

## The Capability of Biochar-Based CaAl and MgAl Composite Materials as Adsorbent for Removal Cr(VI) in Aqueous Solution

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### Abstract

The development of layered double hydroxide materials into composites with carbon-based materials in the form of CaAl-Biochar and MgAl-Biochar has been successfully carried out. The success parameters of the preparation process include XRD, FT-IR, Adsorption-Desorption N<sub>2</sub>, SEM, and TG-DTA. The success through XRD is evidenced by the appearance of the typical diffraction peaks of double-layer hydroxy around  $2\theta = 11^\circ(003)$ ,  $20^\circ(006)$ , and  $60^\circ(113)$ . In addition, there is diffraction around  $22^\circ(002)$  which is the typical diffraction of biochar. FT-IR analysis showed successful preparation in the presence of functional groups around  $1381\text{cm}^{-1}$  which indicated nitrate vibrations from double-layer hydroxy. Another spectrum that also appears on  $1103\text{cm}^{-1}$  is a characteristic of biochar ( $\nu$  Si-O-Si). Adsorption-Desorption N<sub>2</sub> analysis showed that the surface area data of CaAl-Biochar was greater than MgAl-Biochar, which were  $150.987\text{m}^2.\text{g}^{-1}$  and  $111,404\text{m}^2.\text{g}^{-1}$ , respectively. The adsorption capacity of CaAl-Biochar reached  $588.235\text{mg}.\text{g}^{-1}$  and  $426.316\text{mg}.\text{g}^{-1}$  for MgAl-Biochar. The adsorbent materials of CaAl, MgAl, Biochar, CaAl-Biochar, and MgAl-Biochar tend to follow the Langmuir isotherm model with adsorption processes that tend to be spontaneous. The results of regeneration of the composite material lasted up to 5 cycles. The first cycle of CaAl-Biochar reached 96.647% to 82.666% in the last cycle, while MgAl-Biochar reached 90.885% in the first cycle to 73.454% in the last cycle.

### Keywords

Adsorption, Cr(VI), Regeneration, Biochar, Layered Double Hydroxide

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### 1. INTRODUCTION

Layered double hydroxide (Fig. 1) is a material that is quite widely developed today because of its good ability to overcome contaminants. The layered double hydroxide known as anionic clays has attracted attention in various fields such as catalysis, hydrogenation, oxidation, ion exchange, and adsorption (Lee et al., 2019a). Layered double hydroxide in great demand because it has a layered structure, flexible, and has a large surface area. In many studies, layered double hydroxide is used as medicine Pšenička et al. (2020), supercapacitor Xue et al. (2020), catalyst Yang et al. (2020), and layered double hydroxide the most widely applied adsorbent. Layered double hydroxide is widely used as an adsorbent because it has a large surface area and high adsorption ability. However, the structure of the Layered double hydroxide is less stable and the layers peel off easily during repeated use processes. This allows the material to be modified so that it has good adsorption performance and can be used

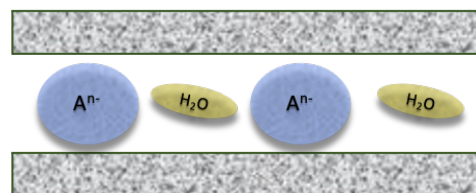


Figure 1. Schematic illustration of layered double hydroxide

repeatedly to increase efficiency.

Another study that also used Ca/Al-Cl as a Cr(VI) adsorbent achieved an adsorption capacity of  $1.40\text{mg}.\text{g}^{-1}$ . Other adsorbents used to adsorb Cr(VI) are Mg/Al and Zn/Al with an adsorption capacity of  $0.52$  and  $1.31\text{mg}.\text{g}^{-1}$  respectively (Milagres et al., 2017). The flexible nature of the layered double hydroxide allows it to be modified with the support material so that the adsorption performance of the material is increased.

Composite material is a modified result of layered double hydroxide with other supporting materials. One material that has good capabilities is carbon-based. Several carbon-based materials that can be used as multiple-layer hydroxy support materials are graphite, hydrochar, and biochar because they have a large enough surface area. Biochar is a carbon-based material that has many active sites such as,  $-\text{OH}$ ,  $\text{CHO}-$ ,  $\text{C}-\text{C}$ ,  $\text{M}-\text{O}$ ,  $\text{C}=\text{C}$ ,  $\text{COOH}$ , aromatic carbon skeleton, mineral crystal phase, and other oxygen-containing functional groups, making biochar a multifunctional adsorbent [Hassan et al. \(2020\)](#).

The biochar production process is carried out through thermochemical conversion using organic materials under oxygen-deficient conditions as known as pyrolysis at temperatures around  $700^\circ\text{C}$  [Zhang et al. \(2017\)](#). The use of biochar as a support material for composite can be produced using a variety of biomass, such as crop residues [Rajapaksha et al. \(2019\)](#), wood waste [Yang et al. \(2019b\)](#), food waste [Yang et al. \(2019a\)](#), municipal solid waste [Ashiq et al. \(2019\)](#), sewage sludge [Zhang et al. \(2020\)](#), bamboo [Zhang et al. \(2020\)](#) rice husk [Huong et al. \(2020\)](#).

The ability of composite materials from layered double hydroxide specifically CaAl and MgAl with biochar as adsorbent has been widely proven by various studies. [Palapa et al. \(2020c\)](#) in their research on Mg/Al and Mg/Al-biochar layered double hydroxide as adsorbent of methylene blue and rhodamine-B substances. The maximum adsorption capacity achieved by Mg/Al in each adsorbent was 62.32 and 11.56 mg/g. The adsorption capacity increases in Mg/Al-biochar to 91.44 and 69.23  $\text{mg}\cdot\text{g}^{-1}$ , respectively. [Lesbani et al. \(2020\)](#) carried out the adsorption process of methylene blue with adsorbents in the form of Ca/Al layered double hydroxide and Ca/Al-biochar composites. The adsorption capacity of the layered double hydroxide Ca/Al reached 22.936  $\text{mg}\cdot\text{g}^{-1}$ , while the composite material had a capacity of 23.310  $\text{mg}\cdot\text{g}^{-1}$ . The development of biochar-based adsorbent, CuAl-rice husk biochar developed by [Palapa et al. \(2020d\)](#) has increased the surface area from 46.2  $\text{m}^2/\text{g}$  to 200.90  $\text{m}^2/\text{g}$ . The adsorption ability of CuAl-rice husk biochar was tested to overcome cationic dyes with a maximum capacity of 74.125  $\text{mg}\cdot\text{L}^{-1}$  ([Palapa et al., 2020d](#)). On the other hand, research conducted by [Mohadi et al. \(2021\)](#) utilized CaAl-biochar composite as an adsorbent for a mixture of cationic dyes malachite green, rhodamine-B, and methylene blue with an adsorption capacity of 71.429  $\text{mg}\cdot\text{L}^{-1}$ . [Siregar et al. \(2021\)](#) in their research used NiAl-LDH based on biochar for the adsorption of Congo Red, which resulted in a maximum capacity of up to 312.5  $\text{mg}\cdot\text{L}^{-1}$ .

In this research, a layered double hydroxide material CaAl and MgAl was developed into a composite with a carbon-based material in the form of biochar. The resulting composites were in the form of CaAl-Biochar and MgAl-Biochar. The material will be applied as an adsorbent of Cr(VI). The success of the layered double hydroxide modification process CaAl and MgAl into a composite material of CaAl-Biochar and MgAl-Biochar is proven by characterization data, among others, XRD, FT-IR,  $\text{N}_2$  adsorption-desorption, TG-DTA, and SEM. Comparison of the ability of the adsorbent before and after the composite process will be proven by several parameters such as regeneration,

isotherm, and thermodynamics adsorption.

## 2. EXPERIMENTAL SECTION

### 2.1 Materials and Instruments

The materials used in this research such as,  $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  (Merck, 236.15 g/mol),  $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  (Merck, 375.13 g/mol),  $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  (Merck, 256.41 g/mol),  $\text{Na}_2\text{CO}_3$  (Merck, 105.88 g/mol), NaOH (Merck, 40.00 g/mol), HCl 37% by MallinckrodtAR®,  $\text{C}_2\text{H}_5\text{OH}$  (Avantor, 99%), Biochar. Water was obtained using a Purite® water purification system from the Research Center of Inorganic Materials and Complexes. The concentration of the dye was analyzed using spectrophotometer UV-Visible Biobase BK-UV 1800PC.

### 2.2 Preparation of Layered Double Hydroxide Material

As much as 100 mL of  $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$  0.75 M was mixed with 100 mL of  $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  0.25 M then stirred for 30 minutes. Next, adjust the pH of the mixture to reach pH 10 with the addition of 2 M NaOH. The resulting mixture was then stirred at a temperature of  $65^\circ\text{C}$  for 24 hours. After that, the sample was filtered and washed with distilled water and then dried in an oven at a temperature of  $100^\circ\text{C}$  to obtain a layered double hydroxide Ca/Al. Then the Ca/Al layered double hydroxide which has been obtained was characterized using XRD, FT-IR, BET, SEM, and TG-DTA.

The synthesis of Mg/Al material was carried out by mixing 100 mL of 0.75  $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$  and as much as 100 mL x  $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  as much as 100 mL. Then the two solutions were stirred for 30 minutes. After that, the mixture was dropped 2 M NaOH until it reached pH 10. The mixture was kept at a temperature of  $80^\circ\text{C}$  for 24 hours until a white solid was obtained. Then the solid is dried in an oven at a temperature of  $100^\circ\text{C}$ . The results of the layered double hydroxide Mg/Al were characterized using XRD, FT-IR, BET, SEM, and TG-DTA.

### 2.3 Preparation of Composite (CaAl-Biochar and MgAl-Biochar)

As much as 30 mL of 0.25 M  $\text{M}^{2+}$  (Ca, Mg) were mixed into 30 mL of  $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$  0.75 M solution then stirred and added 3 grams of biochar. The NaOH solution with a concentration of 2 M is slowly dripped in the mixture until it reaches a pH of 10. A solid will form after 3 days of stirring at a temperature of  $80^\circ\text{C}$ . Furthermore, the solid is filtered and washed with distilled water. The composite material obtained was dried at a temperature of  $100^\circ\text{C}$ , then characterized using XRD, FT-IR, BET, SEM, and TG-DTA.

### 2.4 Adsorption Study

Adsorption studies were carried out to determine the kinetics, thermodynamic, and isotherm parameters of adsorption. The kinetics parameters were carried out by varying the adsorption time from 5-180 minutes. while the isotherm and thermodynamic parameters were carried out by varying the concentration of adsorbate (50, 75, 100, 125, and 150)  $\text{mg}\cdot\text{L}^{-1}$  and the adsorption temperature at (303, 313, 323, and 333)K. The concentration

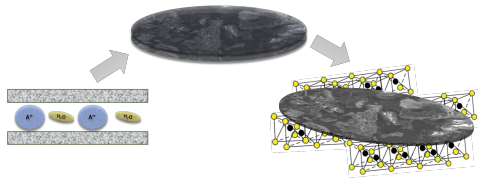


Figure 2. Layered double hydroxide modified by biochar

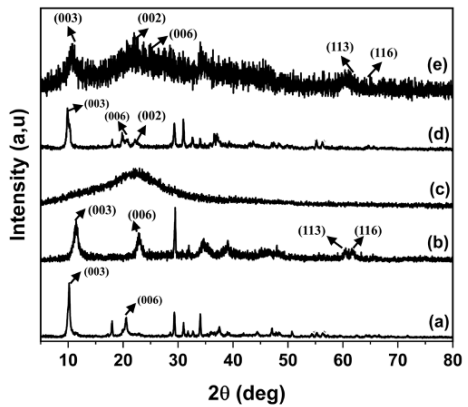


Figure 3. XRD pattern of CaAl (a), MgAl (b), Hc (c), CaAl-Biochar (d) MgAl-Biochar (e)

of adsorbed Cr(VI) was measured by a complex process using diphenylcarbazide at a wavelength of 543 nm.

### 2.5 Regeneration Study

A regeneration study was carried out by 20 mL of 100 ppm Cr(VI) with 2 g of adsorbent then stirred for 2 hours. Furthermore, the centrifugation process is carried out to separate the adsorbent and the adsorbate residue. Residual adsorbate was measured using a UV-Vis spectrophotometer and the adsorbent was dried for desorption using water, hydrochloric acid, sodium hydroxide, and acetone. The desorption process is carried out with several solvents to obtain a suitable solvent. The regeneration process is carried out by the adsorption-desorption process repeatedly in 5 cycles.

## 3. RESULTS AND DISCUSSION

The success of the MgAl-Biochar composite material preparation process is proven by characterization data which includes XRD, FT-IR, BET, SEM, and TG-DTA. The main characterization of the preparation process is XRD, where this analysis is used to determine the important diffraction peaks and the crystallinity of the prepared material. Figure 3 presents a diffractogram of CaAl (a), MgAl (b), Biochar (c), CaAl (d), and MgAl-Bc (e) materials as a comparison of success.

The success of the CaAl-Biochar composite preparation process refers to the JCPDS data No. 87-0493 [Herald et al. \(2017\)](#), that the typical diffraction of CaAl is around  $2\theta = 11^\circ(003)$  and  $23^\circ(006)$ . The analysis results obtained, the diffraction of CaAl (Fig. 3a) was  $10.18^\circ(003)$ , and  $20.61^\circ(006)$ , while the CaAl-Biochar

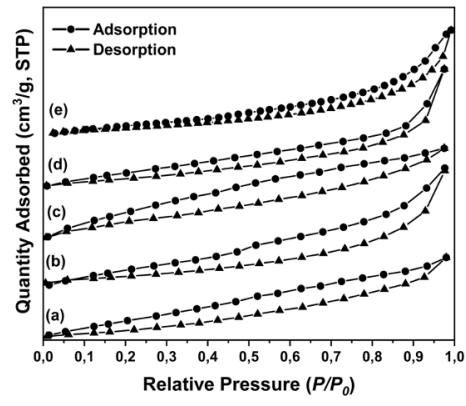


Figure 4. Adsorption desorption N<sub>2</sub> on to the CaAl (a), MgAl (b), Biochar (c), CaAl-Biochar (d), and MgAl-Biochar (e)

composite increased 1 peak of biochar (Fig. 3c) at  $22^\circ(002)$ .

Based on data from the Joint Committee on Powder Diffraction Standards (JCPDS) File No. 20-0658 in [Kashani et al \(2020\)](#) [Ahmadi-Kashani and Dehghani \(2020\)](#) the diffractogram of MgAl is around angles  $11.8^\circ(003)$ ,  $23.6^\circ(006)$ ,  $62.3^\circ(113)$  and  $66.3^\circ(116)$ . Figure 3(a) is a diffractogram of MgAl which shows the peaks at  $11.47^\circ(003)$ ,  $22.86^\circ(006)$ ,  $61.62^\circ(113)$ , and  $65.5^\circ(116)$ . This proves that the MgAl synthesis process has been successfully carried out. The diffractogram of a layered double hydroxide MgAl composite with a carbon-based material in the form of biochar (MgAl-Biochar) is presented in Figure 3(c). The MgAl-Biochar diffractogram resembles the diffractogram of MgAl and the Biochar material in Figure 3(b), where the characteristic peak is at  $2\theta = 22^\circ(002)$  which is the characteristic of amorphous material. On the other hand, broader diffraction in biochar indicates a high organic content ([Lesbani et al., 2020](#)).

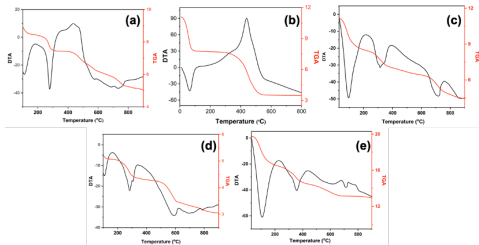
The next supporting analysis is the N<sub>2</sub> adsorption-desorption analysis was also carried out to determine the surface area of the material. The isotherm pattern of the adsorbent material is presented in Figure 4.

Based on IUPAC, the overall N<sub>2</sub> adsorption isotherm profile in Figure 4 follows type IV that shows a hysteresis loop, that is, the difference between the adsorption and desorption processes ([Shaji and Zachariah, 2017](#)). BET characterizes the surface area of a mesoporous substance, which may be a material with a pore diameter of between 2 and 50 nm. Hysteresis H4 explains that the adsorbent has slit-shaped pores with a micropore size distribution ([Alsamman et al., 2017](#)).

The results of determining the surface area, pore size, and pore volume are presented in Table 1. CaAl-based materials tend to have a larger surface area than MgAl. CaAl layered double hydroxide has a surface area of  $47.027 \text{ m}^2/\text{g}$  and increases to  $150.987 \text{ m}^2/\text{g}$ . On the other hand, the MgAl layered double hydroxide with a surface area of  $23.150 \text{ mm}^2/\text{g}$  increased to  $111.404 \text{ mm}^2/\text{g}$  after the composite process. the CaAl-Biochar material may have a greater adsorption ability, which is shown in Table 1.

**Table 1.** BET Surface Area Analysis

Materials	Surface Area (m <sup>2</sup> /g)	Pore Size (nm), BJH	Pore Volume (cm <sup>3</sup> /g),BJH
CaAl	47.027	0.075	4.006
MgAl	23.15	0.092	0.028
Biochar	30.595	0.044	3.561
CaAl-Biochar	150.987	0.062	10.918
MgAl-Biochar	111.404	0.475	3.583



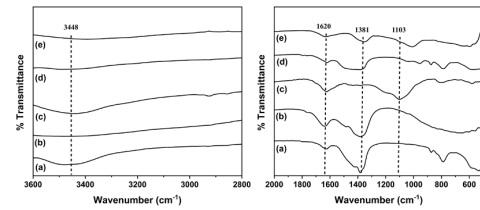
**Figure 5.** TG-DTA profile of CaAl (a), MgAl (b), Biochar (c), CaAl-Biochar (d), and MgAl-Biochar (e)

Further characterization of the adsorbent material was carried out by thermogravimetric analysis shown in Figure 5. CaAl shows three exothermic peaks at 110°C indicating the decomposition of water. The second peak is at 300°C which is the decomposition of the nitrate ion in the interlayer of the layered double hydroxide. The third peak is around 600°C which indicates that the CaAl layered double hydroxide has completely decomposed.

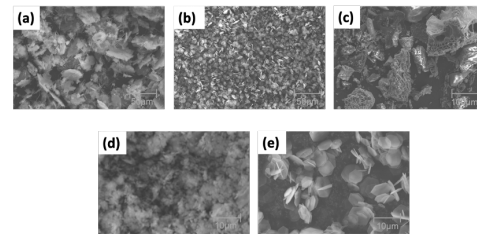
MgAl layered double hydroxide shows three exothermic peaks at 100°C, 320°C, and 730°C. In contrast, to layered double hydroxide, biochar has an exothermic peak at 90°C which indicates water decomposition. another peak is at 430°C which indicates the occurrence of the oxidation process in biochar. Composite materials from double-layer hydroxy with biochar, both CaAl-Biochar and MgAl-Biochar, show peak similarities with the constituent materials. Figures 5(d) and 5(e) obtained 3 peaks of decomposition of the layered double hydroxide characteristics and one endothermic peak of biochar.

Apart from the three characterizations above, the FTIR is used to detect the presence of functional groups in the material. The FTIR spectrum of MgAl, Biochar, and MgAl-Biochar in Figure 6 shows the similarity of functional groups at 3400 and 1600 cm<sup>-1</sup>. According to Palapa et al. (2020b), the spectrum is a stretching and bending vibration of the hydroxyl.

Figure 6 shows the presence of nitrate vibrations in 1381 which is one of the characteristics of the layered double hydroxide Palapa et al. (2020d). Figure 6(c) is a spectrum of biochar showing vibrations at 3448 and 1103. According to Lesbani, the vibrations at 3448 are stretching vibrations from -OH, while 1103 indicates the presence of Si-O-Si bonds. The success of the composite material preparation was also analyzed by SEM as presented in Figure 7.



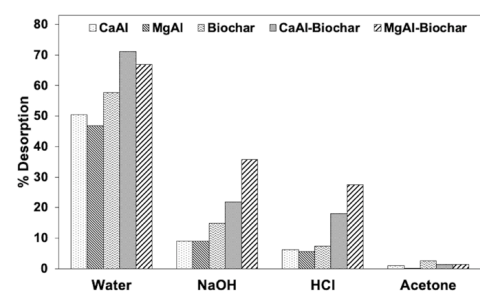
**Figure 6.** FT-IR spectra of CaAl (a), MgAl (b), Biochar (c), CaAl-Biochar (d), and MgAl-Biochar (e)



**Figure 7.** SEM morphology of CaAl (a), MgAl (b), Biochar (c), CaAl-Biochar (d), and MgAl-Biochar (e)

The next characterization in the form of SEM analysis is presented in Figure 7. Figure 7(a) is CaAl and 7(b) MgAl, showing that the layered double hydroxide has been successfully synthesized in the form of pieces. Biochar morphology in Figure 7(c) shows a small pore shape. CaAl-Biochar and MgAl-Biochar composite materials in Figures 7(d) and 7(e) show the shape of the plate sheet.

The ability of the adsorbent material is proven by several parameters, such as regeneration, isotherm, and adsorption thermodynamics. In this case, the regeneration process is carried out for 5 cycles for each adsorbent. Regeneration is carried out by first using the adsorption process, then desorption using water, the results of which are presented in Figure 8.

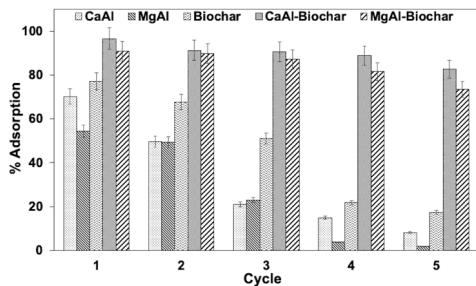


**Figure 8.** Desorption process using adsorbent materials

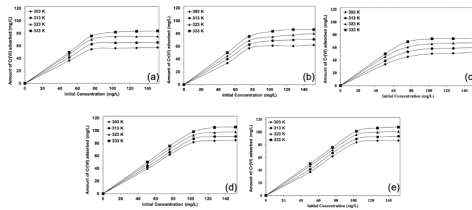
The adsorbent materials CaAl, MgAl, Biochar, CaAl-Biochar, and MgAl-Biochar showed the same results in the desorption process. The highest desorption ability of each reagent in Figure 8 shows that the water solvent is suitable for use as a desorption agent. This is evidenced by the ability of water as a desorption agent which reaches 50.357%, 46.828%, 57.609%, 71.113%, and 67.001%, respectively. Furthermore, these two processes are

**Table 2.** Isotherm parameter of adsorbent materials

Materials	Langmuir			Freundlich		
	$k_L$	$Q_{max}$ ( $\text{mg}\cdot\text{g}^{-1}$ )	$R^2$	$k_F$	$n$	$R^2$
CaAl	0.215	89.286	0.999	1.039	0.528	0.999
MgAl	2.17	86.957	0.999	1.175	0.549	0.623
Biochar	2.233	74.627	0.999	1.203	0.575	0.913
CaAl-Biochar	0.027	588.235	0.981	6.196	1.028	0.951
MgAl-Biochar	0.081	426.316	0.994	1.631	0.595	0.565



**Figure 9.** Regeneration process using adsorbent materials



**Figure 10.** Effect of concentration and temperature on the adsorption of CaAl (a), MgAl (b), Biochar (c), CaAl-Biochar (d), and MgAl-Biochar (e)

repeated for 5 cycles. The results of the regeneration process are presented in Figure 9.

The layered double hydroxide of CaAl and MgAl showed a drastic decrease in the adsorption ability in the third cycle. CaAl, which is initially 70.246% and 49.658%, in the last cycle, decreases to 8.251%. Whereas in MgAl, which was originally 54.427% and 49.388%, in the last cycle it decreased to 1.874. Good regeneration ability is shown by the composite material in Figures 9(d) and 9(e). CaAl-Biochar and MgAl-Biochar composites were able to maintain the adsorption capacity in the 90-70% range.

The data on the adsorption capability of the adsorbent is supported by the isotherm parameter data and the adsorption thermodynamics. It can be seen that the adsorption ability of each adsorbent increases with increasing concentration and temperature. This data can be seen from the graph in Figure 10 which tends to continue to increase.

The graph shows that both CaAl and CaAl-Biochar materials have a higher adsorption ability compared to MgAl and MgAl-

Biochar. This is evidenced by the data from the surface area analysis in Table 1 which shows that CaAl-based materials have a higher surface area than MgAl. Based on Siregar et al. (2021), Cr(VI) adsorption isotherm parameters were determined using the Langmuir and Freundlich isotherm model. Table 2 presents the results in the form of the maximum adsorption capacity of Cr(VI) using CaAl, MgAl, Biochar, CaAl-Biochar, and MgAl-Biochar as well as the determination of the adsorption isotherm model. The maximum capacity of layered double hydroxide increases even up to 5 times after going through the composite process. The maximum capacity of CaAl which was originally  $89.286 \text{ mg}\cdot\text{g}^{-1}$  increased to  $588.235 \text{ mg}\cdot\text{g}^{-1}$  after becoming a CaAl-Biochar composite.

The determination of the adsorption isotherm model according to Palapa et al. (2020a) is based on a linear regression value that is closer to 1. Overall CaAl, MgAl, Biochar, CaAl-Biochar, and MgAl-Biochar more likely to follow the Langmuir isotherm model because it has a linear regression value that is closer to 1. Langmuir isotherm model which assumes the adsorption sites are identical and that there are no interactions between adsorbed molecules (Chen et al., 2020). According to Onder et al. (2020), the adsorption process that follows the Langmuir isotherm model tends to be chemisorption and the adsorption process occur in monolayer.

Furthermore, the thermodynamic parameters of the adsorption were determined to determine the adsorption energy that took place. According to Badri et al. (2021) Thermodynamic parameters which include entropy ( $\Delta S^\circ$ ), enthalpy ( $\Delta H^\circ$ ), and Gibbs free energy ( $\Delta G^\circ$ ) are presented in Table 3.

Overall, the enthalpy ( $\Delta H^\circ$ ) shown in Table 3 is positive, according to Li et al. (2020), this confirms that the Cr(VI) adsorption process is endothermic. The enthalpy range which is at 1-40 kJ/mol indicates that the Cr(VI) adsorption takes place in physisorption, meanwhile,  $\Delta H^\circ$  which is in the 40-120 kJ/mol range indicates that the adsorption process takes place chemisorption (Lee et al., 2019b). The  $\Delta H^\circ$  values of CaAl, MgAl, Biochar, CaAl-Biochar, and MgAl-Biochar in Table 3 are in the range of 16-60 kJ/mol, this indicates that the Cr(VI) adsorption process tends to take place physisorption.

The entropy value ( $\Delta S^\circ$ ) in Table 3, according to Sahmoune (2019), indicates that there is increased randomness at the solid/solution interface. The Gibbs free energy shown in Table 3, with the adsor-

**Table 3.** Thermodynamics parameter of adsorbent materials

Material	$\Delta H^\circ$ (kJ/mol)	$\Delta S^\circ$ (J/mol.K)	$\Delta G^\circ$ (kJ/mol)			
			303 K	313 K	323 K	333 K
CaAl	60.543	0.207	-2.236	-4.308	-6.38	-8.452
	64.04	0.219	-2.216	-4.402	-6.589	-8.776
	33.272	0.111	-0.371	-1.482	-2.592	-3.702
	18.459	0.06	0.197	-0.405	-1.008	-1.611
MgAl	19.958	0.062	1.265	0.649	0.032	-0.585
	60.609	0.208	-2.322	-4.399	-6.475	-8.552
	57.249	0.201	-3.586	-5.594	-7.602	-9.609
	69.435	0.239	-3.025	-5.417	-7.808	-10.2
Biochar	24.522	0.087	-1.788	-2.656	-3.524	-4.393
	17.281	0.059	-0.706	-1.299	-1.893	-2.487
	61.371	0.208	-1.524	-3.6	-5.675	-7.751
	40.392	0.136	-0.952	-2.317	-3.681	-5.046
CaAl-Biochar	26.721	0.088	0.164	-0.712	-1.589	-2.465
	20.617	0.065	1.031	0.385	-0.261	-0.908
	16.496	0.049	1.57	1.077	0.584	0.092
	47.184	0.166	-3.07	-4.728	-6.387	-8.046
MgAl-Biochar	46.765	0.166	-3.534	-5.194	-6.854	-8.514
	46.255	0.163	-3.072	-4.7	-6.328	-7.956
	24.532	0.086	-1.584	-2.446	-3.308	-4.17
	16.635	0.057	-0.575	-1.143	-1.711	-2.279
MgAl-Biochar	56.667	0.193	-1.706	-3.633	-5.559	-7.486
	49.364	0.172	-2.642	-4.358	-6.074	-7.791
	29.3	0.1	-0.854	-1.849	-2.844	-3.839
	23.459	0.077	0.26	-0.506	-1.271	-2.037
	18.303	0.057	0.884	0.309	-0.266	-0.841

bents of CaAl, MgAl, Biochar, CaAl-Biochar, and MgAl-Biochar has negative values indicating that the Cr(VI) adsorption process was spontaneous Li et al. (2020).

#### 4. CONCLUSIONS

The adsorption ability of the composite material CaAl-Biochar and MgAl-Biochar has been proven by the increased maximum capacity value of the constituent layered double hydroxide material. CaAl layered double hydroxide which was originally  $89.286 \text{ g}^{-1}$  increased to  $588.235 \text{ mg.g}^{-1}$ , while the initial MgAl was  $86.957 \text{ g}^{-1}$  to  $426.316 \text{ g}^{-1}$ . The determination of the composite material adsorption isotherm model is more likely to follow the Langmuir isotherm model with a process that takes place spontaneously. The success of the synthesis of CaAl-Biochar and MgAl-Biochar composite materials was proven by XRD analysis which showed the characteristic diffraction of layered double hydroxide  $2\theta = 11^\circ(003)$  and biochar  $22^\circ(002)$ . This data is supported by an increase in the surface area of the CaAl layered double hydroxide material from  $47.027 \text{ m}^2/\text{s}$  to  $150.987 \text{ m}^2/\text{s}$  and MgAl from  $23.150 \text{ m}^2/\text{s}$  to  $111.404 \text{ m}^2/\text{s}$ .

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