Efficient Removal of Methylene Blue by Adsorption Using Composite Based Ca/Al Layered Double Hydroxide-Biochar

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ABSTRACT

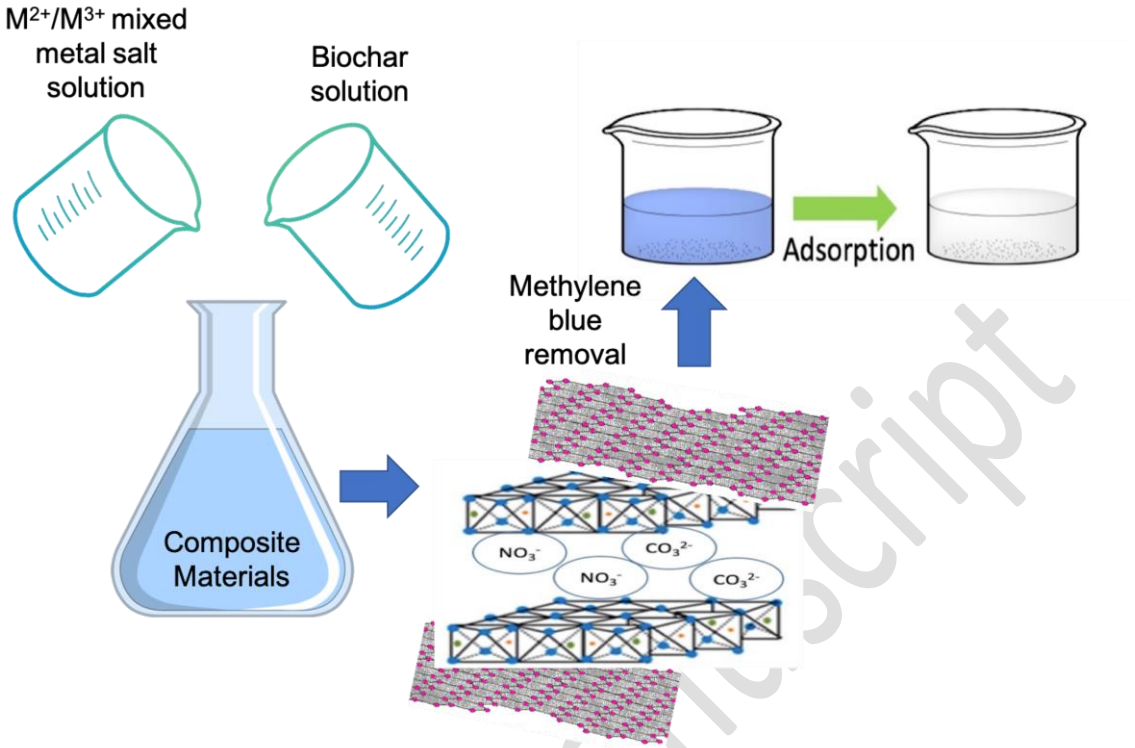
Composite based Ca/Al layered double hydroxide and biochar was prepared using mixing coprecipitation method at pH 10. Composite and the starting materials was characterized using X-ray, FTIR, BET, thermal, and SEM-EDX analyses. Furthermore, composite was used as adsorbent of methylene blue from aqueous solution. Several factors that influencing the adsorption process was investigated such as adsorption time, initial concentration, and temperature adsorption. The performance of composite as adsorbent was evaluated by reusability process.

The results showed that composite has diffraction peak at 9.82, 17.99, 19.86, 20.55, 29.32, 30.95, 32.65, 36.61, 37.00, 43.49, 47.15, 55.12, and 56.12 deg, which was based on diffraction of Ca/Al layered double hydroxide and biochar as starting materials. The surface area of composite was 158.291 m^2/g and largely higher than starting materials. The morphology of composite also shows regularity shape than Ca/Al layered double hydroxide and biochar.

Adsorption of methylene blue on composite showed that higher adsorption capacity (32.535 mg/g) than starting materials. The reusability of adsorbent showed that composite can be used several times ad adsorbent without loss adsorption capacity and these phenomena indicated composite is excellent material to remove dye from aqueous solution.

Keywords: composite, Ca/Al layered double hydroxide, biochar, methylene blue, adsorption

GRAPHICAL ABSTRACT



1. Introduction

The existence of hazardous dyes in wastewater from many activities expecially industrial process is one of the environmental problem in this decade (Schwarzenbach *et al.*, 2010; Yang *et al.*, 2016). The sources of dyes due to utilization of dyes from textile, cosmetic, food, paper, and pharmaceutical industries (Blaisi *et al.*, 2018). These dyes from industries is highly toxic not only to human but also ecosystem in the environment. One of the toxic dyes is methylene blue. Methylene blue is difficult to degrade due to light stable and difficult to oxidize (Sharifpour *et al.*, 2019). Several methods have been developed to reduce methylene blue from wastewater such as filtration, membrane process, and adsorption (Meili *et al.*, 2019; Yan *et al.*, 2013). Adsorption is the most suitable method to remove methylene blue from aqueous solution among these methods because simple way, easy to conduct, low cost operation, and also high efficiency (Abbasi and Asgari, 2018; Zubair *et al.*, 2017). The effectivity of adsorption is

turning on the ability of adsorbent which has depended on the variation of mass adsorbent or concentration of adsorbate. Several adsorbents have been used to remove methylene blue from solution such as chitosan, bentonite, zeolite, and also layered double hydroxide (Amor *et al.*, 2018; Haile *et al.*, 2015; Naseeruteen *et al.*, 2018; Taher *et al.*, 2018).

Layered double hydroxide (LDH) is inorganic layered structure, which also known as hydrotalcite compound. LDH consist divalent and trivalent metal ions, water, and exchangeable anion with general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]+xA_x^{-n}mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal ions and A^{n-} is anion with n valent (Mishra *et al.*, 2018; Oktriyanti *et al.*, 2020). The anion between interlayer can be exchangeable depending on synthetic condition and application. The total LDH has positively charged due to incorporating anionic species on interlayer space of LDH (Duan *et al.*, 2011).

LDH has high adsorption capacity due to wide surface area. Adsorbate bind to LDH through several ways such as electrostatic interaction, hydrogen bond, and also pore interaction by dipole or van der walls connections (Chen *et al.*, 2011). However, LDH has structural instability toward regeneration because the LDH structure can be sprayed and exfoliated (Zhu *et al.*, 2018). Thus, for economic reasons the LDH should be supported by large and stable molecule such as biochar. Biochar was obtained from renewable feedstocks such as rice husk (Bustamante *et al.*, 2016; Xu *et al.*, 2013).

Biochar has been used as stable adsorbent matrix and support to form composite with LDH for environmental applications. MgAl-LDH/Biochar was used as adsorbent of methylene blue with removal >95% (Meili *et al.*, 2019). MgFe-LDH was modified with biochar to form adsorbent for nitrate removal. The maximum adsorption capacity of these MgFe-LDH-biochar was 24.8 mg/g (Xue *et al.*, 2016). Removal of organic pollutants such as phosphate was also conducted using biochar/MgAl LDH with effective results due to biochar serve as an effective matrix and separate colloidal or nanosize LDH shape, which increase active site of adsorbent (Zhang *et*

al., 2013). Mg/Al LDH-biochar was also applied as effective adsorbent for removal phosphate from aqueous solution in which adsorbent was prepared by co-pyrolysis of LDH preload rice husk (Lee *et al.*, 2018). Thus, adsorbent based LDH-biochar is widely used as efficient adsorbent to reduce organic pollutants from wastewater.

Therefore, this study prepared composite biochar-Ca/Al LDH by mixing-coprecipitation method as adsorbent of methylene blue. Composite was characterized using X-ray, FTIR, BET, thermal, and SEM-EDX analyses. Further, the adsorption was studied through effect of pH, adsorption time, initial concentration, and temperature adsorption. The regeneration study was also studied to show the potency of composite as adsorbent.

2. Materials and methods

2.1 Chemical and Instrumentation

Chemicals such as calcium nitrate, aluminum nitrate, sodium carbonate, sodium hydroxide were purchased from Merck and Sigma-Aldrich. All these chemicals used without further purification. Biochar based local rice husk was obtained from Bukata Organic, Java Island Indonesia. Water was obtained from Research Center of Inorganic Materials and Complexes FMIPA Universitas Sriwijaya by ion exchange purification water system. Characterization of adsorbent was performed using X-Ray Rigaku Miniflex-6000 and sample was scanned in the range 5-80 deg with scan speed 1^{o}/min. Infra-red spectrum was recorder using FTIR Shimadzu Prestige-21 using KBr pellet and sample was recorded at wavenumber 400-400 cm^{-1}. Surface area analysis was performed using ASAP Micrometric at 77 K and sample was degassed several times prior analysis. Thermal analysis was performed using TG-DTA Shimadzu under atmospheric nitrogen. Morphology and composition of adsorbent was carried out using SEM-EDX Quanta-650 Oxford Instrument. Analysis of methylene blue was performed using UV-Visible spectrophotometer BIO-Base BK-UV 1800 PC at 664 nm.

2.2. Synthesis of Ca/Al LDH

Ca/Al LDH was synthesized by coprecipitation method according to previous literature as follow (Xu *et al.*, 2010). The equal volume of calcium nitrate and aluminum nitrate were mixed with concentration ratio 3:1. The mixtures were constantly stirred and 2M sodium hydroxide was added slowly with similar volume to calcium and aluminum. The pH was adjusted to 11 by adding sodium hydroxide. The reaction mixture was kept for 12 hours at 70 ^{o}C to form white suspension. The Ca/Al was obtained by filtration of suspension, washed with water and dried at 105 ^{o}C overnight.

2.3. Preparation of composite

Preparation of composite using Ca/Al LDH and biochar was conducted using mixing coprecipitation method. A 300 mg of biochar was added to 30 mL solution of calcium nitrate and 30 mL solution aluminum nitrate with molar ratio 3:1. The mixtures were constantly stirred and solution of sodium hydroxide was added slowly to the solution until pH 10. The reaction mixtures were stirred for 3 days at 70 ^{o}C and suspension solid was formed. Composite was obtained after filtration and washed with water several times. Composite was dried at 110 ^{o}C overnight and ready to characterize.

2.4. Adsorption study

Adsorption of methylene blue on composite was performed by batch system through variation of contact time, variation of initial concentration, and variation of temperature. The variation contact time of adsorption was 0-200 minutes. The initial concentration variation was 5-40 mg/L for temperature 30, 40, 50, and 60 ^{o}C. The concentration of methylene blue for each adsorption treatment was measured using UV-Visible spectrophotometer at 664 nm.

2.5. Desorption and regeneration study

The desorption process was conducted using several solvents ranging from non-polar to polar solvent such as diethyl ether to ethanol and water. Desorption of methylene blue was conducted after adsorption process and adsorbent was collected for regeneration study.

The regeneration study was conducted similar as adsorption process using optimum adsorption time and the filtrate was measured using UV-Vis spectrophotometer. The regeneration study was performed until three cycle process.

3. Results and Discussion

The XRD powder patterns of Ca/Al LDH, biochar, and composite were shown in Figure 1. The XRD pattern of Ca/Al LDH has unique diffraction at 10.18 (002), 20.61 (104), 29.31 (014), which was appropriate with JCPDS No.87-0493 (Plank *et al.*, 2016; Taher *et al.*, 2019). These patterns was also similar with the results of Xu *et al.*, (2010). Thus Ca/Al LDH can be used as precursor of composite based biochar.

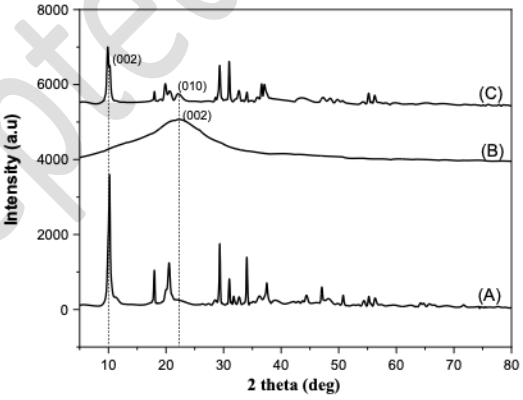


Figure 1. XRD powder patterns of Ca/Al LDH (A), biochar (B), and composite (C)

The XRD pattern of biochar as shown in Figure 1(B) has broader pattern due to high organic content on biochar (Wei, 2013). The diffraction has peak at 29.03 deg and indicated the low crystallinity of biochar. Composite of Ca/Al LDH-biochar has diffraction peak as shown in Figure 1(C). The high crystallinity of composite was obtained, which was largely different

from biochar. The diffraction peak of composite was appeared at 9.82, 17.99, 19.86, 20.55, 29.32, 30.95, 32.65, 36.61, 37.00, 43.49, 47.15, 55.12, and 56.12. All diffraction of Ca/Al LDH and biochar were found on composite. Thus composite based Ca/Al LDH and biochar was successfully synthesized.

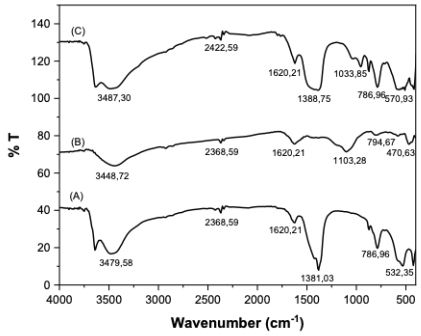


Figure 2. IR spectrum of Ca/Al LDH (A), biochar (B), and composite (C)

The FTIR spectrum of Ca/Al LDH, biochar, and composite were shown in Figure 2. The IR spectrum of Ca/Al LDH has specific vibration of nitrate, which was located on interlayer of LDH together with water. These nitrate vibrations were appeared at wavenumber 1381 cm^{-1}. Vibration stretching and bending of -OH from water was found at wavenumber 3480 cm^{-1} and 1620 cm^{-1}, respectively (Forano *et al.*, 2013). The vibration of metal divalent and trivalent was found at wavenumber 787 cm^{-1} and 532 cm^{-1} as shown in Figure 2(A). The vibration of biochar was appeared at 3448 cm^{-1} (υ-OH stretching), 1620 cm^{-1} (υ-OH bending), 1103 cm^{-1} (υ-Si-O-Si), and 470 cm^{-1} (υ-Al-O). Due to source material of biochar is from local rice husk and contain silica and alumina thus on biochar these elements are still appeared.

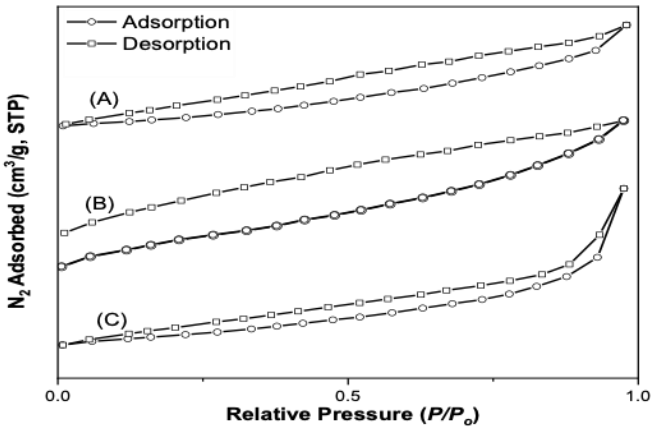


Figure 3. BET profile of Ca/Al LDH (A), biochar (B), and composite (C)

The nitrogen adsorption desorption of composite and starting materials is presented in Figure 3. There is hysteresis loop on the isotherm adsorption desorption and the isotherm was classifying as type IV with mesoporous class materials (Jiang *et al.*, 2019). The BET analysis of composite and starting materials is shown in Table 1.

Table 1. Surface area properties of materials

Materials	**Surface Area (m^2/g)**	**Pore $Volume_{BJH}$ (cm^3/g)**	**Pore $Diameter_{BJH}$ (nm)**
Ca-Al	29.333	0.0072	13.033
Biochar	50.936	0.00475	12.089
Ca-Al/biochar 1:0.1	158.291	0.0174	12.474

The surface area of composite is higher three folds than starting materials of biochar. The increasing of these surface area properties is probably due to opening of Ca/Al LDH pore assisted by carbon of biochar. However, the increasing of surface area for composite material affected from the biochar's lignin was removed (Ntaflou and Vakros., 2020). As predicted with previous reported literature that composite based LDH-biochar can increase the surface area of materials. On the other hand, the pore volume and pore diameter were decreased as results of high increasing of surface material.

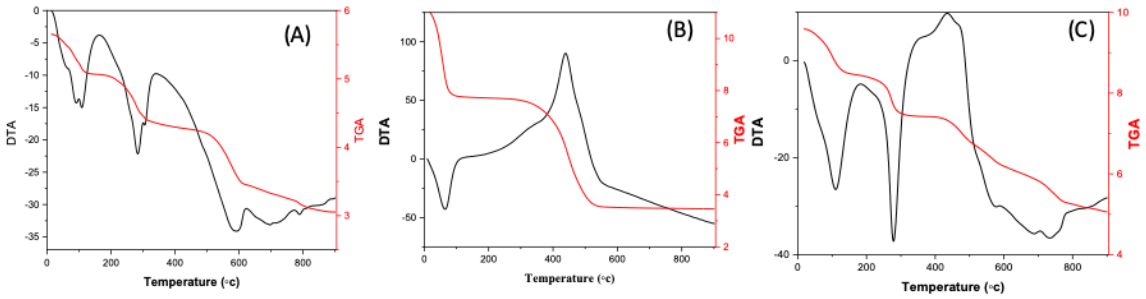


Figure 4. TG-DTA profile of materials

Further characterization of composite was attempt using thermogravimetric analysis as shown in Figure 4. The Ca/Al LDH shows three exothermic peaks and assigned as decomposition and loss of water at 110 0C, decomposition of nitrate on interlayer LDH at around 300 ^{o}C and decomposition of Ca/Al around 600 ^{o}C. The profile decomposition of biochar has a little different with inorganic materials like LDH. Temperature at 90 ^{o}C is assigned as loss water of crystallization on LDH and another peak is endotherm peak at 430 ^{o}C due to oxidation process on biochar material (Chen *et al.*, 2018). The composite has decomposition peaks of all starting materials as shown in Figure 4(C) i.e. three peaks of exothermic and one peak of endothermic process.

Figure 5. Photos morphology of materials

Composite was also characterized by SEM-EDX analysis as shown in Figure 5. The layer structure was appeared in Figure 5(A) indicating Ca/Al LDH was successfully synthesized although irregular layer was formed. Biochar has small pore as shown in Figure 5(B). The irregular distribution of pore was found together with block shape. On the other hand,

composite has regular form with plate sheet form. The composition of these materials was analyzed by EDX as shown in Table 2.

Table 2. Composition analysis by EDX

Ca/Al LDH		**Biochar**		**Composite**	
Element	**(%)**	**Element**	**(%)**	**Element**	**(%)**
Ca	21.8	C	58.3	Ca	24.5
Al	9.9	O	27.3	Al	8.2
O	57.6	Si	11.0	Si	2.5
N	10.8	Al	3.3	O	54.4
				N	10.4

Table 2 shows Ca/Al LDH has mayor elements calcium, aluminum, oxygen, and nitrogen. Biochar is organic material thus carbon is dominated on the sample. Composite is consisting of LDH and biochar and all elements are found except carbon probably due to analysis and associated with oxygen. According to Ntaflou and Vakros (2020), in base phases, lignin of biochar were remove due to treatment.

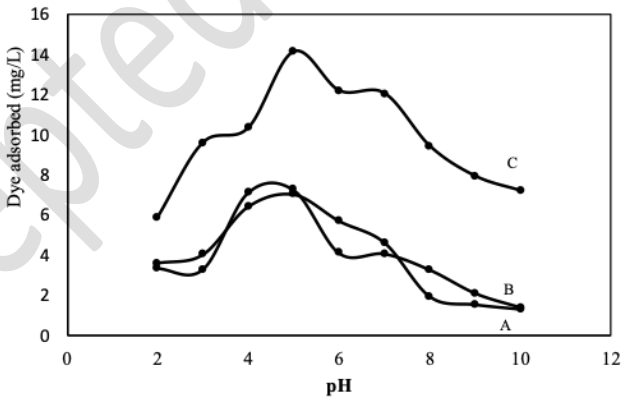


Figure 6. The influence of pH medium on methylene blue adsorption

The first investigation of adsorption is the influence of pH medium as shown in Figure 6. The pH optimum of methylene blue adsorption on Ca/Al LDH, biochar, and composite was pH 5. Thus the adsorption of methylene blue on these adsorbents will be conducted at these pH optimum value.

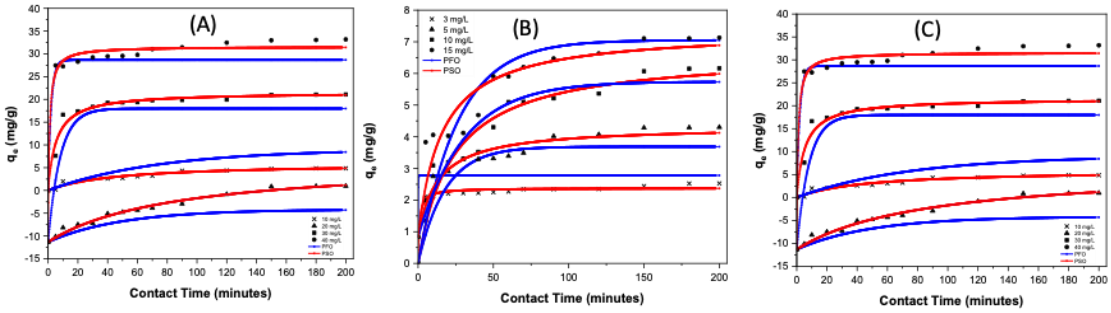


Figure 7. The contact time adsorption of methylene blue on Ca/Al LDH (A), biochar (B), and composite (C)

The effect of methylene blue adsorption time on composite and starting materials was shown in Figure 7. The adsorption amount was gradually increased with increasing adsorption time and reach equilibrium almost more than 100 minutes for all adsorbents. The results of adsorption time were fitted with pseudo first-order (PFO) and pseudo second-order (PSO) kinetic model as follows (He *et al.*, 2019; Palapa *et al.*, 2020):

PFO:

$$\log (q_e - q_t) = \log q_e - \left(\frac{k_1}{2{,}303}\right) t \quad . \qquad (1)$$

where: qe is the adsorption maximum at equilibrium (mg g^{-1}); qt is adsorption maximum at t (mg g^{-1}); t is time of adsorption (minute); and k_1 is adsorption kinetic rate at PFO ($minute^{-1}$).

PSO:

$$\frac{t}{qt} = \frac{1}{k2qe^2} + \frac{1}{qe} t \qquad (2)$$

where qe is the adsorption maximum at equilibrium (mg g^{-1}); qt is adsorption maximum at t (mg g^{-1}); t is time of adsorption (minute); and k_2 is adsorption kinetic rate at FSO (g mg^{-1} $minute^{-1}$).

The PFO and PFO was calculated at every concentration, which was investigated deeply in this research as shown in Table 3.

Table 3. Pseudo first-order and second order of kinetic adsorption

Adsorbents	Parameter	3 mg/L	5 mg/L	10 mg/L	15 mg/L
Ca/Al LDH					
Pseudo First	Q_e exp (mg/g)	1.833	2.175	3.074	6.064
Order	Q_e calc (mg/g)	0.229	1.256	2.519	4.212
	k_1 (min^{-1})	0.034	0.029	0.003	0.031
	R^2	0.731	0.936	0.818	0.839
Pseudo Second	Q_e exp (mg/g)	1.833	2.175	3.074	6.064
Order	Q_e calc (mg/g)	1.847	2.216	3.219	6.254
	k_2 (min^{-1})	0.439	0.106	0.023	0.017
	R^2	0.999	0.999	0.995	0.995
Biochar					
Pseudo First	Q_e exp (mg/g)	1.263	2.053	3.080	3.733
Order	Q_e calc (mg/g)	2.517	2.037	7.952	2.661
	k_1 (min^{-1})	0.020	0.030	0.382	0.020
	R^2	0.738	0.924	0.723	0.928
Pseudo Second	Q_e exp (mg/g)	1.263	2.053	3.080	3.733
Order	Q_e calc (mg/g)	1.270	2.229	3.448	4.108
	k_2 (min^{-1})	0.166	0.024	0.011	0.012
	R^2	0.998	0.991	0.988	0.988
Composite					
Pseudo First	Q_e exp (mg/g)	2.432	4.193	10.53	15.17
Order	Q_e calc (mg/g)	2.295	6.702	5.075	4.086
	k_1 (min^{-1})	0.019	0.029	0.029	0.025
	R^2	0.912	0.866	0.888	0.895
Pseudo Second	Q_e exp (mg/g)	2.432	4.193	10.53	15.17
Order	Q_e calc (mg/g)	2.959	5.727	10.73	15.29
	k_2 (min^{-1})	0.008	0.002	0.018	0.023
	R^2	0.968	0.955	0.998	0.999

For all concentration of methylene blue, the PFO and PSO has R^2 value almost close to one. The k_1 and k_2 is adsorption rate constant at that order on various concentration. The data in

table 3 showed that the value of k_1 and k_2 for Ca/Al LDH and biochar was decreased with increasing concentration of methylene blue. This phenomenon is due to increasing the methylene blue will decrease rate of adsorption on adsorbent. On the other hand, the composite has different phenomena, while increasing concentration of methylene blue will increase the k_1 and k_2 value. Composite has larger surface area and consist of several components thus that item will assist to increase the adsorption constant rate. The slightly different between Qe experimental and Qe calculation is due to data fitting equation of PFO and PSO.

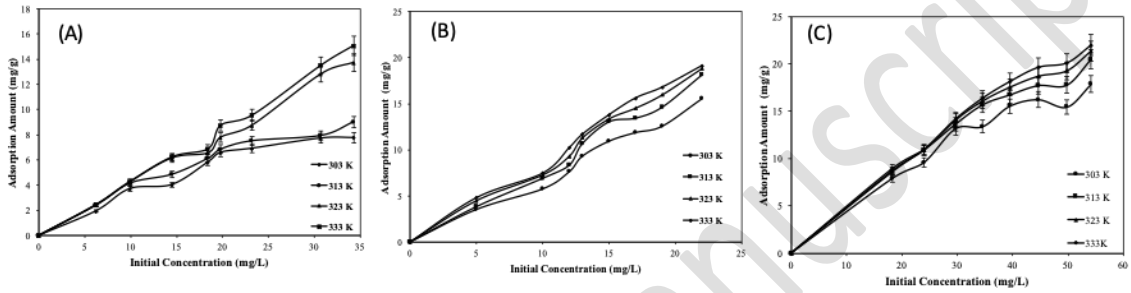


Figure 8. The initial concentration and temperature adsorption of methylene blue on Ca/Al LDH, biochar, and composite

The effect of initial concentration and temperature of methylene blue on adsorption was shown in Figure 8. The amount of methylene blue adsorbed on adsorbent was gradually increased with increasing initial concentration and temperature. The data in Figure 8 can be used to obtain isotherm data using Langmuir and Freundlich isotherm equations as follow (Lee *et al.*, 2018; Segun Esan, 2019):

Langmuir isotherm:

$$\frac{C}{m} = \frac{1}{bK} + \frac{C}{b} \quad (3) \qquad (3)$$

where: C is a saturated concentration of adsorbate; m is the amount of adsorbate; b is the maximum adsorption capacity (mg/g), and K_L is the Langmuir constant (L/mg).

Freundlich isotherm:

$$\text{Log } q_e = \log K_F + 1/n \log C_e \quad (4) \qquad (4)$$

Where: qe is adsorption capacity at equilibrium (mg/g); Ce is the concentration of adsorbate at equilibrium (mg/L), and K_F is Freundlich constant. The Langmuir and Freundlich isotherm data are shown in Table 4.

Table 4. The Langmuir and Freundlich isotherm adsorption

Adsorbents	**Temperature (K)**	**Isotherm**					
		Langmuir			**Freundlich**		
		Q_m	**K_L**	**R^2**	**n**	**K_F**	**R^2**
Ca/Al LDH	303	8.278	0.496	0.972	3.156	3.221	0.710
	313	7.536	0.581	0.810	2.144	2.682	0.662
	323	4.440	0.070	0.795	1.560	3.450	0.917
	333	22.936	0.174	0.974	1.411	3.551	0.986
Biochar	303	0.686	0.238	0.694	0.170	359.170	0.893
	313	0.297	0.425	0.876	1.249	29957.116	0.973
	323	0.135	0.364	0.973	0.092	75613.615	0.975
	333	22.676	0.021	0.881	1.209	1.775	0.999
Composite	303	19.493	0.321	0.957	3.185	6.599	0.713
	313	20.921	0.665	0.984	3.481	9.462	0.857
	323	0.839	0.115	0.908	2.996	10.610	0.865
	333	23.310	0.923	0.977	3.791	11.945	0.814

The value of Q_m for various temperature given is relative equal for all adsorbents and the R^2 value is in the range 0.7-0.9. The Freundlich isotherm adsorption is suitable for Ca/Al LDH and biochar, while Langmuir isotherm is appropriate for composite. The thermodynamic data also can be obtained from data in Figure 8. The thermodynamic adsorption data of methylene blue on Ca/Al LDH, biochar, and composite is presented in Table 5.

Table 5. The thermodynamic adsorption of methylene blue

Adsorbents	**C**	**T (K)**	**Q_e (mg/g)**	**ΔH (kJ/mol)**	**ΔS (kJ/mol)**	**ΔG (kJ/mol)**
Ca/Al LDH	30 mg/L	303	15.722	59.190	0.195	0.212
		313	18.034			-1.735

		323	25.614			-3.681
		333	27.012			-5.628
		303	17.550			0.328
	35 mg/L	313	19.539	57.873	0.190	-1.571
		323	27.443			-3.470
		333	30.152			-5.369
		303	14.940	28.79	0.1086	-3.128
	18 mg/L	313	15.595			-4.181
		323	15.810			-5.234
		333	16.612			-6.288
Biochar		303	18.327	6.64	0.0392	-25.278
	20 mg/L	313	18.982			-26.331
		323	18.671			-27.385
		333	18.945			-28.438
		303	26.674			-5.458
	30 mg/L	313	27.233	25.258	0.101	-6.472
		323	28.055			-7.485
		333	28.313			-8.499
Composite		303	26.768	41.239	0.148	-3.488
	35 mg/L	313	30.940			-4.964
		323	31.826			-6.441
		333	32.535			-7.917

The data in Table 5 showed that for all adsorbents the value of ΔG is negative and indicated that adsorption of methylene blue was spontaneously occurred. On the other side, the ΔH value is in the range 6-59 kJ/mol and that value means that adsorption of methylene blue on Ca/Al LDH, biochar, and composite was physical adsorption and also increasing randomness on composite than LDH and biochar. The highest Qe value was obtained on composite (32.535 mg/g). These high Qe value is related with increasing surface area of composite compared with Ca/Al LDH and biochar.

The performance of adsorbent for methylene blue adsorption was evaluated using adsorbent reusability process. Prior these steps, desorption was conducted using several solvents as shown in Figure 9.

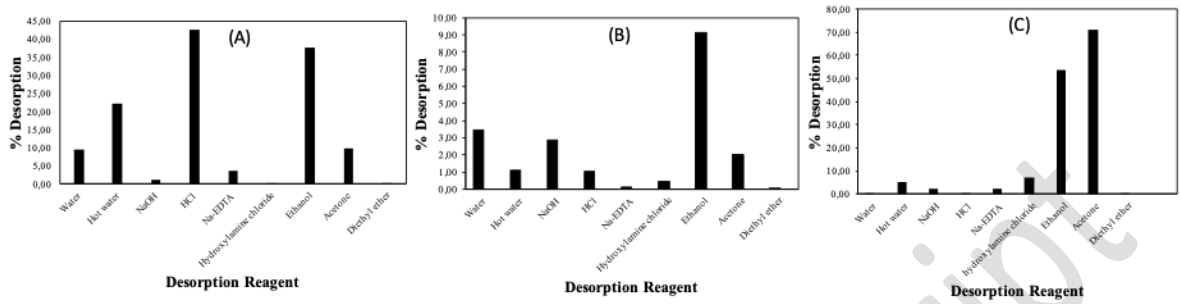


Figure 9. Desorption of methylene blue

The data of desorption showed that for hydrochloric acid and ethanol was appropriate solvent to remove methylene blue from Ca/Al LDH. As for biochar and composite, organic solvent such as ethanol and acetone is suitable to remove methylene blue from adsorbent. The reason is probably due to like and dissolve like principle (Extremera *et al.*, 2012).

The adsorption of methylene blue was conducted again using similar adsorbent after desorption process. In this step, adsorbent was desorp, washed with water several times, and dried at 100 ^{o}C thus adsorbent can be used for the next cycle. The reusability process of adsorbent was presented in Figure 10.

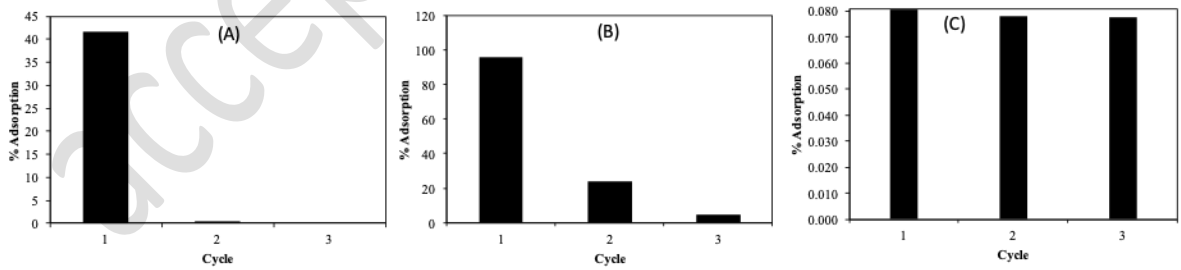


Figure 10. Reusability of adsorbents: Ca/Al LDH, biochar, and composite

The data in Figure 10 showed that Ca/Al LDH and biochar as starting material of composite have low reusability process. The adsorption capacity is sharply decreased in cycle 2 and 3. On the other hand, composite has high reusability process and stable until three times adsorbent

cycle although the adsorption capacity is low. This data showed that composite was synthesized in this research has high ability and stability under reuse adsorbent and can be promised for smart adsorbent to remove dye pollutant from wastewater.

4. Conclusion

Composite Ca/Al LDH-biochar has specific diffraction at 9.82, 20.55, 29.32, 30.95, 32.65, 36.61, 55.12, and 56.12 deg which was originally comes from diffraction of Ca/Al LDH and biochar. The surface area of composite (158.291 m^2/g) was higher than Ca/Al LDH (29.333 m^2/g) and biochar (50.936 m^2/g). The adsorption capacity of methylene blue of composite was also larger than Ca/Al LDH and biochar. The reusability of adsorbent showed that composite can be used until three time cycle without significant loss of adsorption capacity, while Ca/Al LDH and biochar is largely different and cannot be reuse several times.

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