto Ca/Al LDH, BC and Ca/Al-Biochar were shown in Figure 7 indicating the thermodynamic parameters. The thermodynamic parameters of the adsorption process such as a change in standard free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were obtained from experiments at various temperatures using the following equations:

$$\Delta G = -RT \ln K \quad (3)$$

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (4)$$

where K is the distribution coefficient; R is the gas constants; T is temperature adsorption absolute (K); ΔH is Enthalpy (kJ/mol); ΔS is entropy (J/mol.K); ΔG is Gibbs free energy (kJ/mol). Table 4 listed the value of these parameters. As a results in Table 5, the low to

Table 4. MG adsorption by several adsorbents comparison.

Adsorbents	Adsorption condition pH	MG adsorption capacity (mg/g)	Ref.
Pristine Lignin	2	31.2	[22]
Neem Sawdust	7.2	4.35	[23]
Ginger Waste	9	84.3	[24]
Novel Graphene Oxide	2.6	113.5	[25]
Red Clay	5.16	64.75	[26]
NiFe Intercalated POM LDH	–	8.81	[27]
Activated Carbon Lime	–	47.0	[28]
Ca/Al LDH	–	70.42	This work
Rice Husk BC	–	51.02	This work
Ca/Al-Biochar	–	71.429	This work

Table 5. Adsorption thermodynamic parameter.

Concentration	T (K)	Q_e (mg/g)	ΔH (kJ/mol)	ΔS (J/mol.K)	ΔG (kJ/mol)
BC	303	35.077	13.914	4.600	−0.029
	313	38.526			−0.489
	323	41.260			−0.950
	333	43.639			−1.410
Ca/Al LDH	303	36.504	26.404	8.880	−0.186
	313	42.212			−1.063
	323	46.492			−1.941
	333	51.861			−2.819
Ca/Al-Biochar	303	50.297	52.029	17.78	−1.971
	313	55.309			−3.754
	323	60.363			−5.536
	333	66.227			−7.318

high adsorption energy was obtained, which was related to the adsorption belongs chemisorption. The enthalpy of Ca/Al-Biochar was more than 40 kJ/mol [31]. The negative value of ΔG at various temperatures implies the spontaneity adsorption process and it is favorable at high temperatures. The positive value of ΔS on MG adsorption by Ca/Al LDH, BC and Ca/Al-Biochar had corresponded to the randomness of the solid-liquid interface during the adsorption process. The positive value of ΔH indicated the reaction of adsorption become endothermic due to the dye adsorbed was an increase on increasing temperature. The Ca/Al-Biochar had the highest value indicated that the interaction between adsorbate and adsorbent was more effective of MG adsorption.

4. Conclusions

In conclusion, the Ca/Al LDH, BC, and Ca/Al-Biochar were successfully prepared and applied to selective adsorption of MG toward cationic MB and Rh-B. The selectivity study showed that MG was more selective than MB and Rh-B for all adsorbent. MB was removed entirely after 90 min. The MG adsorption kinetics was followed the PSO model with a coefficient correlation closed to one. The adsorption isotherms could be expertly matched using the Langmuir model. The adsorption capacity of MG onto Ca/Al-Biochar, Ca/Al LDH, and BC were 71.429 mg/g, 70.423 mg/g, and 51.020 mg/g, respectively. The thermodynamic analysis indicates that the MG adsorption in all adsorbents was spontaneous (ΔG<0), endothermic, the randomness of solid-liquid phase interface and the adsorption process was belonged to chemisorption.

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